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SOFT MATTER COMPOSITES

Annual Meeting 2021

Collection of Abstracts

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Yielding of amorphous solids

L. Berthier [1,2]

[1] *Laboratoire Charles Coulomb (L2C), Université de Montpellier, CNRS, Montpellier, France*
[2] *Department of Chemistry, University of Cambridge, Cambridge, United Kingdom*
Corresponding author:ludovic.berthier@umontpellier.fr

Understanding how amorphous solids yield in response to external deformations is crucial both for practical applications and for theoretical reasons. We have shown [1, 2] that despite large differences in the materials' microscopic interactions, a degree of universality emerges as there are only two ways in which amorphous solids respond to a deformation: One, typical of well-annealed materials, is characterized by an abrupt failure with a macroscopic stress drop and the sudden emergence of sharp shear bands; the other, typical of poorly annealed materials, shows merely a smooth crossover. By varying the preparation protocol, one can change the response of a given material from one to the other, and this change is controlled by a random critical point.

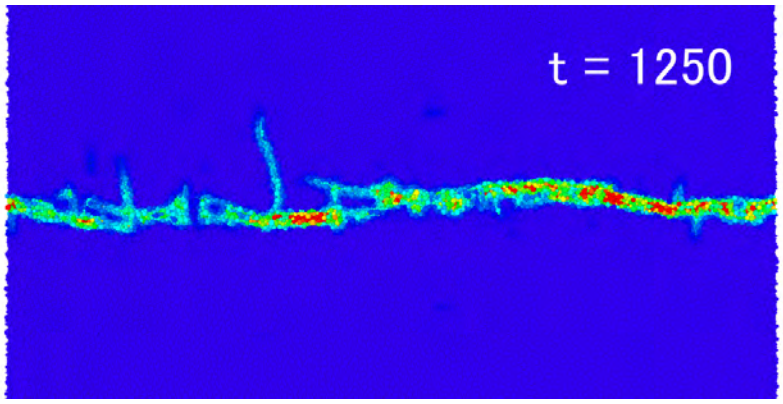

Figure 1: *Brittle yielding and shear-band formation in a two-dimensional amorphous solid.*

We have also shown that brittle yielding originates at rare soft regions, similarly to Griffiths effects in disordered systems [3]. We numerically demonstrated how localised plastic events in such soft regions trigger macroscopic failure via the propagation of a shear band, see Fig. 1. This physical picture, which no longer holds in poorly annealed ductile materials, allows us to discuss the role of finite-size effects in brittle yielding and reinforces the similarities between yielding and other disorder-controlled nonequilibrium phase transitions such as depinning and hysteresis.

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Feel the Force; Unravelling mechanical cues in plants and their attackers

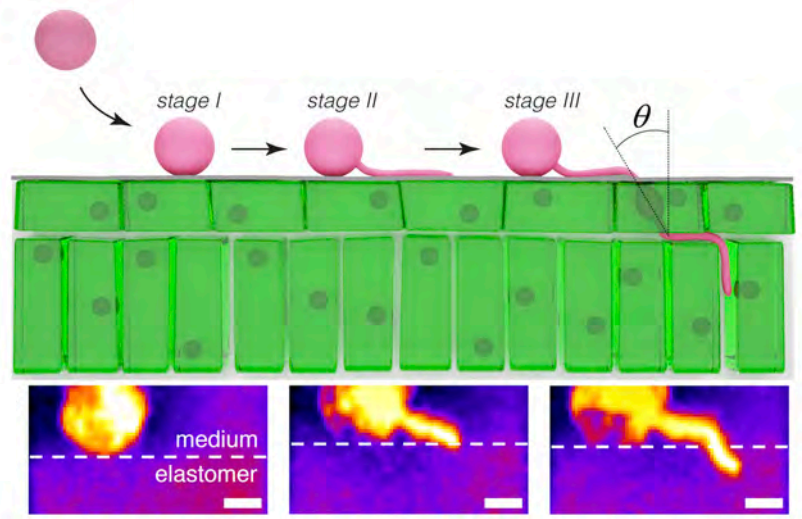
J. Sprakel[1]

[1]*Physical Chemistry and Soft Matter, Wageningen University, Wageningen, the Netherlands*

Corresponding author: joris.sprakel@wur.nl

Mechanical forces are crucial morphogens in a wide variety of phenomena in the growth, development and function of plants and in the way they are placed under siege during pathogenic attack. Plant cells internalize mechanical signals and couple these to their intrinsic biochemical and genetic machinery, giving rise to complex mechano-chemical feedback mechanisms that control a vast array of biological processes. Plant pathogens, which have devastating effects on crop yields and food security, utilize mechanical stress to invade their hosts. Mechanical host entry is the gateway for many microbial plant diseases to commence. Until recently, it remained highly challenging to unravel these processes as direct approaches to measure mechanical features inside plant tissues, with sub-cellular resolution, or at the pathogen-host interface were lacking.

Here I will discuss work from our team over the past 5 years aimed at resolving these issues by applying notions of soft matter and mechanochemistry to problem sets in plant and phytopathogen biology. I will discuss how molecular mechanoprobes, molecule-scale mechanical testers tailored for use in living plants, can be used to obtain nanomechanical maps of intact and growing tissues and illuminate mechanical inhomogeneities that underly mechano-biological signalling. I will then discuss how we used these, and other micromechanical imaging tools, to unravel the mechanical pathways of host entry by one of the most devastating phytopathogens, *Phytophthora infestans*, the causative agent of late potato blight and one of the root causes of large famines such as the great Irish famine. By unravelling the mechanics of host entry, we could identified new physical targets for control that offer opportunities to combat these pathogens that until now remain notoriously challenging to erradicate. I will conclude with an outlook of ongoing work, that uses this toolbox to address novel challenges in plant biology and physical phytopathology.



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Lubrication performance of microgels: an oral perspective

A. Sarkar[1]

[1]Food Colloids and Bioprocessing Group, School of Food Science and Nutrition, University of Leeds

Corresponding author: A.Sarkar@leeds.ac.uk

Oral tribology has emerged as a key paradigm in the tribology field to quantify friction in soft sliding oral contact surfaces such as tongue-palate, tongue-food etc[1,2] and is providing fundamental insights into the physics of oral processing and sensory perception. In this field, biocompatible microgels have been recently demonstrated to act as excellent lubricants in oral tribological contacts, with applications in dry mouth therapy and design of fat mimetics[3]. Using a combination of experimental techniques and theoretical considerations, this talk will cover three case studies[4-6] on tribology of soft elastomeric surfaces (with different wetting properties and surface roughness) in the presence of biopolymeric microgels with well-defined deformability, composition, cross-linking densities and particle sizes. Some of these microgels show aqueous 'ball-bearing' abilities depending upon their volume fraction[4]. A case study[5] will be presented on how these microgels can act as viscosity modifiers of the continuum particularly in case of complex fluids, where the lubrication performance can be quantitatively described using the second Newtonian plateau value (η_∞). Finally, recent fabrication of novel 3D soft tribo-surfaces of optimized topography, wettability and deformability to emulate the highly sophisticated tongue surfaces engineered by the nature will be highlighted[6].

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Acknowledgements

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Hybrid nanoparticles and hydrogels for biomedical applications

Luisa De Cola
Istituto di Ricerche Farmacologiche Mario Negri IRCCS
Via Mario Negri, 2 - 20156 Milano, Italy and University of Milano

Corresponding author: luisa.decola@marionegri.it

Advancements in the use of nanoparticles for biomedical applications have clearly shown their potential for the preparation of improved imaging and drug-delivery systems. However, only a few successfully translate into clinical practice, because, a common "barrier" preventing nanoparticles from delivering efficiently their payload to the target site after administration, is related to the nanoparticle uptake by macrophages. We have recently reported disulfide-bridged organosilica nanoparticles with cage-like morphology, and assessed in detail their bioaccumulation *in vivo*. [1] The fate of intravenously injected 20 nm nanocages was investigated in both healthy and tumor bearing mice. Interestingly, the nanoparticles exclusively co-localize with hepatic sinusoidal endothelial cells (LSECs), while avoiding Kupffer-cell uptake (less than 6%), in both physiological and pathological condition. Our findings suggest that organosilica nanocages hold the potential to be used as nanotools for LSECs modulation, potentially impacting key biological processes such as tumor cell extravasation and hepatic immunity to invading metastatic cells or a tolerogenic state in intrahepatic immune cells in autoimmune diseases.

Recently we have also shown that nanoparticles can be an interesting component for hybrid hydrogels. [2,3] We have shown that injectable nanocomposite hydrogel able to form *in situ* a tissue mimicking matrix as an innovative material can be employed for the treatment of esophageal fistulas. [4]

The hydrogel is based on hyaluronic acid (HA), the cross-linking process occurs at physiological conditions leading to a hydrogel made of >96% by water and with a large-pore microarchitecture. The material, easily injectable with an endoscopic needle, is formed in a time compatible with the surgical procedure and has final mechanical properties suitable for cell proliferation. The *in vivo* experiments (porcine model) on esophageal-cutaneous fistulas, showed improved healing in the animals treated with the hydrogel compared with the control group.

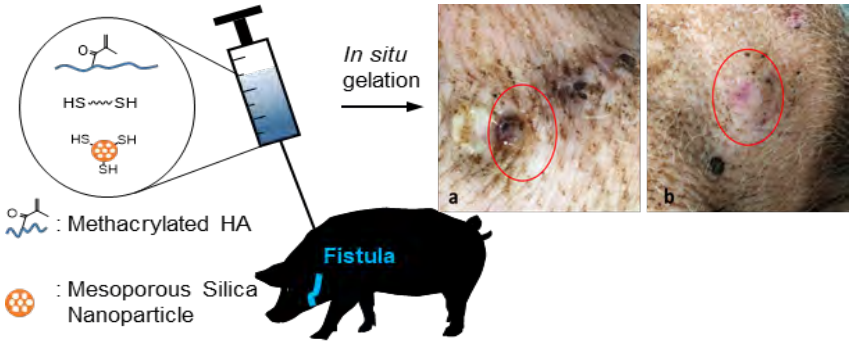

Figure 1: *Schematic representation of the hybrid hydrogel and of the fistula treatment.*
The in vivo results showing the treated and untreated fistulas

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Make biology simple again

P. Schwille [1]

[1] *Max Planck Institute of Biochemistry, Dept. Cellular and Molecular Biophysics , Martinsried, Germany*

Corresponding author:schwille@biochem.mpg.de

In the past years, a growing selection of ultrasensitive analytical techniques have been applied to established biological systems, either cell cultures or model organisms. While they have much contributed to the quantitative understanding of these systems and generated loads of data that remain to be digested by cutting-edge bioinformatics, little progress has been made on a more first-principle based understanding of living entities. Thus, in the past decade, we proposed and have since been pursuing a fully new approach towards biology, i.e., "bottom-up synthetic biology". The underlying idea is that only a radical simplification and abstraction of a biological cell will allow us to understand the distinctive features of life, because even the simplest life forms on earth have accumulated a huge degree of redundance in order to remain viable in a hostile and competitive environment. Abstracting from this massive and in large parts non-hierarchical complexity of interactions in a living system, otherwise being the hallmark of the physicist's approach, is doomed to failure. Thus, in order to arrive at a self-sustaining minimal system of molecular interactions with the ability to evolve – a minimal living system - we likely need to build it from scratch. Technically speaking, we need to assemble functional modules from the bottom-up until the system emerges basic functions of life.

Mechanics of Macromolecular Interfaces

E. Dufresne[1]
[1]*ETH Zürich, Department of Materials, Mechanics of Macromolecular Interfaces*
Corresponding author:eric.dufresne@mat.ethz.ch

The mechanical properties of interfaces underly a huge array of phenomena, from wetting and adhesion to the stability of emulsions and foams. When the bulk phases are simple fluids and/or stiff solids, the essential mechanics seem to have been worked out. The soft matter community has revealed a lot of fascinating and useful phenomena when interfaces between simple fluids are decorated with surfactants.

Here, I will focus on interfaces of macromolecular solids and fluids.

In the first part, I will describe experiments with gels: polymer networks swollen with a liquid solvent. I will address two fundamental questions. 1. Does surface tension change as the material is deformed? If the solvent dominates, the answer should be no. If the network dominates, the answer could be yes. 2. What is the equilibrium contact angle of a droplet on a gel when the droplet and gel's solvent have the same composition?

In the second part, I will briefly describe experiments on phase-separated protein droplets. I will sketch how a classical method from interfacial science can be applied to quantify the ultra-low surface tension of these systems, and give examples of how these interfacial properties can be manipulated.

General Session 1

Monday 31 May 11:30 – 12:30

Semiflexible polymers under oscillatory shear flow

A. Lamura [1], R. G. Winkler[2], G. Gompper[2]
[1] *CNR, IAC, Bari, Italy*
[2] *Forschungszentrum Jülich, IAS and ICS, Jülich, Germany*
Corresponding author:antonio.lamura@cnr.it

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

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Rheological behavior of highly loaded suspensions for dense ceramics stereolithography application

S. Fournier[1]; G. Baeza[1], H.Reveron[1], J.Chevalier[1]
[1] *Univ Lyon, INSA Lyon, UCBL, CNRS, MATEIS, UMR5510, 69621 Villeurbanne, France*

Corresponding author: sylvain.fournier@insa-lyon.fr

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

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

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

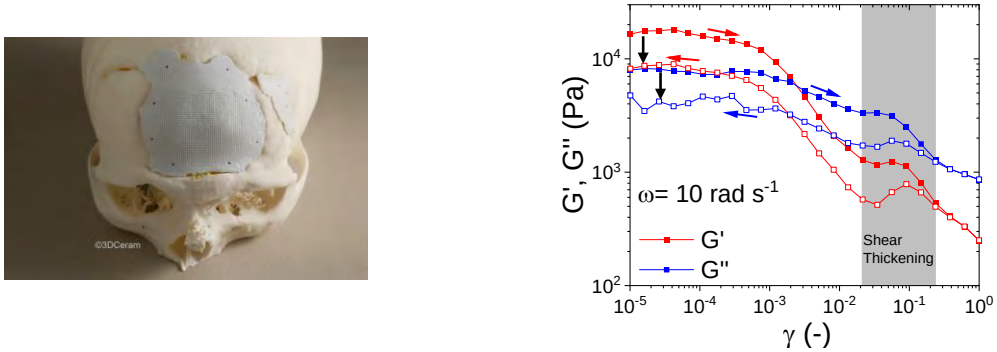

Figure 1: *a) A 3D-printed ceramic cranial implant made by SLA.* b) *Dynamic strain amplitude sweep of a commercial 3Y-TZP SLA paste.*

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

M. Gunnarsson[1], E. H. Mojumdar[1,2], D. Topgaard[1], E. Sparr[1]
[1] *Lund University, Physical Chemistry, Lund, Sweden*
[2] *Malmö University, Department of Biomedical Science, Faculty of Health and Society, Malmö University & Biofilms Research Center for Biointerfaces (BRCB), Malmö, Sweden*
Corresponding author:maria.gunnarsson@fkem1.lu.se

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

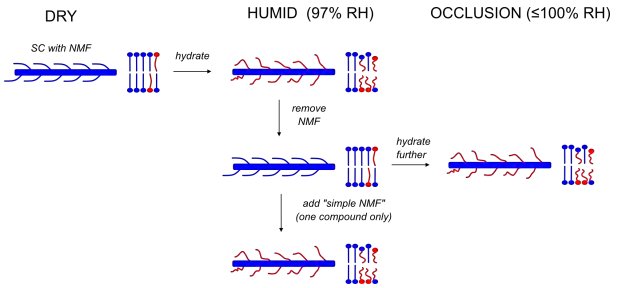

Figure 1: *Schematic illustration of how the molecular mobility of the keratin filaments and lipids in SC are affected by the presences of polar compounds.*

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General Session 2

Monday 31 May 11:30 – 12:30

Active Turbulence in Swarming Microswimmers

R. G. Winkler, K. Qi, G. Gompper
Theoretical Physics of Living Matter, Institute for Advanced Simulation and
Institute of Biological Information Processing, Forschungszentrum Jülich, D-52425 Jülich
Corresponding author:r.winkler@fz-juelich.de

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

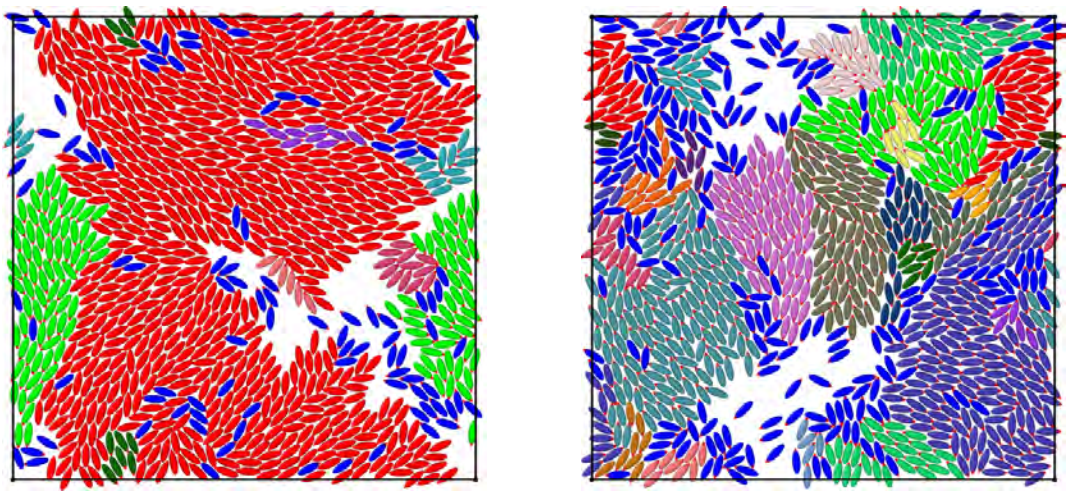

Figure 1: *Snapshots of squirmer configurations for zero (left) and finite (right) rotlet dipole. The colors indicate collective moving clusters, which are significantly smaller in presence of a rotlet dipole.*

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Probing the dynamics of bicontinuous Pickering emulsions with diffusion wave spectroscopy

J. Tavacoli[1], M. Reeves[2], J. Thijssen[2]
[1]*Faculty of Physics and Center for NanoScience, Ludwig-Maximilians-Universität, Germany*
[2]*SUPA School of Physics and Astronomy, The University of Edinburgh, UK*
Corresponding author:j.tavacoli@lmu.de

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

Chemical Feedback in Templated Reaction-Assembly Networks

Inge Bos[1], Camilla Terenzi[2], Joris Sprakel[1]

[1] *Wageningen University and Research, Physical Chemistry and Soft Matter, Wageningen, The Netherlands*

[2] *Wageningen University and Research, Laboratory of Biophysics, Wageningen, The Netherlands*

Corresponding author:ingem.bos@wur.nl

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

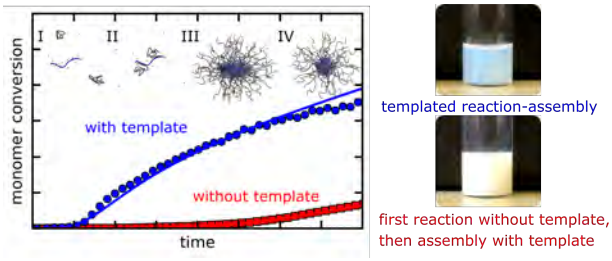

Figure 1: *Combining the reaction and the assembly process affects both the polymerisation kinetics (left plot) and the final structures formed (right pictures). During the reaction-assembly process four different phases could be distinguished, schematically depicted at the top left.*

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Student Organised Session

Monday 31 May 16:10 – 18:00

Dynamic stabilisation of polymer solution thin liquid films

E. Chatzigiannakis[1], Jan Vermant[1]
[1] *ETH Zurich, Department of Materials, Zurich, Switzerland*
Corresponding author: jan.vermant@mat.ethz.ch

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

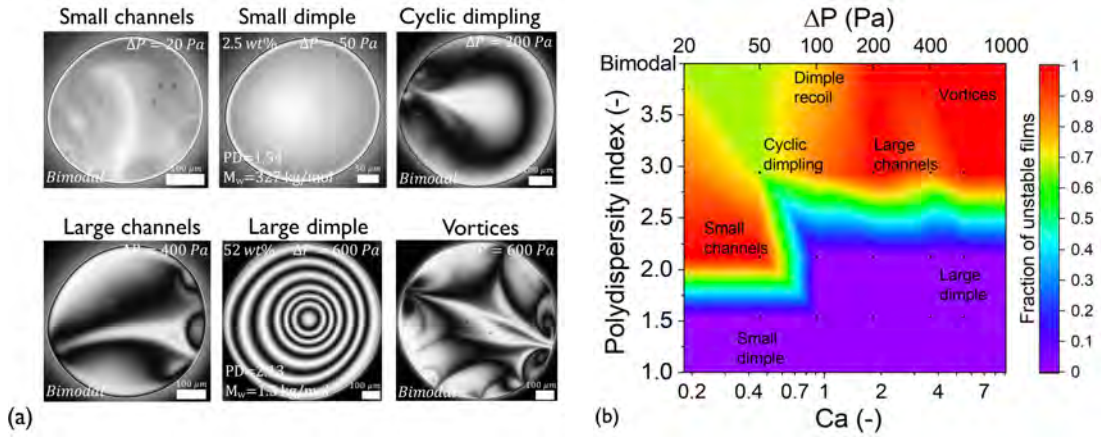

Figure 1: *(a) Microinterferometric images of polymer films of different polydispersities. (b) State diagram describing the propensity for asymmetric drainage as a function of Ca and ΔP for films containing polymers of different polydispersities.*

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

References

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Melting of Entropically Stabilized Solid

Presenting Azizi [1], I. Azizi[1], Y. Rabin[1]

