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Collection of Abstracts

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Plenary lectures

Assembling responsive colloids

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Responsive colloids such as thermo- or pH-sensitive microgels are ideal model systems to investigate the relationship between the nature of interparticle interactions and the plethora of self-assembled structures that can form in colloidal suspensions. They allow for a variation of the form, strength and range of the interaction potential almost at will. Moreover, due to their soft nature, we can create dispersions with concentrations far above random close packing. These ultra-dense suspensions exhibit fascinating flow properties and can form a variety of different amorphous and crystalline structures [1]. Particularly interesting are ionic microgels [2]. Due to their large number of internal counterions they possess very large polarisabilities, and we can thus use external electrical ac fields to generate large dipolar contributions to the interparticle interaction potential [3]. This leads to a number of new crystal phases, and we can trigger crystal-crystal phase transitions through the appropriate choice of the field strength [4]. However, while the responsiveness and softness of these particles result in intriguing properties, they also pose considerable problems when attempting to characterize the response of individual particles to their environment at high packing fractions, where particles can adapt their shape, de-swell as well as partially interpenetrate. Here I will demonstrate how we can use scattering techniques as an ideal set of tools to obtain in-situ information about the structure of the individual particles as well as that of the assembled arrays on all relevant length scales. These experiments provide for example detailed information such as the internal density profile of the individual microgel and its response to various stimuli and packing fractions, and the structural correlations between particles in the different fluid and solid states. I will highlight in particular the use of small-angle neutron scattering together with appropriate contrast variation experiments, and combined with complementary techniques such as small-angle x-ray scattering and confocal microscopy, in order to obtain a quantitative understanding of the structural properties of dense and highly correlated microgel suspensions [2,5,6]. Moreover, I will also demonstrate the effect of particle anisotropy in field-driven assembly.

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Tuning strain stiffening and fracture of composite fibre networks

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Living tissues show an extraordinary adaptiveness to strain, which is crucial for their proper biological functioning. The physical origin of this mechanical behaviour has been widely investigated using reconstituted networks of collagen fibres, the principal load-bearing component of tissues. However, collagen fibres in tissues are embedded in a soft hydrated polysaccharide matrix which generates substantial internal stresses whose effect on tissue mechanics is unknown. Here, by combining mechanical measurements and computer simulations, we show that networks composed of collagen fibres and a hyaluronan matrix exhibit synergistic mechanics characterized by an enhanced stiffness and delayed strain-stiffening [1]. We demonstrate that the polysaccharide matrix has a dual effect on the composite response involving both internal stress and elastic reinforcement. Moreover, the matrix has a pronounced effect on fracture of the networks, leading to enhanced toughness and a transition from brittle to ductile behaviour. Our findings elucidate how tissues can tune their strain-sensitivity over a wide range and provide a novel design principle for synthetic materials with programmable mechanical properties.

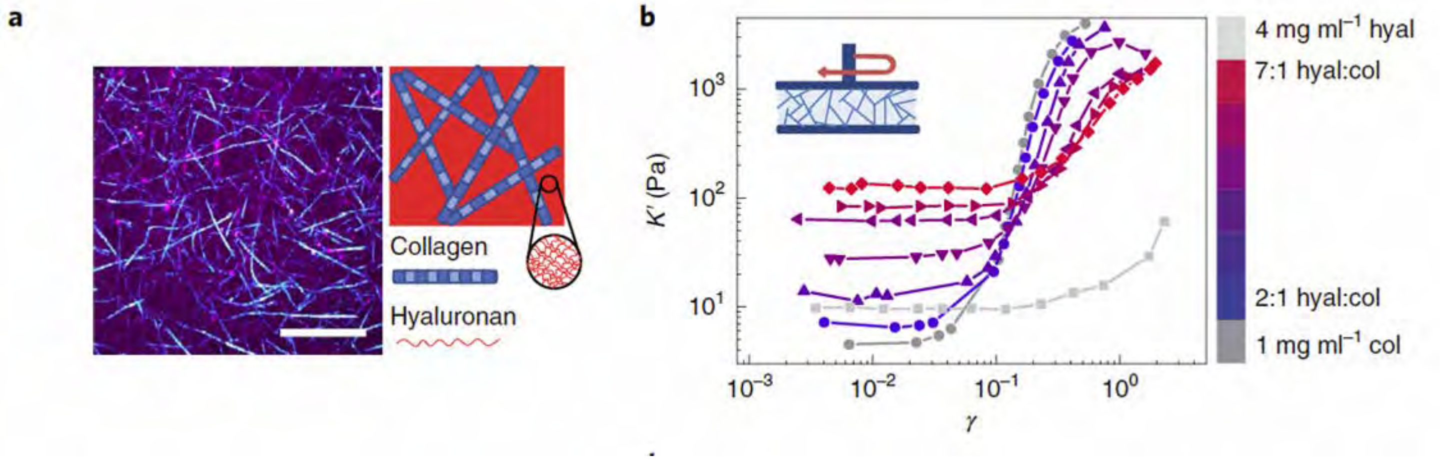

Figure 1. (a) Confocal image and schematic picture of composite collagen/hyaluronan network. (b) Differential elastic modulus as a function of strain for networks with different hyaluronan concentrations, showing both an enhanced stiffness and a delayed strain stiffening with increasing matrix concentration (from [1]).

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3D Printing of Soft Matter into Bioinspired Architectured Materials

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Biological materials exhibit heterogeneous architectures that are tuned to fulfill the functional demands and mechanical loading conditions of their specific environment. Examples range from the cellulose-based organic structure of plants to collagen-based skeletal parts like bone, teeth and cartilage. Because they are often utilized to combine opposing properties such as strength and low-density or stiffness and wear resistance, the heterogeneous architecture of natural materials can potentially address several of the technical limitations of artificial implants or composites in general. However, current man-made manufacturing technologies do not allow for the level of composition and fiber orientation control found in natural heterogeneous systems. In this talk, I will show that 3D printing routes using self-assembly inks offer an exciting pathway for the fabrication of biologically-inspired materials with unprecedented heterogeneous architectures and functional properties.

The Power of One: What Can We Learn from Singe Molecule Fluorescence Microscopy Measurements?

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Single molecule spectroscopy has tremendously impacted every field in which the technique was applied, ranging from catalysis over plasmonics, polymer physics, biophysics to cell biology and DNA sequencing. Furthermore, single molecule techniques have allowed researchers to push the resolution of fluorescence microscopy past the diffraction limit. In this presentation, I will give an overview of recent single molecule experiments in my laboratory. Progress in instrumentation, in polymer research (1), in plasmonics (2), in emissive silver clusters (3), in perovskite nano-particle research (4) and in DNA mapping (5) will be discussed.

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Of Microbes, Mechanics and Materials

Translating emergent traits to ecological functions

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Understanding how microbes interface, exchange and communicate with their local surroundings is central to the grand quest for a theory of microbial ecology. From simple to complex fluids, from compliant to rigid surfaces, microbes inhabit plethora of micro-environments spanning vastly different structures, dynamics, and internal energies. Currently we lack a biophysical framework that could explain, generalize, and crucially, predict the *if-s*, the *how-s*, and the *why-s* of the microbe-environment interactions. Research in my lab aims to fill this gap by interfacing soft matter physics and fluid mechanics with microbiology and genetic engineering. In this talk I will discuss that microbes – across individual, species and community scales – are inherently coupled to their micro-environments, and that their behavioural and physiological traits emerge as a consequence of active biophysical feedbacks between the material, information and energy transport processes. Using vignettes from our recent experiments in model gut and aquatic microbial systems, I will demonstrate how microbes and their micro-environments crosstalk via biomechanical coupling, leading to emergence of traits that ultimately translate into ecological and eco-physiological functions. I will discuss the generality of our results across microbial worlds, specifically touching upon the role and ramification of fluctuations in microbial environments. I will conclude by discussing why our efforts to unpack the microbe-mechanics-materials nexus are central to deciphering microbial fitness, succession, and selection, not least for their emerging prospects in medical diagnostics, biotechnology, and bioremediation during current climatic trends.

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Active Filaments, Membranes, and Cells

Thorsten Auth, Jens Elgeti, Roland G. Winkler, and Gerhard Gompper

Active matter exhibits a wealth of emerging non-equilibrium behaviors [1]. A paradigmatic example is the interior of cells, where active components, such as the cytoskeleton, are responsible for its structural organization and the dynamics of the various components. Of particular interest are the properties of active polymers and filaments [2]. The intimate coupling of active forces. thermal noise, hydrodynamic interactions, and polymer connectivity implies the emergence of novel structural and dynamical features.

Different propulsion mechanisms capture the physics of a variety of systems, such as chains of active Brownian particles [3], polar filaments propelled along their contours [4,5], or cytoskeletal filaments propelled by motor bundles [6]. This leads to interesting single-particle behavior, such as a softening of a semiflexible filament of active Brownian particles at intermediate levels of activity [3], or a sperm-like beating motion of a filament pushing a load. At high polymer densities in two dimensions, collective dynamics characterized by active turbulence is observed [5].

Closed polymer rings (in two-dimensions) can be considered as a model of membranes, where, active components lead to enhanced fluctuations [7]. For cells, motility arises from the pulling and pushing forces generated by the cytoskeleton. By studying a system of self-propelled filaments in a deformable membrane confinement, we show that motility is determined by an intimate interplay of propulsion forces, membrane deformability, cell shape, and sensing of and reactivity to the environment [8,9].

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EUSMI / SoftComp
General sessions

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Is gluten a polymer gel like any others?
A journey into the complexity of wheat proteins

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The origin of the unique rheological properties of wheat gluten, the water-insoluble protein fraction of wheat grain, is crucial in bread-making processes and questions scientists since the 18th century. Gluten is a complex mixture of two families of proteins, monomeric gliadins (Gli) and polymeric glutenins (Glu). To better understand the respective role of the different classes of proteins in the supramolecular structure of gluten and its link to the material properties, we have developed model gluten systems comprising controlled amounts of Gli and Glu in a food-grade good solvent for the proteins.

In this talk I will present experimental results using our model systems based on an approach that combines soft matter physics, food science and biochemistry. I will show that, despite gluten protein complexity, phase-behavior, and structural and rheological properties of gluten can be largely rationalized using theoretical models built up for synthetic polymers.

Overall, our experimental results will illustrate the relevance of model gluten gels to unravel the unique and complex behavior of gluten.

An atomistic description of interfaces using NMR

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Interfaces play a key role in soft matter materials, such as nanocomposites, colloids, thin-films or foams. The characterization of the structures and dynamics at atomic level near the interfaces of those systems is a powerful approach to improve the properties of these systems in a rational way. Solid-State Nuclear Magnetic Resonance (SSNMR) spectroscopy is suited to the study of interfaces because it can give information on the local structure. However, the lack of sensitivity of this technique poses limit for the characterization of surfaces.

Recently it has been shown that this issue can be circumvented by the use of high magnetic fields as well as the microwave-driven transfer of electron polarization to the nuclei, a phenomenon called Dynamic Nuclear Polarization (DNP). We have notably employed ^{1}H, ^{29}Si and $^{47,49}Ti$ solid-state NMR experiments to understand the coating of dendritic fibrous silica nanoparticles by TiO_2.[1] These silica-titania hybrid materials have been shown to be efficient photocatalysts. $^{47,49}Ti$ NMR spectra at 18.8 T indicate the formation of disordered TiO_2 anatase at the silica surface. Furthermore, the transfer of ^{1}H polarization to ^{29}Si nuclei reveals the rupture of Si−O−Ti bonds during the transformation of amorphous TiO_2 layer into anatase.

We have also introduced novel techniques for the selective observation of quadrupolar nuclei with $I \geq 1$, such as ^{27}Al, ^{17}O, ^{95}Mo and $^{47,49}Ti$, near surfaces. These techniques have been combined with DNP and employed to characterize the structure of surface and subsurface regions of MoO_3 supported on TiO_2 nanoparticles, a heterogeneous catalyst widely used for the oxidation of hydrocarbons and alcohols. The ^{17}O NMR spectra, acquired in natural abundance (0.038%), indicate the presence of uncoated TiO_2 surface associated to the formation of polyoxometalates or multi-layered MoO_3 and the existence of $HOMo_2$ and $HOMo_3$ acid sites.

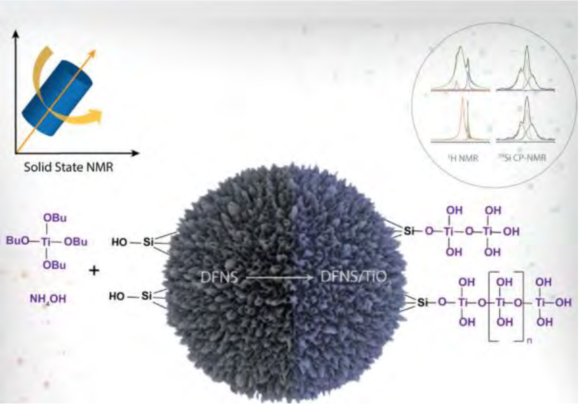

Figure 1. NMR observation of the interfaces of silica nanoparticles coated with TiO_2.

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H-bonding in Terpyridine Functionnalized Polymer Nanocomposites

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Beyond their usual combination with metal-ions[1,2], we show that terpyridine (TPy) functionalized polymers can be associated with inorganic particles to form transient networks via hydrogen bonding. These interactions are first evidenced by differential scanning calorimetry where a growing fraction in Fe_3O_4 nanoparticles (9, 18, and 24%) is seen to shifts-up and broadens significantly the glass transition of PnBA-TPy (+ 8 °C). On the contrary, no shift is observed when a neat PnBA matrix is used to prepare the corresponding nanocomposites. The formation of a physical network is then evidenced by rheological measurements highlighting the extra-friction caused by the TPy groups. Although the increase in nanoparticles content is seen to delay the relaxation mechanisms in all the materials, longer times and higher reinforcement are systematically observed in PnBA-TPy based nanocomposites than its homologous reference (Figure 1). We believe that this work opens the way to the formation of double supramolecular networks based on metal-ligand and H-bonds from a unique polymer.

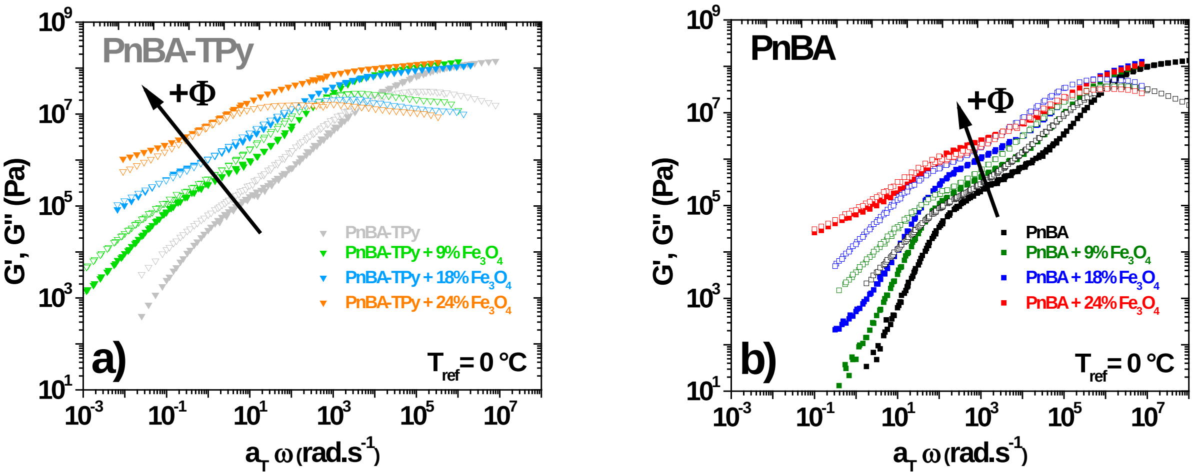

Figure 1. Effect of the particle content on *G'*, *G''* master curves built at 0 °C for a) PnBA-TPy and b) PnBA based nanocomposites.

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Induction Stimulated Phase-changing Rubber: Where does the heat come from?

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Rubber based materials suffer recently from a terrible reputation for being prominent materials in the waste generation. A third of the micro-plastic found in the oceans are actually believed to come from tires and other similar consumer goods.[1] However, these materials remain key for many applications making their production at the industrial level seemingly unavoidable. In this project, we address the question of the materials' reparation by designing a strong and phase changing rubber. Unlike supramolecular materials, they possess high strength and toughness in service, and rely on abundant ingredients: a thermoplastic polyurethane (segmented copolymer) and a responsive (nano-)filler. We voluntarily abandon the *self-healing* paradigm, to move to the *healing on-demand*, being more realistic for the production of truly healable materials endowed with high mechanical properties.

In this context, rubber healing consists in the dissociation of crystalline "hard" segments encompassed within the soft matrix, allowing the chain diffusion and the subsequent cicatrisation. Although this phenomenon is usually controlled through the external temperature, we propose to use induction heating to open new perspectives in this field (higher efficacy, contact-less technology, localized heating …).[2] Because the latter originates from different mechanisms according to the particles' chemical nature, size, and eventually viscosity of the environment [3,4] – it is key to understand them with the aim to optimize the (nano)composite formulation. To do so, we have performed a series of thermal imaging experiments (Fig. 1a), following the temperature of rubber pieces under a high-frequency induction field. We will discuss particularly the contribution of each mechanism to the overall heating of the material. (Fig. 1b)

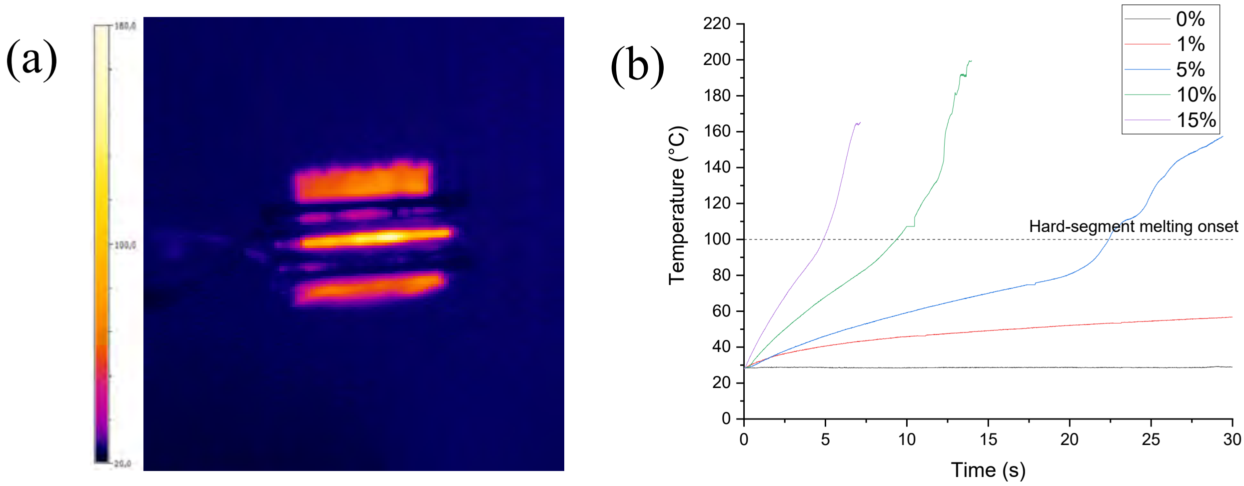

Figure 1. Induction heating performed in micro-Fe filled TPU. (a) Example of IR-based thermal imaging (double coil inductor). (b) Maximal temperature measurements of TPU filled with various amounts of filler along with time.

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Compression-induced anti-nematic ordering in glassy and semicrystalline polymers

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The effect of deformation mode on conformational and microstructural rearrangement of polymers, especially in the strain-hardening regime, still remains elusive. Using molecular dynamics simulations, we investigate the asymmetry between uniaxial tensile and compressive deformation of glassy and semicrystalline polymers. The difference between the two responses strongly depends on the chain length and is the largest at intermediate chain lengths. we provide new insights into the molecular origin of asymmetry between the two responses. The intra- and interchain organization of polymers under tension and compression are remarkably different. The chains align themselves along the tensile axis leading to a net global nematic order of the bonds and end-to-end vectors whereas under compression, the polymers arrange themselves in planes perpendicular to the compressive axis resulting in emergence of an anti-nematic order of the bonds and end-to-end vectors. Moreover, the degree of polymers unfolding is greater under tension and they deform less affinely in comparison to chains under compression.