[1] *Bar-Ilan University, Department of Physics, and Institute of Nanotechnology and Advanced Materials, Ramat Gan,Israel*

Corresponding author: itay.azizi@gmail.com

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

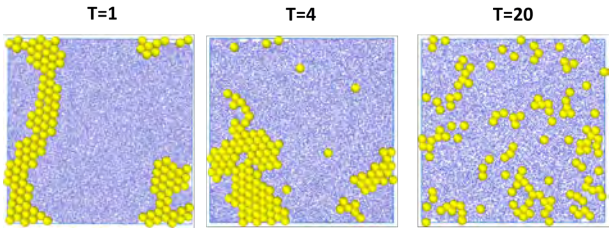

Figure 1: *Melting of a solid cluster of big particles* $\phi_{big} = 0.25, \phi_{small} = 0.35$ *at T=1,4, 20*

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

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Unravelling the transient network topology of hydrophobically associating multiblock copolymers

A. Huysecom[1], W. Thielemans[2], R. Cardinaels[1], P. Moldenaers[1]

[1] *Soft Matter, Rheology and Technology, Departement of Chemical Engineering, KU Leuven, Leuven, Belgium*

[2] *Sustainable Materials lab, Department of Chemical Engineering, KU Leuven Kulak, Kortrijk, Belgium*

Corresponding author:paula.moldenaers@kuleuven.be

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

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

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

Benjamin S. Hanson[1]; Lorna Dougan[1,2]
University of Leeds, School of Physics and Astronomy, Leeds, UK, LS2 9JT
[2] *University of Leeds, Astbury Centre for Structural Molecular Biology, Leeds, UK, LS2 9JT*

Corresponding author: b.s.hanson@leeds.ac.uk

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

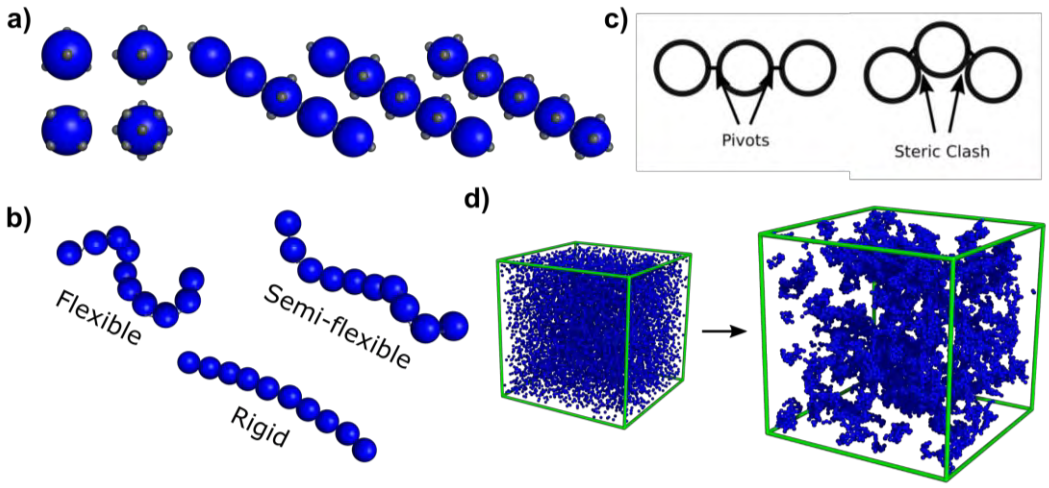

Figure 1: *The range of protein hydrogel systems we are currently investigating. a) Variations in cross-link site topology across monomeric and polymeric structures. b) Polyprotein persistence length can also be varied. c) Our bespoke model, BioNet, includes localized connectivity between subunits to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

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From force-responsive to force-resistant microgels

E. Izak-Nau[1], S. Braun[1,2], A. Pich[1,2,3], R. Göstl[1,2]
[1]*DWI – Leibniz Institute for Interactive Materials, Aachen, Germany*
[2]*RWTH Aachen University, Aachen, Germany*
[3]*Aachen Maastricht Institute for Biobased Materials, Maastricht University, Geleen, The Netherlands*

Corresponding author: izak-nau@dwi.rwth-aachen.de

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

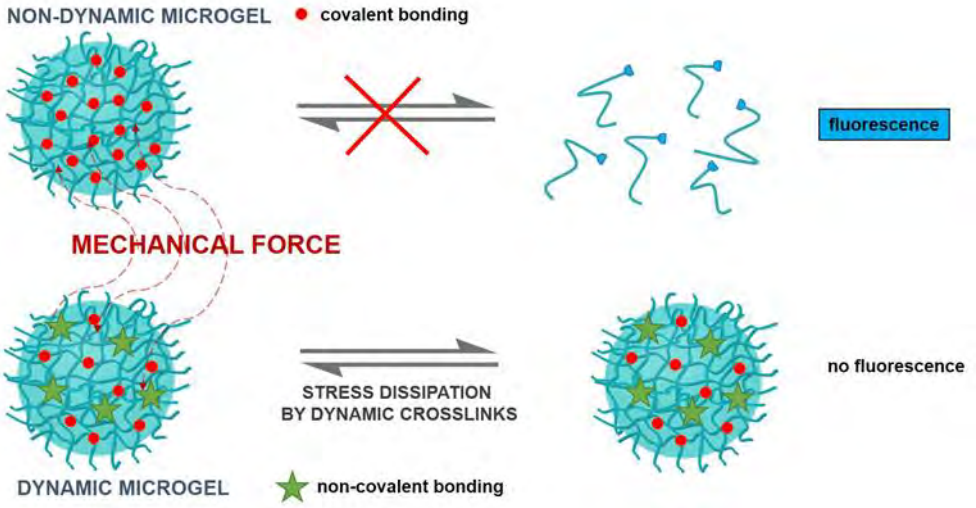

Figure 1: *Mechanical behavior of microgels with static and dynamic crosslinks.*

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

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

L. Tran[1]

[1]*Utrecht University, Soft Condensed Matter & Biophysics, Debye Institute of Nanomaterials, Department of Physics, Utrecht, The Netherlands*

Corresponding author: l.tran@uu.nl

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

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

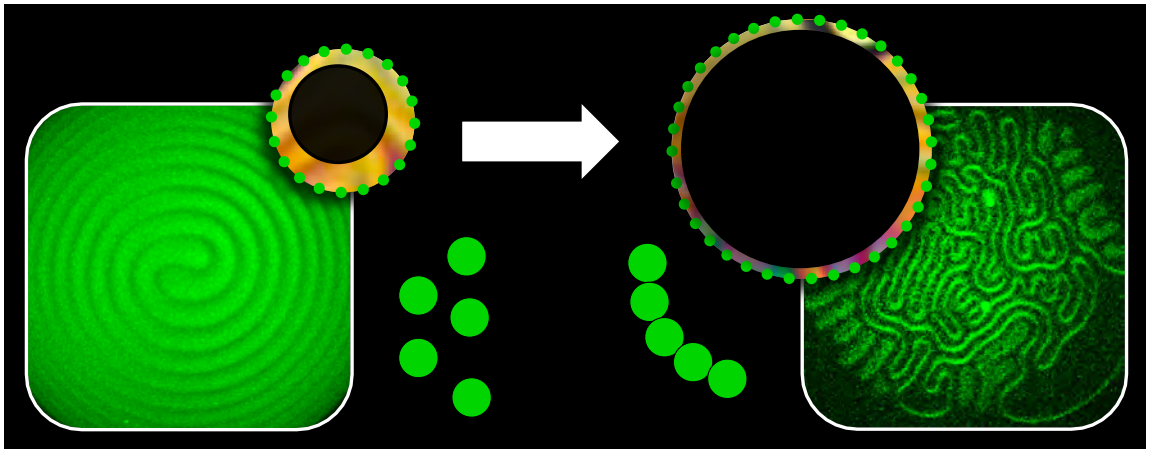

Figure 1: *Fluorescently labelled particles (green) at the interface of chiral liquid crystal shells can be dynamically shaped into linear structures by swelling the shell, dynamically altering the underlying liquid crystal structures.*

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General Session 3

Monday 31 May 16:10 – 18:00

Topological Tuning of DNA Mobility in Entangled Solutions of Supercoiled DNA

D. Michieletto[1]

[1]*School of Physics and Astronomy, University of Edinburgh*

Corresponding author: davide.michieletto@ed.ac.uk

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

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

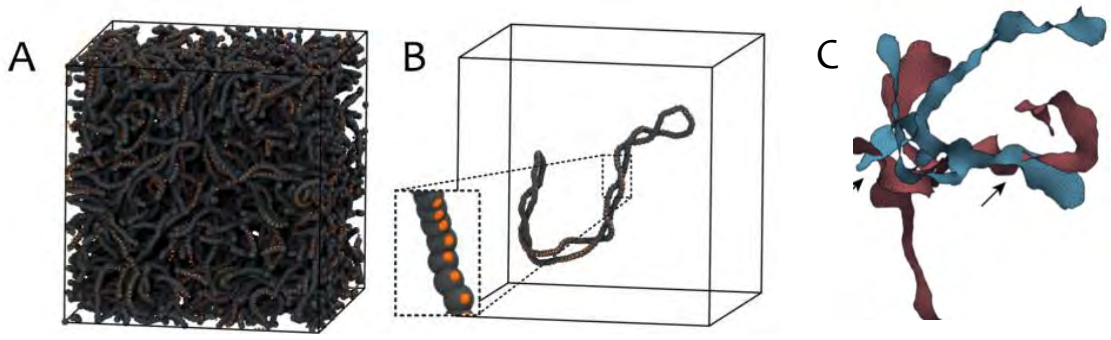

Figure 1: *A-B. Large scale simulations of entangled supercoiled DNA plasmids. C. Identifying threadings between plasmids using minimal surfaces.*

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

M. Nagaraj, R. Morris, J. C. Jones
School of Physics and Astronomy, University of Leeds, Leeds, United Kingdom

Corresponding author: m.nagaraj@leeds.ac.uk

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

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

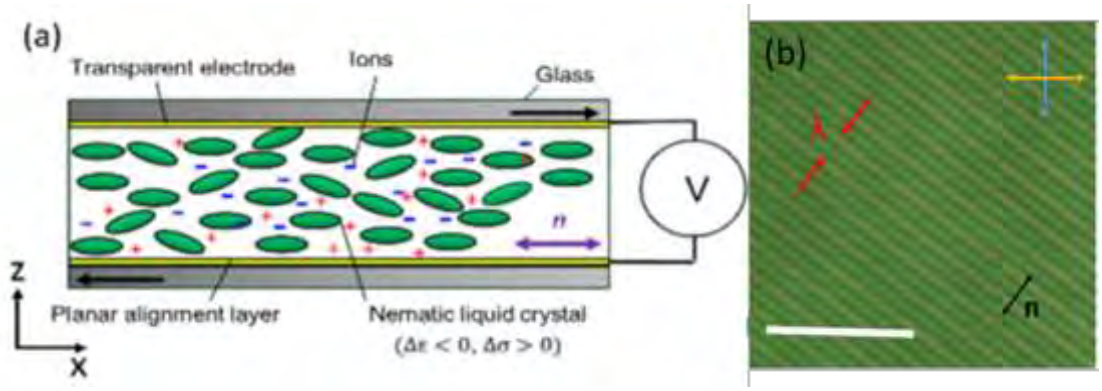

Figure 1: (a) Schematic representation of a liquid crystal device used for EHDI studies, when no voltage is applied.(b) Polarising optical microscopy image of EHDI normal rolls pattern obtained after a critical voltage applied to the liquid crystal. The length of white bar is 50μm, λ is the period, n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

References

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Stretching Polymeric Membranes

R.J. Goodband[1] C.D. Bain[2], M. Staykova[1]
[1]*Durham University, Department of Physics, Durham, UK*
[2]*Durham University, Department of Chemistry, Durham, UK*

Corresponding author: rachel.goodband@durham.ac.uk

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

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

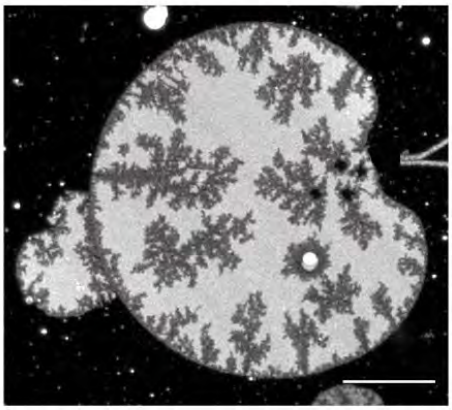

Figure 1: *Fingering-like pore morphologies after rapid polymeric membrane stretch. Scale bar 20 μm.*

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

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Some aspects of nanoparticle assembly and polymer dynamics in rubber systems

J. Oberdisse, D. Musino, A.C. Genix
Laboratoire Charles Coulomb (L2C), University of Montpellier, CNRS, 34095 Montpellier, France.
Corresponding author: julian.oberdisse@umontpellier.fr

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

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

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Particle Wrapping and Uptake at Cells and Vesicles

T. Auth, Q. Yu, S. Dasgupta, G. Gompper
Forschungszentrum Jülich, Theoretical Physics of Living Matter, Jülich, Germany
Corresponding authors: t.auth@fz-juelich.de; g.gompper@fz-juelich.de

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

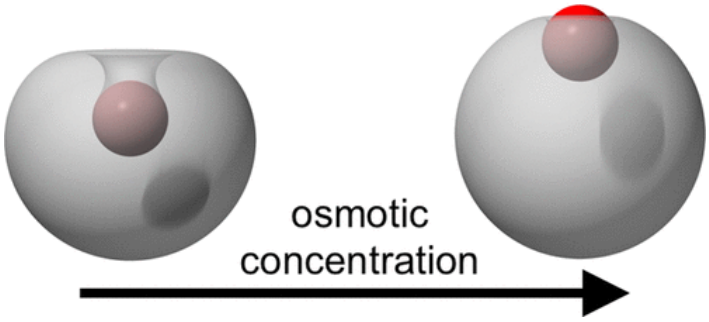

Figure 1: *Particle wrapping at an initially tensionless spherical vesicle in solvent with low (left) and high (right) concentration of solute for fixed wrapping fraction. Reproduced from Ref. [4].*

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Industry Session

Tuesday 01 June 10:40 – 12:40

Making Natural Beauty Happen – performance without compromise

J. Borné [1]
[1] *AAK Sweden AB, Karlshamn Sweden*
Corresponding author:johanna.borne@aak.com

Cosmetic innovations are not only about identifying new sources, ingredients or product offerings. It is a about finding high performing creative solutions delivering into the macro and consumer trends. The consumer trend within the cosmetic industry is currently driving a growing demand for more clean, natural skin care products with sustainable credentials. Natural, however, does not always equate to good or effective. The chemical profile of the natural raw material needs optimization to be used in cosmetic applications and deliver on the efficacy, functionality, and sensory appeal.

A typical skin care product compromises water, emollients, emulsifiers and other ingredients, wherein the shea butter is the most common natural lipid-based emollient. This presentation will focus on how shea-derived emollients and the formulation need to be expertly processed for optimized functionality and performance. It will be demonstrated how a formulator and manufacturer can benefit from the shea-derived functionality rapidly crystalizing into the optimal polymorphic form, resulting in unique textural transformation, enhanced sensory benefits, long-lasting moisturization and thermal stability. In parallel, it will be shown that the success of the work is due to the employment of a combination of X-Ray-Diffractometer, Microscopy, and Trans-Epidermal Water-Loss measurements (TEWL).

Finally, the presentation will highlight advanced imaging techniques to future explore, potentially providing insight into the natural emollients impact on moisturization, skin health and ageing.

Innovative environmentally friendly protected wood: The molecular monitoring of modified wood

Salman Hassanzadeh[1]
[1] *OrganoClick AB, R&D Department, Stockholm, Sweden*
Corresponding author:Salman.Hassanzadeh@organoclick.com

As a renewable material with unique properties and characteristic structures, wood has been used in many applications and situations. However, as wood is organically constituted, it is slowly destroyed by the long-term impact of oxygen, UV radiations, water, contaminants and biological attacks especially in the exterior uses. Wood protection can be obtained by applying various chemicals and application methods. The most common way for harsh outdoor environment is impregnation methods which provide a deeper penetration and higher uptake of protective. However, most of the impregnating chemicals are classified as toxic, dangerous to the environment and they are not or only slowly biodegradable. Aiming to substitute the toxic preservative-based chemistries in the wood market, new generations of the bioinspired and nontoxic functional/protected wood are under development continuously at OrganoClick AB. Using SEM/EDX and Solid-state 13C NMR spectrometer studies, we could evaluate and monitor the protected wood down to the molecular level to shape a fundamental structure-property understanding of the developed sustainable technology. By performing SEM/EDX tests on the treated wood samples, the state of the used chemicals and their fixation mechanism into porous wood structures were studied. Additionally, the penetration depth and morphology of the treated wood were examined carefully. The aging mechanism and natural durability of the wood structure and impregnated chemicals could be followed up by comparative study of the surface and cross-section images together with elemental analyses of the not-treated, treated and treated/aged wood samples (woods aged by both accelerated lab techniques and natural weathering). The Solid-state 13C NMR spectroscopy was used to identify the chemical structure

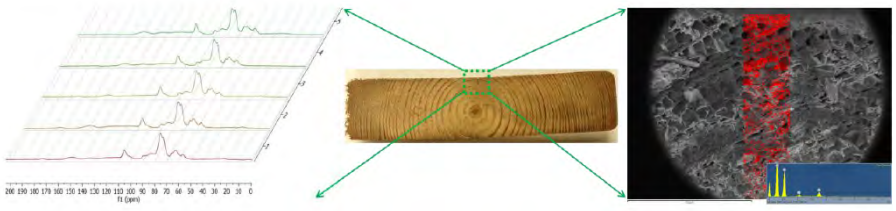

Figure 1: *Graphical abstract of the performed SEM/ EDX and Solid-state 400 MHz NMR spectrometer on the modified wood.*

of the treated wood. The chemical changes of the cellulose, hemicellulose and lignin as main components and functional building blocks of wood were monitored by comparative analysis of the structures before and after treatments. A comparative study between the different treatments and technologies was also performed by checking the crystallinity of cellulose, determined as crystallinity index (CrI) and calculated by deconvolution from the area of the crystalline cellulose (86-92 ppm) and the area of the amorphous cellulose (79-86 ppm)[1]. The obtained structure-property knowledge of the developed wood protection technology by OrganoClick AB has successfully accelerated the implementation of new generation of the environmentally friendly alternative with superior properties over the present toxic products in the market.

References

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(Scattering) Some light on liquid laundry formulations incorporating Betafib®, a biobased structurant.

C.M. van Kats[1]; F.A.L.M. Staps[1], M. Gubitosi[2]
P. Holmqvist[3],
[1]*Cosun Beet Company, Biobased Experts, Dinteloord, The Netherlands*
[2]*CR Competence, Lund, Sweden*
[3]*Lund University, Physical Chemistry, Department of Chemistry, Lund, Sweden*

Corresponding author: CarlosvanKats@Cosun.com

Cosun Biobased Experts is part of Cosun Beet Company with its head office in the Netherlands. Cosun focuses on a strategy for the development of innovative biobased chemicals and materials from renewable, vegetable resources.

Betafib® [1] a biobased cellulosic microfibe.r is one of their products. It can be used as a structurant, for instance in liquid laundry formulations to stabilize encapsulated fragrances since it provides a high yield stress.

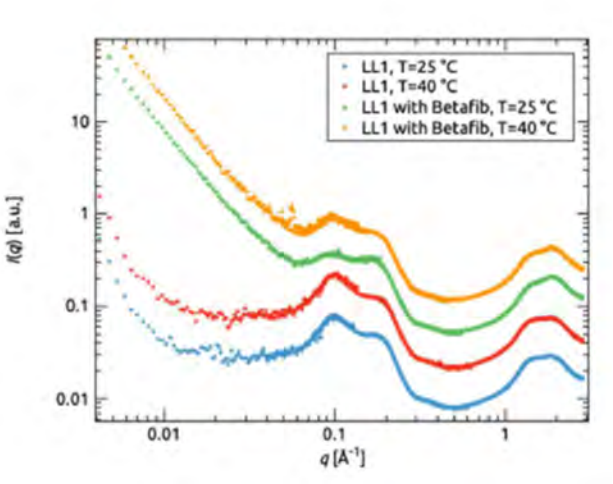

Figure 1: *Example of SAXS data of a Liquid Laundry (LL) composition with and without Betafib® .*

To shine some (X-Ray) light on incorporation of Betafib® in various commercial liquid laundry formulations, SAXS/WAXS and DLS studies were performed at Lund University via the EUSMI program. The hypothesis was checked whether nanostructures of surfactant self-aggregates can hinder the incorporation of Betafib® in some formulations.

Scattering techniques (small-angle X-ray and light scattering) turn out to be a powerful tool to elucidate the structures of these materials at the nanoscale.

The learnings from the measurements performed (through EUSMI) at Lund University will be discussed and open questions for future research will be addressed.

References

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Patient centric Drug Delivery and Manufacturing approaches – Challenges remains

S. Abrahmsén Alami[1]

[1]*Innovation Science & External Liaisons, Pharmaceutical Technology and Development, AstraZeneca Gothenburg, Sweden*

Corresponding author:Susanna.Abrahmsen-Alami@astrazeneca.com

The pharmaceutical products we design and develop should deliver the drug at the right place and to the right extent to assure effectiveness. For the patient and the society it is key that we develop products that are as precise as possible but still cost efficient and accepted by the patients. Today this is handled through mass production. In this talk a few historical oral modified release development case studies will be presented, highlighting formulation and characterization challenges as well as opportunities. Key critical aspects such as need to understand and control fundamental mechanisms occurring during manufacturing, storage and release will be discussed as well as tools that can be applied to gain insight. Aspects of relevance for manufacturing via traditional batch, as well as continuous and more futuristic modular design will be covered. The latter design principles offer opportunities for future's more cost-efficient patient focused therapies with predictive in-vivo dissolution, performance and customer outcomes.

General Session 4

Tuesday 01 June 10:40 – 12:30

Wrinkling Patterns and the Physics of Brain Folding

J. Elgeti, L. Campos, G. Gompper, S. Caspers
Theoretical Physics of Living Matter (IBI-5/IAS-2), Forschungszentrum Jülich

Corresponding author: j.elgeti@fz-juelich.de

We are all aware of the facinating structure of the Brain. Its "Walnut" like apearance with folds and vallys serves regularly as an Icon for thinking and knowledge. There are several hypotheses out there about the origin and function of this wrinkling pattern. In this talk, I want to discuss one, that is particularly interesting for the SoftMatter community. The "Differential Growth Hypothesis" states, that the gray matter (the "outer layer") of the brain grows more than the white matter. This leads to a buckling instability and folding patterns. The underlying physics are equivalent to the wrinkling patterns studied e.g. on streched PDMS Gels. We demonstrate how inhomogeneities in the Cortical thickness can lead to folding patterns much more reminicent of brain structures than homogeneous thickness [1]. Finally, I will touch some aspects and pitfalls in simulating brain folding.

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Exploring microscopic rearrangements in flowing complex fluids using differential dynamic microscopy

J. A. Richards [1], V. A. Martinez[1], J. Arlt[1]
[1] *The University of Edinburgh, School of Physics and Astronomy, Edinburgh, United Kingdom*
Corresponding author:james.a.richards@ed.ac.uk

As complex fluids are stressed and deformed their mechanical properties can change dramatically, for example yielding from a solid to a liquid-like state with increasing stress. These changes are driven by how the fluid components, *e.g.* droplets in an emulsion, interact and rearrange under flow. By probing this relative motion, we can reveal why the properties evolve and suggest how to control the transition. However, such insight is currently limited to model systems where particles can be precisely tracked. Here, we demonstrate how shear-induced rearrangements can be analysed by differential dynamic microscopy (DDM), a Fourier technique where particle resolution is not required. Imaging a silicone oil in water-glycerol emulsion using rheo-confocal microscopy, we show how the speed of droplet rearrangement depends on the rate of shear via an extension of DDM for flowing systems [1]. We also reveal how both the proportion of droplets that move and the speed of rearrangement depends on how far the system is deformed in an oscillatory shear test through a novel analysis: strobo-DDM. These microscopic parameters are then linked back to the bulk rheology to illuminate the mechanisms behind yielding. Together, these techniques open up a host of possibilities for characterising the microscopic dynamics of complex fluids under flow.

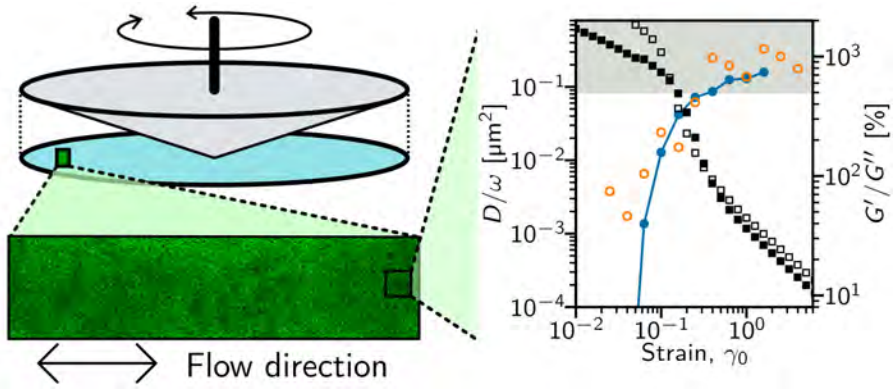

Figure 1: *Left:* Rheo-confocal imaging of a jammed emulsion under oscillatory shear. *Right:* analysis to give microscopic rearrangement rates [D (coloured circles)] compared to bulk rheology [storage modulus to loss modulus ratio, G'/G'' (black squares)]. Filled symbols at 1 Hz and open symbols at lower frequency of 0.1 Hz.

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A novel droplet interface bilayer platform for drug discovery relevant permeation studies

R. Strutt[1,2]; F. Sheffield[1,2], J.D. Harling[3], A.J. Flemming[4], R.V.Law[1,2], N.J.Brooks[1,2], L.M.C. Barter[1,2], O.Ces[1,2]

[1]*Imperial College London, Department of Chemistry, London, UK*
[2]*Institute of Chemical Biology, Imperial College London, London, UK*
[3]*GSK, Medicinal Chemistry, Stevenage, UK*
[4]*Syngenta, Jealott's Hill international Research Centre, Bracknell, UK*

Corresponding author: o.ces@imperial.ac.uk

For a drug candidate to reach an intracellular target it must overcome the cellular plasma membrane; a complex biological organelle of interwoven lipids, sugars and proteins. Both lipids and proteins enable major transport pathways for the drug of interest, where transport via simple diffusion through the lipid matrix has strongly influenced drug design. Current assays to uncover a drugs structural dependency on this transport route have been limited, where typically the translocation interface is oversimplified. Droplet interface bilayer (DIB) technology is centred around a bilayer formed at the interface between two monolayer coated droplets. DIBs have shown vast potential in multiple biophysical and synthetic biology applications broadly acting as an experimental complement to typical vesicle experiments. Permeation studies within DIBs have traditionally relied on fluorescent microscopy read out, limiting their application as a permeation assay with respect to the broad physicochemical space presented in drug discovery. Here we present a novel label-free approach that addresses this technological bottleneck and has enabled us to undertake structure-function relationship studies across DOPC and DPhPC bilayers demonstrating the complementarity of this platform to current widely used drug discovery assays.

References

Drying Microgel Dispersions: at the Crosspoint of Colloidal and Molecular Scales

J.J. Crassous[1]; K. Roger[2]
[1]*RWTH Aachen University, Institute of Physical Chemistry, Aachen, Germany*
[2]*Laboratoire de Génie Chimique, Université de Toulouse, CNRS, Institut National Polytechnique de Toulouse, Université Paul Sabatier, Toulouse, France.*

Corresponding author: crassous@pc.rwth-aachen.de

Bringing an aqueous dispersion or solution into open air leads to water evaporation. The resulting drying process initiates the build-up of spatial heterogeneities as non-volatile solutes and colloids concentrate. Such gradients lead to complex flow within multicomponent systems, which has triggered a large research effort to describe the resulting hydrodynamics. However, less attention has been paid to the deviations from thermodynamic ideality stemming from water depletion in the vicinity of the air/liquid interface. Here, we show that these thermodynamic effects are crucial in the drying of hydrophilic microgel dispersions. We evidence an original drying behavior intermediate between colloidal and solution drying, in which a diffusional scaling is observed together with a weak dependence on the air relative humidity. Mapping composition and structuration gradients using Raman spectroscopy and small-angle scattering techniques, we show that this behavior stems from the ability of microgels to both interpenetrate and compact. As a result, water activity and transport is drastically decreased in the vicinity of the air/liquid interface. This mechanism will be at play in a large diversity of complex colloidal systems and is pivotal for the mastering of drying processes.

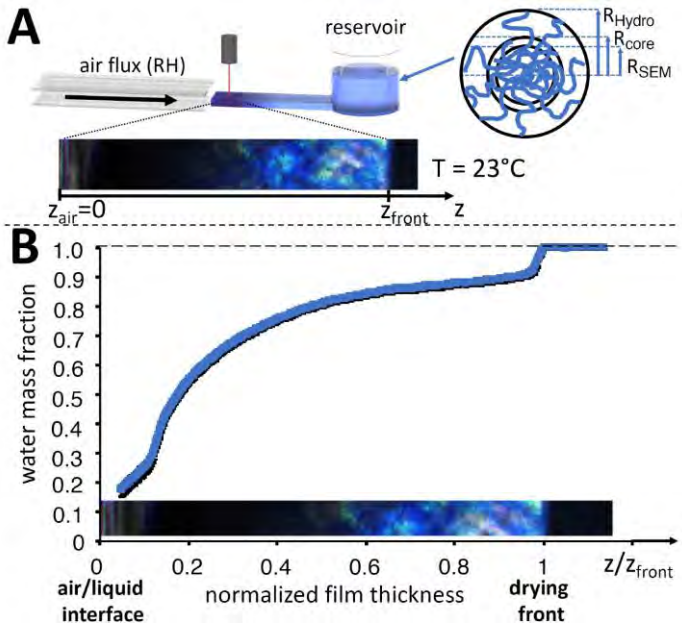

Figure 1: *(**A**) Schematic view of the millifluidic setup, which consists of a rectangular capillary connected on one end to a reservoir containing a 1wt% microgel dispersion and exposed on its other end to an air flux of controlled relative humidity (RH). As water evaporates, microgel particles pack at the air/liquid interface and form a film, displayed in the polarized microscopy image. (**B**) Water gradient through the film measured by Raman confocal microscopy (RH = 50%). Close to the air/liquid interface, water is scarce and the gradient is linear. Moving further away beyond this water-poor and cracked area, water fractions steadily increase with a more complex profile up to the drying front. From there, there is no significant water gradient, which corresponds to bulk conditions.*

Conversion of colloidal CdSe nanoplatelets into quantum rings by thermochemical reconfiguration

B.B.V. Salzmann[1]; J.F. Vliem[1], D.N. Maaskant[1], L.C. Post[1], C. Li[2], S. Bals[2], D. Vanmaekelbergh[1]
[1]*Condensed Matter & Interfaces, Department of Chemistry, Utrecht, The Netherlands*
[2]*EMAT and NanoLab Centre of Excellence, Antwerp University, Antwerp, Belgium*

Corresponding author: d.vanmaekelbergh@uu.nl

While thermodynamics points to quasi-spherical nanocrystals as most stable shape, numerous other morphologies of CdX (X = Se, S, Te) nanocrystals have been reported in the past decades, ranging from cubes to one-dimensional wires and two-dimensional platelets. Since the opto-electronical properties of the nanocrystals are strongly dependent on their shape, the morphology is of major importance. Semiconducting nanoparticles are, due to their characteristic absorption and emission of light, of interest for applications in *e.g.* solar cells and LEDs. In 2016, the family of CdSe nanocrystals was extended to quantum rings by reshaping CdSe nanoplatelets, being previously synthetically inaccessible.[1] This new shape of is high interest as the toroidal morphology could give rise to unprecedented features. For example, previous research on solid-state grown ZnTe/ZnSe quantum rings showed the presence of magneto-excitonic photoluminescence [2], being of interest for future opto-electronic devices. However, due to the relative novelty of CdSe quantum rings, not much knowledge about the conversion mechanism, morphology, crystallinity, and opto-electronical properties have been reported yet.

In here, we monitor the reshaping of CdSe nanoplatelets into quantum rings *ex situ* by combining atomically resolved structural characterization with optical absorption and emission spectroscopy. The CdSe nanoplatelets are treated with elemental selenium at elevated temperatures. During the conversion we observe a reconfiguration and recrystallization of CdSe units from the edges to the top and bottom of the platelet, thereby forming a donut with a membrane in the centre. In the final heating step, we observe perforation at the center. Moreover, we can relate the reconfiguration in shape to the red shifts in optical absorption and emission spectra. Abberation-corrected HAADF-STEM imaging shows high crystallinity of the quantum rings and ocassionally partial perforation.

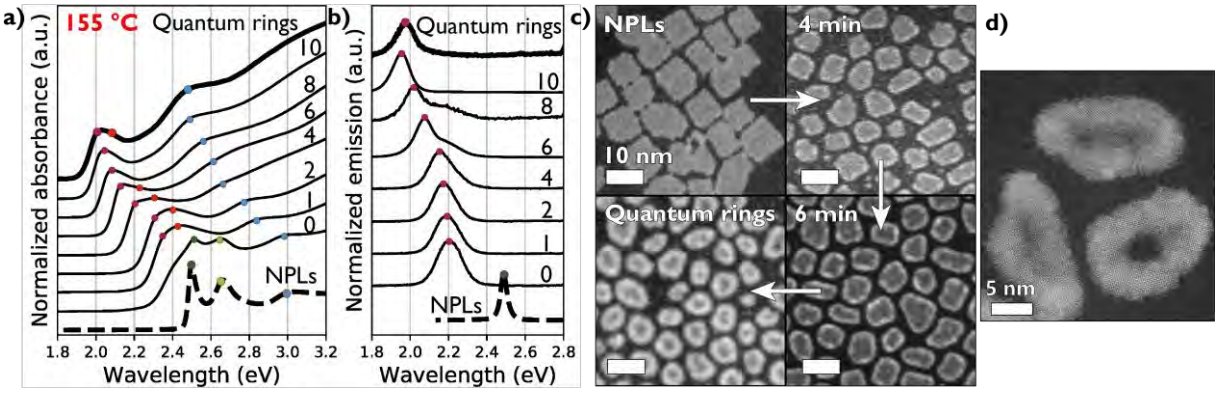

Figure 1: *Characterization of the conversion of CdSe nanoplatelets (NPLs) into quantum rings. Absorption a) and emission spectra b), together with HAADF-STEM images c), showing the gradual conversion. High resolution HAADF-STEM d) shows the single-crystalline nature and (partial) perforation of the rings.*

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Topical Session
Responsive Matter

Tuesday 01 June 16:10 – 18:10

Controlling Biological Systems by Ultrasound: Sonopharmacology and Sonogenetics

A. Herrmann[1]

[1]*DWI - Leibniz Institute for Interactive Materials and Chair of Macromolecular Materials and SystemsRWTH Aachen University*

Corresponding author: herrmann@dwi.rwth-aachen.de

The field of optogenetics has enabled the fundamental scientific understanding of how specific cell types contribute to the function of biological tissues such as neural circuits in vivo.[1] Moreover, this optical technology led to insights into various neural disorders including Parkinson's disease, autism and schizophrenia.[2,3] However, current optogenetic techniques require invasive surgical procedures to deliver light of specific wavelengths to target cells to activate or silence them. Therefore, ultrasound (US) was used as alternative trigger to overcome these shortcomings since US can deeply penetrate tissue (multiple centimeters) and can be applied with millimeter precision. While others target mechanosensitive channel proteins employing low-intensity US to control and to regulate cell behavior,[4] our group deals with general design principles to control protein activity by US.[5] Moreover, we devise mechanochemical macromolecular systems that rely on covalent or non-covalent bond cleavage induced by collapsing US-induced cavitation bubbles. These systems allow the activation of small bioactive molecules, probes and drugs that can interfere with biological systems or cure diseases.[6,7,8] A particular emphasis is paid to reducing US energies to make these sonogenetic and sonopharmacological systems compatible with living matter.

References

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Sculpting hydrogels using advective assembly

Alexandra V. Bayles[1]; Tazio Pleij[1], Martin Hofmann[1], Jan Vermant[1]
[1]*ETH Zürich, Materials, Zürich, Switzerland*

Corresponding author: alexandra.bayles@mat.ethz.ch

Polymeric hydrogels, water-laden 3D crosslinked networks, find broad application as advanced biomaterials and functional materials due to their biocompatibility, stimuli responsiveness, and affordability. In these materials, the crosslinking density reports critical material properties such as elasticity, permeability, transparency, and swelling propensity, but can be challenging to alter across the sample volume polymerized. Here, we report a novel processing scheme that uses laminar flow to direct the organization of hydrogel crosslinking density across a single sample. Inspired by techniques used to structure polymeric melts, we design custom millifluidic devices that force disparate streams through serpentine splitting, rotation, and recombination elements. These elements multiply the incoming 2D macromer concentration field across the cross-sectional area while preserving its relative spacing and orientation. Serial repetition of elements compounds multiplication, allowing the heterogeneous distribution to be efficiently shrunk before it is dissipated by diffusive mixing. These so-called 'advective assemblers' are well-suited to assemble fluid streams parallel and perpendicular to one another, ultimately enabling the extrusion of hydrogel precursors with laminated and dendritic concentration distributions. Photopolymerization of the sculpted precursor secures the distribution in place, resulting in gel filaments with heterogenous distributions.

As an example of the potential applications this technology may serve, we use advective assembly to fabricate poly(ethylene glycol) diacrylate hydrogel actuators. Gel precursors of different polymer compositions are first blended with a poly(acrylic acid) microgel dispersion, which serves as a yield stress carrier fluid that promotes plug flow and preserves the fidelity of patterned concentration maps. After polymerization, the distribution of crosslinking density (tens of microns) causes gel filaments to swell differentially when immersed in aqueous environments, giving rise to shape changes that persist over tens of centimeters. Actuation is predictively programed by changing the concentration density map through simple adjustment of the relative flow rates of incoming streams. Inclusion of comb-like flow elements promote a high degree of interfacial adhesion, and ultimately creates filaments that are robust to high deformation strains. Combining this novel processing method with traditional 3D printing allows for the fabrication of hierarchical actuators. The unique structures achieved, and the geometrically dictated, chemistry-agnostic operating principles used to achieve them, provide a new means to engineer hydrogels to suit a variety of applications.

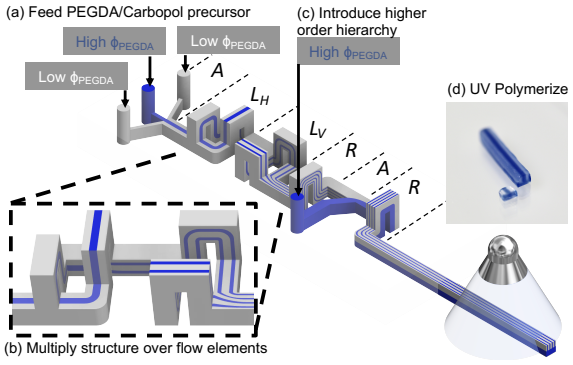

Figure 1: *Advective assemblers sculpt hydrogel crosslinking density along the laminar streamlines of the serpentine device geometry. Here, a 'comb' is produced by (a) feeding disparate hydrogel inks through (b) layer multiplication elements, and (c) adding a second layer perpendicular to the teeth. This illustrative design consists of a $AL_HL_VR + AR$ element sequence; other cross-sections can be achieved by combining or omitting different flow elements. Post-extrusion, the variable crosslinking density is secured via (d) UV polymerization.*

Light responsive all-DNA microgels

R. Merindol[1]; N. Martin[2]; T. Beneyton[2]; J.-C. Baret[2,3], S. Ravaine[2].
[1]*CNRS, University of Montpellier, Laboratoire Charles Coulomb, Montpellier, France*
[2]*CNRS, University of Bordeaux, Centre de Recherche Paul Pascal,Pessac, France*
[3]*France Institut Universitaire de France, Paris, France*

Corresponding author: remi.merindol@umontpellier.fr

Inspired by biological soft-tissues, the fabrication of responsive, biocompatible and hierarchically structured materials is a key challenge for material science, nanotechnology and medicine.[1] DNA provides synthetics materials with the highest level of molecular structural control (*e.g.* DNA Origami), yet processes to create responsive DNA micro-structures are scarce. Here, we describe a process to create monodisperse micron-sized microgels and embed them with light responsive properties.

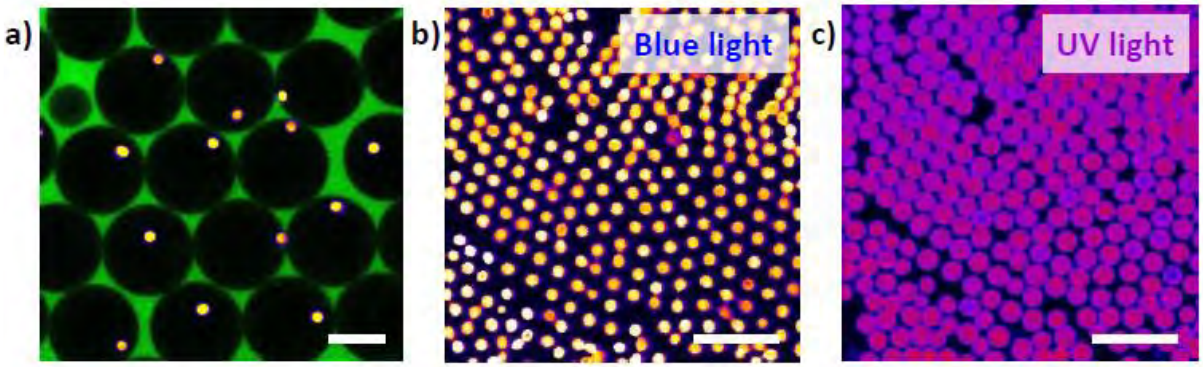

Figure 1: *Confocal laser scanning micrographs (CLSM) showing: a) All-DNA microgels (orange) in the microfluidic emulsion (green) after phase separation. b) Surface immobilized photo-responsive DNA microgels compacted under blue light irradiation and c) swollen under UV light. Scale bars are 20 µm.*

We use enzymatic synthesis to produce large amounts (mg) of sequence controlled ssDNA that can be used to assemble macroscale materials. We recently showed that, in presence of divalent cations, such ssDNA undergoes heat induced phase separation similar to that of polyNIPAM.[2] Combined with DNA hybridization, this phase separation allows one to produce **polydisperse** DNA microgels. Here, we bring this process to the next level by using microfluidic confinement in order to produce **monodisperse** all-DNA microgels (Figure 1a). We embedded these mesoscale building blocks with light responsive properties using a cationic azobenzene photoswitch (azobenzenetrimethyl-ammonium bromide, azoTAB). Light-triggered *trans-cis* photoisomerisation of azoTAB decreases its binding affinity to DNA chains and induces globule-coil transition of the backbone conformation which result in microgel swelling (Figure 1b,c). The process is reversible and yields up to 17-fold volume change in optimized conditions. Finally we demonstrate the assembly of light responsive microgel superstructures as proof-of-concept hierarchical all-DNA materials.[3]

References

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Breaking isolation to form new networks: pH-triggered changes in connectivity inside lipid nanoparticles

Z.X Xu[1,2]; J.M. Seddon[3], P.A. Beales[3], M. Rappolt[1], A.I.I. Tyler[1]
[1] *University of Leeds, School of Food Science and Nutrition, Leeds, United Kingdom*
[2] *University of Leeds, School of Chemistry and Astbury Centre for Structural Molecular Biology, Leeds, United Kingdom*
[3] *Department of Chemistry, Imperial College London, London, United Kingdom*

Corresponding author: A.I.I.Tyler@leeds.ac.uk

There is a growing demand to develop smart nanomaterials that are structure-responsive as they have the potential to offer enhanced dose, temporal and spatial control of compounds and chemical processes. The naturally occurring pH gradients found throughout the body make pH an attractive stimulus for guiding the response of a nanocarrier to specific locations or (sub)cellular compartments in the body. Here we have engineered highly sensitive lyotropic liquid crystalline nanoparticles (LCNPs) that reversibly respond to changes in pH by altering the connectivity within their structure at both room temperature and physiological temperature. At pH ~7, the nanoparticles have an internal structure consisting of discontinuous inverse micellar 'aqueous pockets' based on space group Fd3m. When the pH is ≤6, the nanoparticles change from a compartmentalized to an accessible porous internal structure based on a 2D inverse hexagonal phase (H_{II}, plane group p6mm). We validate the internal symmetry of the nanoparticles using Small Angle X-ray Scattering (SAXS) and cryogenic Transmission Electron Microscopy (cryo-TEM). The high resolution electron microscopy images obtained have allowed us for the first time to directly visualize the internal structure of the Fd3m nanoparticles and resolve the two different-sized inverse micelles that make up the structural motif within the Fd3m unit cell, which upon structural analysis reveal excellent agreement with theoretical geometrical models.