Dynamics of thin liquid films: Implications for beer foam stability

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Beer foam stability is believed to be enhanced by a rigid protein-stabilized thin liquid film (TLF) formed between two neighboring CO_2 bubbles. Such a film is expected to hinder drainage, coalescence and even Ostwald ripening [1], which are the main foam destabilization mechanisms. Although the synthesis or addition of certain proteins during the brewing process is common industrial practice, the mechanism by which they act still remains unclear. We present a combined experimental-numerical study to unravel the mechanisms by which beer foam can be stabilized.

The thin film drainage of three commercial beers was evaluated experimentally using a newly developed variation of the thin film balance technique coupled with interferometry [2]. The influence of surface tension, particle size, bulk and interfacial rheological properties on TLF stability was assessed by Wilhelmy-plate tensiometry, dynamic light scattering, double-wall ring interfacial rheometry and bulk viscosity measurements.

The surface tension and the bulk viscosity of the different beers did not show large variations. However, their drainage behavior differed significantly. Increased film stability, highly heterogeneous film thicknesses and slower thinning rates were observed for the beers of higher fermentation. Although the comparison between the experimental drainage curves and the predictions of the Reynolds model [3] indicates that the interfaces are highly stress-carrying, the mechanism of stabilization was found to differ. For two of the beers, it was observed that the drainage time increases with the interfacial shear viscoelasticity, while the most stable one was stabilized through Marangoni stresses.

These effects were investigated in more detail by performing simulations using the finite element method, which solves the full set of flow- and transport equations. It is shown that film drainage can be delayed by orders of magnitude, as compared to clean surfaces, by two distinct mechanisms: 1) an inhomogeneous surfactant distribution, leading to Marangoni stresses and 2) surface viscosity effects, possibly including anisotropic surface stresses. If both of the mechanisms are present, a non-trivial coupling is observed, which was systematically investigated.

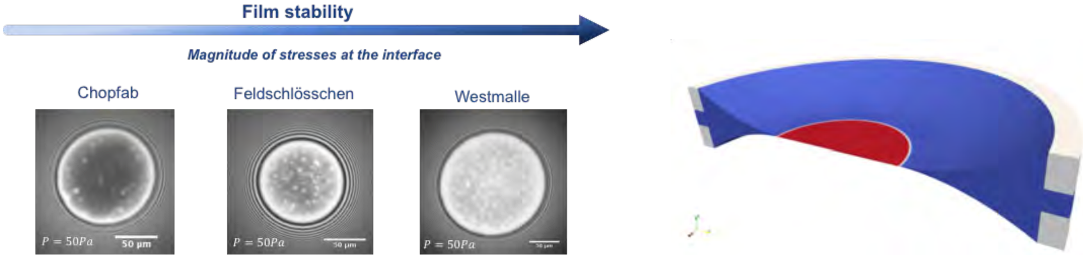

Figure 1. Left: Microinterferometry images of the films of the studied beers and right: FEM simulation of the drainage of a thin liquid film. The color indicates the pressure.

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The role of extensional viscosity in the expansion dynamics of sheets formed by drop impact of a viscoelastic thinning fluid

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When a drop of a viscoelastic fluid hits a solid surface in minimal dissipations conditions, (achieved using either a small solid target or a repellent surface), it expands radially until reaching a maximum diameter and subsequently recedes. Experiments indicate the presence of two expansion regimes: the capillary regime, where the maximum expansion does not depend on the fluid's zero-shear viscosity, and the viscous regime, where the expansion is reduced with increasing zero-shear viscosity due to viscous dissipation. Two classes of viscoelastic fluids have been investigated: (i) solutions of living polymers of various concentrations, an (ii) simple homopolymer of very high molecular weight solutions. Both exhibit strong shear thinning in the non linear regime. In the viscous regime, we we find that the *equibiaxial* viscosity is the appropriate quantity to describe the maximum expansion of both viscoelastic and viscous sheets. For solutions of viscoelastic thinning fluids, shear dissipation is negligible compared to extensional dissipation. We propose an approach towards a rational description of the phenomenon for Newtonian and non-Newtonian fluids by evaluating the viscous dissipation due to shear and extensional deformations, yielding a quantitative prediction of the maximum spreading factor of the sheet as a function of the relevant viscosity. For solutions of viscoelastic thinning fluids, we demonstrate that the biaxial viscosity is the appropriate quantity to rationalize the maximum expansion of the sheets.

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Water Dynamics and Self-Assembly of Single Chain Nano-Particles in Concentrated Solutions

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Single-chain polymer nano-particles (SCNPs) are soft nano-objects consisting of uni-macromolecular chains collapsed to a certain degree by intramolecular crosslinking [1]. The similarities between the behavior of SCNPs and that of intrinsically disordered proteins suggest that SCNPs in concentrated solutions can be used as models to design artificial micro-environments, which mimic many of the general physical and chemical aspects of cellular environments.

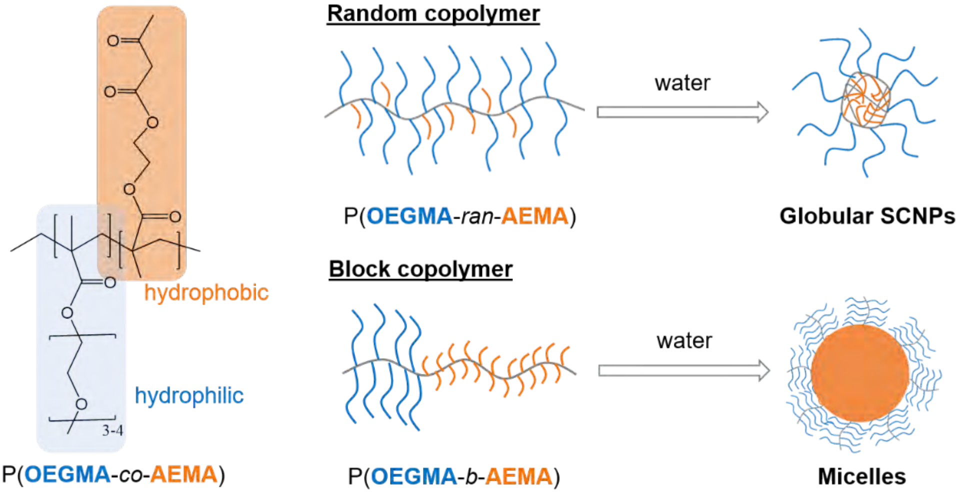

Figure 1: Schematic representation of P(OEGMA-*ran*-AEMA) and P(OEGMA-*b*-AEMA) molecules and their self-assembly into SCNP and micelles in water.

In this work, the self-assembly into SCNPs of an amphiphilic random copolymer, composed by oligo(ethylene glycol) methyl ether methacrylate (OEGMA) and 2-acetoacetoxy ethyl methacrylate (AEMA) (see Figure 1), has been investigated by means of the dielectric relaxation of water. Direct evidence of segregation of the AEMA repeating units is provided by comparison with the dielectric relaxation of water in similar solutions of the linear hydrophilic polymer, P(OEGMA). Furthermore, the results of comparative studies with similar water solutions of an amphiphilic block-copolymer forming micelles support the single-chain character of the self-assembly of the random copolymer. The overall obtained results confirm the self-assembly of the amphiphilic random copolymers into globular like core-shell single-chain nanoparticles at a concentration well above the overlap concentration.

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Spontaneous surface wrinkling for tuneable gratings and photonics application

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Naturally occurring surface topographies, such as those found in animals and plants, often exhibit properties including super-hydrophobicity, drag reduction, antimicrobial resistance and structural colour that are desirable in a number of practical applications. Depending on the pattern morphology, optical effects ranging from tuneable diffraction/reflection to photonic bandgaps can be observed. Spontaneous wrinkling of bi-layered materials allows for the facile and precise patterning of periodic structures ranging from 10s of nm to 100s of μm and beyond. Wrinkling occurs spontaneously when a bi-layer system of a stiff film on a soft substrate undergoes a compression upon exceeding a critical strain value. Here, we systematically investigate the manipulation of light propagation with different surface patterns formed via spontaneous wrinkling of bi-layer systems generated via plasma oxidation of polydimethylsiloxane (PDMS). This process generates a thin glassy layer on top of the soft elastomeric substrate under a controlled strain field. Once the stress is relieved, ordered sinusoidal and higher order patterns can be generated by adjusting the plasma parameters and strain field.[1-3] More complex patterns can be attained under multi-directional strains, providing a route to mimicking natural surfaces. In this work, we systematically investigate model wrinkled surfaces as tuneable diffraction gratings, employing PDMS plasma oxidation rather than film floating [4] to create bilayers. Plasma-induced glassy conversion of PDMS is a directional process yielding a conversion front whose impact on optical response has not been investigated. Laser light diffraction experiments were carried out as function of strain and glassy skin thickness, as well as strain field order parameter, enabling us to resolve film nano/microstructure and demonstrating the potential of this method.

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Spinning drop dynamics in miscible and immiscible environments

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Rotating droplets are among the most studied cases of liquids deformed by an external field as they are relevant in many situations: rotation plays a pivotal role on the structure and evolution of large-scale flows taking place in oceans, atmosphere and in the very body of planets and stars. Freely-suspended droplets rotating at high speed tend to deform due to centrifugal forcing. Droplets change shape following a minimum energy principle, taking the lowest energy state for a given rotational frequency.

While several experiments suggest that largely deformed spinning drops in immiscible fluids relax exponentially towards an equilibrium shape after a jump of centrifugal forcing, a quantitative description of the relaxation time and a clear understanding of the relevant parameters that determine its value are still missing. On the other hand, research on drops in a miscible background fluid is much less advanced. A full experimental characterization of drops showing pure extensional dynamics has never been reported: indeed, in most cases miscible drops undergo also a radial deformation due to secondary flows that set in a spinning capillary [1] and this greatly complicates both measurements and modelling.

By using a customized spinning drop tensiometer we have investigated the extensional dynamics of spinning drops in miscible and immiscible background fluids following a rotation speed jump.

By investigating both miscible and immiscible fluids we have observed two radically different behaviors. Drops in immiscible environments relax exponentially to their equilibrium shape, with a relaxation time that depends only on the interfacial tension, the viscosity of the fluids and the drop volume [2]. We find an excellent quantitative agreement with the relaxation time predicted for quasi-spherical drops by Stone and Bush [3], while other models proposed in the literature fail to capture our data. By contrast, drops with a low concentration gradient with respect to a miscible background fluid do not relax to a steady shape: they elongate indefinitely, their length following a power-law $l(t){\sim}t^{2/5}$ [2] in very good agreement with the dynamics predicted by Lister and Stone [4] for inviscid drops.

These results represent a solid starting point for studying spinning drops in miscible fluids with large compositional gradients, where we may expect the presence of non-negligible capillary effects [5,6]. In such a case we have found that the shape of a miscible drop continuously evolves, in contrast to the saturation effect reported in previous investigations that explored a smaller temporal range [7]. Furthermore, drops assume systematically a dumbbell shape, that, during elongation, is not only determined by the density and viscosity contrast between the drop and the surrounding fluid, but strikingly also by their chemistry. This crucial result rules out the possibility that the drop dynamics are purely dictated by hydrodynamics and strongly hints at the existence of an effective interfacial tension [5,6] in molecular liquids.

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Molecular Exchange in Clusters and Flowerlike Micelles

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In this contribution we present a study on molecular exchange in clusters and flowerlike micelles by time-resolved small angle neutron scattering. In a previous work we have investigated the structure of mixtures of poly(ethylene oxide)-mono and di n-alkylethers, C_n-PEO5 and C_n-PEO10-C_n in water by SANS. The data reveal that for large $n > 22$ the solution contains individual flowerlike micelles while for smaller $n \leq 22$ predominantly clusters of micelles are found. [1]

The main focus of the present work is to study exchange kinetics of telechelic chains in these self-assembled structures. Since pure C_n-PEO10-C_n triblock polymers in water tend to phase-separate in dilute and semi-dilute concentrations we have used mixtures of diblocks and triblocks, C_n-PEO5 and C_n-PEO10-C_n with n=22,28), which form homogeneous solutions at low concentrations. Generally, we expect from the kinetic study microscopic information about the exchange dynamics in particular from the triblocks which should help to understand macroscopic recovery and self-healing processes in physically cross-linked networks. Chain exchange was accessed by TR-SANS employing the kinetic zero average contrast technique developed at JCNS. [2] The results show that the characteristic time τ_{di} and the activation energy $E_{a,di}$ of the diblock is exactly identical in the mixture and in pure diblock micelles. As expected the characteristic time of the triblock, $\tau_{tri} > \tau_{di}$ is significantly larger but , interestingly, with the same activation energy: $E_{a,di} = E_{a,tri}$.

These results may be explained by a sequential expulsion of the hydrophobic block from the micellar core. For the case of a simultaneous release of both chain ends the activation energy would be twice $E_{a,di}$. The characteristic time on the other hand is slower for the triblocks as two alkanes need to leave the core to get a successful intermixing of chains. In earlier studies we found that in dilute solution the exchange is concentration independent indicating single unimer exchange as the main mechanism. [3] In contrast to the exchange of diblocks the exchange of the triblocks is clearly concentration dependent. This can be pictured by a "walking" mechanism [4], where the diffusion between different micelles proceeds stepwise with always one chain end belonging to a micellar core. This mechanism becomes faster the smaller the mean distance between micelles and thus should depend on concentration. Free diffusion of telechelic chains with both ends in solution is obviously energetically unfavored. This may also explain that there was no fundamental difference observed in the exchange between block copolymers forming flowerlike micelles or clusters.

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Direct Observation of the Time-dependent Dynamic Tube Dilation in Entangled Polymer Blends

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The viscoelastic properties and processing conditions of high molecular weight polymers are given by their entanglement dynamics. It is well known that in asymmetric polymer blends, the finite lifetime of constraints leads to a dilation of the tube. However, less in known about how the tube dilates. Here, we show the microscopic observation of the time-dependent dynamic tube dilation process on bidisperse melts. By combining neutron spin echo (NSE), rheology and dielectric techniques on blends of long polyisoprene (PI) chains with short PI additives with different topology, we access the dynamics of the tube dilation process on a molecular scale. The time-dependent tube dilation can be directly inferred from the NSE data. It shows itself in an additional time dependence of the dynamic structure factor in the local reptation regime. We identify the characteristic time of tube dilation as the terminal time of the short component.

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New rheometric tools for advanced soft matter research

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A broad range of standard rheological tests are used to characterize the rheological behaviour of soft matter. Nevertheless there are still limitations, or parameters which haven't been considered extensively until now. Aim of the contribution is to highlight several new testing capabilities and tools suited for soft matter research.

A rheometer platform based on a combined motor transducer (CMT) rheomter equipped with an electrically commutated synchronous motor on the upper side facilitates the use of a second motor on the bottom side. The second motor could either be a rotational or a linear drive. By using a rotational motor as a drive and the second as a torque transducer the device is turned into a separate motor transducer (SMT) rheometer. A SMT mode has some advantages in sensitivity under certain measurement conditions and allows the use of special tools such as for example a cone-partitioned-plate (CPP), which enables measurements even if edge fracture would hinder them in standard geometries. In addition it can operate in a counter rotational mode, where both motors rotate or oscillate in opposite directions and thus enabling the creation of a stagnation line in the sample at which it is sheared but not moved from its position. Counter rotation is especially useful for the investigation of Tayler-Couette instabilities or for rheo-microscopy, since the structures under investigation are not moving out of the field of view when shear is applied. Co-rotating of both motors with different rotational speeds applies a shear while the whole geometry is rotating. Such a mode was used e.g. to recover the full volume microstructural evolution of dense granular suspension by ultrafast X-Ray tomography while controlling or measuring all relevant macroscopic rheological parameters. Combining the upper rotational motor with a linear drive in the bottom permits new testing capabilities such a Dynamic Mechanical Analysis (DMA) testing on more solid like samples or, by using both the rotational and the linear drive in a synchronized fashion during the same experiment, orthogonal superposition rheology, in which the rotational motor applies a steady shear and the linear motor applies an oscillatory motion in orthogonal direction, as well as 2D-SAOS, where both drives perform oscillatory testing, is possible.

Shear-induced polarized light imaging (SIPLI) - provides a unique opportunity to monitor a complete sample during rheological measurements. SIPLI has been used e.g. for oriented lamellar phase of block copolymers, cellulose nanocrystals and liquid crystals as well as for investigations on flow-induced crystallization of semi-crystalline polymers. Combined rheo-Raman spectroscopy is another new rheo-optical technique for following chemical or structural changes simultaneously to rheological measurements.

The VGA-FLC: A grating-aligned ferroelectric liquid crystal electro-optic shutter for fast-switching and shock-resistant applications

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Ferroelectric liquid crystals (FLCs) were a highly popular research subject for the display industry in the 1980s and 1990s, due to their sub-millisecond switching times and inherent bistability [1]. Such materials are susceptible to shock induced flow, rendering them unsuited for large area displays. Their fast switching speed remains desirable, for instance allowing frame sequential colour in projector display applications. Liquid Crystal on Silicon (LCoS) spatial light modulators based on FLCs are commercially successful and are far less sensitive to shock, but new shock-insensitive modes are still important to develop.

A simple but novel geometry for FLC electro-optic shutters is presented, based on near-sinusoidal surface-relief gratings to controllably align the FLC **c**-director: the VGA-FLC. The gratings are surface treated to induce a homeotropic, or vertical, alignment to the FLC layer normal. Such alignment exhibits greater shock stability due to the initial alignment of the smectic layers relative to the direction of the induced liquid flow. When this geometry is pressed, flow remains in the cell plane such that there is no distortion to the layers, and just to the **c**-director. The grating provides a preferred orientation for the **c**-director to which the director returns after a mechanical or electrical shock, seemingly self-healing. When combined with interdigitated electrodes the device switches between dark and bright states at sub-microsecond times. This relatively simple geometry has led to a working prototype of a device that demonstrates both resistance to mechanical shock as well as millisecond switching times. Improvements are suggested that will help optimise the device. A schematic diagram of the components and construction of the device is shown in Figure 1.

On optimisation, the VGA-FLC device has great potential for use in LCoS spatial light modulators, for use in high-speed adaptive optics, head-mounted displays for virtual/augmented reality and telecommunications.

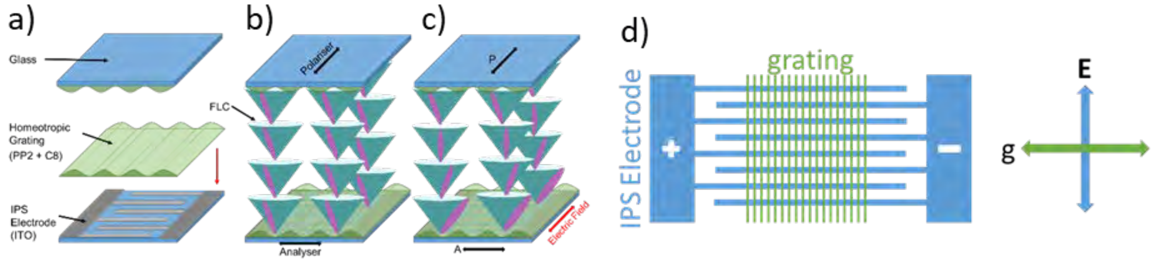

Figure 1: A schematic diagram of the prototype devices' geometry. a): the orientation of the gratings with respect to the in-plane electrodes. b): the device in the OFF/dark state, with no applied electric field, where the ***c****-director is homogeneously aligned through the cell. c): the device with a sufficiently strong electric field applied to rotate the* ***c****-director* 90° *through the cell. d): A 2D schematic diagram representing the orientation of the IDE w.r.t. the grating vector,* ***g****.*

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SELF-ASSEMBLY AND DYNAMICS OF ELLIPSOIDAL COLLOIDS AND THE INFLUENCE OF AN EXTERNAL MAGNETIC FIELD STUDIED BY SAXS AND XPCS

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Anisotropic colloids are known to exhibit a rich phase behaviour. In addition to the usual gas, liquid, crystal and glassy states found for spherical particles, anisotropic particles such as rods are known to exhibit additional liquid crystalline phases. Here we present the self-assembly and dynamics of ellipsoidal colloids in the presence and absence of an external magnetic field. Being made up of hematite cores and silica shells, these particles align in a direction perpendicular to the applied magnetic field. In the absence of the external field both the diffraction patterns and the dynamics are isotropic over the concentration range studied. However, once the field is switched on the particles not only align perpendicular to the field direction but also self-assemble into different liquid crystalline phases like nematic and smectic. The self-assembly and (an)isotropic dynamics of these particles are investigated over a wide concentration and magnetic field range using SAXS and multispeckle ultrasmall-angle X-ray photon correlation spectroscopy (USAXPCS). We also explore the relation between the resulting diffusion coefficients and the structure factor of the self-assembled structures. The results indicate that both along and perpendicular to the field direction, the particle dynamics strongly depends on the structure factor, exhibiting a clear *de-Gennes narrowing*. Further, the diffusion coefficients at the nearest neighbour length scale slow down considerably at high concentrations as expected both with and without an external field.