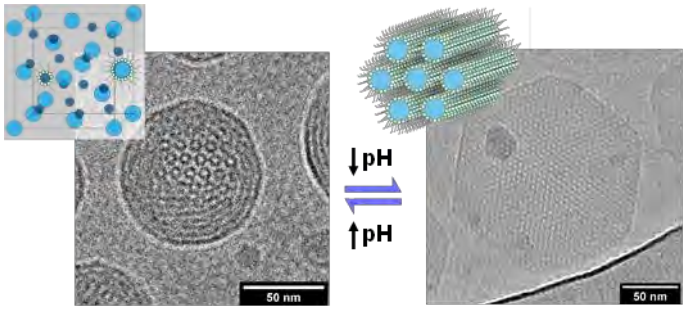

Figure 1: *pH-induced reversible structural transition between Fd3m (left) and H_{II} (right) of LCNPs.*

Mechano-pigments for high dynamic range mechano-sensing in polymeric materials

J. M. Clough*; C. Weder, S. Schrettl

Adolphe Merkle Institute, University of Fribourg, Chemin des Verdiers 4, Fribourg 1700, Switzerland

Corresponding author: jessica.clough@unifr.ch

Polymers are ubiquitous in the modern world, composing materials as diverse as deformable elastomers in car tires, soft hydrogels for tissue mimics and strong, tough ballistic glass. Understanding their ability to bear an applied mechanical strain or stress is essential to engineering these materials. The recent development of optically mechano-sensing polymeric materials has been driven by this fundamental and technological necessity.[1–3] However, the force sensitivity of existing mechano-sensing systems remains restricted, activating at just one, usually high, critical stress threshold.

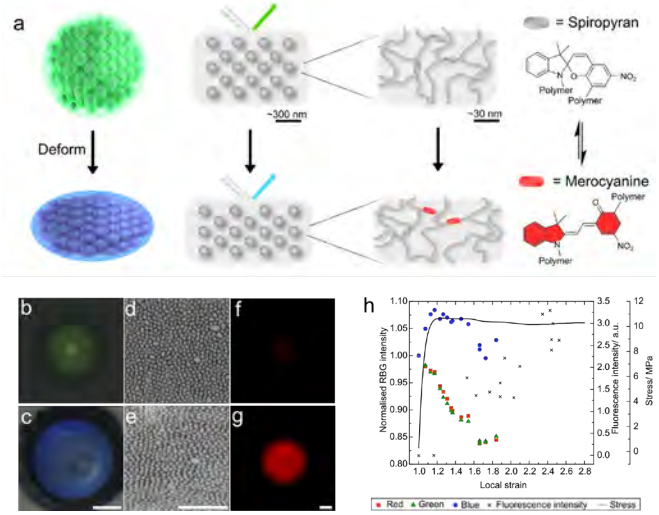

Figure 1: *Mechano-pigments with microstructural and molecular mechanochromism: a) schematic; reflectance images of b) uncompressed and c) compressed sensors (scale-bar 50 µm); d), e) FIB-SEM images of interior colloidal arrangement for sensors in b) and c) (scale-bar 2 µm); fluorescence images of f) uncompressed and g) compressed sensors (scale-bar 50 µm); h) spectral response of sensors to tension in LLDPE*

This contribution presents broadly applicable, high dynamic range mechano-sensors, or "mechano-pigments", capable of reporting on a wide range of deformations. The sensors are spherical, photonic assemblies of silica colloids, embedded in a soft, polymeric matrix cross-linked by a molecular mechano-sensor, spiropyran. The photonic array changes color at smaller deformations, and the spiropyran transforms to fluorescent merocyanine at larger deformations. Compression of single pigments revealed that the onset and extent of molecular mechano-activation is dependent upon the volume fraction of silica colloids in the structure. The mechano-pigments were also readily dispersed in different polymeric matrices, and used to investigate necking in linear low-density polyethylene.

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General Session 5

Tuesday 01 June 16:10 – 18:00

Interfacial dynamics of turbid samples can be measured by dynamic light scattering

Antonio Giuliani[1,2], Benoit Loppinet [1],
[1]*Iinstitute for Electronic Structure and Laser, FORTH, Heraklion Greece*
[2]*Ipresent address : University of Wageningen , the Netherlands*

Corresponding author: benoit@iesl.forth.gr

Dynamic light scattering (DLS) is a pillar of experimental study of dynamics in soft matter. Due to its broad range of probed time scale it has been applied to a very large range of samples in different intentions from particle sizing to complex dynamics including microrheology. The total internal reflection version, known as evanescent wave DLS (EWDLS) has been used to investigate near wall dynamics. It has been applied to colloids or polymers at rest and also to evaluate velocity profile and slip length [1]. We here discuss the case of EWDLS in the presence of strongly scattering samples (i.e multiple scattering)[2].

Using ray-tracing simulation, we show that a significant portion of the detected photons in a EWDLS experiment with turbid sample has been scattered only once (single scattering. We proposed that the measured correlation functions can be separated in two contributions from near wall single scattering and from multiple scattering distributed through the sample. It provides the possibility to separate the two contributions and therefore to retrieve the near wall dynamics. The validity of the method is confirmed using experiments with turbid dispersion of latex particles at rest and under flow. In the former, the near wall diffusion can be retrieved. The near wall velocity can be retrieved in a straightforward fashion in the latter, as the near wall and bulk dynamics are well separated due to the shear flow. Information on both the near wall flow (possibly including slip length) and the bulk flow can then be retrieved from a single experiment. When applied to high concentration colloidal dispersions under shear, the techniques evidenced the onset of wall slip.

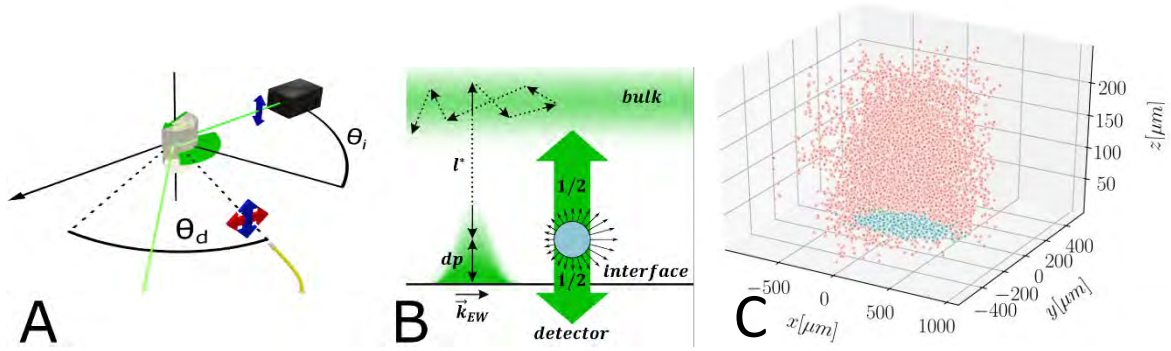

Figure 1 : Geometry of scattering experiment (A,B) and of scattering events (single & multiple) (C)

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Dynamic facilitation and the chain-length-dependent relaxation dynamics in polymeric glass-formers

J. Mattsson[1]; D. Baker[1], M. Reynolds[1], R. Masurel[2], P.D. Olmsted[2]
[1]*University of Leeds, School of Physics and Astronomy, Leeds, United Kingdom*
[2]*Georgetown University, Department of Physics and Institute for Soft Matter Synthesis and Metrology, Washington DC, United States*

Corresponding author: k.j.l.matttsson@leeds.ac.uk

The glass transition temperature T_g in polymers increases with increasing molecular weight M, but the detailed $T_g(M)$ dependence in polymers is not well understood. Here, we present experimental results of the M-dependence of both the structural (alpha) relaxation process, which controls the glass transition, and faster secondary relaxation processes for a range of polymers of varying chain flexibility. Based on our results, we propose that these relaxations are linked through *dynamic facilitation*. This leads to the conclusion that the chain-length-dependent alpha relaxation, and thus $T_g(M)$, in most polymers is controlled by a relatively 'local' fundamental relaxation, for which the relevant metric is linked to local chain flexibility. Thus, following earlier work of many others, we argue that local dihedral barriers play an important role in controlling the dynamics. We identify regimes in M where intra- and inter-molecular relaxation dynamics play different roles in defining the dynamics (and thus T_g). We argue that this naturally gives rise to clear differences in behaviour compared to that observed in non-polymeric glass-formers with simpler 'rigid' structures, or in barrier-free models of polymers.

Solutions of Linear and Ring Single Chain Nanoparticles with Reversible Bonds: effective interactions and beyond.

M. Paciolla[1]; C. Likos[3]; A. J. Moreno[1,2]

[1]*Centro de Física de Materiales (CSIC-UPV/EHU) and Materials Physics Center MPC, Paseo Manuel de Lardizabal 5, 20018 San Sebastián, Spain;*

[2] *Donostia International Physics Center , Paseo Manuel de Lardizabal 4, 20018 San Sebastián, Spain;*

[3] *Faculty of Physics, University of Vienna, Boltzmanngasse 5, A-1090 Vienna, Austria;*

Corresponding author: mpaciolla001@ikasle.ehu.eus

Single-chain nanoparticles (SCNPs) are soft nano-objects synthesized through purely intramolecular cross-linking of functionalized polymers, [1]. Design and function of SCNPs is a rapidly growing area of research due to their promising applications as catalysts, drug delivery vehicles, biosensors or rheology modifying agents. Due to the increasing number of synthesis routes developed is nowadays possible to obtain SCNPs from linear and ring [2] polymers enhancing the possibility to obtain objects with very different properties.

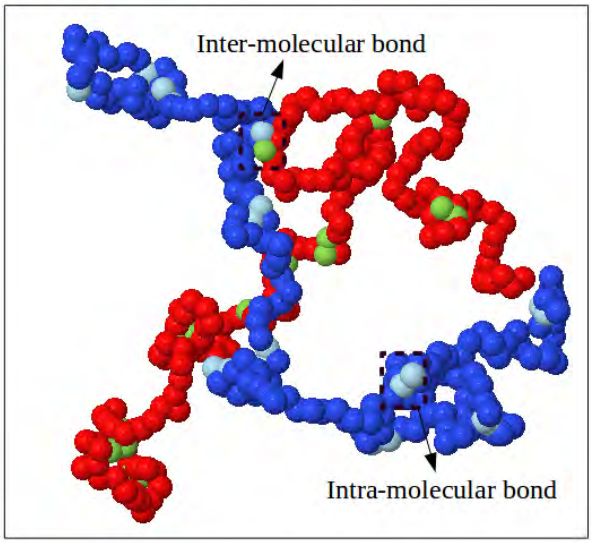

Figure 1: *Representative snapshot from MD simulations for the computation of the effective interactions between linear-SCNPs with reversible bonds.*

In recent years growing efforts have been dedicated to broaden their functionalities and areas of applicability through the implementation of reversible bonds (non-covalent and dynamically covalent). Thus, the competition between intra- and intermolecular bonding can allow for switching between a fluid solution of SCNPs and an arrested reversible gel through changing the conditions of the environment. Then in order to investigate the phase behaviour of solutions of SCNPs, the effective potentials have been determined through Molecular Dynamics simulations and allow us to access and simulate large spatial scales and a broad region of the phase diagram. The emerging general scenarios for reversible gelation of linear-SCNPs [3] and ring-SCNP are explored with an emphasis on the interactions in a binary mixture of two species of linear-SCNPs .

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Solid-state NMR and Crystal Structure Prediction: overcoming difficulties on a route to crystal structure of elusive polymorphs

Marta K. Dudek[1]; Piotr Paluch[1], Edyta Pindelska[2] Karol Nartowski[3], Graeme M. Day[4]
[1]*Center of Molecular and Macromolecular Studies, Polish Academy of Science, Lodz, Poland*
[2]*Faculty of Pharmacy, Medical University of Warsaw, Poland.*
[3]*Department of Drug Form Technology, Wroclaw Medical University, Wroclaw, Poland*
[4]*Computational Systems Chemistry, School of Chemistry, University of Southampton, UK.*

Corresponding author: mdudek@cbmm.lodz.pl

Crystal structure of two polymorphs of furazidin [1] and of methanol solvate-hemihydrate of (+)-catechin [2] were determined by 2D solid-state NMR measurements and crystal structure prediction (CSP). All three solids yield only microcrystalline powders upon crystallization, leading to difficulties in the elucidation of their crystal structure. In such cases, alternative methods have to be used. Among them, a unique combination of high resolution solid-state NMR experiments and quantum chemical calculations is an excellent route to unveil elusive crystal structures of solids. On the other hand, when dealing with flexible, multicomponent systems, noumerous obstacles have to be overcome. Here, we show the strenghts and limitations of the CSP-NMR approach, indicating possible ways of dealing with issues arising on the way to crystal structure determination. Furazidin crystallizes in two previously uncharacterized neat crystal forms, Z'=2 (form I) and Z'=1 (form II). Solid-state NMR measurements indicate that the two structures are built by different conformers. While finding a correct crystal structure using CSP for a Z'=1 polymorph is rather straight-forward, this is not the case of a Z'=2 polymorph. Here, a number of the computationally generated structures showed serendipitous agreement in terms of ^{1}H or ^{13}C NMR data with the solid-state NMR experiments (false-positive matches, Figure 1). We show how such agreement translates into common structural features and formulate conditions that have to be met in order to indicate a correct crystal structure. This knowledge is used to determine the crystal structure of a more complicated system, methanol solvate – hemihydrate of catechin. We also demonstrate a useful short-cut allowing for limiting the number of conformations considered in a very demanding calculations (five-component system, 68 stable conformers).

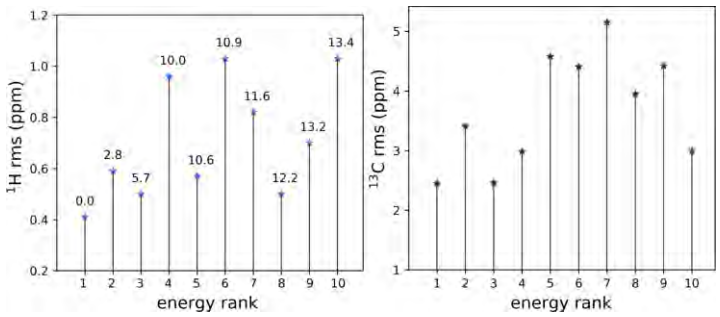

Figure 1: *^{1}H and ^{13}C RMS values obtained after comparison of experimental and theoretical NMR parameters for Z'=2 polymorph of furazidin.*

This work was financially supported by Polish National Science Center (UMO-2018/31/D/ST4/01995). PL-GRID is is gratefully acknowledged for providing computational resources

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Sculpting vesicles with active particles

M. Hoore[1], C. Abaurrea-Velasco[1], H. R. Vutukuri[2], T. Auth[1], J. Vermant[2], G. Gompper[1], **D. A. Fedosov**[1]

[1] *Forschungszentrum Jülich, Institute of Biological Information Processing and Institute for Advanced Simulation, Jülich, Germany*

[2] *ETH Zürich, Department of Materials, , Zürich, Switzerland*

Corresponding author:d.fedosov@fz-juelich.de

Biological cells are able to generate intricate structures and respond to external stimuli, sculpting their membrane from inside. Simplified biomimetic systems can aid in understanding the principles which govern these shape changes and elucidate the response of the cell membrane under strong deformations. We employ a combined simulation and experimental approach to investigate different non-equilibrium shapes and active shape fluctuations of vesicles enclosing self-propelled particles [1]. Interestingly, the most pronounced shape changes are observed at relatively low particle loadings, starting with the formation of tether-like protrusions to highly branched, dendritic structures shown in figure 1. At high volume fractions, globally deformed vesicle shapes are observed. The obtained state diagram of vesicles sculpted by active particles predicts the conditions under which local internal forces can generate dramatic cell shape changes, such as branched structures in neurons.

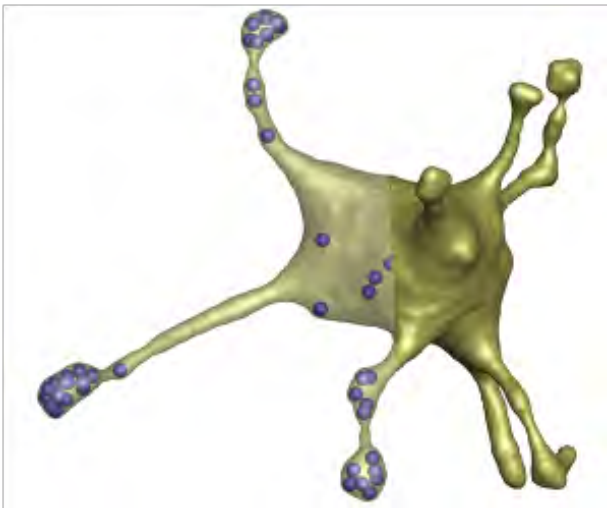

Figure 1: *Dynamic formation of an astrocyte-like shape from a 3D simulation of a vesicle enclosing active particles.*

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Topical Session
Artificial Cell

Wednesday 02 June 10:40 – 12:30

Active cell deformation through actin assembly, a biomimetic approach

Cécile Sykes

Team "Active Cell Matter", Département de Physique, Ecole Normale Supérieure, LPENS UMR 8023
24 rue Lhomond, 75005 Paris, France

Corresponding author: cecile.sykes@phys.ens.fr

The mechanism of cell functions such as motility and division are approached using soft matter physics. We conceive stripped-down experimental systems that reproduce cellular behaviours in simplified conditions: cytoskeleton dynamics are reproduced on liposome membranes[i],[ii] (Figure 1). Complementary to the encapsulation approach[iii] , the "outside geometry" allows for soft matter variables to be tuned, such as membrane tension and the structural details of the cytoskeleton architecture. We obtain a phase diagram for conditions of inward or outward membrane deformations generated by actin dynamics[iv]. We also observe buckling and wrinkling under osmotic deflation[v], thereby confirming that actin networks are elastic and follow the generic mechanism of buckling and wrinkling found in various systems spanning from pollen grains to the development of the gut or the brain.

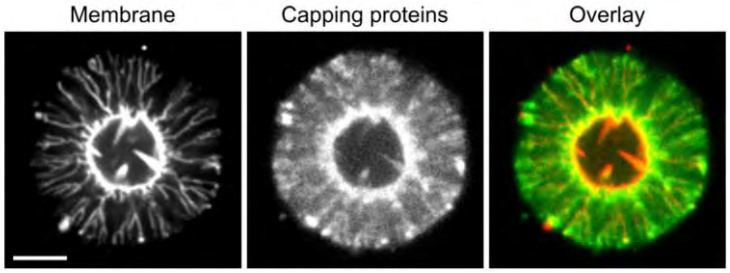

Figure 1: The dynamic actin cytoskeleton (marked by the presence of capping proteins, *Alexa Fluor 488 C5-maleimide, green*) is able to deform the membrane (*TexasRed-DHPE, red*) inward (spikes towards the liposome center) and outward (tubes emanating from the liposome membrane). Scale bar: 5µm.

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Soft Matter, **15**, 9647 – 9653 doi: 10.1039/c9sm01902b (2019)

A toolkit for artificial cell construction: droplets, opto- fluidics and biomembrane engineering

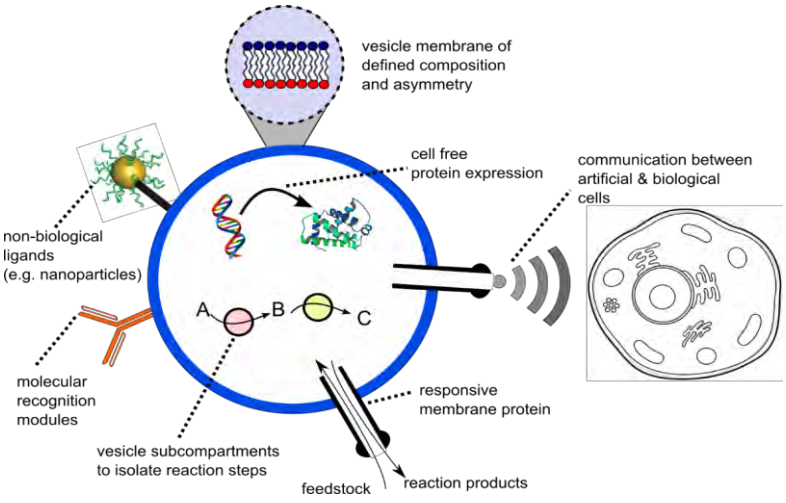
Yuval Elani[1]

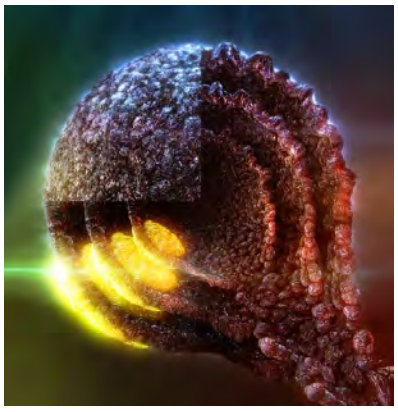
[1] *Department of Chemical Engineering, Imperial College London, London, UK*
[2] *fabriCELL, Imperial College London, UK*

Corresponding author: y.elani@imperial.ac.uk

Artificial cells are cell-like entities constructed from the bottom-up using molecular building blocks, which resemble real biological cells in form and function. They are used both as simplified models of biological cells, and as smart soft-matter microdevices with a range of potential applications in industrial and clinical biotechnology. However, due to the lack of cellular infrastructure and absence of spatial organisation, the capabilities of artificial cells have not matched their biological counterparts. In this talk, I will present work from our group which aims to address this gap.

We have developed a series of technologies that allow us (i) to build cells of defined sizes, lamellarity, level of compartmentalisation, and internal architecture and (ii) to manipulate them in order to recapitulate various membranous motifs found in biology (e.g. double membranes, gap junctions, and tunnelling nanotubes). By deploying molecular bioengineering principles and by transplanting cellular machinery, we can programme our cells to possess the behaviours that are the hallmarks of life: communication, signalling, motility, sense/response, and biosynthesis. To further enhance artificial cell functionality, we use living cells and organelles as discrete functional modules that are embedded inside artificial cells. The resultant 'hybrid' cells are composed of a synthetic host and a living organelle, which enjoy a mutually beneficial relationship, and can be considered a novel living/synthetic cellular bionic material.





Synthetic cells: De novo assembly with DNA nanotechnology

K. Göpfrich[1,2], K. Jahnke[1,2], Y. Dreher[1,2]
[1]*Max Planck Institute for Medical Research, Biophysical Engineering Group, Heidelberg, Germany*
[2]*Heidelberg University, Department of Physics and Astronomy, Heidelberg, Germany*

Corresponding author: kerstin.goepfrich@mr.mpg.de

The future of manufacturing entails the construction of biological systems and synthetic cells from the bottom up. Instead of relying exclusively on biological building blocks, the integration of new tools and new materials may be a shortcut towards the assembly of active and eventually fully functional synthetic cells [1]. This is especially apparent when considering recent advances in DNA nanotechnology and microfluidics. Exemplifying this approach, we use microfluidics for the assembly of synthetic cellular compartments that we equip with natural or DNA-based synthetic cytoskeletons [2,3]. We find that the choice of fluorophore strongly influences dynamic DNA nanostructures, which can be exploited to tune the energy landscapes for their reconfiguration [4]. We further demonstrate the division of giant unilamellar lipid vesicles (GUVs) based on osmosis and phase separation [5] or spontaneous curvature [6] rather than the biological building blocks of a cell's division machinery. We derive a parameter-free analytical model which makes quantitative predictions that we verify experimentally [5]. All in all, we believe that precision technologies, like DNA nanotechnology, can help to accelerate synthetic biology research.

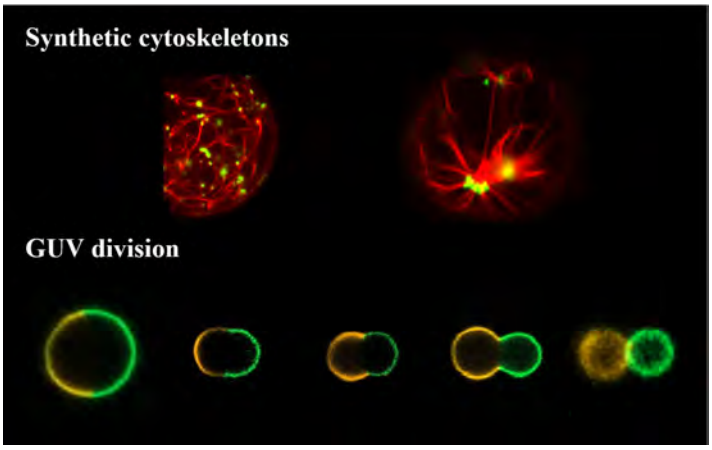


Figure 1: *Top: Confocal images of synthetic cytoskeletons inside microfluidic droplets. Bottom: Division of phase-separated GUVs.*

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

M. Arribas Perez[1,2]; P.A. Beales[1,2,3]
[1] *Astbury Centre for Structural Molecular Biology, University of Leeds, Leeds, UK*
[2], *School of Chemistry, University of Leeds, Leeds, UK*
[3] *Bragg Centre for Materials Research, University of Leeds, Leeds, UK*
Corresponding author: cmmap@leeds.ac.uk

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

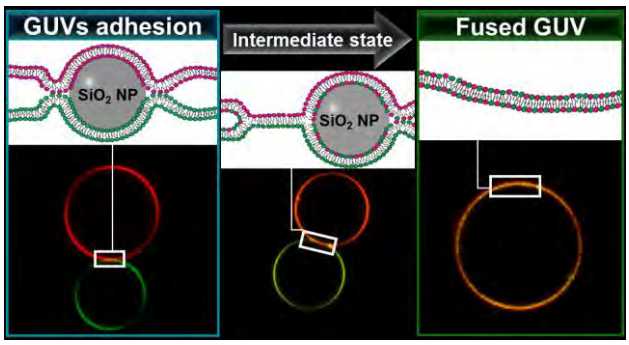

Figure 1: *Confocal microscopy images of GUVs during different stages of fusion mediated by SiO2 NPs along with a schematic representation of the potential state of the membranes at each of those stages.*

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

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Metabolic Adaptation in DNA Protocells

A. Samanta,[1] V. Sabatino,[2] T. R. Ward,[2] A. Walther[1]

[1]Department of Chemistry, *Johannes Gutenberg University of Mainz, Mainz, Germany*
[2] Department of Chemistry, *University of Basel, Basel, Switzerland*

Corresponding author: avik.samanta@uni-mainz.de

The bottom-up approaches in designing (artificial) protocells (PC) exhibiting adaptive behaviours and downstream signal propagation are emerging challenges in synthetic biology.[1] The fundamental cellular processes (differentiation, morphogenesis, and communication) stem from numerous interwoven metabolic reaction pathways that instigate the physical changes in the periplasm in response to the external environment's trigger. The ability to mimic elementary aspects of these non-equilibrium processes in the protocells could pave the way towards designing life-like systems orchestrating complex spatiotemporal transformations. Recently, we unraveled a polymer-like phase-separation behavior in multiblock single-stranded DNA by activating a nucleobase-specific lower critical solution temperature, which provides an opportunity to fabricate all-DNA protocells with several encoded sequences for post-functionalization with spatiotemporal control.[2]

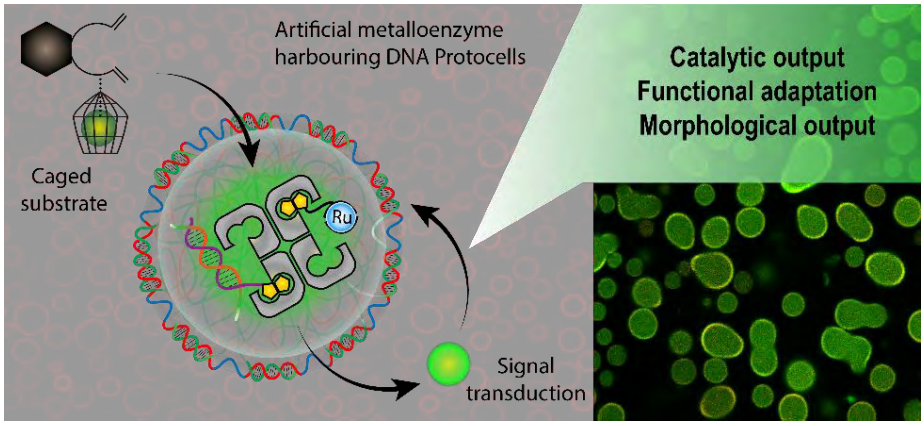

Fig. 1. Artifical metalloenzyme prompted morphological and functional adapatation in all-DNA protocells.

We recently introduced the first concept for functional and morphological adaptation driven by a bioorthogonal metabolic reaction in *all*-DNA protocells (PC).[3] To achieve a metabolic transformation, we encapsulated an artificial metalloenzyme (ArM)[4] whose ring-closing metathesis activity on a pro-fluorescent substrate generated a green-fluorescent metabolite that weakened the A-T (adenine-thymine) duplexes of the PC shell by intercalation. This metabolic reaction led to PC growth, DNA mechanosensor activation, and interparticle PC fusion (Fig. 1). Genetic engineering of the metalloenzyme increased the catalytic efficiency, and significant molecular crowding effects were observed.

Even though cross-disciplinary approaches to explore the design, structure, function, and evolutionary potential of metabolic PC with genetically evolved proteinaceous catalysts are in their early stages, our approach offers valuable insights into the achievement of chemically triggered adaptive behaviour of prebiotic coacervates and towards a minimalistic design of life-like abiotic systems.

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General Session 6

Wednesday 02 June 10:40 – 12:30

Influence of the magnetic content and short-range particle-interactions in the micro-structure and field response of colloidal magnetic brushes.

Joan J. Cerdà [1], Carles Bona-Casas [1], Antonio Cerrato [1], Tomàs Sintes [2], and Joan Massó [1]
[1] [a] *Dpt. de Física UIB i Institut d'Aplicacions Computacionals de Codi Comunitari (IAC3), Palma de Mallorca, Spain.*
[2] [b] *Instituto de Física Interdisciplinar y Sistemas Complejos, IFISC (CSIC-UIB). Universitat de les Illes Balears. E-07122 Palma de Mallorca, Spain.*
Corresponding author:jj.cerda@uib.cat

In this work we address the study of supramolecular brushes [1], whose filaments have both magnetic and non-magnetic moieties distributed along their filaments. Our study is motivated by the possibility of using these magnetic brushes as highly efficient responsive coatings that expand and contract according to an imposed external field in order to develop new types of nano-actuators. Langevin dynamics simulations have been used to study two types of brushes: sticky or Stockmayer brushes (SB) and non-sticky magnetic brushes (NSB). Our numerical results show that partially magnetic brushes have a magnetic microstructure and behaviour that in general are very different from those observed for brushes being fully magnetic, in spite of the fact that for some macroscopic observables, like magnetization, they may behave very similarly. Inside the partially magnetic class, strong differences are also observed between Stockmayer and non-sticky magnetic brushes. Results also point out that partially magnetic brushes can be much more interesting for certain purposes than their fully magnetic counterparts. These results are very promising because they show us that partially magnetic Stockmayer brushes have a great potential for applications.

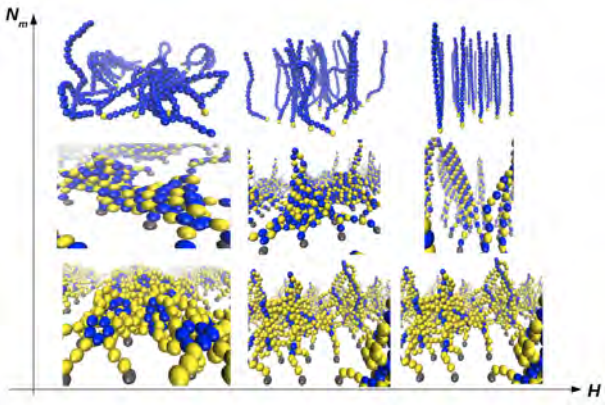

Figure 1: *Schematic diagram showing the microstructure of colloidal magnetic brushes with filaments of length* $N = 20$ *colloids as a function of the number of magnetic colloidal particles they contain,* N_m *, and the external magnetic field applied,* H*.*

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Flow-Induced Crystallization of a Multi-Block Copolymer under Large Amplitude Oscillatory Shear: Experiments and Modelling

G. P. Baeza[1]; M. Nébouy[1], L. Chazeau[1], J. Morthomas[1], C. Fusco[1], P. Dieudonné-George[2]

[1] *Univ Lyon, INSA-Lyon, CNRS, MATEIS, UMR 5510, 7 avenue Jean Capelle, F-69621, Villeurbanne, France*

[2] *University of Montpellier, CNRS, Laboratoire Charles Coulomb, UMR 5221, Place Eugène Bataillon, F-34095, Montpellier, France*

Corresponding author: guilhem.baeza@insa-lyon.fr

Following a previous work investigating the flow-induced crystallization (FIC) of PBT-PTHF multi-block copolymers under steady shear, [1] we propose here to deal with the case of large amplitude oscillatory shear (LAOS). [2] For this purpose, we focus on a single copolymer made, in average, of a sequence of nine soft- and eight hard-segments. We show unambiguously that LAOS accelerates the polymer crystallization when increasing (i) the frequency from 0.5 up to 50 rad s-1 (at constant strain amplitude of 100 %), or (ii) the strain amplitude from 10 to 300 % (at constant frequency of 2.5 rad s^{-1}) – see Figure 1. Based on this data, we demonstrate that high oscillatory shear rates have similar effects as the steady shear rate regarding the gelation time, i.e., that frequency and strain amplitude related effects are secondary. We carefully analyze the stress response through Fourier-Transform decomposition that emphasizes the rich rheological behavior of our material during its liquid-to-solid phase transition. With the help of X-ray scattering experiments (ex-situ SAXS and WAXS), we then propose a global scenario rationalizing the whole set of rheological observations based on the copolymer structure. In parallel, we propose to use a recent model that we developed to simulate the stress response in the case of steady shear promoted FIC and adapt it to the case of LAOS. Remarkably, our model which is based on modified Doi-Edwards equations only, provides good qualitative agreement with the data when varying the strain amplitude or the frequency. Furthermore, it is found to predict quantitatively the gelation time of the system.

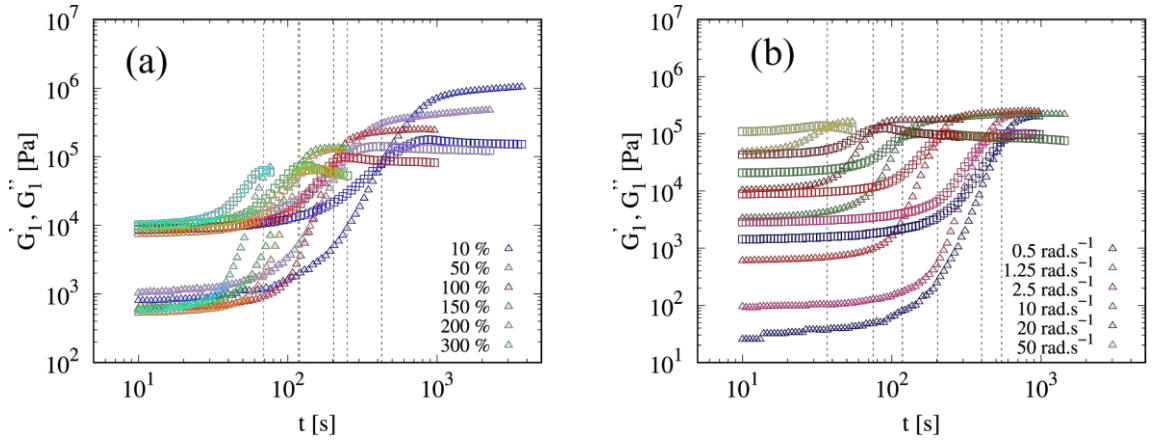

Figure 1: *Storage ($G'_1 - triangles$) and loss ($G''_1 - squares$) dynamic moduli as a function of time during the crystallization of a PBT-PTHF multi-block copolymer varying a) the strain amplitude and b) the frequency of the LAOS solicitation. [2]*

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Structure and dynamics of aqueous locust bean gum solutions

A. M. O'Connell[1], Y. González-Espinosa[2], F. M. Goycoolea[2], A. Gulotta[3], P. Holmqvist[3], J. Mattsson[1]

[1] *University of Leeds, School of Physics and Astronomy, Leeds, United Kingdom*
[2] *University of Leeds, School of Food Science and Nutrition, Leeds, United Kingdom*
[3] *Lund University, Division of Physical Chemistry, Lund, Sweden*
Corresponding author: k.j.l.mattsson@leeds.ac.uk

Locust bean gum (LBG) is a high molecular weight polysaccharide of great industrial interest due to its natural origins and strong thickening ability. In aqueous solution, LBG is known to demonstrate interesting phase behaviour such as gelation upon long-term storage or freeze-thaw cycling. However, many uncertainties remain around the solution state properties of LBG. The high molecular weight, tendency to form aggregates, and dependence on solubilisation procedure are likely causes for some of these uncertainties, and necessitate great care in characterisation.

We present a comprehensive experimental study of aqueous LBG solutions, with results obtained using steady shear rheology, static and dynamic light scattering (SLS and DLS), ultra-small-angle light scattering (USALS), and asymmetric flow field-flow fractionation (AF4) coupled to multi-angle light scattering, refractive index, and UV absorption detectors. This range of complementary techniques allows for a detailed understanding of the solution behaviour.

We identify the solutions to be mixtures of well dispersed polymer and aggregates, where the latter may be removed following a strict filtration procedure. The AF4 technique hydrodynamically separates these fractions, allowing for accurate size and molecular weight characterisation. The well-dispersed LBG is consistent with a neutral flexible polymer in good solvent conditions, while the aggregates appear highly compact and dominate the bulk solution scattering profile. The zero-shear viscosity scaling indicates three concentration regimes (dilute, semidilute unentangled, and semidilute entangled), and the intrinsic viscosity is used to determine the molecular weight, in good agreement with the value found by AF4-MALS for the dispersed polymer fraction. DLS reveals internal relaxations occurring under Zimm dynamics, apparent as a primary decay mode present at all measured concentrations. Above the entanglement concentration, a faster diffusive mode is also observed. The solution structure is probed over a wide range of lengthscales using static light scattering and USALS.

Furthermore, we determine the frequency-dependent rheology of these solutions using bulk rheometry and a range of microrheological techniques, allowing for characterisation over a broad frequency range.

Our work provides a thorough experimental characterisation of LBG solutions, revealing their behaviour over a range of concentrations from dilute to entangled regimes.

Dynamics of hydrogels having permanent and transient crosslinks – sticky Rouse mode?

Louis DEBERTRAND, Jingwen ZHAO; Costantino CRETON; **Tetsuharu NARITA**
Laboratoire Sciences et Ingénierie de la Matière Molle, ESPCI Paris, 75005 Paris, France.

tetsuharu.narita@espci.fr

Mechanical reinforcement of hydrogels has become an important topic of the gel science. Hydrogels having simultaneously permanent crosslinks and transient crosslinks can exhibit improved mechanical properties compared to the corresponding chemical gels. These "dual crosslink" gels also show unique viscoelastic properties, while the effects of the crosslinking ratios on them have not been fully understood. In this work, in order to comprehend the dynamics of the dual crosslink gels, we synthesized model dual crosslink gels with a variable ratio of permanent and transient crosslinks, and measured their linear and nonlinear mechanical properties by both torsion and tensile tests to characterize the transient crosslinker concentration dependence, by proposing molecular interpretations of the dynamics.

Poly(vinyl alcohol) hydrogels were synthesized, with glutaraldehyde as permanent chemical (covalent) crosslinker and borate ion as transient (dynamic covalent) crosslinker. Small amplitude oscillatory shear tests (torsion tests in parallel plate geometry) and uniaxial traction tests (tensile tests) were performed. We fitted the experimental data of both torsion and tensile tests with a constitutive model to describe the dynamic properties with only four parameters.

The dynamic moduli of the dual crosslink gel can be described by (1) the low frequency elastic modulus corresponding to that of the chemical gel, (2) the high frequency elastic modulus of both permanent and transient crosslinks which are additive, (3) relaxation time of the network (at the peak of the viscous modulus) and (4) the power-law exponent of the decay in both moduli after the peak, indicating the spectrum of the relaxation time (Fig.1(a)). This power-law decay was interpreted as sticky Rouse mode, or release of the longer Rouse mode by breaking of "sticky" transient bonds. However, when the permanent and transient crosslinker concentration dependence was studied we found that the power-law exponent depends both permanent and transient crosslinkers while the relaxation time decreased with increase in the transient crosslinker concentration but independent of the permanent crosslinker concentration. We show that the power-law exponent is the function of the number of the relaxation modes, which can be defined as the number of the transient crosslinkers per permanent chain, and with increase in the number of the relaxation mode, change from Maxwell-like to Rouse-like dynamics is observed (Fig.1(b)).