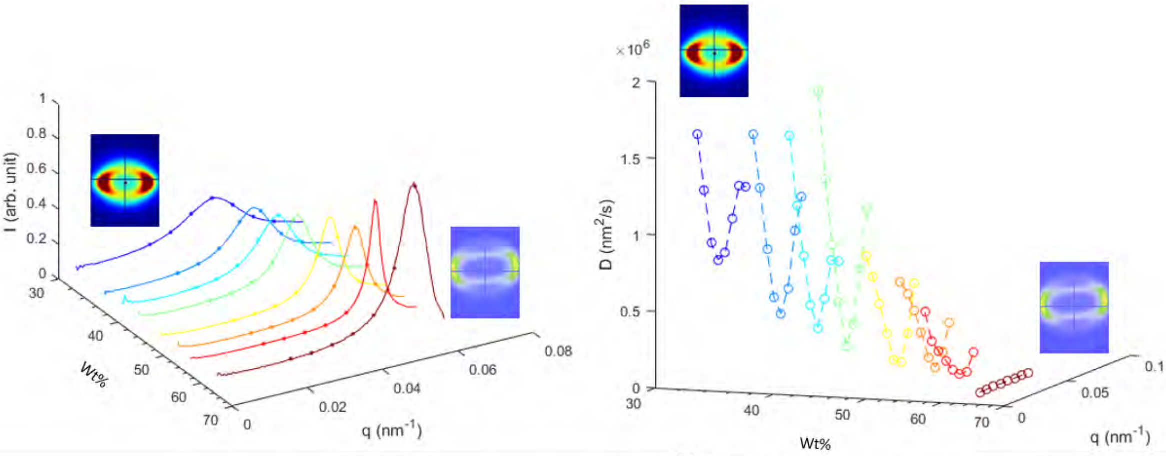

Fig1. Left: Scattering intensity (I) as a function of q for different concentrations (wt%) of the particles; insets show the diffraction patterns for the lowest and highest concentrations. All the data correspond to 1000mT and along the direction of the field.
Right: Diffusion coefficients (D) at particular values of q (indicated by the dots on the intensity profiles in the left graph). Different colors correspond to different wt% of the particles.

Stabilisation of water-water emulsions (PEO-dextran) by linear homo-polyelectrolytes

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Emulsions are formed when to non-miscible liquids are mixed, the most known are oil-in-water emulsions (cosmetic cream) or water-in-oil emulsions, but it also is possible to make other types of emulsions such oil-in-oil or water-in-water (W/W) emulsions. To obtain the latter, two aqueous solutions of incompatible polymers are mixed. In order to use these kinds of emulsions for instance in the food industry, one has to stabilize them. Unlike oil-water emulsions, the use of molecular surfactants to stabilize W/W emulsions is not possible, because they have a very low interfacial tension and a broad interface.

Stabilization of W/W emulsions are well studied in the literature, mainly by gelling of the continuous phase, or by using particles as interface stabilizer, so-called Pickering effect. In this study, the objective was to stabilize W/W emulsions by polymers have an affinity with both phases and locate at the interface.,For that purpose, we used a model emulsion made of PEO (P) and dextran (D) as incompatible polymers. It was found that out of 16 polymers tested, mainly polysaccharides, only three show a stabilizing effect of emulsions: chitosan, diethylaminoethyl dextran (DEAED) and propylene glycol alginate (PGA).

Chitosan and PGA showed a better stabilization of D in P than P in D emulsions whereas DEAED was able to stabilize both D/P and P/D emulsions. Interactions of these polymers with PEO and dextran were investigated with light scattering and the microstructures was studied by confocal laser scanning microscopy. The effects of pH, ionic strength, interfacial tension and polymer concentration were studied to understand mechanism of stabilisation.

Dynamics of Arrested Phase Transition in Protein Solutions Studied by X-ray Photon Correlation Spectroscopy

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In protein and colloidal solutions, the interplay between liquid-liquid phase separation (LLPS) and glass formation can lead to a dynamic arrested state [1-3]. While the kinetics of this process has been advanced in recent studies, little is known about the dynamics of domains approaching and in the arrested state. Here we report a study using X-ray photon correlation spectroscopy (XPCS) in USAXS model with a tunable delay time. We use a bovine gamma-globulin (IgG) and polyethylene glycol (PEG) mixture as a model system which features a LLPS upon quenching [2]. By recording the two-time correlation functions in different time periods (Fig.1a), we are able to following the dynamics of domains (micrometer length scale) during coarsening and under arrest. The intermediate scattering function can be well described using the Kohlrausch-Williams-Watts (KWW) equation with double exponentials featuring an exponent around 1.5 which is typical for driven-phase transitions. The relaxation time as a function of aging time shows clearly two stages with an exponential increase in the early stage and a much slower power increase in the later stage (Fig.1b), in good agreement with the literature on dynamics of aging and gelation process [4,5].

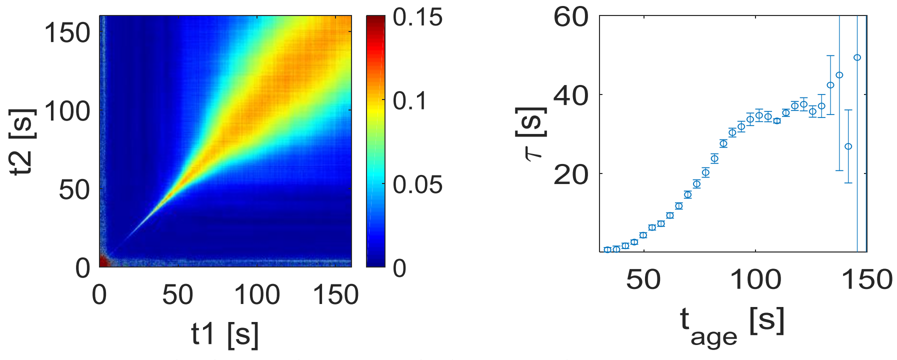

Figure. 1. (a) Typical two-time correlation function from XPCS measurements for an IgG-PEG mixture during LLPS at -2ºC, and the corresponding relaxation time as a function of aging time.

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Stable oil-in-water emulsions using an hydrophobically modified xanthan

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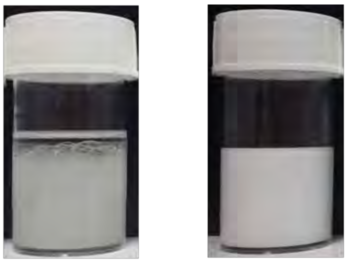
Polysaccharides are widely employed in many industries such as food or cosmetic mainly to stabilize oil-in-water emulsions and to control their rheological properties. Among the others, xanthan gum is the most used due to its outstanding thickening properties of aqueous solutions. However, because of its poor interfacial properties, it requires the addition of an emulsifier to disperse and stabilize the oil droplets. Unfortunately, the use of low molecular weight surfactants has many disadvantages related to toxicological and environmental considerations. On this basis, macromolecular surfactants have been developed during the last decades, most being synthetics while the nowadays demand of natural ones is considerably growing. To overcome this problem, octyl residues were grafted onto the backbone of xanthan to confer new amphiphilic properties [1]. Moreover, xanthan can adopt two different conformations [2], with distinct rheological properties [3] depending on the experimental conditions: an ordered semi-rigid helical structure or a disordered flexible coil.

The objective of the present work is to study and understand the phenomenon involved in the stability of oil-in-water emulsions containing amphiphilic xanthan.

Oil-in-water emulsions using no surfactant but containing pristine or modified xanthan have been studied and compared. As expected in emulsion, unmodified xanthan is not able to stabilize the emulsions as phase separation occurred within only few hours. Oppositely, emulsions obtained with modified xanthan are stable over months (see fig. 1). These results clearly demonstrate the high potential for hydrophobically modified xanthan as emulsion's stabilizer which has been studied as a function concentration and grafting density [4].



Emulsion with xanthan after 1 day

Emulsion with modified xanthan after 2 months

Figure 1: Oil in water emulsions containing 1g/L of pristine xanthan one day after preparation (left) and modified xanthan 2 months after preparation(right)

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Tailor-made covalent nanocomposites based on magnetic nanoparticles and elastic polymers

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The incorporation of magnetic nanoparticles into polymeric matrices, such as gels and elastomers, leads to magnetically tunable hybrid materials. By employing magnetic nanoparticles as multifunctional, inorganic crosslinkers, we obtain magnetic node networks with a novel particle-matrix interaction due to a direct covalent coupling between magnetic and elastic component.[1, 2] Moreover, direction-dependent properties are induced in these magnetic node networks by incorporation of magnetic nanoparticles, that show as well geometric as magnetic anisotropy.

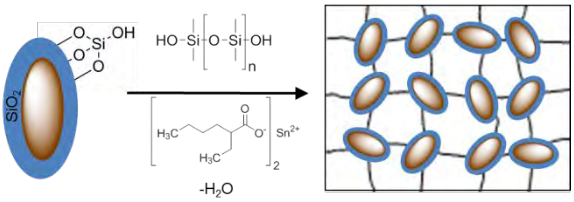

Fig. 1. Reaction scheme for the formation of particle crosslinked elastomers.

Here, we present the synthesis of magnetic node networks based on spindle-like α-Fe_2O_3 particles in an elastomeric matrix. These materials are prepared by a polycondensation reaction, schematically shown in Fig. 1, leading to a network formation based on a large number of effectively connecting polymer segments per magnetic node particle. Due to the covalent attachment of the magnetic nanoparticles to the elastic matrix, homogenous elastomers with high particle contents of up to 35 m% can be achieved.

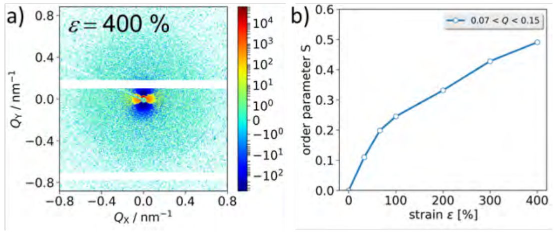

Fig. 2. a) 2D difference scattering pattering of the sample at ε = 400 %. b) Order parameter S depending on the applied strain.

The mechanical properties of the magnetic node networks strongly depend on the particle volume fraction. With increasing particle volume fraction, an increasing Young´s modulus and a decrease of the strain at break are observed, attributed to both a variation of the crosslinking density and a particle filler effect, respectively. In small angle X-ray scattering (SAXS) experiments, upon increasing the strain anisotropic 2D scattering patterns are observed, attributed to the orientation of the anisotropic crosslinker particles with their long axis parallel to the strain vector (Fig. 2.). By analysis of the azimuthally averaged scattering intensity, we extract the order parameter that shows steady increase with the applied strain. The hybrid elastomer thus offers a tunable, strain-dependent anisotropy.[3] In magneto-rheological experiments, a field-induced increase of the storage modulus of up to 60 % is observed. This magneto-rheological effect is attributed to a decrease in the rotational mobility of the crosslinking particles due to their interaction with the applied field.

As shown, by the incorporation of spindle-like hematite particles into these elastomers, direction-dependent properties are induced which are a key step for the realization of actuators showing a reversible contraction along one axis.[4] This new type of smart polymeric material is expected to have promising applications for dampers or in robotics, where the mechanical properties need to be reversibly manipulated.[5]

Acknowledgments

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Elaboration and characterization of aqueous colloidal suspensions of C_{60} fullerene stabilized by an amphiphilic copolymer

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Mots-clés : C_{60} fullerene, amphiphilic copolymers, light scattering, hydrogels

Since the end of last century, fullerenes (C_{60}) have been widely studied for their potential applications in biomedicine and electrochemistry [1]. However, their dispersion in water is difficult and can be improved by mechanical stirring or using ultrasound which often requires the use of a surfactant to achieve stable colloidal particles based on aggregated fullerenes. [2,3].

We propose to use an amphiphilic copolymer instead (Fig.1) in order to promote various kinds of interactions between the polymer and fullerenes (hydrophobic, π-stacking).

To produce these colloidal suspensions, we will explore the ultrasound as described earlier, and the Ouzo effect, which results in the spontaneous formation of a colloidal dispersion by dissolving an apolar specie (C_{60}) in a polar organic solvent and quickly pouring water in this solution [4].

The obtained colloidal suspensions will be studied by UV-visible spectroscopy and light scattering. The final goal is to incorporate these nanoparticles into a hydrogel in order to reinforce it which will result in an organic/organic nanocomposite.

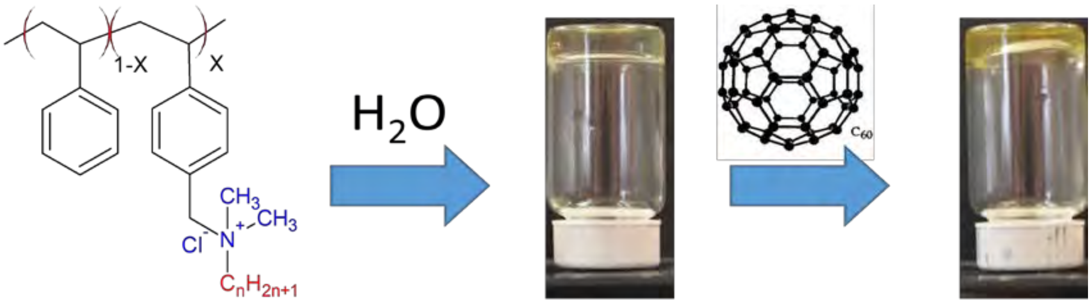

Figure 1 : Structure of the amphiphilic copolymer and hydrogels with and without C_{60}

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Abstract for oral contribution, EUSMI/SoftComp general session

Locally-resolved ionic conductivity of polymer electrolytes thin films

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Recently, AFM-based electrical measurements in polymers are increasingly used to map the nanoscale conductivity in systems with potential applications, as nanocomposites, semiconductors and electrolytes. Most of the current electrical techniques require setting-up an electrical contact with the polymer surface, usually done by bringing the AFM probe into direct contact with the sample. However, since polymers are soft materials, most of the suitable techniques require the use of intermittent contact AFM protocols, to avoid sample scratching and plastic deformation. In this work, we present an intermittent contact AFM technique that allows the electrical mapping of polymer surfaces. nanoDielectric Imaging (nDI) works by applying an AC bias to the AFM probe at a fixed electric field frequency (f). The technique provides nanoscale maps with information related to the components of the complex dielectric permittivity ($\varepsilon^*(f)$) of the samples. With this approach, we can achieve a lateral resolution better than 40 nm. In addition, it is possible to carry out frequency dependent dielectric measurements (f = 1 Hz – 100 kHz) at fixed points on the sample's surface [1,2]. These measurements (nanoDielectric Spectroscopy (nDS)) provide the information about the site-dependent molecular dynamics and charge-carrier motions in the system. As a case of study, we will present dielectric experiments on poly(ethylene oxide) (PEO) thin films. PEO is a semicrystalline polymer that at room temperature shows a dielectric relaxation signal related to charge trapping between amorphous/crystalline interfaces. This phenomenon is connected to the ionic conductivity of the amorphous phase of the material. We will present nDI maps and nDS frequency dependent spectra of PEO thin films at room temperature, and in a humidity range of 15 – 60%. The ability of performing humidity-controlled experiments were developed and carried out under the EUSMI program. Our results allowed providing relevant physical parameters such as the DC-conductivity of the amorphous phase, and its dependence with relative humidity.

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Colloids on curved surfaces: migrating matter

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In uniform three-dimensional space and flat two-dimensional space, the various states of matter can exist anywhere because of the translational and rotational invariance of space. In two dimensions, the introduction of uniform curvature (the surface of a sphere) can strongly affect structure, phase transitions and dynamics of particles confined to the surface [1-3], but all locations are still equivalent. In contrast, on non-uniformly curved surfaces, different states of matter may have structural or thermodynamic preferences for regions of different curvature [4]. Hence, phase transitions may be accompanied by the migration of matter to a new position. In this talk, I will use specially designed simulations to investigate this coupling of phase and location for colloids on toroidal and sinusoidal surfaces. We predict that migration at phase transitions could arise in any non-uniformly curved soft-matter system including templated surfaces and biological membranes. Furthermore, the nature of the coupling is strongly influenced by the range of the attractive interactions between the particles.

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3D SERS imaging of complex biological structures

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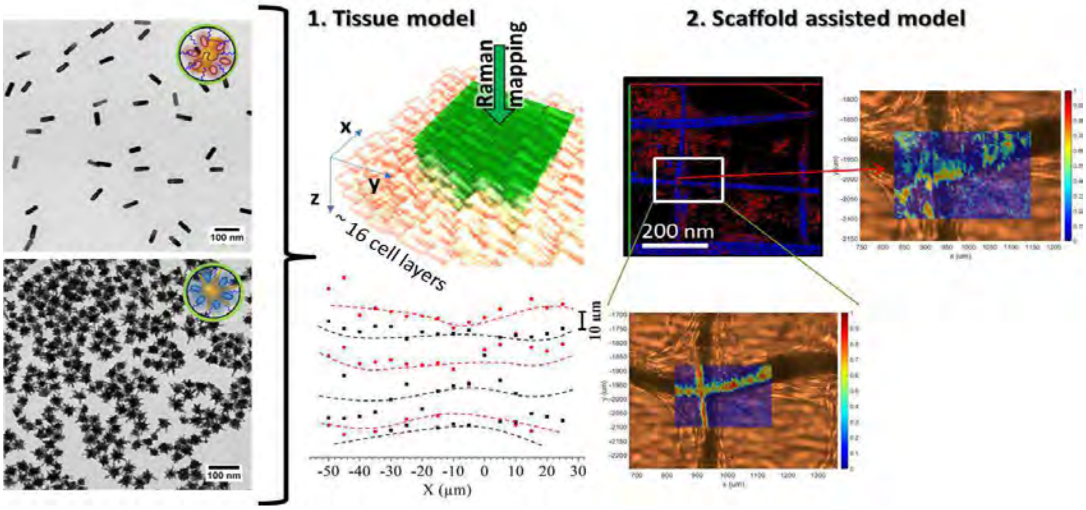
3D cell culture models are increasingly taking importance in medical research, given the need to create models that better represent the situation occurring in tissues and real situations. There are different methods to produce such 3D cell models, such as self-assembly of cells (spheroids), bioreactors, or assisted by scaffolds that can be produced using 3D printers.[1,2] These sophisticated models not only require improvements in cell engineering techniques, or the development of new materials, but also advanced imaging tools to accurately characterize them, hence providing fast and precise diagnostics and follow-up care.[3] To image such systems, high penetration depth, no photobleaching and minimum signal overlap is desired. Thus, confocal surface-enhanced Raman scattering (SERS) imaging has revealed itself as a promising alternative technique to monitor 3D cell ensembles. Commonly, this method involves the use of SERS-labelled plasmonic nanoparticles, called "SERS tags", as contrast agents. We developed a robust synthetic method to fabricate SERS tags which are responsive to NIR illumination, thereby providing deeper penetration depth in biological systems. [4,5]

Even though confocal SERS imaging is emerging as a promising imaging technique, further progress is still needed.[6] In order to understand the capabilities of the technique, we first studied a 3D cell model consisting of Human dermal fibroblasts pre-incubated with SERS tags, forming a layered or "sandwich" structure. A second, more complex system, comprises the culture of cells within a SERS-labelled scaffold. We aim at monitoring the growth of cells over time, inside a tessellated scaffold. Thanks to the non-invasive character of SERS, which avoids the need for fixing cells, imaging was conducted using a NIR laser (785nm) over various days.