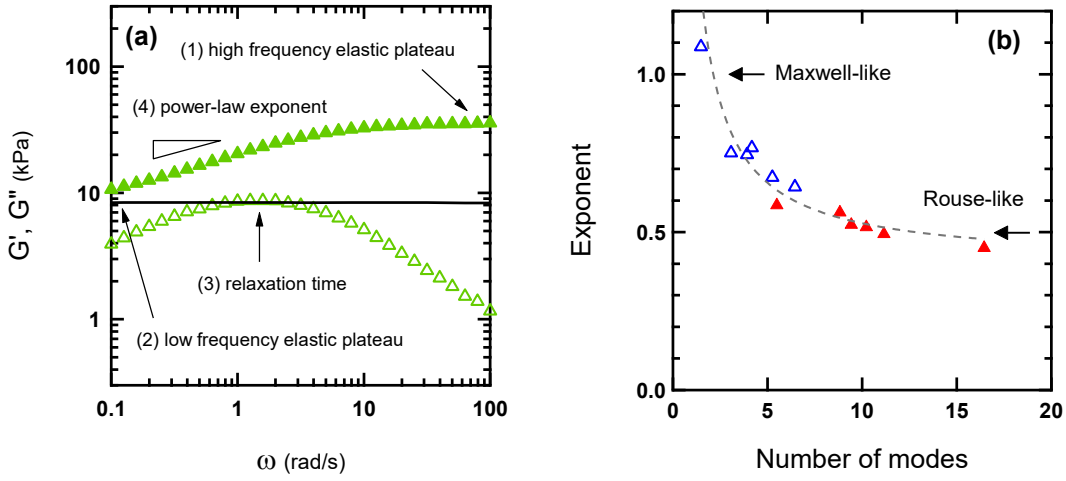

Figure 1: *(a) dynamic moduli of the dual crosslink gel. (b) Power-law exponent vs the number of modes (number of transient crosslinks per chemical chain).*

SAXS and microfluidics as a characterization tool to study the anisotropy of lyotropic liquid crystals during flow

A. Rodriguez-Palomo[1], V. Lutz-Bueno[2], X. Cao[3], R. Kádár[4], M. Andersson[5], M. Liebi[1,6]

[1]*Chalmers University of Technology, Dep. of Physics, Gothenburg, Sweden.*
[2]*Paul Scherrer Institute, Swiss Light Source, Villigen, Switzerland.*
[3]*ETH Zurich, Institute for Chemical and Bioengineering, Zurich, Switzerland.*
[4]*Chalmers University of Technology, Dep. of Industrial and Materials Science, Gothenburg, Sweden.*
[5]*Chalmers University of Technology, Dep. of Chemistry and Chemical Engineering, Gothenburg, Sweden.*
[6]*EMPA, Swiss Federal Laboratories for Materials Science and Technology, Centre for X-ray Analytics, St. Gallen, Switzerland.*

Corresponding author: adrian.rodriguez@chalmers.se

Extrusion-based 3D printing is a promising tool to produce hierarchical structures with controlled architecture. Complex structures with high anisotropy can be created by combining additive manufacturing and self-assembled materials. Understanding these self-assembled structures under flow is a requirement to design materials with fine-tuned properties. Lyotropic liquid crystals based on block co-polymers are a good example of hierarchical materials with self-assembled structures in different length-scales. To visualize the anisotropy and nanostructure during flow inside the 3D printing nozzle, microfluidic channels were used to reproduce the nozzle geometry in combination with scanning small angle X-ray scattering (SAXS). In this study we used Pluronic-based lyotropic liquid crystals self-assembled in the hexagonal and lamellar phase, which can be used to create hierarchical composites [1,2]. The hexagonal phase showed regions with orientation perpendicular to the flow. Only in areas with shear rate higher than a threshold, an orientation in the flow direction was found. Complementary rheological measurements showed strain overshoot, which is believed to be a consequence of reoriented and ruptured structures which define a well-defined multidomain structure. For the lamellar phase a structural transition from ordered lamellae to multilamellar vesicles was observed in the scattering signal. Such transition was reversible, and the structure returned to aligned lamellae at high shear rates. These results identify the structural changes and key mechanisms of reorientation during flow, which can be expanded and applied to various similar systems [3].

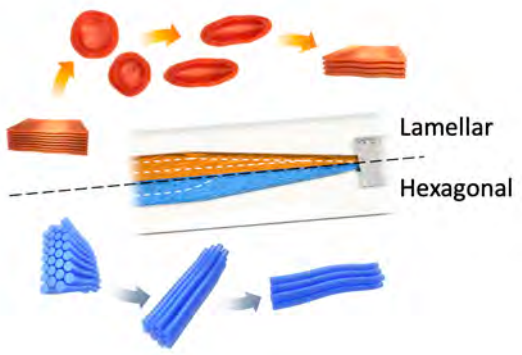

Figure 1: *Schematic illustration of the changes in the morphology and orientation of the lamellar and hexagonal self-assembled phases inside the microfluidic channels.*

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General Session 7

Wednesday 02 June 15:30 – 17:20

Control of Superselectivity by Crowding in Three-Dimensional Hosts

H. Kusumaatmaja[1]; A. T. R. Christy[1,2], M. A. Miller[2]
[1]*Durham University, Department of Physics, Durham, UK*
[2] *Durham University, Department of Chemistry, Durham, UK*
[1]*Institution3, Department3, City3, Country3*

Corresponding author: halim.kusumaatmaja@durham.ac.uk

Motivated by the fine compositional control observed in membraneless droplet organelles in cells, we investigate how a sharp binding-unbinding transition can occur between multivalent client molecules and receptors embedded in a porous three-dimensional structure. In contrast to similar superselective binding previously observed at surfaces, we have identified that a key effect in a three-dimensional environment is that the presence of inert crowding agents can significantly enhance or even introduce superselectivity [1]. In essence, molecular crowding initially suppresses binding via an entropic penalty, but the clients can then more easily form many bonds simultaneously. We demonstrate the robustness of the superselective behavior with respect to client valency, linker length, and binding interactions in Monte Carlo simulations of an archetypal lattice polymer model.

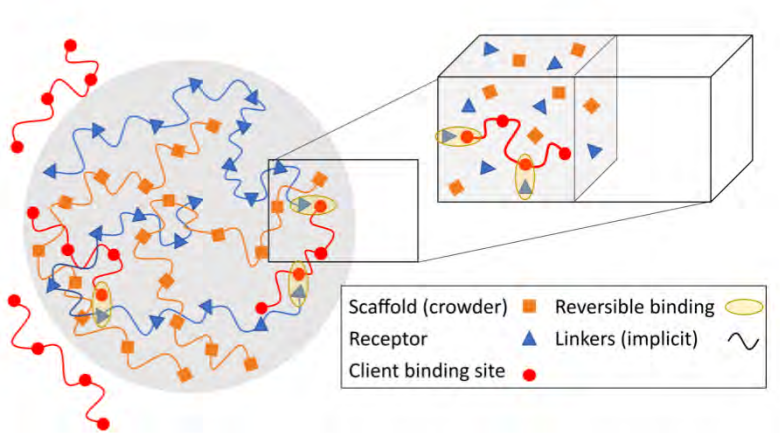

Figure 1: *Binding of multivalent clients to receptors embedded in a porous three-dimensional structure. Introducing inert crowding agents can give rise to a sharp binding-unbinding transition.*

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Analytical description of self-propelled polar flexible filaments

C. A. Philipps, G. Gompper, R. G. Winkler
Forschungszentrum Jülich, Institute of Biological Information Processing and Institute for Advanced Simulations, Jülich, Germany
Corresponding author:c.philipps@fz-juelich.de

Nature provides a variety of active matter agents, which are self-propelled units consuming either internal energy or extracting energy from their environment. The biological spectrum ranges from the macroscopic scale of a flock of birds, school of fish and mammalian herds, to self-propelled bacteria, sperm and algae, to the cellular level of the active semiflexible filaments of the cytoskeleton in living cells. In the latter, actin filaments are driven forward by myosin motors walking along the filaments [1]. This constant conversion of chemical into kinetic energy via the hydrolyzation of ATP leads to many interesting out of equilibrium phenomena. In general, active "polymers" exhibit interesting conformational and dynamical properties, even in dilute solution, which are absent in passive systems [2]. From a theoretical point of view, an analytical description of a polar active polymer is rather challenging, specifically due to the directed propulsion by the polar forces. Driving the Rouse model out of equilibrium by adding an active force tangentially to the local curvature of each monomer segment, a non-Hermitian eigenvalue problem is obtained. This transformation from a symmetric polymer to a directed A-B structure requires an adaptation of the free-ends boundary conditions and the eigenfunctions. A biorthogonal basis with respective distinct boundary conditions is established in combination with a normal mode analysis. An analytical solution of a polar filament with tangential driving forces is presented, where the filament itself is described by the Gaussian flexible polymer model [3]. It is found that the statistical properties strongly depend on the modality of applying the active force [4]. Surprisingly, conformational properties of continuous filaments are independent of activity [5]. Here, a description in terms of a discrete model has to be performed with care to avoid discretization effects. On the contrary, dynamics is activity enhanced, with the center-of-mass mean-square displacement changing from diffusion to a ballistic regime for intermediate times and back to diffusion for long times with an activity-dependent diffusion coefficient. Similarly, the decay of end-to-end vector correlation function is accelerated by activity.

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Unravelling Nature's Networks: Control of intra-protein nano-staples defines architecture and mechanics of protein networks due to *in situ* unfolding

Matt D G Hughes[1], Benjamin S Hanson[1,2], Sophie Cussons[2,3], Najet Mahmoudi[4], David J Brockwell[2,3], *Lorna Dougan*[1,2]

1 School of Physics and Astronomy, University of Leeds, UK
2 Astbury Centre for Structural Molecular Biology, University of Leeds, UK
3 School of Molecular and Cellular Biology, Faculty of Biological Sciences, University of Leeds, UK
4 ISIS Neutron and Muon Spallation Source, STFC Rutherford Appleton Laboratory, UK
Corresponding Author*: Lorna Dougan,* L.Dougan@leeds.ac.uk

Hierarchical assemblies of semi-flexible biopolymers, such as proteins, exhibit a wide-range of material properties that are exploited both in nature and by mankind. Recent work has focused on understanding the importance of the building block stability[1], however little is understood about the importance of the transition from the protein's native folded state to its unfolded state in network assembly. To determine the importance of *in situ* unfolding on network properties we control the force lability of a single protein building block, by reducing the natively disulphide reinforced bovine serum albumin (BSA).[2]

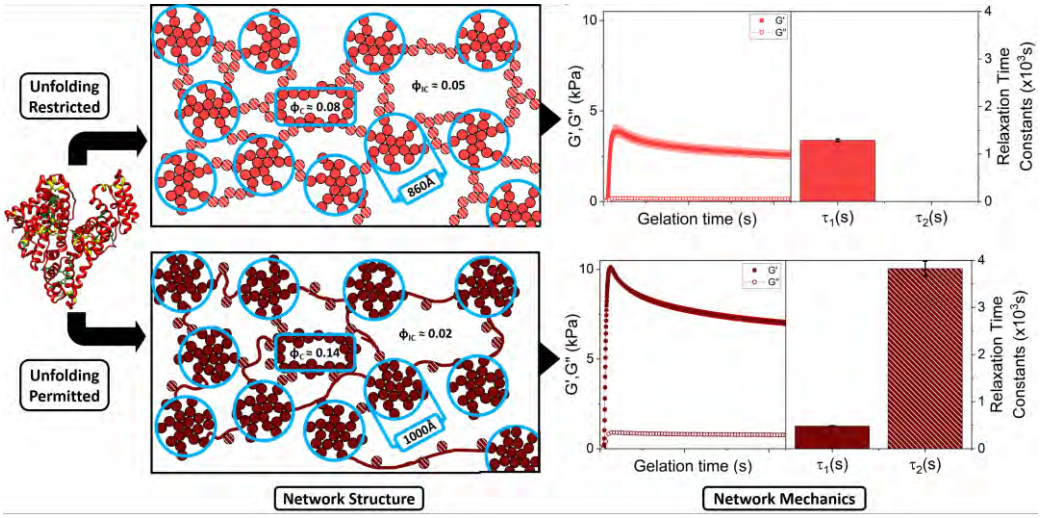

Figure 1: (left) Crystal structure of BSA (PDB code: 3V03). (middle) Predicted network architectures of BSA hydrogels in the (top) absence and (bottom) presence of the reducing agent DTT. (right) Gelation curves of BSA hydrogels showing storage and loss moduli as a function of gelation time and the extracted of post-photo-chemical cross-linking relaxation time constants in the (top) absence and (bottom) presence of DTT (where τ_1 and τ_2 relaxations are attributed to network rearrangement and *in situ* unfolding respectively).

Employing a combination of circular dichroism spectroscopy, small-angle scattering, rheology and modelling we show that restricting unfolding leads to homogeneous networks of cross-linked fractal-like clusters connected by an inter-cluster region of folded protein. Conversely, allowing in situ unfolding results in more heterogeneous networks of denser fractal-like clusters connected by an inter-cluster region populated by unfolded protein. In addition, gelation-induced protein unfolding and crosslinking in the inter-cluster region changes the hydrogel mechanics, as measured by a 3-fold enhancement of the storage modulus, an increase in both the loss ratio and energy dissipation, and markedly different relaxation behaviour. By controlling the protein's ability to unfold through nanoscale stapling, we demonstrate the importance of in situ unfolding in defining both network architecture and mechanics, providing insight into fundamental hierarchical mechanics and a novel route to tune biomaterial for future applications.

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On the interaction of β-glucosidase with Wrinkled SiO_2 nanoparticles: the protein corona formation

G. Pota[1]; D. Cavasso[2]; I. Russo Krauss[2,3]; V. Califano[4]; L. Paduano[2,3]; A. Costantini[1]; G. Vitiello[1,3]

[1]*University of Naples Federico II, Department of Chemical, Materials and Production Engineering, Naples, Italy*
[2]*University of Naples Federico II, Department of Chemical Sciences, Naples, Italy*
[3]*CSGI, Center for Colloid and Surface Science, Sesto Fiorentino (FI), Italy*
[4]*Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili STEMS-CNR, Naples, Italy*

Corresponding author: giulio.pota@unina.it

β-Glucosidase (BG) is an enzyme involved in the conversion of lignocellulosic biomass to obtain biofuel. It catalyzes the hydrolysis of cellobiose into glucose, which can be fermented to produce bioethanol. However, BG is costly, slightly thermally unstable at the reaction operative conditions as well as difficult to rescue from the reaction environment. Enzyme immobilization onto solid supports helps overcome these issues [1]. In this context, Wrinkled Silica Nanoparticles (WSN), a type of nanoparticles with central-radial pore structure [2], represent an ideal support for BG immobilization (Fig. 1a, 1b). The aim of the present study is to investigate the interaction mechanism of BG with WSN, unveiling the relationship between the enzyme organization onto the WSN surface and the catalytic performance. Herein, the kinetics of immobilization at different support-to-enzyme ratios were investigated by Dynamic Light Scattering (DLS), Circular Dichroism (CD) and Fourier Transform Infrared Spectroscopy (FTIR). DLS results showed that a 6:1 support-to-enzyme ratio provides the highest colloidal stability for the biocatalyst. CD spectra (Fig. 1c) assessed that the protein retains almost completely its structure during the process of adsorption as confirmed by the deconvolution of Amide I band (1650 cm^{-1}) in the FTIR spectrum of the sample [3]. Moreover, CD intensity decreases with time, likely because the protein gets inside the pore structure and its shielded from UV rays by the silica skeleton of the nanoparticles. Thermal denaturation curves of free and immobilized enzymes were compared indicating that the supported biocatalyst experiences no denaturation, whereas half the protein in its free form is denatured at 74 °C. Finally, immobilized biocatalyst exhibits a full activity with respect to the free enzyme in the hydrolysis of cellobiose to glucose.

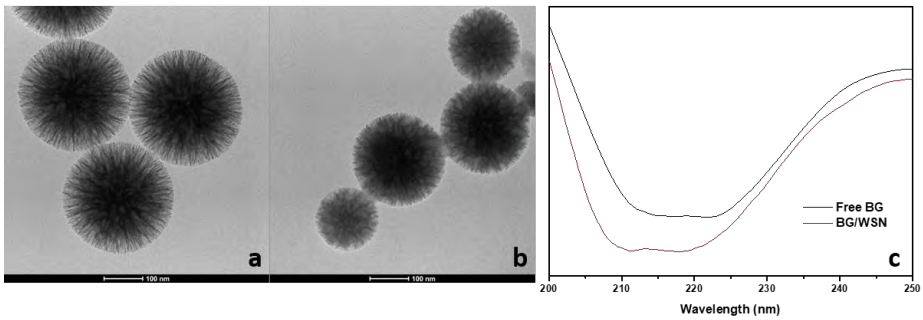

Figure 1: TEM images of bare WSN (**a**) and BG-immobilized WSN (**b**). CD spectra of free and immobilized BG onto WSN surface (**c**).

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Self-assembly of alternated lipo/hydrophilic copolymers in water: domain of occurrence and structure of the ouzo phase.

H. Trevisan[1]; F. Tournilhac[1]

[1]*ESPCI-Paris, Molecular, Macromolecular Chemistry, and Materials Lab, UMR 7167, Paris, France*

Corresponding author: francois.tournilhac@espci.fr

Selection of monomer couples, ensuring reactivity ratios close to zero, is an effective strategy to induce spontaneous copolymerization into an alternated sequence.[1,2] In addition, monomer design and customization of the solvent-monomer interactions opens the way to functional copolymers showing molecular self-assembly relevant to their regular amphipathic structure.[2] In this work, we show that the design of comonomers with adequate reactivities and interactions can be used to direct copolymer self-assembly on a mesoscopic scale. We investigate spontaneous formation of nanoparticles through solvent/non-solvent interaction using the so-called "ouzo effect". In this way, an ouzo diagram was built to determine the operation window for the self-assembly of alternated copolymers consisting of vinyl phenol and maleimide units carrying long alkyl-pendant groups ($C_{12}H_{25}$ or $C_{18}H_{37}$) in aqueous solutions (Figure 1). Also, investigations were pursued to account the influence of the lateral lipophilic pendant units on the size and structure of the nanoaggregates formed during one-shot water addition. Structure characterization by light scattering techniques (DLS and SLS), small-angle neutron scattering (SANS) and cryogenic transmission electron microscopy (Cryo-TEM) confirms the self-assembly of copolymer chains into nanoparticles (hydrodynamic radius range: 60 – 300 nm), which size is affected by the lipophilicity of the alternating copolymers and the solvent diffusion in water. Altogether, we present here the spontaneous ouzo effect as a simple method to produce stable alternating copolymer nanoparticles in water without the addition of stabilizing agents.

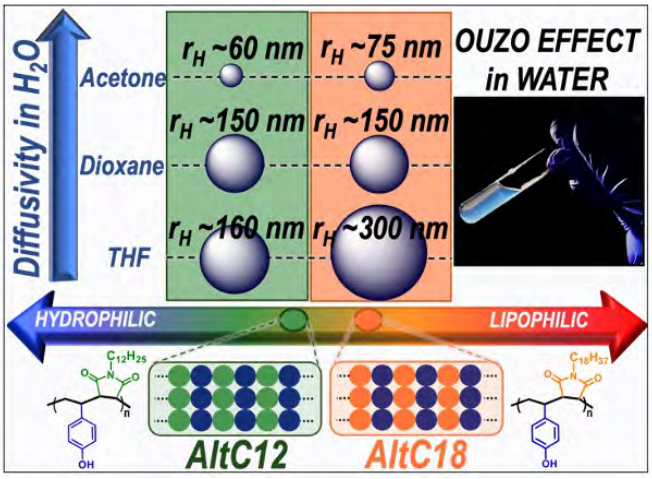

Figure 1: *Lateral alkyl pendant-groups ($C_{12}H_{25}$ or $C_{18}H_{37}$) on sequence alternated copolymers (AltC12 and AltC18, respectively) confers tuneable lipophilicity, allowing the spontaneous formation of nanoparticles in aqueous suspension with different sizes and structures, that vary with solvent diffusion in water.*

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General Session 8

Wednesday 02 June 15:30 – 17:20

Can the roles of polar and non-polar moieties be reversed in non-polar solvents?

C. J. Dongmo Foumthuim [1], M. Carrer[2], M. Houvet[3], T. Škrbić[1,4], G. Graziano[5], A. Giacometti[1,6]

[1] *Università Ca' Foscari di Venezia, Dipartimento di Scienze Molecolari e Nanosistemi, Venezia Mestre, Italy*
[2] *University of Oslo, Department of Chemistry and Hylleraas Centre for Quantum Molecular Sciences, Oslo, Norway*
[3] *Polytech Nantes-Engineering School of the University of Nantes, Nantes Cedex 3, France*
[4] *University of Oregon, Department of Physics and Institute for Fundamental Science, Eugene, USA*
[5] *University of Sannio-Benevento, Department of Science and Technology, Benevento, Italy*
[6] *6European Centre for Living Technology (ECLT), Venice, Italy*

Corresponding author:cedrix.dongmo@unive.it

Using thermodynamic integration, we study the solvation free energy of 18 amino acid side chain equivalents in solvents with different polarities, ranging from the most polar water to the most non-polar cyclohexane. The amino acid side chain equivalents are obtained from the 20 natural amino acids by replacing the backbone part with a hydrogen atom, and discarding proline and glycine that have special properties. A detailed analysis of the relative solvation free energies suggests how it is possible to achieve a robust and unambiguous hydrophobic scale for the amino acids (see Fig.1 below). By discriminating the relative contributions of the entropic and enthalpic terms, we find strong negative correlations in water and ethanol, associated with the well-known entropy-enthalpy compensation, and a much reduced correlation in cyclohexane. This shows that in general the role of the polar and non-polar moieties cannot be reversed in a non-polar solvent. Our findings are compared with past experimental as well as numerical results, and may shed additional light on the unique role of water as a biological solvent.