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Complex relaxation behaviour in crowded solutions of eye lens proteins

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An essential optical constituent of the mammalian eye is the lens, which contains an aqueous mixture of concentrated proteins, known as crystallin proteins. These proteins and their interactions guarantee the high index of refraction, transparency and deformability of the lens, which are required for the eye's function. Within the lens fluid, three major protein fractions exist: α, β and Ɣ crystallin. Common pathologies such as cataract or presbyopia have been the major drivers in lens protein research. Our current understanding is that they are linked to phase transitions, and that the proteins undergo condensation and/or liquid-liquid phase separation in the case of cataract, and an arrest transition in presbyopia. However, while liquid-liquid phase separation has been on the focus of the research community for decades, much less is known about the dynamical properties of concentrated lens protein solutions.

We have thus performed a systematic investigation of the dynamics of lens protein solutions and mixtures ($\alpha + \beta$ crystallin and $\alpha +$ Ɣ crystallin) at different volume fractions as a model systems for the eye lens. We combine dynamic and static light scattering, neutron spin echo measurements, X-ray photon correlation spectroscopy and microrheology in order to obtain the required dynamic information over a large range of time and length scales. Overall, collective diffusion coefficients exhibit a non-additive contribution by the single proteins, suggesting significant protein interactions that affect gradient diffusion at elevated volume fractions. A particularly interesting feature can be observed in *q*-dependent DLS experiments on α- crystallin solutions and protein mixtures close to the glass transition, which show unequivocally three relaxation modes, all characterized by diffusive dynamics. According to previous investigations [1], DLS results on α crystallin showed two characteristic relaxation modes attributed to the so-called *caging* effect, consistent with polydisperse hard spheres. Hence, the nature of the third relaxation process remains unclear. Additional systematic large-scale computer simulations are therefore performed, in combination with colloid theory such as mode-coupling theory, in order to shed light on these surprising findings and arrive at a comprehensive picture for dynamical arrest in eye lens solutions.

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Mucus microscopic dynamics under controlled strain

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Mucus is a thixotropic gel whose complex organization on different length scales is at the basis of its biological functionality. The main component responsible of its functionality is a glycosylated protein called mucin, which has marked interactional properties. The network formed by mucin macromolecules has a transient nature where bonds are incessantly broken and reformed under the action of internal and/or external loads. Here we present a consistent picture of the mucus dynamics under the action of an applied external strain. Data are obtained combining rheological stress-relaxation tests in torsion to simultaneous DLS measurements collected through transparent plates.

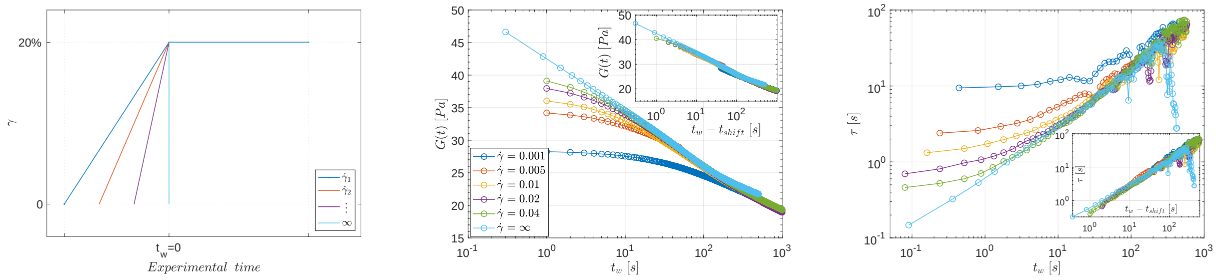

Figure Coupled Rheo-DLS relaxation data at 20% strain for different strain rates: (left) applied deformation; (central) Shear modulus versus waiting time; (right) Characteristic relaxation time ($\tau_{0.5}$) versus waiting time. Insets report rescaled data with respect to a common shifting time t_{shift}.

The picture emerging from the experimental data indicates the presence of a wide distribution of relaxation times, which entirely regulate the micro and macroscopic behavior of the mucus. We speculate that the structural disorder and the transient nature of the mucin bonds are responsible of the observed distribution of relaxation times. We believe that the elucidated mechanism is relevant in all biophysical processes, such as mucociliary clearance, where the microscopic mechanics rules the mucus functionality.

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Nematic doping of nematics with particles of different anisotropies

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The ability to control nematic phases in thermotropic liquid crystals (LC) by external fields opens a wide range for applications, e.g. in optical devices. While it is common to use electric voltage in such devices, the employment of magnetic fields is limited by the low magnetic anisotropy of the mesogens.

However, the incorporation of dipolar magnetic particles in nematic phases is expected to result in ferronematic phases that are readily responsive at moderate magnetic field strengths. [1] One of the main challenges for the experimental realization is the strong tendency of the nanoparticles to agglomerate, as a consequence of the strong molecular interactions of the mesogens and the dipolar interactions between the particles. [2] Thus, compatibilization is a key step for the development of ferronematics. Our novel approach towards ferromagnetically doped LCs with enhanced volume fraction and stability is based on nanoparticles that are surface-modified with a side-chain LC polymer brush. We employ two different synthetic pathways with a variation of shell thickness, mesogen density and the spacer length. This results in an effective steric stabilization of the particles against agglomeration and offers a high degree of functionalization with respect to the mesogen.

The impact of the modified particles, differing in size, shape and magnetic anisotropy, on the phase behavior of 5CB (B_{th} = 250 mT at a layer thickness of d = 25 µm) is investigated with respect to particle concentration. By differential scanning calorimetry and determination of the order parameter we show a significant improvement in compatibilization as compared to conventionally stabilized particles. The magnetic response of the ferronematic phases is investigated by capacitance measurements in a magnetic field. As compared to 5CB, the critical field strength is shifted to lower magnetic fields, and the shape of the Fréederickzs transition indicates an effective ferronematic coupling between the magnetic particles and the LC matrix (Figure 1b).

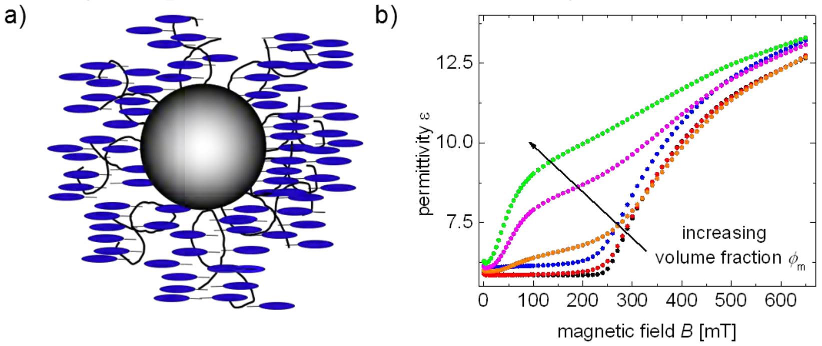

Figure 1. a) Scheme of LC polymer brush particle, b) Capacitance measurements in parallel B and E field for pure 5CB (black), and for 5CB doped with 9OCB-PHMS@$CoFe_2O_4$ with a volume fraction between 0.01 vol% and 0.1 vol%.

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Designing Nanostructured Porous Polymeric Gas Sensors: from Solution Thermodynamics to Phase Inversion

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Micro- and nanoporous polymeric materials are important for a wide range of applications and, in particular separations and sensing, and it is thus important to fundamentally understand their design, synthesis and functionality [1]. Porous polymers can be designed, either at the molecular level (bottom up approach) or through a secondary process (top down approach), to have a defined and controllable pore sizes and connectivity [2]. These are extensively employed in membranes [3], nanoparticles [4] and hollow capsules [5] given the easy processibility and versatility of polymer solution and process design, with applications, including but not limited to carbon capture, gas storage, separation and purification, catalysis, drug delivery, and sensing.

The porous polymer material of particular interest in this work is poly(2,6-diphenyl-p-phenylene oxide) (PPPO), currently used as an adsorbent medium in gas chromatography for air analysis. PPPO nanoporous materials are produced via a demixing process from solution, generally via spinodal decomposition, caused by the addition of a non-solvent (heptane) and subsequent phase inversion and kinetic arrest. Partial crystallisation of the polymer-rich phase expedites this kinetic arrest and likely enables the formation of nano-sized phase domains. This work provides a detailed understanding of the system thermodynamics, demixing mechanisms and kinetics, towards enabling the predictive and versatile design on PPPO nanoporous adsorbers and the widening of current applications [6].

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Topical session
Biophysics

Cell adhesion to soft interfaces under flow

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The adhesion of cells to soft interfaces under shear flow is a common and important phenomenon in biological systems. The endothelial glycocalyx, for example, is a soft, glycan rich film that lines the inner walls of all blood vessels and acts as a 'gate keeper' providing for selective and coordinated trafficking of cells from the blood circulation into tissues. How the endothelial glycocalyx accomplishes this function, e.g. permitting certain immune cells to migrate to sites of infection/inflammation whilst retaining other cells in the circulation, and how tumor cells hijack the system to metastasize in distant organs, is not well understood.

This is a complex question that requires explicit consideration of biochemical factors (such as the bonds between receptors on the circulating cell and ligands at the soft interface) and physical factors (such as hydrodynamics and interface mechanics). In this talk I will present experimental and theoretical tools we have developed to study the role of soft glycocalyx layers in cell adhesion under shear flow, across scales from individual molecular bonds to cells. The insights gained have general implications for cell adhesion to soft interfaces.

Mechanomodulation of lipid membranes by weakly aggregating silver nanoparticles

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Due to their advantageous antibiotic and optical properties, silver nanoparticles (AgNPs) are widely used in consumer products and are being actively developed for biomedical applications in therarpy and diagnostics. However AgNPs have been reported to occasionally cause serious injuries to eukaryotic cells, but the mechanisms behind this cytotoxicity are still not well understood. Here we investigate the how the medium composition of the dispersion affects the colloidal stability of AgNPs and how this modulates AgNP interactions with lipid vesicle models of the biomembrane. We find that AgNPs in a low ionic strength glucose buffer are colloidally stable for at least several days and do not perturb lipid membrane properties. Conversely, in physiological ionic strength saline buffer, AgNPs weakly aggregate with an attachment efficiency of less than 2% during particle collisions. Under these conditions we start to observe sporadic yet significant perturbation of vesicle membranes. Disruption of membrane integrity (transient poration) increases in a dose-dependent manner and rare but statistically significant membrane remodelling is observed in the form of pearling tubules invaginating within the vesicle lumen. Adsorption of AgNPs on the membrane within this weakly aggregating regime results in an average 16% decrease in membrane fluidity. More interestingly, we observe a small sub-population of the vesicles exhibit significant modulation of their mechanical properties with lower bending rigidity and higher membrane tension. We argue that this mechanomodulation of the membranes is caused by low probability AgNP aggregation events at the membrane and these could be the cause of the sporadic membrane perturbation events that we observe.

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The role of adhesion on the microfluidic flow of biomimetic tissues

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The aim of this study is to design a biomimetic cohesive tissue with a tunable degree of internal adhesion and determine its flow behavior in controlled microfluidic settings. The final goal of the project is to elucidate, by means of a biomimetic system, the role of cellular adhesion on the flow of epithelial tissues. The artificial tissue is obtained by the controlled assembly of giant unilamellar vesicles [1], which constitute a suitable model system for cells. Intercellular adhesion is mediated by the inclusion of ligand-receptor complexes [2,3], which allows us to control the occurrence (or not) of cell-cell assembly, the strength of the adhesion, as well as the typical size of the formed aggregates. An example of GUV aggregate obtained using the streptavidin-biotin pair is shown in the figure. Aspiration experiments in microfluidic constrictions are performed in order to characterize the flow behavior of the designed tissues. Our preliminary results show that, depending on the aspect ratio between the aggregate and the constriction size, the tissue adopts different strategies in order to advance through the constriction: aggregate reorientation, flow localization, or cell deformation.

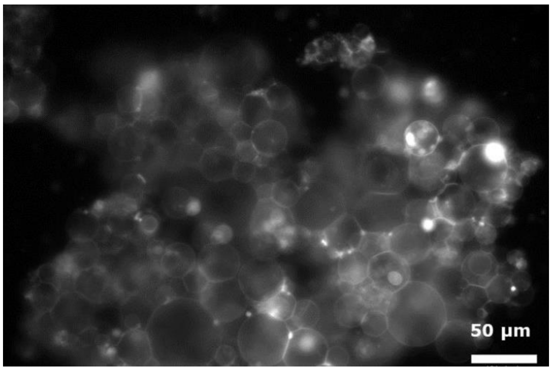

Figure: GUV aggregate obtained using the biotin-streptavidin complex.

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Allosteric modulation of local reactivity in DNA origami

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Here, we characterize the structure and dynamics of a triangular-shape DNA origami with the use of Langevin-type molecular dynamics simulations, using the coarse-grained OxDNA model. In particular, we focus on two different network geometries and analyse the different fluctuations properties to characterize the digital behaviour of restriction enzymes over sites contained in the folded M13 sequence, which we recently reported [1]. We link the local and global conformational changes, and the local DNA network properties, to the binding propensity of restriction enzyme HinP1I. Finally, we will attempt to use the Michaelis-Menten model to connect the prediction of molecular dynamics simulations with gel electrophoresis experiments.

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Transmigration of non-ionic synthetic polymers through lipid membranes

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Polymers with balanced hydrophilicity can translocate through biological membranes without doing damage. We have synthesized such balanced, alternating hydrophobic/hydrophilic polymers and studied their translocation properties using Pulsed Field Gradient (PFG) NMR.

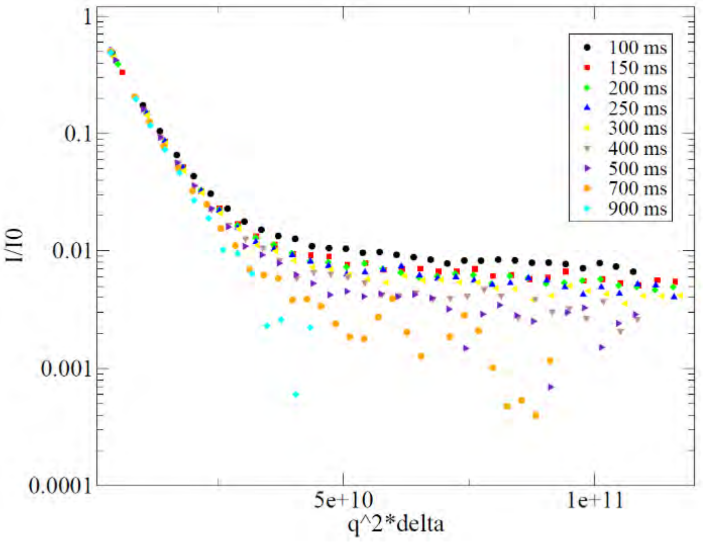

Fig. 1. PFG NMR measurement for mixture of liposomes and amphiphilic polymers. Colors represent different time between two gradient pulses.

Normally the hydrophobic inner part of lipid membranes blocks passive diffusion of molecules through the membrane. In the case of synthetic polymers there are only few reports of translocation using charged polymers [1-2]. For non-charged polymers translocation phenomena were predicted theoretically [3] but not verified experimentally.

In a previous work we found that amphiphilic copolymers containing alternating hydrophilic and hydrophobic segments translocate through lipid membranes without destroying it [4].

The investigated polymers contain polyethylene glycol (PEG) as a hydrophilic part and dicarboxylic acids as the hydrophobic one. As a model cell membrane we used unilamellar liposomes of different lipids (DOPC, POPC, DMPC). Dynamic light scattering (DLS) and small angle x-ray scattering (SAXS) were used to characterize liposomes in terms of structure and stability without and in the presence of the polymer.

Translocation properties were measured by PFG NMR and analyzed by a two-phase diffusion model [5]. Two dynamical phases of the polymers were observed in their mixture with liposomes (Fig. 1). One phase is attributed to the free polymers and the other one characterizes their interaction with liposomes. The time dependence of the ratio between these two phases indicates the translocation process. The exchange process was observed in the time range from 50 to 900 ms.

Using the two-phase diffusion model, the dependence of translocation time on the polymer molecular weight and liposome composition was studied. First calculations show slight increase of the exchange time with increasing of polymer molecular weight and strong dependence of the exchange time on thickness of lipid bilayer.

Because of the non-ionic nature of the polymers only small interactions with biological compounds are expected and the materials might be interesting candidates for drug delivery and other applications.

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Topical session
3D printing

Microfluidic device fabrication via µSL utilizing tailored photopolymer formulations

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Additive manufacturing based on micro-stereolithography (µSL) is currently revolutionizing the fabrication of microfluidic systems replacing well-established micromolding based on poly(dimethylsiloxane) (PDMS). By illuminating a liquid photopolymer formulation (resin) by dynamic mask projection in a layer-by-layer fashion, truly three-dimensional geometries are obtained in a single fabrication step with micrometer-resolution. However, commercial photopolymer formulations often provide rather limited versatility regarding transparency, elasticity, XYZ-resolution, and biocompatibility. For realizing microfluidic functional units such as valves and pumps or tailored microchannel surfaces for cell adhesion and emulsion formation, we require exact control over composition, polymerization kinetics, viscosity, and functionality of photopolymer formulations for µSL.

On this account, this talks addresses key parameters in photopolymer formulation design and processing via µSL towards microfluidic devices with XYZ resolution as found in conventional PDMS-based microfluidics. Utilizing such tailored, “home-made” resins, µSL-based fabrication of microfluidic devices for forming emulsions and polymer microparticles will be discussed as well as design criteria of photopolymer formulations for manufacturing elastic and/or biocompatible polymer materials with micron-scale resolution.

Novel non-dimensional groups describing transition criteria between scaling regimes in capillary thinning of complex fluids

Christian Clasen
KU Leuven

Capillary breakup extensional rheometry of complex fluids has proven to be a powerful tool for the investigation of extensional material functions of low viscous and weakly viscoelastic fluids and suspensions. In particular the identification of scaling laws for the minimum filament diameter decay, when either the microstructure influenced viscosity, elasticity, as well as inertia, or combinations thereof dominate the fluid response, allows to fit the thinning profile in order to extract relaxation times, apparent extensional viscosities or generally relevant capillary time scales .

One problem that arises, however, is the identification of the applicable scaling law for an observed filament thinning. This arises because the transition between scaling regimes is often broad, and different dominant material properties can lead to similar scaling laws that differ only in their respective coefficients, so that selection of the correct scaling law even in the absence of a transition can be ambiguous.

In this paper we present therefore for the first time a two-dimensional map spanned by a novel axial Ohnesorge number Oh_L and the viscosity ratio p between the fluid viscosity and the viscosity of the outer medium, that allows to identify the filament diameters at the transitions between different thinning regime. We demonstrate that a quantitative description requires the incorporation of an additional dimensionless geometrical parameter a that accounts also for the critical axial length scale of the filament. The validity of this map is demonstrated over six orders of magnitude for the Ohnesorge number, as well as nine orders of magnitude for the viscosity ratio, by experimental observation of filament thinning dynamics of model silicon oil and water/glycerol mixtures, structured with micron-sized particles, as well as finite element numerical simulations for experimentally not accessible regimes.

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3D printing based technique for bioinspired surface patterning

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Patterned surfaces and interfaces are of paramount importance for various animal species to perform tasks for their survival. One such example can be found in the Gecko, which shows an exceptional ability to stick and run on any vertical and inverted surface [1] due to the presence of micron to nanometer size features on their toes; see Figure 1(a) . Also, in the plant world, 3D patterned surfaces with hooks can be found in Catchweed or *Galium aparine* that can adhere to many surfaces [2]; see Figure 1(b) . To understand the fundamental physical mechanisms that govern such adhesive behavior, recreating bioinspired patterned surfaces is essential. Indeed, such studies can also inspire innovative designs of interfacial mechanics for new applications such as soft robotics.

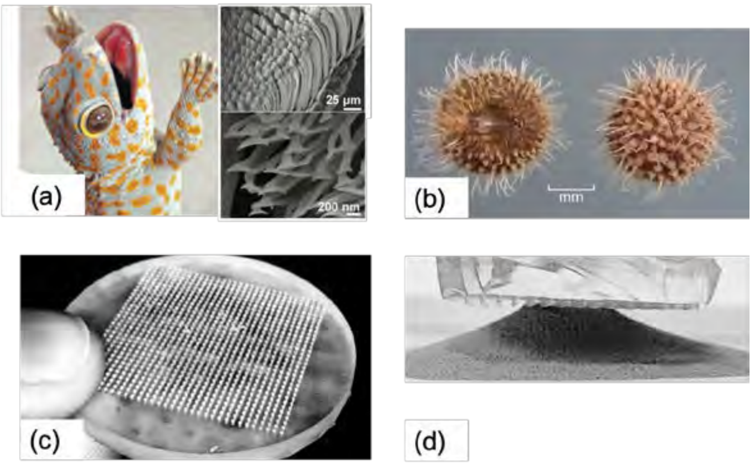

Figure 1: Patterned interfaces found in nature: (a) Image of a Gecko along with SEM pictures of its toe showing micro and nanometric pattern [1], (b) Galium aparine seeds with micrometric hooks responsible for mechanical interlocking [2], (c) a picture of 3D printed pattern with mushroom features on it and (d) adhesion on a stretchable textile fabric of the moulded mushroom pattern in soft polymer.

Currently, 3D printers are the easiest and most economized tool for the direct realization of complex 3D features. Based on 3D printing and moulding techniques, we propose an inexpensive and simple method of preparing microscopic patterned surfaces in soft polymers having 3D complex features with controlled shape, protrusion angle and spacing spanning between 200 μm and 1 mm (Figure 1(c)). We show that the surface patterns we can make have the desired mechanical functionality; specifically, we created surface patterns that can adhere to different fabrics, see Figure 1(d). The design protocol allows us to produce the soft patterned surfaces inexpensively and create many different interfacial properties such as adhesion, friction or hydrophobocity.

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3D Printing of Spatially Patterned Single- and Double-Network Magnetically Responsive Hydrogels

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Responsive functional soft nanocomposite materials remain a significant focus of scientific effort worldwide due in part to their applications in biomedicine ranging from cancer treatment to biomolecule/drug delivery through to cell supports[1]. Their responses to electric and/or magnetic fields, temperature, salts, pH, and light can be engineered through precise physicochemical modifications across multiple length scales and also by spatial patterning using 3D printing technologies[2]. Magnetic nanoparticles (MNPs) and also their clusters are used in the biomedical field in a wide range of applications from cancer treatment to MRI imaging[3]. The combination of MNPs and established 3D printable polymeric hydrogel formulations can provide multifunctional and stimuli-sensitive nanocomposite delivery systems with spatial-, temporal- and dosage-controlled release properties (***Figure 1***). We are interested in exploring these possibilities for tissue engineering and biomedical applications.

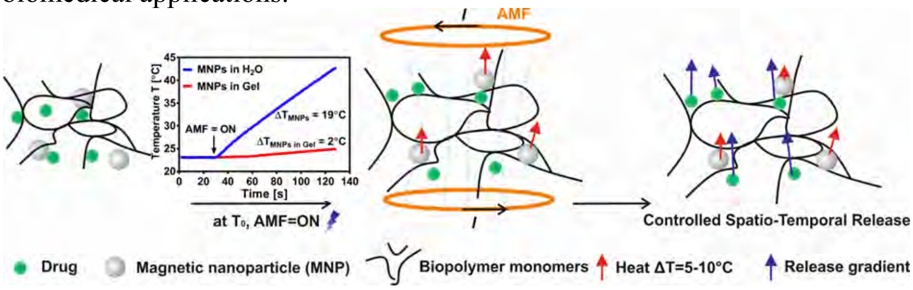

Figure 1*: Scheme showing the heating of magnetic nanoparticles encapsulated in hydrogels.*

A multi-head 3D printer was successfully built in-house and modified to allow extrusion of Pluronic F127 hydrogels and composite gels including F127 and polyethylene glycol diacrylate (PEGDA) with parameters of moderate temperature and pressure that would support cell viability. Magnetic nanoparticles were synthesised, stabilized and incorporated homogenously; oscillatory rheology measurements confirmed the viscoelastic properties with G′ (storage modulus) values in the ~20 kPa range providing ideal materials for 3D printing well-defined architectures with high fidelity for both magnetic and non-magnetic streams. The hybrid inks showed complete shear- and temperature- recoverability/reversibility to their initial state, confirming that at particle concentrations that enable magnetic responses the necessary printability is not lost. Various complex structures were printed with high resolution (~100 micron) with independent magnetic and non-magnetic patterned components and these were shown to be reproducible and robust and their fidelity and degradation could further be controlled by immediately curing post-printing.

For AC-magnetic field responsiveness, high resolution IR thermography confirmed that incorporated magnetic nanoparticles retain sufficient magnetic response to provide spatial temperature gradients for cell stimulus and for stimulus-responsive release. The advantages of spatial patterning of thermally active components will be described. In addition, we recently synthesized selection of thermoresponsive nanogels with varied critical transition temperatures (LCSTs) in the tissue engineering relevant ranges. These current efforts will also be discussed for potential enhanced stimuli-responsive applications.

In summary we demonstrate; (i) reproducible and robust extrusion of hybrid magnetic hydrogels with controllable physicochemical properties; (ii) spatial patterning of thermally active components and drug loading, and; (iii) in situ manipulation using applied magnetic fields with high resolution thermal mapping.

Acknowledgements

The authors acknowledge support from Science Foundation Ireland (16/IA/4584 and 13/IA/1840).

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SERS ACTIVE INKS FOR 4D BIOPRINTING

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Bioinks are the basic building blocks for the fabrication of 3D printed scaffolds. Depending on the desired scaffold properties many potential bioinks can be used [1, 2]. Moreover, bioinks can also possess extra functionalities or changing properties, introducing an additional dimension to the printed scaffolds and, thus, leading to the concept of 4D bioprinting [3]. In this way, the scaffold could act also as a sensing material and monitor in real-time the evolution of tissue or tumour growth. In this work, we evaluate the properties of a series of Surface Enhanced Raman Scattering (SERS) active bioinks as potential materials to monitor relevant bioanalytes within cells and tissues, produced during the development of diseases. To produce bioinks with sensing properties, different biopolymers have been combined and incorporated to plasmonic nanoparticle suspensions, such as gold nanorods (AuNRs) suspensions. The viscoelastic properties and the printing ability of the different bioinks, as well as the AuNRs dispersion within the matrix were evaluated. It is expected that the 3D printed plasmonic scaffolds would drive possibilities in advanced biosensing and bioimaging applications.

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Topical session
Single molecule methods

Single-molecule biophysics: From monitoring DNA polymerases *in vitro* to target search of CRISPR-Cas *in vivo*.

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Single-molecule detection schemes offer powerful means to overcome static and dynamic heterogeneity inherent to complex samples. Probing interactions and reactions with high throughput and high spatiotemporal resolution, however, remains challenging.

In the first part, I will introduce DNA based FRET sensors that allow binding of DNA polymerases and even DNA synthesis to be monitored at the single-molecule level and in real time (1). The sensors are further characterized in novel glass-made nanofluidic devices that confine the diffusional movement of the probes thereby enabling high throughput measurements and, in a mixing geometry, even the continuous observation of chemical reactions (2).

In the second part, I will talk about our work on super-resolution microscopy. Although frequently employed in the life sciences, the number of freely accessible microscopy frameworks, especially for single particle tracking photo-activation localization microscopy (sptPALM), remains limited. We therefore designed the miCube: a versatile super-resolution capable fluorescence microscope, which combines high spatiotemporal resolution, good adaptability, and easy installation (3). We further achieved fast data analysis via a novel phasor-based localization algorithm (4). The capabilities of the miCube are assessed with a sptPALM assay relying on the heterogeneous expression of catalytically inactive Cas9 (dead Cas9) in live Lactococcus lactis bacteria.

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Superresolution fluorescence microscopy enlightens functional, responsive microgels.

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The elucidation of the structure and functionalization of materials in the sub-micron range is a key to their further development and application. Microgels are a class of such soft materials with high potential for multiple fields. Several groups have learnt to functionalize and structure microgels in sophisticated ways, but the evaluation of a successful functionalization or the envisioned properties are often limited by the ways of analysis and visualization. The development of modern super-resolved fluorescence microscopy methods opened up new ways of nanoscopic visualization that had not been possible previously due to the diffraction limit of light prohibiting spatial resolution beyond approx. 200 nm.

In my contribution, our results on super-resolution fluorescence microscopy in microgels and other soft matter systems will be presented. The possibilities to elucidate shape and functionalization, to visualize single cross-linker positions and to address local polarity in a microgel with 3D super-resolution fluorescence imaging will be discussed and ways presented to address and answer scientific questions in soft matter science.

Title: Light from Within: Sensing weak strains and femtoNewton forces in single molecules
(Ties van de Laar & Joris Sprakel)

Abstract:

Weak forces acting on individual molecules control a wide variety of chemical and physical processes. Mechanical cues at the molecular scale are an essential link in the mechanotransduction cascade, shape the pathways of supramolecular assembly and govern elasticity and rupture. The action of forces on molecules is typically inferred from the response they elicit at larger scales or probed using force spectroscopic methods that cannot be easily applied deep within a material. Quantifying weak mechanical stresses and strains at the molecular scale, deep within materials, in a non-invasive way has remained a foremost challenge. In this talk, we demonstrate the use of doped conjugated polymers as strain sensors at the single-molecule scale with a non-invasive optical read-out. Using simulations and single-molecule experiments

we show how these molecular sensors report in grayscale at picoNewton resolution and how their performance can be optimized through their chemical design. This paves the way towards non-invasive, high-resolution and quantitative stress- and strain mapping in complex systems down to the molecular scale.

Tailoring Fluorescence Correlation Spectroscopy for demanding applications

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Fluorescence Correlation Spectroscopy (FCS) is a microscope-based fluorescence technique that allows to interpret qualitatively the shape and rate of fluctuations of the fluorescence signal induced by a focused laser beam. The sensitivity of the technique is such that the signal from a single molecule is sufficient to characterize the diffusion rate or the chemical reaction rate constant. As the source of the signal is spatially limited to the sub-micron size of the focal spot of a microscope objective, diffusive properties can be mapped with a microscopic precision. In complex media with a characteristic size of building blocks, the diffusion rate changes not only with the probe size but also with the ratio of the probe size to the building blocks length scale (micro-viscosity) [1,2]. Moreover, the size of the focal spot defines the range over which diffusion is measured. In all cases objectives with a correction collar had to be used in order to compensate the aberration effects. Typically, FCS experiments are performed at ambient temperature and pressure, mainly because optimum light collection conditions are reached with immersion objectives. We showed that not only immersion objectives but also dry ones can be used to obtain accurate FCS correlation functions in a reasonable time, opening a way to study length scale dependence of the diffusion process [3]. The use of air objectives opened possibilities for studying temperature dependencies in a broad range of temperatures (-100 to +200°C) [4]. For that purpose, a customized Linkam microscope temperature stage was designed and purchased. Also a dedicated high pressure cell was built which allowed performing FCS measurements at pressures up to 1000 bar in the temperature range 20 - 100°C [5]. For particles comparable in size with the confocal volume, an analog of the form factor in scattering techniques occurs, which not only allowed for proper particle size estimation but also made it possible to estimate the distribution of dye molecules within the colloidal particle (core-shell type) [6,7]. Intra- and inter-particle electrostatic interactions were studied in solutions of small polyelectrolytes [8, 9]. The whole presentation is based on our own studies and illustrated with our results obtained in cooperation with various research centers.

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Single-molecule microscopy at the ice-water interfase to study ‘antifreeze’ proteins

Roderick P. Tas and Ilja K. Voets

The inhibition of internal and external ice formation is important for the survival of a variety of species that live at extremely low temperatures, such as fish, insects, plants and bacteria. They express a class of ice-binding proteins (IBPs) with ‘antifreeze’ activity to depress the freezing-point of water and inhibit the growth of ice-crystals. Even though the functions of IBPs are extensively studied, their mechanisms of action remain debated. Here we establish single-molecule localization microscopy (SMLM) based methods of the ice-water interfase to study the effect of IBPs on ice shaping with diffraction-unlimited resolution. Using time-resolved reconstructions we map the dynamics and features of the changing ice-front. Furthermore, we aim to study the single-molecule biophysics of IBPs to better understand their mechanisms of binding and distribution along ice-front in order to better understand their antifreeze activity.

Young scientists' session

Dynamic and thermodynamic structural investigation of capillary suspensions

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Capillary suspensions are a relatively new class of materials consisting of particles suspended in a bulk fluid, with a small amount of immiscible secondary fluid added to form a percolating network of capillary bridges between the particles. These capillary suspensions have wide-ranging applications, from the synthesis of porous ceramics to the development of low-fat food products[1]. To connect structure and function, Bossler and Koos recently characterized the microstructure of capillary suspensions at rest[2]. The goal of the present study is to directly observe the microstructural changes of capillary suspensions during key rheological transitions, e.g. yield, using confocal microscopy. The reorganization of the microstructure of a capillary suspension of fluorescently labelled silica particles is investigated using a confocal microscope equipped with a linear shear cell. Identical shear profiles are repeated on a commercial rheometer to obtain force measurement data. A custom-made IDL-code is employed to detect and track the particles in the 3D-confocal images. The particle positions and radii are determined using a combination of edge detection with Hough transform. We then use parameters such as the radial distribution function and the coordination number distribution to quantitatively characterize the microstructure, which differs depending on the local particle and secondary fluid volume fractions, as well as the wetting properties. An increase in the particle volume fraction generates more available contacts, thus shows a higher average coordination number. After compressing the $\Phi_{solid} = 0.25$ sample, a large jump in coordination number is observed (Figure 2, right), possibly indicating a critical volume fraction above which the displacement of particle clusters is restricted. Subsequent shearing only results in a slight change in the number of contacts. This research can provide information about yield, shear banding and frictional shear thickening in granular systems in addition to capillary suspensions.

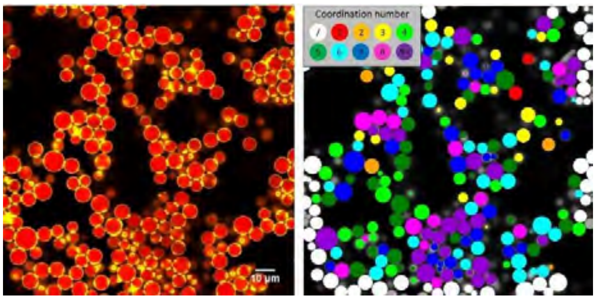

Figure 1, left: Confocal micrograph of a capillary suspension of silica particles (red) with added aqueous glycerol (yellow). Right: The in-plane radii of the particles are colored based on their coordination number. Particles that are detected, but where not all neighbors are known, are shown in white.

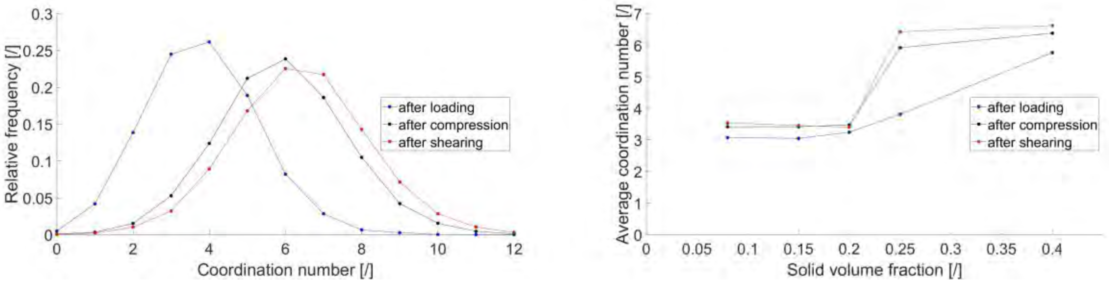

Figure 2, left: Distribution in coordination number for a sample with $\Phi_{solid} = 0.25$ after loading, after going to a gap size of 150 µm and after small amplitude oscillatory shearing. Right: Evolution of average coordination number with particle volume fraction. The $\Phi_{secondary} / \Phi_{solid}$ ratio is constant at 0.1 for all samples.

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Sideways self-propulsion of Janus micro-rods: cargo transport

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In recent years, there is a growing interest among researchers on the self-propulsion of micron-sized particle systems [1, 2]. The ability of particles to generate field gradients in a surrounding medium, resulting in directed motion, makes them promising candidates for sensing operations, moving cargo or transporting active pharmaceutical ingredients in the human body. One of the strategies to induce the directed motion of Janus particles is the convertion of the chemical energy of the fuel into mechanical energy of particle. That implies the production of Janus particles with different catalytic properties on opposite sides [3, 4, 5]. Previous studies were focused mostly on spherical particles and rods propelled along their long axis [4, 5]; our group was among the first who produced and studied the sideways self-propelled rods. They are made by the simple and robust technique: electrospinning of aligned polystyrene fibers with subsequent coating of their opposite sides with platinum and gold. This approach allows to study the motion of sideways self-propelled straight and bent rods in hydrogen peroxide solution [6, 7].

A larger active area makes sideways propelled rods attractive for the possible application in sensing and moving microscale cargo. Therefore, the analysis of cargo towing by self-propelled rods is essential in order to further adjust the Janus rods production and characteristics. With micron-size polystyrene spheres chosen as a model load, we explore how rod collects the cargo and how the velocity of the rod scales with the number of attached particles; these results will be addressed in my presentation.

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Sol-gel transition in gelatin solutions by dynamic measurements: rate and concentration effects

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Thermal gelation of gelatin was investigated by rheological measurements in dynamic mode. Gelatin is a versatile material, with applications in different fields, such as food, pharmaceutical, medical. In the present work, aqueous solutions with various concentrations of pig and calf derived gelatins, at different bloom levels, were characterized. Gelation temperature was investigated by dynamic temperature ramp tests with different cooling and heating rates at a constant frequency and deformation, in linear regime.

In order to explore sol-gel transition, the temperature was varied between 60°C and -5°C, and viceversa. At high temperatures, the sample is liquid-like whereas at low temperatures the sample shows the response of a solid-like material. The gelation is reversible and the dynamic moduli show a hysteris, depending on the heating/cooling rates.

It was observed that the sol-gel transition temperature, $T_{sol\text{-}gel}$, is affected by different factors, such as cooling/heating rate and gelatin concentration, whereas the $T_{gel\text{-}sol}$ is less dependent on the same parameters.

We propose a method for the evaluation of the thermodynamic gelation temperature and gel strength and we discuss results by tuning gelatin concentration and bloom level, as well as heating/cooling rates.

Tracking-free one- and two-point microrheology of soft materials

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Passive particle tracking microrheology (PT-μr) is an experimental technique that exploits the thermal motion of tracer particles to probe the local mechanical properties of small amounts of homogeneous (one-point PT-μr) and microstructured (two-point PT-μr) soft materials [1]. While in one-point PT-μr the trajectories of single particles are analysed to extract their mean squared displacement, in two-point PT-μr the cross correlations between the mean-square displacements of two particles are studied, which provides a means to get rid of artefacts that may arise in PT-μr as a consequence of the interactions of the probes with the sample microstructure. Despite its appealing conceptual simplicity, both approaches require calibration procedures and operating assumptions that constitute a practical barrier to a wider adoption, especially in industrial environments and in particular for two-point PT-μr that requires numerous accurate measurements and a subtle analysis of the acquired data. Here, we present a novel approach to passive one-and two-point microrheology that, not requiring particle tracking, unlocks a calibration-free, automated, operator-independent rheological characterisation of soft materials. We first show how Differential Dynamic Microscopy (DDM) [2] can be used to perform one-point microrheology of different homogeneous complex fluids [3] by relying on the multi-scale, temporal correlation study of the image intensity fluctuations that are observed in microscopy experiments as a consequence of the motion of the tracers. In addition, we show how a novel analysis based on optical flow detection, enables one obtaining accurate two-point microrheology data on both Newtonian fluids and semiflexible polymer networks (solutions of entangled F-actin) [4]. Our results are in good agreement with PT-μr when the latter can be used. In addition, we can extract reliable information even in cases where PT-μr is not a suitable option, demonstrating tracking-free microrheology as a viable alternative and complement to PT-μr and to other rheological probes.