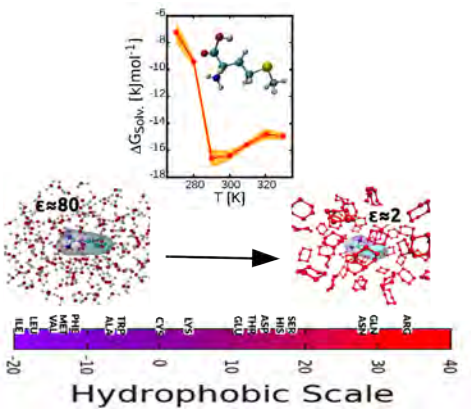

Figure 1: *Temperature dependence of the solvation free energy of methyl-ethylsulfide (methionine) in cyclohexane. The graph further exemplifies the transfer free energy of the latter analyte from a polar solvent, water ($\epsilon \approx 80$) to a non-polar solvent, cyclohexane ($\epsilon \approx 2$). This scheme is demonstrated to provide a robust and unambiguous classification of the relative hydrophobicity scale of amino acids, which indeed includes both physicochemical properties of solvent and solute. The hydrophobic scale suggested by this study is finally displayed on the bottom of the graph.*

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Cyclic Polyethylene Glycol as Nanoparticle Surface Ligand

Fabienne Barroso-Bujans[1,2,3], Mohammad A. Aboudzadeh[1,3], Marek Grzelczak[1,3]
[1]*Donostia International Physics Center, Donostia-San Sebastian, Spain*
[2]*IKERBASQUE - Basque Foundation for Science, Bilbao, Spain*
[3]*Materials Physics Center, CSIC-UPV/EHU, Spain*

Corresponding author: fbarroso@dipc.org

Cyclic polymers behave dramatically different than linear polymers due to the lack of end groups and smaller coil dimensions. We demonstrate that cyclic polyethylene glycol (PEG) can be used as an alternative of classical linear PEG ligands for gold nanoparticle (AuNP) stabilization. To this aim, we introduced a synthetic approach to synthesize cyclic PEG chemically attachable to gold surfaces [1]. Then, cyclic PEG was chemically attached to AuNPs by using standard ligand exchange procedures and the colloidal stability of nanoparticles evaluated [2]. Our results showed that the brush height of cyclic PEG increases identically as that of linear brushes in water with $(N\sigma^{1/2})^{0.7}$ (N, chain length and σ, grafting density) suggesting more extended conformations in the cyclic chains. Such structural effect and the reduced footprint diameter in cyclic brushes helped to explain the distinct response of AuNPs to ionic strength and temperature, respectively, compared to linear analogues.

Our latest studies on the colloidal stability of AuNPs modified with cyclic PEG were performed in ethanol, a solvent where neat PEG exhibit a non-conventional upper critical solution temperature. We observed that linear PEG brushes cause the precipitation of AuNPs (13 nm diameter) in hours without altering their surface plasmon resonance in a non-conventional temperature-reversible process. However, when the polymer brush topology is cyclic the precipitation is avoided while providing a very high colloidal stability to AuNPs in ethanol at -25 ºC for days. We postulated a mechanism where a fast reversible collapse of chain brushes leads to a state that is favorable for the interpenetration of linear chains and precipitation of AuNPs in a slow process, but which is not favorable for the interpenetration of cyclic polymer brushes. Our results evidence that the topology of PEG brushes plays an important role on the colloidal stability of AuNPs.

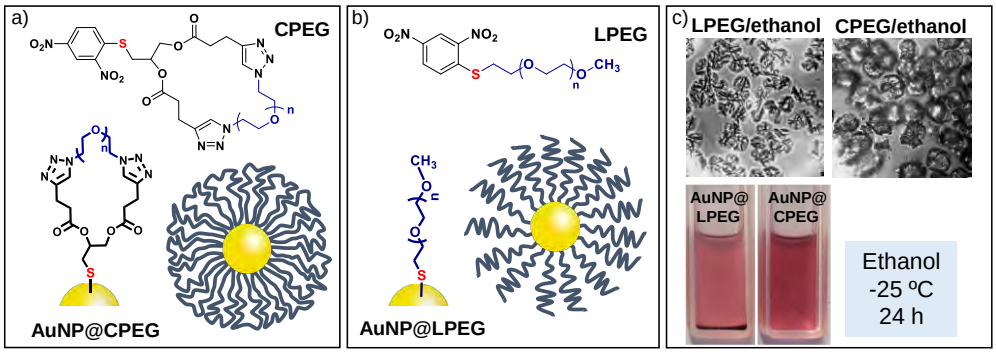

Figure 1: *Gold nanoparticles stabilized with PEG of different topologies. Structure of a) cyclic PEG (CPEG) and b) linear PEG (LPEG) with protected thiol groups. c) Optical microscopy of neat polymers in ethanol at -10 ºC and pictures of AuNPs modified with CPEG and LPEG in ethanol, stored at -25 ºC overnight.*

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Swimming behavior of squirmer dumbbells and polymers

J. Clopés, G. Gompper, R. G. Winkler
Forschungszentrum Jülich, Theoretical Soft Matter and Biophysics, Institute for Advanced Simulation and Institute of Biological Information Processing, Jülich, Germany
Corresponding author: r.winkler@fz-juelich.de

Nature provides a plethora of microswimmers, which can be rather elongated, filament- or polymer-like [1, 2]. Examples are bacteria swarmer cells or marine phytoplankton dinoflagellates assembling in a linear fashion. In order to address the relevance of hydrodynamic interactions for the collective behavior of such organisms, we study the swimming properties of linear polymer-like assemblies by mesoscale hydrodynamic simulations, where an active unit (monomer) is described by a spherical squirmer – which can be 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 (see Figure 1), and consequently the swimming efficiency differs from that of active Brownian linear assemblies. In particular, puller dumbbells and chains 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 [3]. Hence, the large-scale conformational and dynamical properties depend on the specific propulsion mechanism.

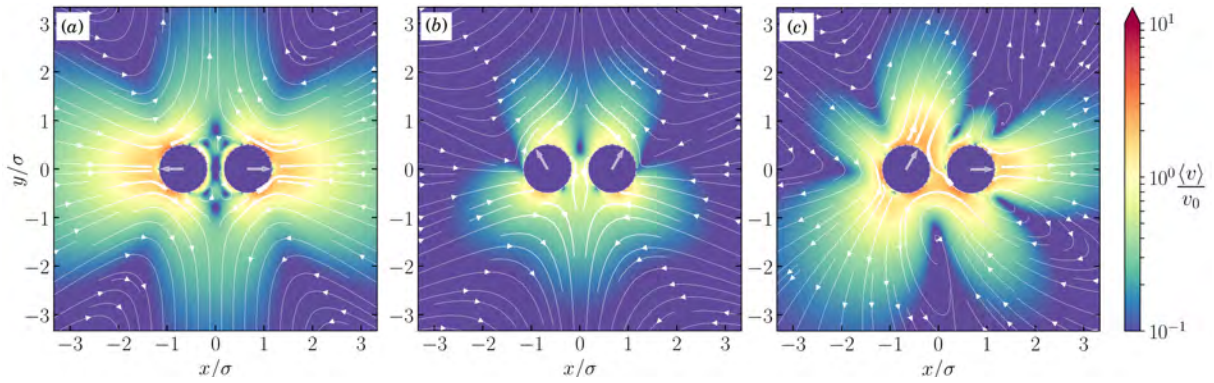

Figure 1: *Flow fields in the laboratory reference frame of most probable squirmer-squirmer relative orientations in dumbbells for different active stresses, β, (a) pullers ($\beta = 5$), (b) weak pushers ($\beta = -1$), (c) strong pushers ($\beta = -5$).*

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Structure and dynamics of supramolecular model polymer: influence of polymer polarity and association strength

Ana Brás[1]; Ana Arizaga,[1] Uxue Agirre,[1] Marie Dorau,[1] Daria Sokolova,[1,2] Judith E. Houston,[3,4] Aurel Radulescu,[4] Sylvain Prévost[5], Margarita Kruteva[6], Wim Pyckhout-Hintzen[6], Annette M. Schmidt[1]

[1]*Institute of Physical Chemistry, University of Cologne, Cologne, Germany*

[2]*Chemistry Department, University of Basel, Basel, Switzerland*

[3]*European Spallation Source ERIC , Lund, Sweden*

[4]*Jülich Centre for Neutron Science (JCNS) at Heinz Maier Leibnitz-Zentrum (MLZ), Forschungszentrum Jülich GmbH, Munich, Germany*

[5]*Institut Laue-Langevin, Life Sciences Group, Grenoble, France*

[6]*Jülich Centre for Neutron Science (JCNS-1) and Institute for Complex Systems (ICS-1), Forschungszentrum Jülich GmbH, Jülich, Germany*

Corresponding author: aeliasbr@uni-koeln.de

Supramolecular polymers, in which non-covalent interactions such as hydrogen bonds or metal coordination keep the repeating units together, offer exciting prospects for materials with novel properties because of the reversibility of the interactions [1]. This new class of materials combines the overall good chemical and mechanical properties of polymers with inherent dynamic reversible supramolecular interactions. Amongst others, hydrogen bonding (H-bonding) represents such a reversible mechanism [2]. The presented work focuses on the self-assembly of polymer model systems in the bulk via H-bonding. Our investigations are based on polymers with either a polypropylene oxide (PPO) or a polyethylene oxide (PEO) backbone, respectively. Diaminotriazine (Dat) and Thymine-1-acetic acid (Thy), as well as 2-ureido-4[1H]-pyrimidinone (Upy) are used as covalently attached functional end groups. Different experimental techniques such as small angle scattering and rheology were combined to study in particular the correlation between the backbone polarity and the different end-groups association strength as Upy is highly self-associative [1,2] in comparison to the heterocomplementary pair Thy/Dat. Results on the structure show that PEO and PPO functionalized with the pair Thy/Dat self-assemble as linear chains [3], while both polymers functionalized with Upy show a sphere-particle morphology corresponding to a Upy rich-phase. The corresponding Upy cluster radius is larger on PEO than on PPO due to the higher chain hydrophilicity. This means that the bonding energy is affected by the different polarities. An analysis of the dynamical behavior indicates not only the formation of a supramolecular network, but also a dramatically change from a typical Newtonian fluid behavior as observed for Thy/Dat groups.

Acknowledgment:

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A Natural, Cellulose-Based Microgel for Water-in-Oil Emulsions

K.S. Lefroy[1]; B.S Murray[1], M. E. Ries,[2] T. D. Curwen[3]
[1]*University of Leeds, School of Food Science and Nutrition, Leeds, UK*
[2]*University of Leeds, School of Physics and Astronomy, Leeds, UK*
[3]*Mondelēz International, Reading Science Centre, Reading, UK*

Corresponding author: fskl@leeds.ac.uk

Non-derivatised cellulose is generally assumed to have poor surface activity and therefore be unsuitable as a water in oil (W/O) emulsifier. In this work, a "natural" cellulose microgel (CMG) is fabricated via a top-down approach and used to stabilise W/O emulsions, without employing chemical modification. The cellulose is coagulated from an ionic liquid through a solvent-exchange process, in the presence and absence of added sunflower oil, in order to tune the cellulose morphology and properties. Detailed characterization of the nature of these microgels and the effect of the solvent change sequence on their emulsifying properties was investigated.

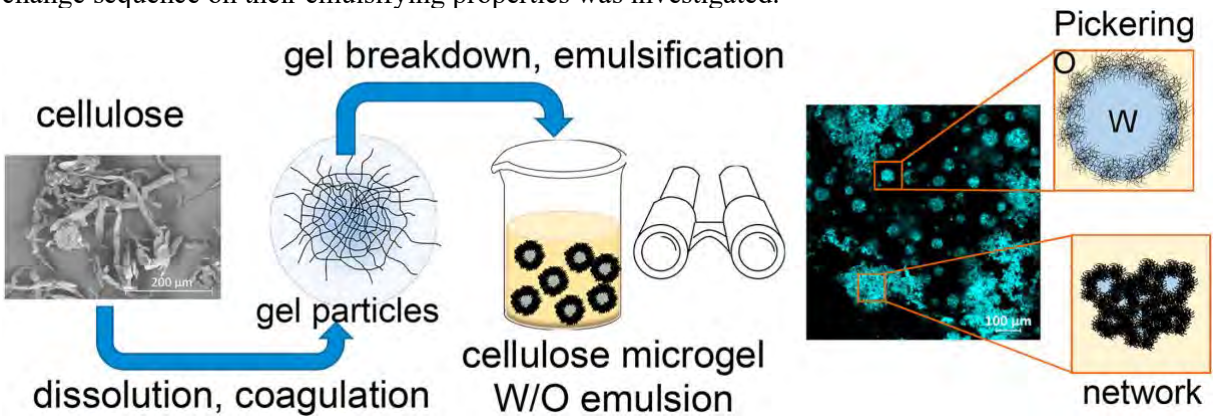

Figure 1: *Process of fabricating cellulose microgels (CMG) via coagulation from an ionic liquid. CMGs are then used to form water-in-oil (W/O) emulsion, through Pickering and network stabilisation .*

In the presence of oil, Fourier transform infrared (FTIR) spectroscopy confirmed the retention of oil in the coagulum during regeneration and the resultant CMGs were more easily dispersed in oil than water, suggesting the fabrication of a "hydrophobic" microgel. Confocal microscopy confirmed the adsorption of CMGs to the water-oil interface and W/O emulsions of up to 20 wt.% water displayed good stability over at least 1 month. This study therefore describes a "novel" route to W/O stabilisation using a natural emulsifier, which could be then used as a method of reducing fat and sugar in food products.

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Poster Session 1

Monday 31 May 14:00 – 15:30

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

M. Arribas Perez[1,2]; P.A. Beales[1,2,3]
[1] *Astbury Centre for Structural Molecular Biology, University of Leeds, Leeds, UK*
[2], *School of Chemistry, University of Leeds, Leeds, UK*
[3] *Bragg Centre for Materials Research, University of Leeds, Leeds, UK*
Corresponding author: cmmap@leeds.ac.uk

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

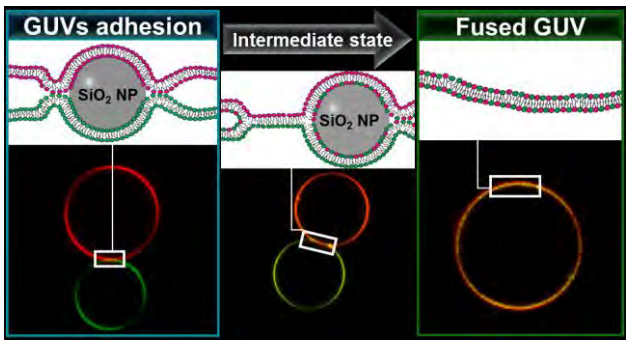

Figure 1: *Confocal microscopy images of GUVs during different stages of fusion mediated by SiO2 NPs along with a schematic representation of the potential state of the membranes at each of those stages.*

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

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

Racha Bayzou[1], Annie-kim Landry[2],Rafael Bianchini Nuernberg[2], Julien Trébosc[1,3], Frédérique Pourpoint[1], Frédéric Le Cras[4], Brigitte Pecquenard[4], Olivier Lafon[1,3]

[1] Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 – UCCS - 59000 Lille, France.
[2] CNRS, Université de Bordeaux, ICMCB et Bordeaux INP, F-33608- Pessac, France.
[3] Univ. Lille, CNRS, INRAE, Centrale Lille, Univ. Artois, FR 2638 – IMEC – Fédération Chevreul, 59000 Lille, France.
[4] Univ.Grenoble Alpes, CEA, LETI, F-38054 Grenoble, France.
[5] Institut Universitaire de France, 1 rue Descartes, 75231 Paris, France.

Corresponding author: Racha.bayzou.etu@univ-lille.fr

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

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

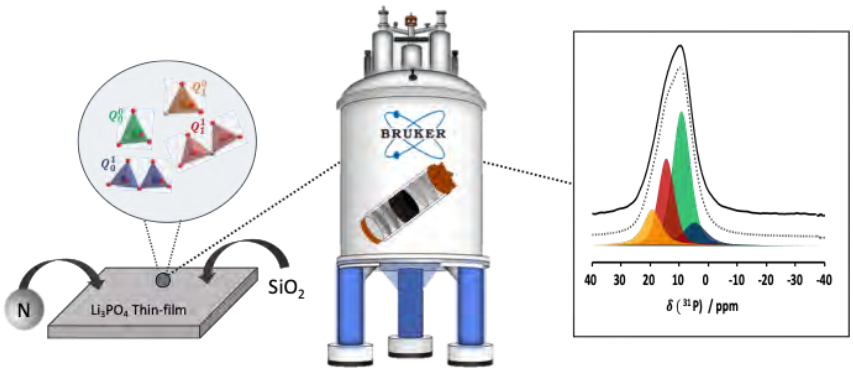

Figure 1. Solid-state NMR was employed to probe the atomic-level structure of LiPON thin-films.

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

Coline Bretz[1]; Andrea VaccaroI[1]

[1]*LS Instruments, Fribourg, Switzerland*

Corresponding author: coline.bretz@lsinstruments.ch

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

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

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Design, conception and microfluidic flow of a vesicle prototissue

L. Casas-Ferrer[1]; G. Massiera[1], L. Casanellas[1]

[1]*Université de Montpellier, Laboratoire Charles Coulomb UMR 5221, Montpellier, France*

Corresponding author: laura.casas-ferrer@umontpellier.fr

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

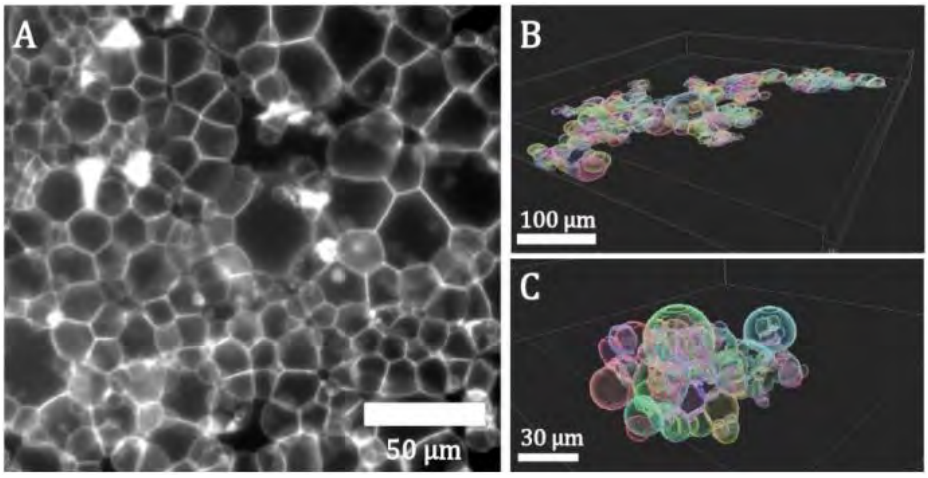

Figure 1: *Prototissue morphologies: 2D-monolayers (A, B) vs. globular aggregates.*

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

Filtration of nanoparticles through porous hydrogel matrix

Malak Alaa Eddine[1,2], Sabrina Belbekhouche[2], Bruno Bresson[1], Cécile Monteux[1]

[1] Laboratory SIMM (Soft Matter Science and Enginneering), PSL Research University, Sorbonne University, CNRS-ESPCI Paris, France

[2] Institut de Chimie et des Matériaux Paris Est,Thiais,France

Corresponding author: malak.alaa-eddine@espci.fr

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

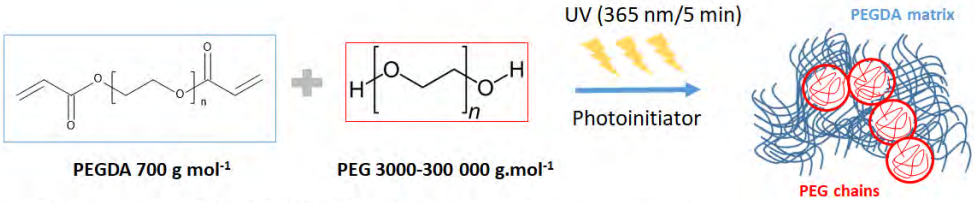

Figure.1 Preparation of PEG/PEGDA hydrogel system by radical polymerization

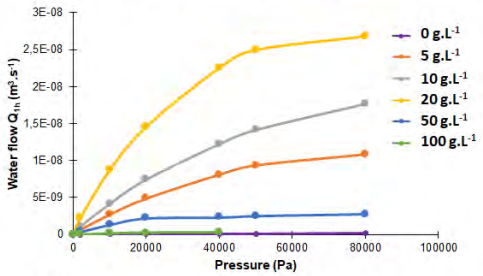

Figure.2 Water flow versus pressure for PEGDA hydrogels membranes prepared with 20 wt % of PEGDA and various PEG-300 000 gmol^{-1} content in prepolymerization mixture.