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Electrostatic coassembly of thermoresponsive double hydrophilic block polyelectrolytes

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Interpolyelectrolyte complexes (IPECs) are formed by mixing oppositely charged polyelectrolytes in solution due to both strong electrostatic interaction and gain in entropy because of release of the low molecular weight counterions. Complexation of double hydrophilic block polyelectrolytes (DHBP), which are diblock copolymers with one charged block and one neutral hydrophilic block, usually results in core-shell micellar structure formation. In this case the micellar core was formed by IPEC insoluble in water, while the micellar corona was formed by hydrophilic neutral chains, which stabilized the core in the aqueous solution. The polyelectrolytes coassembly behavior depends on numerous factors such as composition, charge-to-charge stoichiometry, ionic strength and pH among other factors [1,2]. Due to the possibility of tuning these factors, IPECs can find applications as containers for guest substances including bioactive compounds [1,2].

One of the possible ways to change and control structure of the resulting co-assemblies is the introduction of thermoresponsive fragments in the composition of interacting polyelectrolytes [3]. Thus, in the present communication we analyzed the complexation behavior of positively (Quaternized poly(2-(dimethylamino)ethylmethacrylate)-*b*-poly(*N*-isopropylacrylamide), QPDMAEMA-PNIPAm) and negatively (Poly(acrylic acid)-*b*-poly(*N*-isopropylacrylamide), PAA-PNIPAm) charged DHBPs with a thermosensitive block (PNIPAm) as a function of their charge ratios. Specifically, we followed the coassembly kinetics of these DHBPs at equivalent stoichiometry using a combination of light scattering, SAXS, time-resolved SAXS, TEM and DSC methods.

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The Importance of Building Block Stability in Hierarchically Structured Protein Networks

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Proteins are known as the workhorses of life, performing a huge array of functions from providing mechanical strength to molecular recognition & binding.[1] They are able to perform these functions due to their specific, well-defined folded structures. We are interested in their potential to be used as building blocks for hydrogels in order to determine if their single-molecule properties scale up to macro sized systems or scale out.[2] This involves a multi-length scale approach using a range of mechanical and structural techniques including small angle neutron scattering (SANS), bulk rheology, and circular dichroism. In particular in this study we utilise the natural stabilisation of maltose binding protein upon the binding of its ligand maltose to investigate how this single molecule stabilisation is translated to the network.[3] We demonstrate that stabilising the building block molecule, translates to the network in several ways including an enhancement in the mechanical strength of the network. The ultimate goal of these types of study is to understand the design parameters of folded protein hydrogels, resulting in unparalleled control and tunability of the structural, mechanical and biofunctional properties of hydrogels constructed from folded proteins.

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Rheological insights in the behaviour of supramolecular double network hydrogels – the synergy investigated

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The rising demand for fatigue resistant and self-healing polymeric materials with high stiffness, strength and toughness drives research in the field of multi-dynamic polymer networks. In this regard, double network (DN) hydrogels with two distinct modes of relaxation have emerged as a promising class of novel materials due to their synergistic mechanical properties, resulting in excellent toughness and strength [1,2]. To overcome the limited fatigue resistance of covalently crosslinked networks, the state-of-the-art DNs combine different reversible, physical interactions with distinct binding strengths, thereby mimicking the behaviour of fully chemical or hybrid DNs [3,4]. However, the limited studies available mainly focus on the final mechanical properties of these materials, while a fundamental understanding of their multiple dynamics still remains elusive. In this research, **linear oscillatory shear rheometry** will help us gain insights in the **multiple dynamics of fully physical DN hydrogels** with distinct relaxation times. Hereto, a stiff and brittle thermoresponsive hydrogel based on the **association of hydrophobic blocks** in 3-arm PEO-PPO-PEO block copolymer stars, is combined with 4-arm PEO stars containing telechelic terpyridine ligands. Upon addition of transition metals, the latter forms more soft and ductile hydrogels by **metal-ligand complexation**. The resulting DN hydrogels show **synergistic rheological properties** as compared to a superposition of the separate network responses. The mutual influence of the networks on their individual gelation ability is addressed by systematically studying the separate networks in the presence of the gel precursors of the other network. Moreover, the careful selection of the networks, in which the relaxation modes could be linked to the dissociation of the physical interactions, together with the **different stimuli-responsiveness of these physical interactions** (including temperature, pH and solvent dependence), allow to pinpoint the **different contributions in the DN relaxation spectrum**, thereby also revealing the effect of combining the networks on the individual relaxations. Based on the relaxation spectrum, an attempt is made to explain the synergistic rheological properties of the DN hydrogel. This research contributes to the development of fundamental insight in the excellent mechanical behaviour observed in novel DN hydrogels.

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Ultra thin silica shell growth over AuNP for SERS based Detection

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Metal nanoparticles (such as Au, Ag, and Cu) when irradiated with light of resonant wavelength, undergo collective oscillation of free electrons over a narrow region, resulting in electromagnetic field enhancement close to their surface. This ability of NP to confine free electrons within a nanoscale region under resonant excitation is known as localized surface plasmon resonance (LSPR). The interaction of light and NP is strongly dictated by the shape, size, composition, and environment of the NP. Out of all kinds of metal NP, AuNP have been largely studied due to their biocompatibility, easily tunable LSPR band and large electromagnetic field enhancement.

Although AuNP have been proposed for various applications such as photo-thermal therapy, imaging, and SERS based sensing, they may suffer stability issues due to insufficient surface functionalization and direct interaction with analytes. This ultimately results in NP agglomeration and loss of optical properties. Existing stabilization methods comprise the growth of a chemically inert silica shell over the AuNP surface by the well-known Stöber method, which involves the hydrolysis and condensation to tetraethyl orthosilicate. This yields homogeneous but typically thick silica shells around the Au core. Although the resulting Au@SiO$_2$ core-shell NP display better stability, it hampers the ability of the Au core to amplify the Raman signal of the analyte from its large electromagnetic field enhancement. To address this issue, we have developed an easy and robust protocol for preparation of highly homogeneous Au@SiO$_2$ NP with ultra-thin shell.

We report a one-step protocol to grow highly homogeneous ultrathin silica shells ranging from 2 to 6nm over gold nanoparticles of varying sizes and shapes. The thickness of the silica shell is controlled by varying the concentration of Binol molecule with hexadecyltrimethyl ammonium bromide (CTAB). The Binol molecule seems to play a crucial role in modifying the micellar structure of CTAB, as well as in timely termination of the silica growth. This thin uniform silica shell is optically transparent and chemically inert. Moreover, the thin shell allows us to control the distance of the probe molecule from the Au surface, allowing significant Raman signal amplification from the Au core and ensuring no interference from the processes involving the SERS active core. The potential application of these as-synthesized Au@Si core shell NP is being explored in SERS based sensing for different analytes.

Three-layer onion-like micelles with soft poly(lauryl acrylate) core: co-assembly and morphological transition

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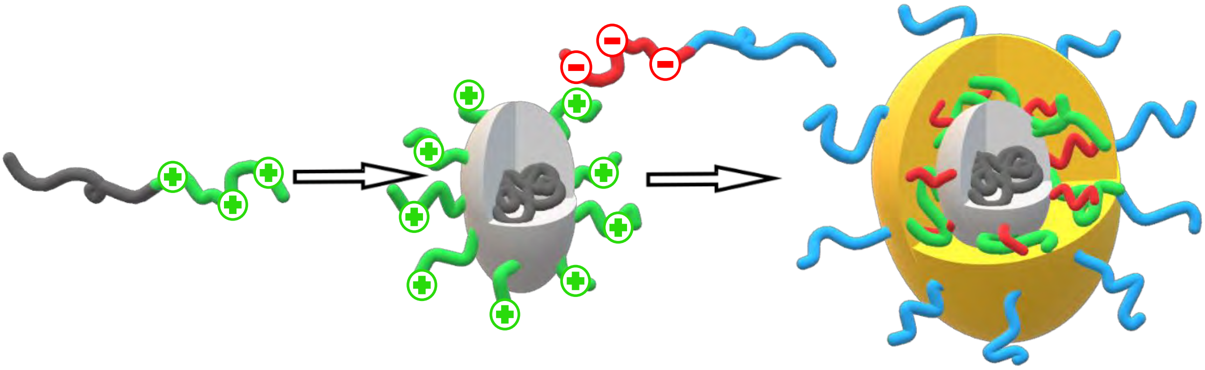
Amphiphilic diblock copolymers consisting of a hydrophilic and a hydrophobic block form micelles in aqueous solutions that can be used as nanocarriers in encapsulation and controlled release. The hydrophobic blocks usually form a glassy micellar core with a rigid structure that limits the applications of these polymers. We studied complexation of poly(ethylene oxide)-block-poly(methacrylic acid) and poly(lauryl acrylate)-block-poly(trimethylaminoethyl acrylate iodide) where hydrophobic block of poly(lauryl acrylate) (PLA) forms fluid micellar cores. We followed complex formation using a combination of scattering, microscopy, calorimetry, nuclear magnetic resonance spectroscopy and surface tension measurements. We proved that the PLA-containing diblock polyelectrolyte forms three-layer onion (core/shell/corona) micelles with a soft PLA core, a middle layer of interpolyelectrolyte complex, and a hydrophilic corona. Moreover, from SAXS measurements we discovered that PLA forms an ellipsoid core with attached chains as an outer shell. Thanks to their unique tunable properties, core/shell/corona micelles with a soft PLA core, an interpolyelectrolyte shell and a hydrophilic corona may be used as nanocapsules with the controllable size, core shape and the middle layer charge and thickness.



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Posters

A Constant Pressure Boundary Condition for Multicomponent Lattice Boltzmann Fluid Simulations

Abstract

The lattice Boltzmann method (LBM) for simulating fluids has received attention for its efficient parallelisation and ease of implementing complex and moving boundaries, a feature that makes it attractive for a wide range of complex flow problems. For the simulation of moving flows, particularly those driven by a pressure differential, constant pressure boundary conditions are desirable. Such a condition has received attention for the single-component fluid LBM, but very few proposals have been made for multicomponent models. Furthermore, none of the proposed approaches are applicable for the 'free energy' multicomponent model.

We have developed a new approach for pressure boundary conditions in the free energy model and this has been assessed using benchmarking tests consisting of simple flows in a capillary channel. The results show good agreement with the theoretical expectations, and the fluid interfaces exhibit less distortion at the boundary in comparison with similar methods. This new method is envisioned to enable new and more accurate simulations in complex multicomponent channel flow applications.

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Confined short-chain *alkanol* in *MCM-41* by **B D S:**

Efects of *matrix* treatments and pore filling

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Abstract:

The dynamic behavior of a representative short-chain ***alkanol**,* namely, **protic polar *n-propanol* (*n-PrOH*)** in the **bulk** state and in a series of the **confined** ones in **regular *Mobile Crystalline Materials* (*MCM-41) matrix*** with the pore size $\boldsymbol{D}_{\mathbf{pore}}$ = 40 Å under various *external* parameters related to conditioning and confining procedures using **broadband dielectric spectroscopy (BDS)** together with a desorption study of the physically adsorbed ***moisture*** (***H_2O***) from the ***MCM-41 matrix*** by **middle-infrared (M-IR) spectroscopy** are reported. These *external* parameters included drying and filling conditions under various atmospheres as well as pore filling factor.

First, because of the hydrophilic character of the **unmodified** (**virgin) regular *MCM-41 matrix,*** several carefull tests of *different* drying and filling procedures under the specific drying temperature/time conditions with the subsequent filling under *distinct* environment (*air* with *moisture, nitrogen, vacuum*) indicating their significant influence on the BDS response of the variously treated ***MCM-41 matrix*** were performed.

Next, for the variously treated ***MCM-41 matrix*** and the variously prepared **fully filled (saturated) *n-PrOH/MCM-41 samples***, a dramatic broadening of the spectra of the confined ***n-PrOH/MCM-41 systems*** with respect to the **bulk *n-PrOH*** are observed.This is ascribed to both the geometric restriction as well as due to the mutual interaction of the **protic polar *n-PrOH molecules*** with the **polar** pore surface of the ***MCM-41 matrix***.

Finally, the effect of the pore filling factor of ***n-PrOH medium*** in the most optimally treated and filled ***MCM-41 matrix*** was investigated. Qualitative and quantitative developments from the unimodal spectral form of the main relaxation feature in the **underfilled *n-PrOH/MCM-41 system*** to the bimodal ones for both the **saturated** and **overfilled *n-PrOH/MCM-41 systems*** with distinct relative intensities of the individual spectral components were found. By comparison with **the BDS response** of the **bulk *n-PrOH medium***, these dynamic findings can be intepreted in terms of the spatial variation of the dynamics, i.e., distinct local mobility of ***n-PrOH molecules*** being slower at the interface surface of the mesoscopic intrapores formed due to a part of the ***n-PrOH molecules*** attached by the inter-molecular *H*-bonds to *polar* ***silano**l* groups in all the three ***n-PrOH/MCM-41* samples** and faster in the bulk-like „core“ region of the mesoscopic intrapores in the **saturated *n-PrOH/MCM-41 system*** as well as in the macroscopic interpores between the grains of ***MCM-41 matrix*** in the **overfilled *n-PrOH/MCM-41 one***.

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Cholesterol-induced destabilization of lipid bilayers around inserted carbon nanotubes

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Abstract

Cholesterol is a crucial component of mammalian cell membranes that takes part in many vital processes. It is generally accepted that cholesterol stabilizes the membrane induce transition into ordered states. In contrast to expectations, we demonstrate that cholesterol can destabilize the membrane by creating an unstable nano-domain around perpendicularly embedded ultra-short CNT, and we show that cholesterol triggers the translocation of the ultra-short CNTs through cell membrane. Using atomistic simulations, we report the existence of a nanoscale domain around an ultra-short carbon nanotube within crossover distance 0.9 nm from the surface of the nanotube, where the properties of the bilayer are different from the bulk: this domain is characterized by increased fluctuations, decreased orientational lipid order parameter and decreased thickness of the membrane. It was confirmed experimentally that cholesterol nanodomains provoke spontaneous translocation of nanotubes through a lipid bilayer even for low membrane tensions.

BoltzmaNN: Heuristic inverse design of pair potentials using neural networks

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In this work we investigate the use of neural networks (NNs) to devise effective equations of state from a given isotropic pair potential using the virial expansion of the pressure. We train the NNs with data from molecular dynamics simulations, sampled in the NVT ensemble at densities covering both the gas- and liquid-like regime. We find that the NNs provide much more accurate results compared to the analytic estimate of the second virial coefficient derived in the low density limit. Further, we design and train NNs for computing the potential of mean force from the radial pair distribution function, g(r), a procedure which is often performed for coarse-graining applications. Here, we find that a good choice for the loss function is crucial for an accurate prediction of the pair potentials. In both use cases, we study in detail how providing additional information about forces and the density impacts the performance of the NNs. We find that including this additional information greatly increases the quality of the predictions, since more correlations are taken into account. Further, the predicted potentials become smoother and are in general much closer to the target potential.

Swimming behavior of squirmer polymers

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Nature provides a plethora of microswimmers, which are typically propelled by flagella or cilia [1]. Such microswimmers can be rather elongated, filament- or polymer-like. Examples are bacteria swarmer cells, *e.g.*, *Proteus mirabilis*, forming up to 100μm long multinucleate structures [2], or marine phytoplankton dinoflagellates assembling in a linear fashion. Artificial polymeric assemblies of microswimmers have also been recently synthesized [3]. In order to address the relevance of hydrodynamic interactions in the motility of these swimmers, we study the swimming properties of linear polymer-like assemblies by mesoscale hydrodynamic simulations (multiparticle collision dynamics [4]), where an active unit (monomer) is described by a spherical squirmer [5]. The latter allows us to control the nature of the propelling unit: a pusher, a neutral swimmer, or a puller. We find that the monomer hydrodynamic flow field leads to correlations in the relative orientation of adjacent monomers, and consequently the swimming efficiency differs from that of active Brownian linear assemblies [7]. In particular, pullers show a pronounced increase in the rotational diffusion coefficient compared to pushers, while for neutral squirmers, the rotational diffusion coefficient is similar to that of active Brownian particles. Hence, the large-scale conformational and dynamical properties depend on the specific propulsion mechanism.

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Red blood cell shows a variety of different shapes in flow due to complex interplay between its membrane elasticity and hydrodynamics [1]. During malaria infection, adhesion of infected red blood cells (iRBC) to endothelial microvasculature is a key step for the parasite survival and its further multiplication. During the parasite development, iRBC morphology, stiffness and adhesiveness changes drastically and its interaction with the flow leads to complex adhesion dynamics such as crawling, flipping and rolling. Using a particle-based mesoscale hydrodynamics approach and coarse-grained model of iRBC, we show that adhesion dynamic state not only depends on the stage of infection or membrane elasticity, but also on the flow shear stress. We show that mid-stage iRBC flips at lower shear stress flows, which is replaced by crawling beyond a critical shear stress. This critical shear stress increases with both membrane stiffness and viscosity contrast between the cytosol and suspending medium [2]. This transition from flipping to crawling resembles tumbling to tank-treading transition of RBCs in free shear flow. Such a change in adhesion dynamics directly affects how iRBCs interact with vascular endothelium [3].

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Shear banding in elastoviscoplastic materials

Shear banding has been shown to occur in a wide range of yield stress fluids [1, 2] as a transient effect during shear startup, when the material yields from an initially solid-like to finally fluid-like state, associated with an overshoot in the bulk signal of stress with respect to time (or equivalently accumulated strain).

The aims of this study are to elucidate the degree to which this phenomenon is universal across all yield stress fluids. In particular, we examine the degree to which it occurs across a suite of different constitutive models, including simplified fluidity models resembling
that in [3], the Isotropic Kinematic Hardening model [4], and the Soft Glassy Rheology Model[5]. The results of this numerical study are then used to make some general remarks concerning the appropriate structure of constitutive models for yield stress fluids. We also ask whether the effect can be reduced or eliminated according to the strain protocol imposed.

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Microfluidic flow-processing of soft matter systems

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Arguably one of the most striking properties of soft matter systems is the propensity to have a major response to minor perturbations. One of such perturbations is flow, which allows to induce phase changes and structural rearrangements.

Here, two pseudo-quaternary systems containing sodium dodecyl sulfate (SDS) and medium to long chain alcohols as co-surfactants in a lamellar phase (L_α) are studied. The structural transformation from planar lamellar sheets to multilamellar vesicles (MLVs) is observed upon the application of shear stress to the solution.

This transformation is characterised with nuclear magnetic resonance (NMR), rheology and small angle neutron scattering (SANS). Furthermore, the kinetics of the transformation is resolved with real-time measurements within a microfluidic device to obtain well-defined shear fields. Time-resolved kinetics are investigated by tracking the changes in birefringence pattern employing cross-polarised microscopy. The results point to MLV formation and indicate that it is a time-dependent and shear-rate dependent process.

The combination of microfluidics with high resolution spatio-temporal measurements allows characterisation of out-of-equilibrium transformations in complex surfactant mixtures.

Cubosomes/AT101 systems for drug delivery: translational diffusion investigated with NMR technique and *in vitro* therapeutic efficiency

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Cubosomes are colloidal nanoparticles with a cubic shape, built of a bicontinuous cubic phase. Their structure resembles exotic membrane systems naturally occurring in cells, which enables the trapping of a number of active pharmaceuticals with different polarity, including chemotherapeutic agents. This feature of such systems leads to an increase of the drug solubility and its *in vitro* and *in vivo* uptake. An important advantage of these systems is also their outstanding stability and the possibility of controlled modification of the curvature of their membranes, and thus the system of water channels responsible for the diffusion of loaded drug molecules.

In this study cubosomes were prepared with the *top-down* method from the gliceryl monooleate, and were loaded with the hydrophobic anti-cancer drug gossypol AT101. The morphology analysis of these systems using transmission electron microscopy (cryo-TEM) and dynamic light scattering (DLS) and zeta potential proved that the obtained cubosomal nanoparticles are structurally complex and stable colloidal systems. Moreover, loaded AT101 molecules in addition to their important role as a drug, additionally have a significant effect on the colloidal stability of these systems. BDOSY analysis (Bayesian Diffusion Ordered Spectroscopy) using the MNova program 12 obtained NMR spectra (Nuclear Magnetic Resonance Spectroscopy) allowed for the determination of the translational diffusion coefficients separately for each of the individual fractions present in the studied systems. The obtained results characterize the polydispersity degree prepared cubosomal nanoparticles and provide insight into their physical stability and confirm the binding efficiency of the drug. Finally, i*n vitro* studies using glioblastoma cancer cells show the high potential of this system for anticancer therapy.

Acknowledgements
This work was supported by the National Science Center, Poland, under grant SONATA BIS 6 "Cubosomes - liquid-crystal nanoparticles as a potential bioimaging systems”.

Effect of bidispersity on the crystallization and the molecular topology of linear semicrystalline polymers by Molecular Dynamics simulations

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Preferred presentation: oral

Keywords: semicrystalline polymers, bimodal molecular weight distribution, Molecular Dynamics, molecular topology

The molecular topology of the amorphous phase is very important to understand the mechanical properties of semicrystalline polymers. In particular, it was argued that tie segments, linking two adjacent crystallites, contribute most effectively to the mechanical behaviour. Previous experimental works have also inferred that the molecular weight distribution is a key factor for the formation of tie molecules. Bimodal Molecular Weight Distribution (MWD) polymers are very attractive since the high-molecular-weight component enhances the mechanical properties, while the low-molecular-weight polymer chains promote the melt to flow easily. However, the influence of a bimodal MWD on the crystallization has not been investigated in detail, and experimental techniques can hardly access the molecular topology. Therefore, in this contribution we resort to molecular simulations in order to overcome difficulties of experimental measurements and to study quantitatively the nonequilibrium process of crystallization at the nanoscale.

We perform extensive Coarse-Grained Molecular Dynamics simulations of the crystallization of uni- and bimodal MWD polymers with different long-chain content: we study the nucleation behaviour and the influence on the final molecular topology. We find that the incubation time, i.e. the time elapsed before the establishment of steady-state nucleation, first decreases with the weight fraction of long chains, reaches a maximum, and then increases. This results from the conflicting effects of free energy barrier and mobility of chain segments. The free energy barrier decreases with the weight fraction of long chains, which is attributed to the transition from intermolecular to intramolecular nucleation, whereas the chain mobility decreases with increasing long-chain content. Nevertheless, the growth rate of crystallites decreases continuously with the weight fraction of long chains, mainly resulting from reduced chain sliding diffusion. We also propose an efficient numerical algorithm to access quantitative data of molecular topology (i.e., loop, tie, and cilia segments). It turns out that the concentration of loop and tie segments increases with the increasing weight fraction of long chains. This work provides useful molecular insight on the role of bimodal MWD on the crystallization of semi-crystalline polymers.

Emergent conformational and dynamical properties in systems of active filaments

A. Martin-Gomez, T. Eisenstecken, G. Gompper, R. G. Winkler

Active matter is comprised of agents which either convert internal energy or exploit energy from the environment to generate directed motion. The associated out-of-equilibrium character of active matter is the origin of a number of fascinating phenomena [1]. In particular, active systems with many internal degrees of freedom like filamentous, polymer-like structures are involved in various biological processes and exhibit novel conformational [2] and dynamical properties [3]. On the nano- and micro- scale, these active agents are typically dissolved in a fluid, and hydrodynamic interactions (HI) are essential for their behavior. Yet, such interactions are usually neglected. To shed light onto the effect of fluid mediate interactions on the conformational and dynamical properties of active polymers, we performed analytical calculations and computer simulations.

The polymer is described as a linear bead-spring chain exposed to a non-Markovian exponentially correlated temporal noise (colored noise), describing activity, and HI are taken into account by the Oseen tensor. Without HI, flexible polymers swell with increasing activity, whereas stiff polymers shrink initially and swell again at even larger activities [2, 3]. The presence of HI leads to an even stronger shrinkage of the polymers, even flexible polymers exhibit shrinkage at moderate activities. Contrarily, self-avoidance seems to hinder such shrinkage for flexible polymers, but becomes irrelevant at higher stiffness. Dynamically, the polymers exhibit an enhanced activity-induced diffusive motion, which is further amplified by HI [4].

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Membrane proteins are involved in several key cellular functions such as signal transduction and intracellular transport. Dysfunction of these proteins is associated with diseases such as cancer, diabetes, and Alzheimer's. In many cases, clustering of membrane proteins is an essential step for them to be able to carry out their functions. There are a large number of studies that have investigated lipid-protein interactions during clustering, in order to understand at a molecular level how nano and mesoscale membrane organization contribute to lateral membrane compartmentalization. However, the physical mechanisms that are responsible for the clustering of membrane proteins are not well understood. Moreover, similar to colloidal forces, the tools to be able to quantify these interactions and precisely measure the forces between the proteins have not been developed. Thus, the central question of our project is: What is the physical nature of the forces that govern the clustering of membrane proteins, and how can they be measured with precision? To address these questions, I am developing a novel FRET and DNA nanotechnology-based force sensor. By coupling the sensor to 2 proteins and having a pair of FRET dyes attached to its arms, the FRET signal provides a direct readout of the distance between the proteins. Furthermore, combining this information with a sensor that is calibrated for stiffness, the forces between membrane-bound or transmembrane proteins can be calculated. To begin with, I am studying the B-subunit of Shiga toxin (STxB) that is able to cluster at the surface of Giant Unilamellar Vesicles (GUVs). It was proposed that this clustering results from attractive Casimir-like forces that have an entropic origin. To test this hypothesis, I will check with our DNA-force sensor how the interaction depends on the GUV tension. In the long term, this sensor could be used on cells to study interactions between membrane proteins on the plasma membrane in general.

3D-DDLS

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Depolarized dynamic light scattering, DDLS, is a usable tool for investigating optically anisotropic colloidal particles. In dilute systems both the translational and rotational diffusion can be determined in a DDLS measurement. The downside of this technic, as with conventional dynamic light scattering, is that it is limited to transparent samples. For conventional dynamic light scattering, DLS, several different methods are being used to overcome the problem with turbidity. We are using a 3D-DLS setup for measuring turbid samples and have now added the possibility to also measuring 3D-DDLS. Due to the focusing of the beams the polarization at the detection is slightly tilted in comparison to the incident beam. This tilt is scattering angle dependent and in different direction for the two beam with a maximum tilt of about 7degree at 90 degree scattering angle. Using this setup we have measured silica coated hematite ellipsoids with different aspect ratio at several scattering angles. We get a q^2 dependence of the extracted relaxation rates, Γ, with an intercept that corresponds to the expected rotational diffusion. The 3D-DLS measurements have been possible to perform down to a transmission of 0.2%. This means that the rotational diffusion will not only be accessible for a larger spectrum of system but also for a broad range of concentrations where interactions start to play a more dominant role. This work is a part of EUSMI Joint Research Activities.

CORRELATION OF SILANE GRAFTING DENSITY WITH RHEOLOGICAL PROPERTIES OF SILICA FILLED RUBBER: COUPLING OF FLOW AND TEMPERATURE

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The development of tires with low rolling resistance passes through the addition of silica into the elastomers especially in the thread. Unfortunately, many volume defects appear during extrusion of the strips which are responsible for a decrease in industrial performance. The understanding of the interactions between the components of the mixture and the analysis of the rheological behavior are then essential to explain the origin of such extrusion defects. This work proposes to provide an understanding and rheological description of the micro-structural origin of the intensity of the volume defect.

To this end, **model non vulcanized** mixtures with a simplified formulation but generating volume defects during their extrusion were studied under controlled mixing conditions (Butadienne rubber BR, Styrene-Butadienne Rubber SBR, Silica + coating agent or coupling agent).

Several rheological descriptors were correlated with the silica / elastomer grafting rates measured by NMR and chemicophysical analyzes. Unsurprisingly, an increase in the rheo-thickening behavior under uniaxial elongational flow is observed with the increase in the degree of grafting. However, the rheological properties are highly dependent on the mixing conditions. These results are explained by interconnection of fillers aggregates by grafted elastomer. This network is promoted by temperature but destroyed by the flow. Therefore, a competition is noticed between the grafting reactions and rupture phenomena which respectively cause the growth or decrease in the size of the connected objects responsible for the rheo-thickening behavior.

A model describing this competition has been developed based on percolation theory in aggregated clusters coupled with the kinetics of clusters breakup under flow. It allows a good estimation of the rheological descriptors according to the mixing conditions.

Few-layer graphene based nanocomposites for potential use in dental/biomedical applications

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Statistically, we chew around 800 times in an average meal - that is almost a million times a year. We put our teeth under huge mechanical strain, and often require fillings to repair them. Fillings are typically made of a mixture of metals, such as copper, mercury, silver and tin, or composites of powdered glass and ceramic. Typical metal fillings can corrode and composite fillings (thus far) are not very strong; Graphene on the other hand is 200 times stronger than steel and doesn’t corrode, making it a prime new candidate for dental fillings. Graphene could therefore, be used to make mechanically stronger composite-dental fillings, which do not corrode. Despite some challenges and the fact that carbon nanotubes-polymer composites are sometimes better in some particular performance, graphene-polymer composites may have wide applications in dentistry due to their outstanding properties and the availability of graphene in a large quantity and at low cost. One of the main problems, for patients, associated with dental-polymers is that of location. This stems from the fact they are within the mouth and this proves to be an extremely demanding setting, where exposure to moisture, high temperatures, and abrasion from toothbrushes plus intake of food all have an effect. These conditions can lead to complications such as mechanical failure, which could negate clinical success and over time mandates remedial work for restoration with associated cost and inconvenience. Graphene has potential applications in dental-polymer materials as it has the required mechanical properties as well as being biocompatible. Here we present new work into the application of graphene for the fabrication of potential dental-polymer materials (Fig. 1).

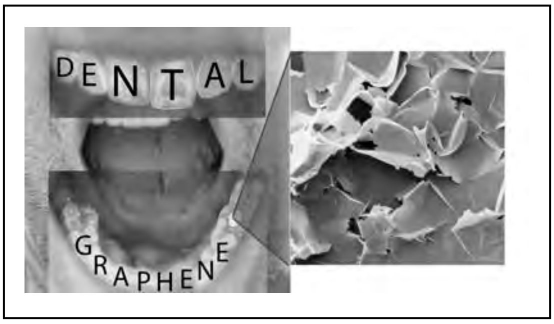

Fig.1 Helium Ion Micrograph of Few-Layer Graphene.

Molecular behaviour of series of alkyltrimethylammonium-based ionic liquids

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An important feature of ionic liquids (ILs) is the possibility to tune their physical, chemical and biological properties by the choice of the cation and anion in order to fit a selected application. ILs have been successfully used as solvents in organic and inorganic synthesis, catalysis, extraction and separation, electrolytes or as functional materials[1]. While many works about ionic liquids focus on their applications, the key to understanding the relation between their structure, properties and eventually their application, is the understanding of their molecular behaviour[2,3].

A set of alkyltriethylammonium bis(trifluoromethanesulfonyl)imides was prepared and characterized. The molecular dynamics of the [N222R][TFSI] ionic liquids was studied by the temperature dependent relaxation and self-diffusion (^{1}H and ^{19}F) NMR measurements, along with thermodynamics studies, and X-ray diffraction. Our study provide quantitative details of the molecular behaviour of the series of alkyltriethylammonium ionic liquids, presenting the variation in their behaviour along with the alkyl chain elongation.

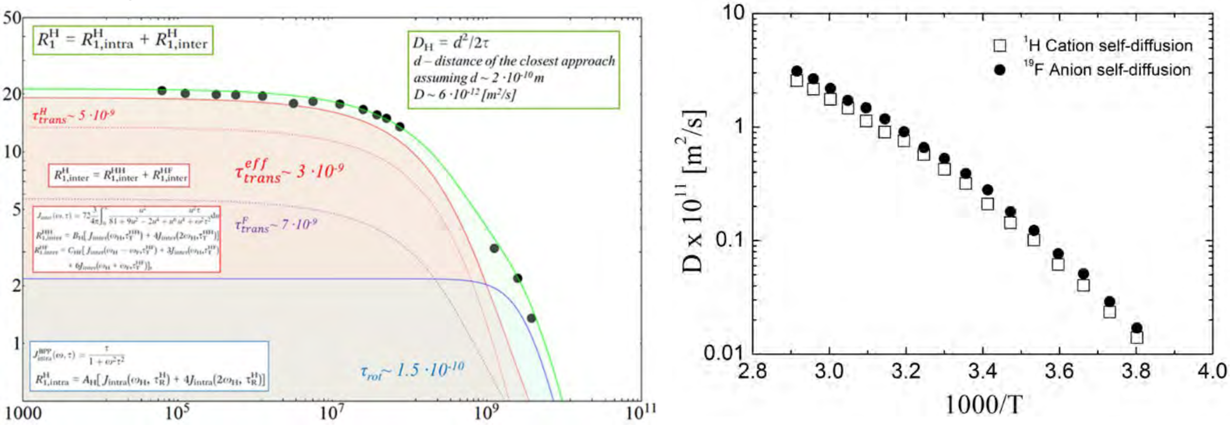

***Fig 1 (left)** Dispersion of spin–lattice relaxation times T1(ω); the fit of the total spin-lattice relaxation rate (green solid curve) is decomposed into the rotational (RotHH) and translational (TrHH) contributions. **(right)** The ^{1}H and ^{19}F PFG-NMR diffusion. Both pictures relate to dodecyltriethylammonium bis(trifluoromethanesulfonyl)imide.*

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Active $CoFe_2O_4$@Pt nanostructures propelled by catalytic reduction of borohydrides

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Abstract:

Developing artificial swimmers at the nano- and microscale has emerged as a new class of active matter. These mobile structures are opening up novel applications ranging from biosensing to drug delivery in environments dominated by a low Reynolds number.[1] While keeping complexity low, such systems should also overcome the influence of Brownian motion, viscous drag and various surface phenomena. Nature has inspired numerous designs founded on the swimming patterns of microorganisms. Mimicking these features might thus enable the design of structures that propel themselves by taking up energy from their surroundings and transforming it into directed motion.[2] The controlled motion of these structures is thereby of interest for both fundamental research and emerging applications. Within this approach, considerable research is focused on the design of catalytically active Janus particles.[1] In general, the propulsion concept of these systems lies in the catalytic activity of anisotropic artificial structures for fuel consumption only at one side of a particle, thereby producing a chemical concentration gradient and steady-state flow of the surrounding medium that impulses the swimming object forward, resulting effectively in self-propulsion.

Here, we present novel heterofunctional $CoFe_2O_4$@Pt nanostructures activated through a coupled chemical fuel system based on the catalytic reduction of borohydrides. The nanostructures are prepared via a seed-mediated growth process, which entails a stable interface linkage between the $CoFe_2O_4$ and Pt domains.[3] The propulsion is generated by a concentration gradient considering fuel and reaction products in the vicinity of the catalytic nanoobject, and by railing their direction using a homogeneous magnetic field in order to reduce the predominant rotational diffusion for nanoscoped swimmers. This investigation includes the systematic synthetic approach implemented to prepare nanostructures in a size range smaller than 50 nm, the development of a new fuel system and the real-time tracking of the motion using dark-field light scattering microscopy.

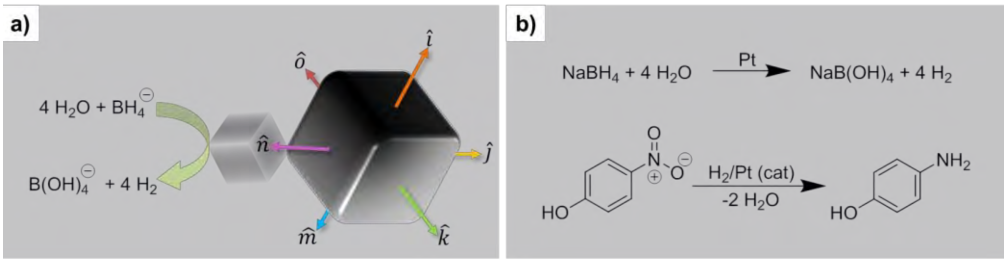

Figure1. Schematic illustrations showing a) $CoFe_2O_4$@Pt nanostructures and b) fuel system proposed in this research

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Modeling shear-induced crystallization of segmented block copolymers: A coarse-grained molecular dynamics study

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Semi-crystalline segmented block copolymers made of hard and soft segments are widely used in the industry as thermoplastic elastomers since the 1960s for their rubbery properties and ease of processing. These materials are known to form phase-separated domains due to the crystallization of the hard part. The kinetics of this process is strongly dependent on the processing conditions. In particular, the enhancement of the structuring due to a mechanical solicitation, often called flow-induced crystallization, is of great interest from an industrial point of view. In a recent paper, we studied the effect of startup shear flow on the crystallization kinetics of these copolymers from both experimental and theoretical points of view. [1] We showed that the transient mechanical response of the material in shear flow could be well described by a Doi-Edwards model modified to account for the slowdown of the amorphous phase dynamics due to crystallization.

Here we propose to investigate the effect of shear on the crystallization kinetics through a series of molecular dynamics simulations. The model for building copolymers is based on a modified version of the Kremer-Grest coarse-grained model leading to a semi-crystalline structure. [2] The differences between hard and soft segments are taken into account by tuning the chain stiffness, density and interaction strength. The enhancement of the crystallization kinetics is then studied in startup flow as a function of the shear rate. While very few apparent effects can be seen on the stress-strain curve, an increase of the crystallization rate is shown by using local order parameter techniques to detect crystallites (see figure below). [3] We found that the induction time for crystallization is essentially driven by the total amount of strain, in agreement with experiments. [1] The effect of the deformation on the chain conformation is also analyzed using the orientation tensor and the nematic order parameter, allowing us to make the link between chain alignment and increase of the nucleation rate.

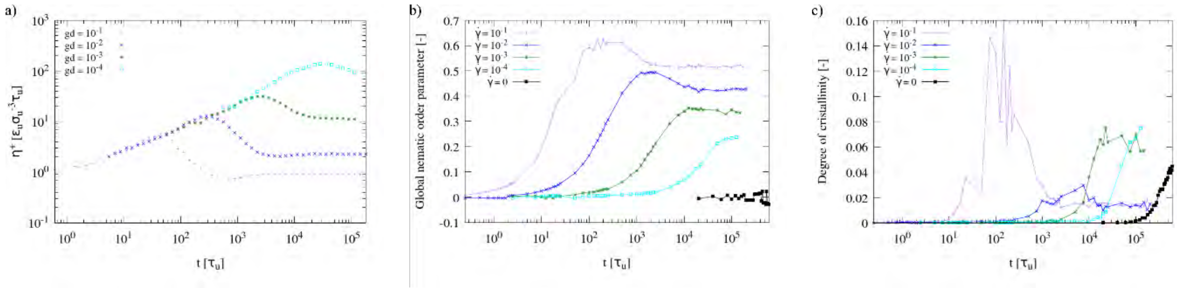

Figure: Evolution of the viscosity (a), global nematic order parameter (b) and degree of crystallinity (c) during startup flow at various shear rates.

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STRUCTURAL MODIFICATIONS OF LIPID LIQUID CRYSTALLINE NANOPARTCLES CAUSED BY PHYSICAL AND CHEMICAL FACTORS

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Lipid liquid crystal nanoparticles (LLC NPs) in form of cubosomes are a group of attractive structures which can be potentially used in biomedical applications. The most important features that determine their usefulness in a biomedical field are: large active surface area, biocompatibility, stable structure, and their most important feature, the ability to absorb and release hydrophobic and hydrophilic molecules. However, not only their practical application is the reason to study their complex nature. The motivation for the basic research is also the uniqueness and variety of their structure and how different factors can influence on cubosomes' phase behavior.

Bicontinuous cubic particles, cubosomes, are composed of curved lipid bilayers dividing a three-dimensional space on the intertwined, but not connected with each other water channels. They are stable colloids in the presence of surfactants. In order to investigate the LLC NPs' structure we used cryo transmission electron microscopy (cryoTEM). This technique allows to follow possible morphological change's in natural, hydrated states of those nanoparticles. Small angle X-rays scattering measurements were also performed to have better insight into crystalline structure taking into account large population of LLC NPs.

Structural changes of LLC NPs were induced in three ways: by simple heating of the system, changing concentration of lipids and ratio of lipids to surfactants, as well as incorporation into the system functional additives. The term "functional" means that additives (quantum dots, iron oxides, drugs) enrich LLC NPs in properties useful from the point of view of biomedical applications like optical and MRI bioimaging.

Acknowledgements: This work was supported by the National Science Center Poland (NCN) under research grant SONATA-BIS 6: 2016/22/E/ST3/00458

Frank-Tobias Hirschmann, Martin Oettel and Hender Lopez

Coarse-graining proteins for better insights into their diffusion behavior in solution

We discuss coarse-graining strategies and resulting models for bovine serum albumin (BSA) and immunoglobulin (Ig) proteins. The models consist of effective beads with intraparticle interactions parametrized by all-atom simulations. Interparticle interactions are adapted to experimental results for the compressibility of protein solution obtained by scattering. Brownian dynamics simulations of diffusion in these coarse-grained systems allow to disentangle translation, rotation and internal bead motion which all contribute to the signal in dynamic scattering experiments.

Influence of wall heterogeneity on polymer nano-sandwiches: a multiscale study

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Many applications of polymeric materials involve their dynamics on rough or chemically heterogeneous surfaces. Examples include adhesion, friction and rubber reinforcement by fillers. Surface heterogeneities lead to significant differences with respect to smooth surfaces, but our understanding of their role remains incomplete. To investigate this issue, we performed extensive molecular dynamic simulations of a recently introduced model of polymer melt confined between surfaces with increasing spatial correlation (patchiness) of weakly and strongly interacting sites [1] (Fig.1). In the first part of the talk, we will focus on the chain dynamics and show that major changes do occur on changing the typical size of the heterogeneities, while keeping constant the surface chemical composition. When the surface patchiness exceeds a certain threshold, a dramatic decoupling between diffusion and structural relaxation occurs, which resembles the Stokes-Einstein breakdown in glass forming materials. Surprisingly, these large dynamical effects are accompanied by minor structural modifications. In the second part of the talk, we will discuss the multiscale counterpart of this behaviour, by investigating the relaxation dynamics over a wide range of probe-lengths, from fractions of monomer diameter up to exceeding the chain gyration radius [2]. Our work suggests that, by proper design of the solid walls, it is possible to tune major dynamic and mechanical changes in nanoscopically confined polymers, and highlights the importance of controlling not just the surface chemistry but also the surface morphology.

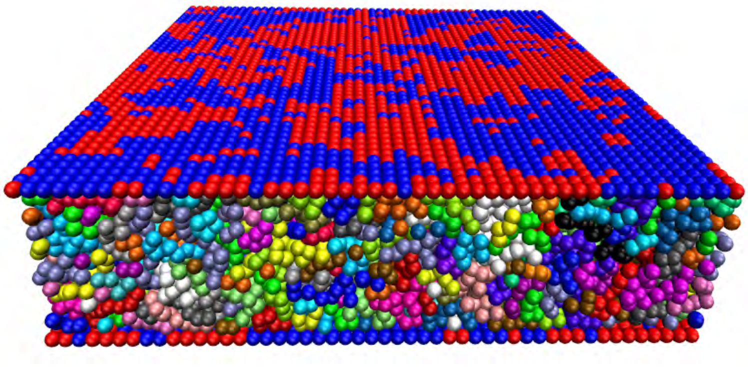

Figure 1. Illustration of the investigated system. Blue and red surface beads correspond to strongly and weakly interacting sites, respectively.

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Optimization of graphene support to enable the direct visualization of surface ligands

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Graphene shows unparalleled properties in terms of structure, conductivity and thickness[1]. These properties have resulted in different applications, such as its use as a sample support in the field of electron microscopy[2]. However, depending on the method to transfer the graphene and its final cleanliness (amount of remaining contaminants) the quality can be severed, avoiding or limiting some applications.

Here we present a home-made transfer of graphene in order to retrieve clean graphene supports. These clean and thin graphene supports enable the investigation of soft materials such as surface ligands[3], for which the characterization is extremely challenging due to their lack of contrast. In this study, we used the optimized graphene supports in combination with exit wave recontruction (EWR) to visualize surface ligands around nanoparticles (Figure 1).

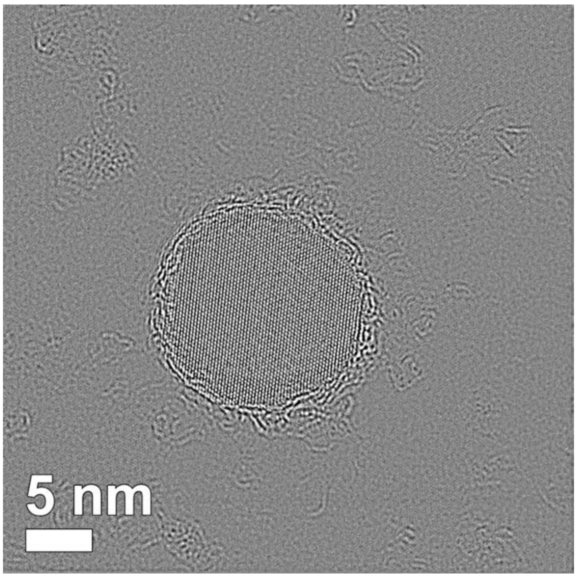

Figure 1. Phase image obtained by EWR from a Au nanosphere surrounded by polyethylene glycol (PEG) deposited on a home-made graphene grid.

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Self-assembling properties of an amphiphilic hopanoid covalently-bonded lipopolysaccharide (LPS)

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Lipopolysaccharides (LPSs), major components of the outer membrane of Gram negative-bacteria, are essential for bacterial growth and survival. They act as a structural barrier and play an important role in the pathogenic or symbiotic interaction with eukaryotic hosts. We have recently demonstrated that a photosynthetic *Bradyrhizobium strain* synthesizes a novel LPS bearing a covalently attached hopanoid to the lipid A portion. Hopanoids are pentacyclic triterpenoid derivatives and constitute an important class of membrane compounds widely distributed in a diverse range of bacteria, including some rhizobia. These molecules are thought to act as membrane stabilizers, control fluidity and permeability and assure integrity of bacterial cell envelope.

In the present research, we investigate the self-assembling properties of an amphiphilic hopanoid covalently-bonded lipopolysaccharide (HoLA), and of its mutant, in the presence of POPE and POPG phospholipids to form lamellar vesicles biomimicking the bacterial outer membrane. A combined experimental strategy is adopted, including dynamic light scattering (DLS), small-angle neutron scattering (SANS) and electron paramagnetic resonance (EPR). The experimental techniques employed in this work allow us to fully characterize the considered systems at different observation scales, from the meso- to the microscopic level, i.e. from the morphology of the vesicles to the structural arrangement of the LPS molecules in the bilayer. Particularly, DLS measurements reveal the formation of liposomes and allow us to estimate their dimension; SANS measurements confirm the formation of unilamellar vesicles and allow us to estimate the thickness of the lipid bilayer; EPR measurements allow us to investigate the dynamics of the lipid hydrophobic tail in the bilayer, giving information on the local microstructure. The final aim of this biophysical analysis is to correlate the structural properties of this novel LPS to the complex architecture of the bacterial outer membrane, which consequently modulates the cell wall resistance.

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INTERNALIZATION, INTRACELLULAR LOCALIZATION AND CYTOTOXICITY OF LIPID-BASED LIQUID CRYSTALLINE NANOPARTICLES AND THEIR HYBRIDS WITH INORGANIC NANOPARTICLES

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Lipid-based liquid crystalline nanoparticles (LLC NPs) in form of cubosomes get an increasing interest as a novel bioimaging agent and drug delivery system. It is mainly because of number of advantages such as an enhanced stability, biocompatibility, high surface area to volume ratio and presence of both hydrophilic and hydrophobic regions.

Here, the glyceryl monooleate (GMO)-based cubosomes were prepared by top-down ultrasonication method. In order to enable the visualization during studies and to obtain optical nanoprobes, two types of systems were prepared: (1) cubosomes hybrids with incorporated CuInZnxS2+x (ZCIS) quantum dots and (2) cubosomes incorporated with fluorescent dye (Nile Red). The physico-chemical characterization and cytotoxicity analysis of prepared cubic systems were conducted. Afterwards, detailed analysis of LLC NPs internalization into mammalian cells and their final localization were performed. Firstly, the influence of different endocytic inhibitors on the cellular uptake was assessed, indicating that there is no one mechanism of their uptake, both the energy independent, cholesterol dependent manner and macropinocytosis can be distinguish. To understand the intracellular behavior of LLC NPs and their hybrids the distribution was visualized by confocal laser scanning microscopy (CLSM), and they were localized in cytoplasm, mainly in its perinuclear region. The exact localization of nanoprobes inside cells at the ultrastructural level was also confirmed with transmission electron microscope (TEM).

The internalization and intracellular localization of nanostructures have a significant impact on their toxicity, drug administration ability and retention time, what in turn influences the further successful use of LLC nanoparticles in theranostics.

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Chain-length dependent relaxation dynamics and transport properties in glass-forming oligomers and polymers

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Understanding how a glass is formed on a microscopic level remains an outstanding problem in condensed matter physics; both the approach towards the glassy state and the molecular behaviour within the glass remain to be fully understood. Moreover, how chain connectivity in oligomers and polymers affect the relevant molecular behaviour and transport properties is not presently clear. The work presented here addresses these questions through a systematic experimental study ranging from small molecules to oligomers and polymers, including molecular systems of different characteristics (flexibility, fragility, etc). The effects of molecular chain-length on rheology, chain, structural and secondary relaxations are explored using a range of experimental techniques. Results attained from rheology, broadband dielectric spectroscopy and calorimetry will be discussed, outlining their role in determining the material response for molecules of different chain-length and chemistries. The work will be presented in the context of established models and behaviour previously reported in the literature.

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Thiol-ene chitosan hydrogels: From macro to microgel

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The thiol-ene click chemistry is a versatile methodology widely used to form bio-hydrogel by crosslinking polysaccharides. In this opportunity, chitosan-based macrogels were prepared through thiol-ene reactions. First, the chitosan (CS) was functionalized with a vinyl group (CS-ene) or thiol groups (CS-SH). Then, two crosslinking strategies (photochemically and thermochemically activated) were compared: (1) CS-ene with CS-SH and (2) CS-ene cross-linked with di(ethylene glycol)-bis(thiol) (dEG-$(SH)_2$). The first strategy, where the crosslinking reaction occurs between two functionalized macromolecules and intra-chains crosslinking reactions are avoided ("no loop"), leads to the formation of weak gels. In this case, rheology displays a critical gel point ($G' \approx G'' \approx \omega^{0.5}$) and the cross-linking density estimated by NMR slightly depends on the substitution degree of pentenoate-modified CS. The second strategy, where the functionalized chitosan (CS-ene) is crosslinked by reaction with a small di-thiol molecule (dEG-$(SH)_2$), provided stronger gels with a faster diffusion of the dEG-$(SH)_2$ during the network formation, which strengthen the gel modulus. The last strategy is the most efficient methodology for the macrogel synthesis, despite that the "loop" formation cannot be fully avoided. Finally, both methodologies were transposed at the microscale through inverse emulsion to attempt to synthesize chitosan-based microgel.

HYDRODYNAMIC DIMERIC AND TRIMERIC PHORETIC SWIMMERS

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ABSTRACT

Self-propelled phoretic colloids have recently emerged as a promising avenue for the design of artificial microswimmers. By studying the hydrodynamics of a single swimmer, we can predict the behaviour of large ensembles of colloids. A hydrodynamic fluctuating mesoscale simulation approach is here employed [1]. We present the hydrodynamic velocity fields of various swimmers with different structural shapes. Dimers, rod-like trimers, and v-like trimer are investigated for swimmers with monomers of equal or different sizes in quasi-two and three dimensional systems. The competition between attractive or repulsive hydrodynamic and phoretic interactions varies as a function of the oligomer geometry and phoretic affinity (philic or phobic), which eventually results in a rich phenomenology such as clustering, swarming, or rotational motions [2].

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Self-assembly of filaments on a curved manifold

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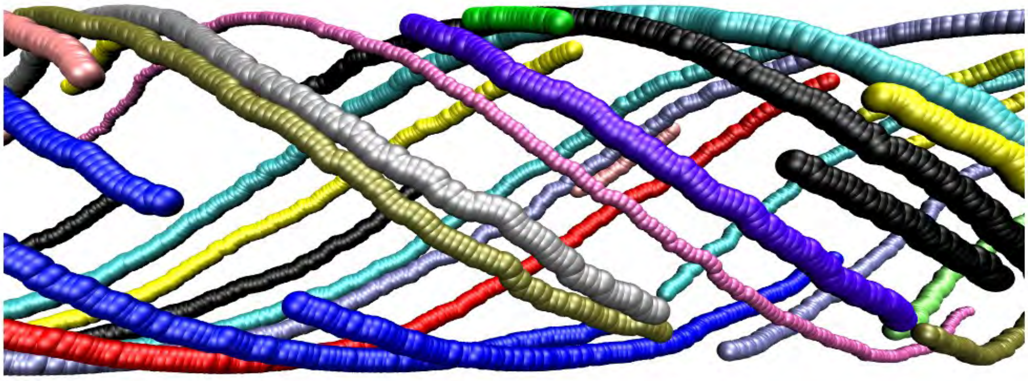

Simulation snapshot of a cylinder with self-assembled trimers

Rod-like proteins, like BAR-domain proteins or RodZ and MreB proteins, have been shown to adsorb on membranes and to regulate the membrane curvature. The formation of large complexes of these proteins plays an important role in celluar processes like membrane trafficking, cytokinesis and cell motion.

In our work, we propose a simplified model to investigate such curvature-dependent self-assembly processes. We simulate the assembly of trimers on the surface of a cylindrical membrane. Anisotropic monomers, modelled as trimer molecules, which have a preferred binding side, interact via pair-wise Lennard-Jones potentials. When several trimers assemble, they form an elastic ribbon with an intrinsic curvature and twist, and a bending and torsional rigidity. Since the trimers are are bound to the curved surface of the cylinder, this leads to a preferred spatial orientation of the ribbion.

We show that these interaction leads to the formation of helices with several windings around the cylinder. The emerging helix angle depends on the rigidities and the preferred curvature and twist values. In particular, a well defined and controllable helix angle emerges in the case of equal bending and twist rigidity.

Density-based protein-protein docking

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Predicting the assembly of multiple proteins into specific complexes is critical to the understanding of their biological function in an organism, and thus the design of drugs to address their malfunction. Proteins are flexible molecules, and this inherently poses a problem to any protein docking computational method, where even a simple rearrangement of the side chain and backbone atoms at the interface of binding partners complicates the successful determination of the correct docked pose. We present STID maps, a structural descriptor capable of simultaneously representing protein surface, electrostatics and local dynamics within a single volumetric descriptor. We then demonstrate that the application of STID maps into a protein-protein docking scenario bypasses the need to accommodate for specific side chain packing and small conformational changes at the interface of binding partners. This representation is leveraged in our de novo protein docking software package, JabberDock, which we show can accurately predict complexes with success rates comparable to or greater than currently available methods.

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Interfacial Tension of Complex Fluids with Microfluidics and Machine Learning

Dale Seddon and João T. Cabral

Interfacial tension is a property that is extremely important to many systems in both nature and industry. The effects of interfacial tension are apparent in the stability of mixtures and emulsions in everyday life with products in the food, household, cosmetic and chemical sectors, among many more. There are several methods for measuring interfacial tension, such as the Pendant drop and Wilhelmy plate. However, these are usually batch methods with low-throughput. Other problems associated with these techniques include limited range of measurement and the lack of applicability to complex fluids such as surfactant systems.

The Taylor analysis, named after G.I. Taylor, was developed in the 1930’s to measure the interfacial tension of two immiscible fluids. The technique examines how a droplet deforms as hydrodynamic shear is applied in a well-defined flow field. This analysis has been applied in microfluidics, studying how droplets deform as they approach a geometric constriction. The microfluidic Taylor analysis allows high-throughput for rapid characterisation of droplet deformation.

Deep learning will be combined with microfluidics to create a rapid, continuously operated system to accurately measure the interfacial tension of soft matter systems. Convolutional neural networks (CNN’s) will be used with images obtained of droplets in a microfluidic constriction to predict the interfacial tension value. The training set will include these images and the ground truth will be the Pendant drop interfacial tension measurements. This approach allows rapid examination of complex non-spheroidal, non-Newtonian droplets that cannot be resolved using conventional Taylor analysis.

Confocal laser scanning microscopy study of stress-sensing poly(*N*-isopropylacrylamide) hydrogel networks crosslinked with mechanofluorophores

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As the extreme softness and intrinsic fragility of polymeric hydrogel networks impose limitations in respect to their mechanical characterization by employing conventional measurement methods, it is important to develop more sophisticated methodologies and characterization techniques.[1] The biological and biomedical applications of hydrogels render both their physicochemical and mechanical response, over a range of hydration levels, of particular interest and their control beyond critical.

Here, we report the integration of the Diels-Alder adduct of a π-extended anthracene and maleimide[2] as covalent crosslinker into poly(*N*-isopropyl acrylamide) (PNIPAAm) structure, a typical and well-investigated thermoresponsive hydrogel with mechanical behavior that can be fine-tuned depending on its water-absorption capability.[3] A hand-induced needle-puncturing process was realized, after swelling the networks with varying amounts of water, as an alternative to conventional force application methods, owing to the sensitivity of the mechanofluorophore that allowed the analysis of low levels of mechanical stress.[4] The subsequent fluorescence caused by covalent bond scission was visualized with confocal laser scanning microscopy (CLSM), and the intensities of the hydrogel samples with different swelling degrees were correlated to the macroscopic fracture mechanics and their elastic moduli recorded with traditional uniaxial compression.

The detection and precise localization of stress accumulation around a defined region of interest *via* CLSM promotes a productive correlation of material properties and mechanophore fluorescence and facilitates the further elucidation of the interrelationship between the molecular structure and the macroscopic properties of chemically crosslinked polymeric hydrogels. This mechanophore-assisted fractography with µm-resolution can establish a new paradigm for the mechanical analysis of soft matter in fields covering traditional polymer and life sciences.

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Viscoelastic Polyelectrolyte Complex Coacervates as Soft Underwater Adhesives

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Associative, liquid-liquid phase-separation of oppositely-charged polyelectrolytes, leading to a polymer-rich coacervate and a polymer-lean supernatant, is called "polyelectrolyte complex coacervation". This phenomenon is ubiquitous in biological systems. For instance, the underwater adhesive of a marine organism called sandcastle worm is based on coacervates.

Inspired by this organism, we have developed viscoelastic complex coacervates from synthetic polyelectrolytes as model systems for underwater adhesion. Due to the electrostatic nature of the ionic bonds between the charged polyelectrolytes, the mechanical properties of these systems are highly sensitive to the ionic strength of the medium. The dynamic properties of the materials are studied over a large range of time scales owing to the application of Time-Salt Superposition principle. The adhesive properties of the coacervates are studied using a custom-built *underwater* probe tack test upon a "salt switch", where coacervates prepared at high salt concentrations are placed in a low salt medium. While this method is a promising way of hardening injectable underwater adhesives, the highest adhesion energies on the order of 15 $J.m^{-2}$ were measured with the coacervate closest the sol-gel transition which did not go through a salt switch. The highly rate-dependent behavior of this coacervate indicates the viscoelastic nature of its underwater adherence. Since these materials can perform in physiological conditions and be directly applied under water, they hold great promise as spontaneous biomedical adhesives without the need to any chemical reactions.