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Soft templates with designed microstructure for energy storage devices

D.J. French[1]; J.H.J. Thijssen[1]
[1]*University of Edinburgh, School of Physics & Astronomy, Edinburgh, UK*

Corresponding author: David.French@ed.ac.uk

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

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

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

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

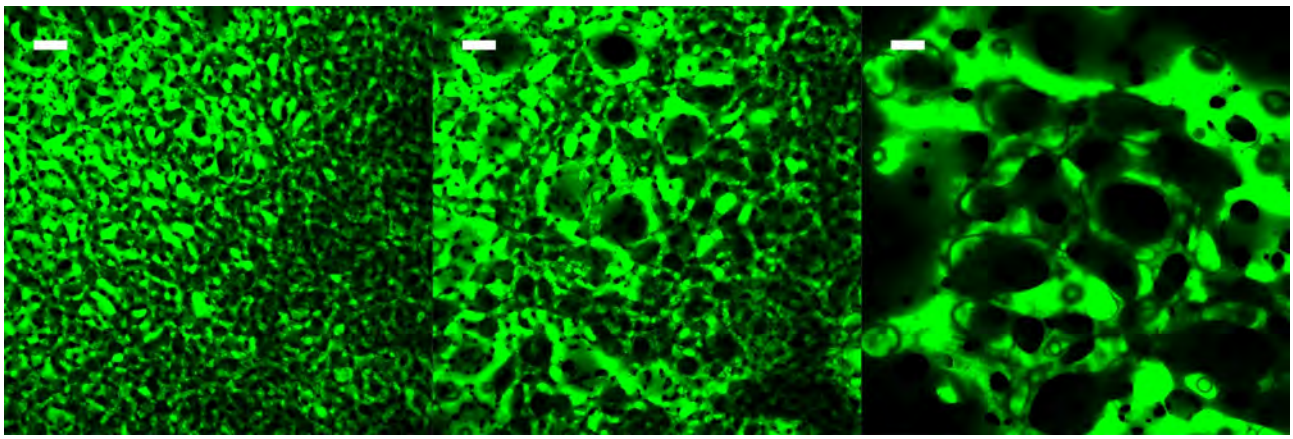

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Figure 1: *Confocal microscopy images from three points in a single bijel. There is a clear gradient in channel width along the sample, which should allow high transport rates whilst maintaining a high interfacial area. The green channel is one liquid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

Controlled activation of communication pathways between living and artificial cells

I. Gispert[1,2,3], Y.Elani[2,3,4], L. Barter[1,2], O. Ces[1,2,3]
[1]*Department of Chemistry, Imperial College London, United Kingdom*
[2]*Institute of Chemical Biology, Imperial College London, United Kingdom*
[3]*fabriCELL, Imperial College London, United Kingdom*
[4]*Department of Chemical Engineering, Imperial College London, United Kingdom*

Corresponding author: y.elani@imperial.ac.uk

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

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

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

*g.zubaite18@imperial.ac.uk, @gretazubaiteart

Detection of microscopic damage by multispeckle diffusing wave spectroscopy

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

Corresponding author: tetsuharu.narita@espci.fr, costantino.creton@espci.fr

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

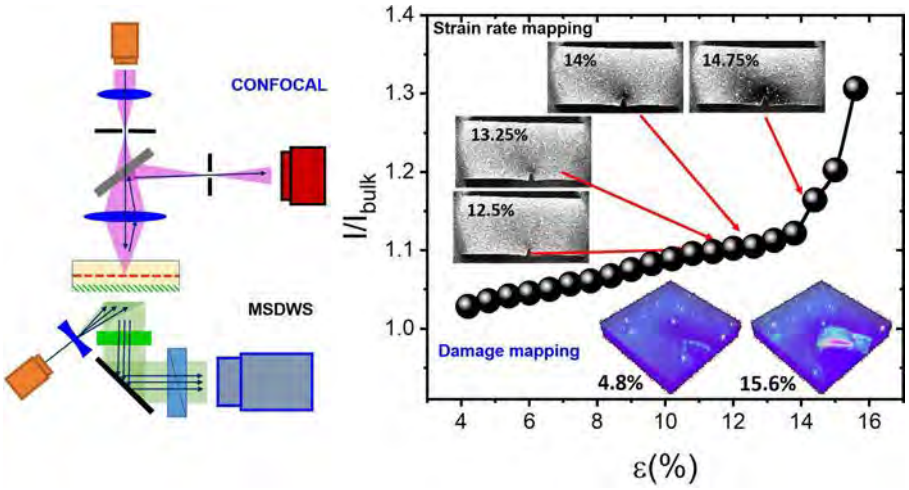

Fig. 1 Simultaneous measurement of MSDWS and confocal microscopy. The increase of heterogeneity long time before macroscopic fracture can be observed, coming with the increase of bonds breaking in a very small length scale.

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

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

D. J. E. Kalnin[1,2]
[1]*ISTOM, Ecole superieur d'agrodeveloppement international, Angers, FRANCE*
[2]*Moltech d'Anjou, University of ANGERS, Angers, FRANCE*

Corresponding author: d.kalnin@istom.fr

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

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

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

Vasileios Koutsos
Institute for Materials and Processes, School of Engineering, The University of Edinburgh, United Kingdom

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

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

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

X. Lacambra-Andreu[1,2,4]; N. Dergham[1,2] , M. Magallanes-Perdomo[1,4], S. Meille[1,4], J. Chevalier[1,4], J-M. Chenal[1,4], A. Maazouz[1,2,3], K. Lamnawar[1,2]

[1] *Université de Lyon, INSA-LYON, F-69621 Lyon, France*
[2] *UMR 5223, IMP, CNRS, INSA Lyon, F-69621 Villeurbanne, France*
[3] *Hassan II Academy of Science and Technology, Rabat, Morocco*
[4] *MATEIS, CNRS UMR 5510, INSA-Lyon, F-69621, Villeurbanne, France*

Corresponding author: xavier.lacambra@insa-lyon.fr

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

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

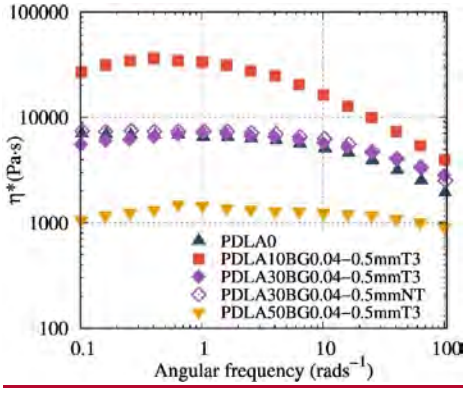

Figure 1*: Evolution of the complex dynamic viscosity modulus versus the angular frequency at 150°C for composites with 30wt% BG as a function of the particle size for Thermal Treated (T3) particles.*

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

S. Laquerbe[1], J. Es Sayed[1], C. Lorthioir[2], C. Meyer[3], T. Narita[1], G. Ducouret[1], P. Perrin[1], N. Sanson[1]
[1]*ESPCI-PSL University-Sorbonne Université-CNRS, Soft Matter Sciences and Engineering, Paris, France*
[2] *Sorbonne Université-CNRS- Collège de France, LCMCP, Paris, France*
[3]*ESPCI-PSL University-CNRS, C3M, Paris, France*

Corresponding author: sandrine.laquerbe@espci.fr

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

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

J. P. E. Machado[1,2]; T. Nicolai[1], L. Benyahia[1]
[1]*Le Mans Université, IMMM UMR-CNRS 6283, Le Mans, France*
[2]*BioPol-Universidade Federal do Paraná, Chemistry Department, Curitiba, Brazil*

Corresponding author: joao_pedro.elias_machado.etu@univ-lemans.fr

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

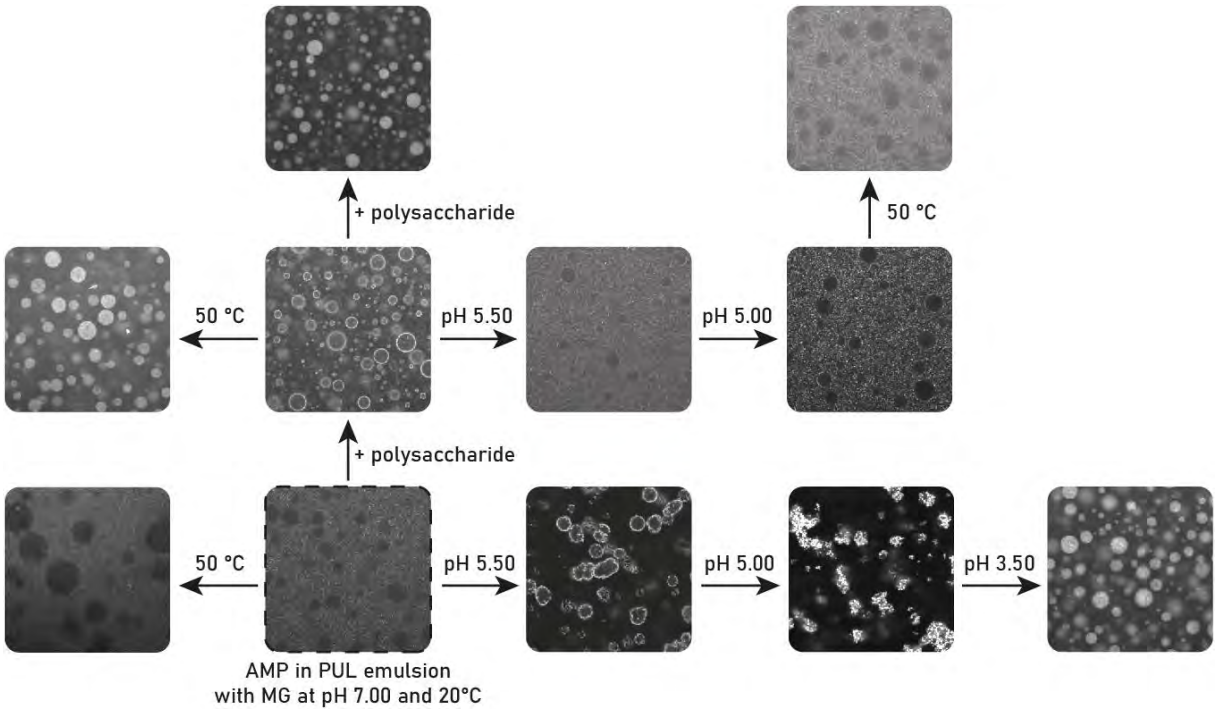

Figure 1. *Confocal laser scanning microscopy images (127 µm × 127 µm) of w/ w emulsions of a AMP rich phase dispersed in a PUL rich phase in the presence of MG showing the effects of adding a polysaccharide, changing the pH, and increasing the temperature.*

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

Yuwen Meng; Taco Nicolai, Lazhar Benyahia, Erwan Nicol
Le Mans Université, IMMM UMR-CNRS 6283, 72085 Le Mans, France

Corresponding author: Taco.nicolai@univ-lemans.fr

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

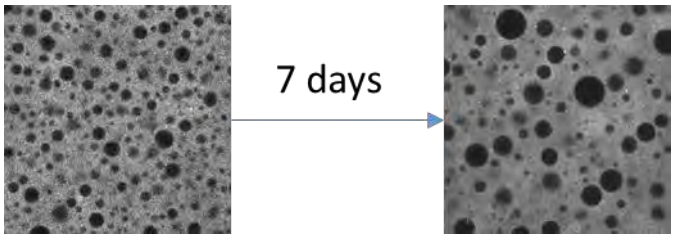

Figure 1: *Emulsion PEO in dextran stabilized by 0.15% of xanthan.*

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

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

S. Mohanakumar[1], S. Wiegand[1,2]
[1]*IBI-4, Forschungszentrum Jülich, 52428 Jülich, Germany*
[2]*Department of Chemistry, Universität zu Köln, Luxemburger Str. 116, 50939 Cologne, Germany*

Corresponding author: s.wiegand@fz-juelich.de

Themophoresis is defined as mass transport of solute molecules in a temperature gradient. The Soret coefficient, S_T, is used to quantify the ratio of the established concentration gradient to the temperature gradient [1]. This phenomenon is very sensitive to the nature of solute-solvent interactions and is used as a tool to monitor protein-ligand binding [2]. Protein-ligand systems are complex systems which include non-ionic and ionic components within it. Hence to reduce the complexity of the systems and as an approach towards understanding, we look into the thermophoretic properties of non-ionic and ionic systems, separately. Non-ionic solute molecules exhibit a clear correlation between thermophoretic properties and hydrophobicity of solute molecules [3]. As a first step into the investigation of ionic solutes we conducted

systematic thermophoretic measurements of aqueous solutions of five potassium salts: potassium chloride, potassium bromide, potassium thiocyanate, potassium acetate and potassium carbonate. The study is conducted in the context of Hofmeister series where the corresponding anions cover the full range: from the most hydrophobic to most hydrophilic [4]. We investigate the thermophoresis of all aqueous salt solutions between 15-45°C, with concentrations being varied from 1-5 mol/kg using infrared thermal diffusion forced Rayleigh scattering (IR-TDFRS). Our study shows how sensitive the thermophoretic phenomenon is to the specific ion species and how a change in ions leads to a drastic change in thermophoretic properties [5]. We discuss our observations in the context of cluster formation with increasing salt concentration and in comparison, with results of non-ionic solutes [3,5].

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

A.A. Parry[1]; D.A. Paterson[1], P. Bao[1], J.C. Jones[1], S.A. Peyman[1], J. Sandoe[2], R. Bushby[1], S.D. Evans[1], H.F. Gleeson[1].

[1]*University of Leeds, School of Physics and Astronomy, Leeds, UK*

[2] *University of Leeds, Leeds Institute of Biomedical and Clinical Science, Leeds, UK*

Corresponding author: py14ap@leeds.ac.uk

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

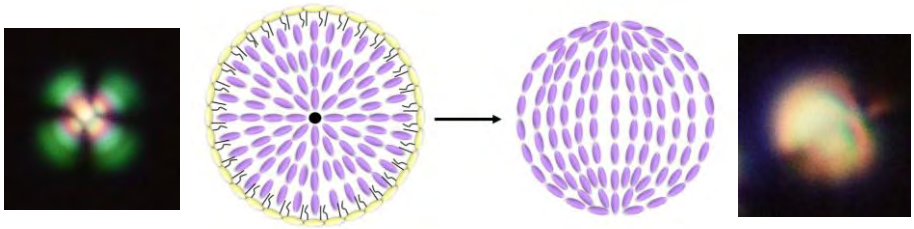

Figure 1: *Switch in alignment of an LC droplet from homeotropic to planar in response to the removal of the lipid monolayer.*

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

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Feeding the future: Protecting crops and ecosystems with Polymers

C. E. Pugsley[1,2]; R. E. Isaac[2], N. J. Warren[1] and O. J. Cayre[1]
[1]*University of Leeds, School of Chemical and Process Engineering, Leeds, United Kingdom*
[2]*University of Leeds, School of Biology, Leeds, United Kingdom*

Corresponding author: fscp@leeds.ac.uk

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

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

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

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The relation between ion transport and relaxation dynamics in polymers

M. Reynolds[1]; H. M. Coubrough[2], D. L. Baker[1], P. C. M. M. Magusin[3], A. I. I. Tyler[4], P. D. Olmsted[5], A. J. Wilson[2], J. Mattsson[1]

[1]*University of Leeds, School of Physics and Astronomy, Leeds, UK*
[2]*University of Leeds, School of Chemistry, Leeds, UK*
[3]*University of Cambridge, Department of Chemistry, Cambridge, UK*
[4]*University of Leeds, School of Food Science and Nutrition, Leeds, UK*
[5]*Georgetown University, Department of Physics, Washington DC, USA*

Corresponding author: K.J.L.Mattsson@leeds.ac.uk

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

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

S. Roca-Bonet; **M. Ripoll**

Theoretical Physics of Living Matter, Institute of Biological Information Processing Forschungszentrum Jülich, Germany

Corresponding author:m.ripoll@fz-juelich.de

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

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

A. Rodriguez-Palomo[1], V. Lutz-Bueno[2], M. Guizar-Sicairos[2], X. Cao[3], R. Kádár[4], M. Andersson[5], M. Liebi[1,6]

[1]*Chalmers University of Technology, Dep. of Physics, Gothenburg, Sweden.*
[2]*Paul Scherrer Institute, Swiss Light Source, Villigen, Switzerland.*
[3]*ETH Zurich, Institute for Chemical and Bioengineering, Zurich, Switzerland.*
[4]*Chalmers University of Technology, Dep. of Industrial and Materials Science, Gothenburg, Sweden.*
[5]*Chalmers University of Technology, Dep. of Chemistry and Chemical Engineering, Gothenburg, Sweden.*
[6]*EMPA, Swiss Federal Laboratories for Materials Science and Technology, Centre for X-ray Analytics, St. Gallen, Switzerland.*

Corresponding author: adrian.rodriguez@chalmers.se

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

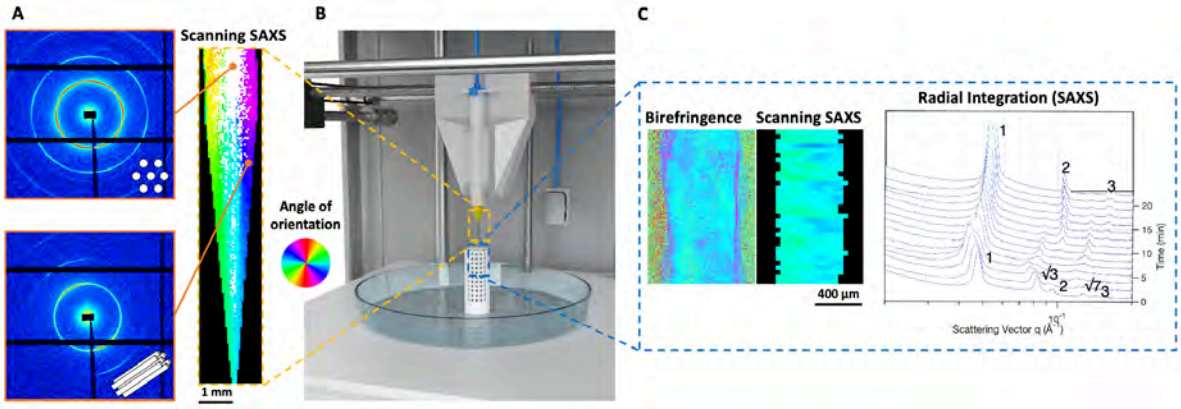

Figure 1: *Scattering signal and orientation of the hexagonal phase inside the nozzle (A) and in the extruded filament (C). The colourful regions show the nanostructure orientation in a specific angle according to the colour wheel.*

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

R.H. Seneviratne[1] ; M. Rappolt[2] ; L.J. Jeuken[3] P.A. Beales[1],
[1]*University of Leeds, School of Chemistry, Leeds, United Kingdom*
[2]*University of Leeds, School of Food Science and Nutrition, Leeds, United Kingdom*
[3]*University of Leeds, School of Biomedical sciences, Leeds, United Kingdom*

Corresponding author: cm12rhs@leeds.ac.uk

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

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

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

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

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

Bruno F. B. Silva[1], Ricardo Gaspar [1], Ana I. Gómez-Varela[1,2], Juan L. Paris[1], Adelaide Miranda[1], Pieter A. A. De Beule[1]

[1]*INL – International Iberian Nanotechnology Laboratory, Braga, Portugal*

[2]*University of Santiago de Compostela, Department of Applied Physics, Santiago de Compostela, Spain*

Corresponding author: bruno.silva@inl.int

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

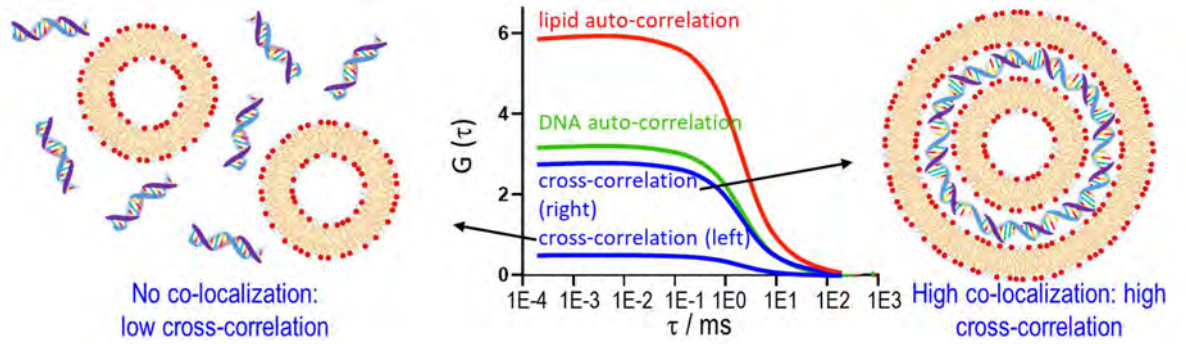

Figure 1: *Schematic illustration of the use of FCCS to monitor the formation of cationic liposome – DNA complexes. Liposomes and DNA are labelled with two spectrally-resolved dyes and their motions are analysed simultaneously, allowing determination of individual auto- and cross-correlation functions.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

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

Yuanyuan WEI, *Costantino CRETON, Tetsuharu NARITA*
Laboratoire Sciences et Ingénierie de la Matière Molle, ESPCI Paris, 75005 Paris, France.

Corresponding author: yuan-yuan.wei@espci.fr

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

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

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

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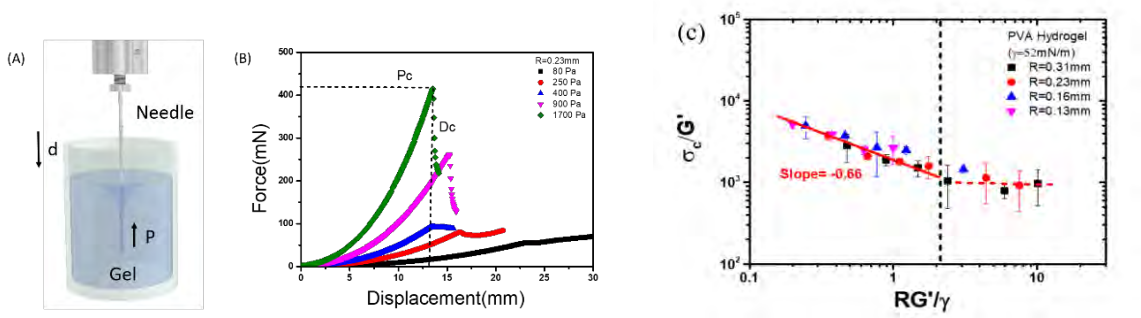


Figure 1. *(A) Schematic of puncture experiment and (B) representative puncture loading curves: puncture force as a function of puncture displacement. P_c is the fracture force marked as the peak force in the loading curve, and D_c is the fracture distance. (C) Critical nominal stress normalized by elastic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

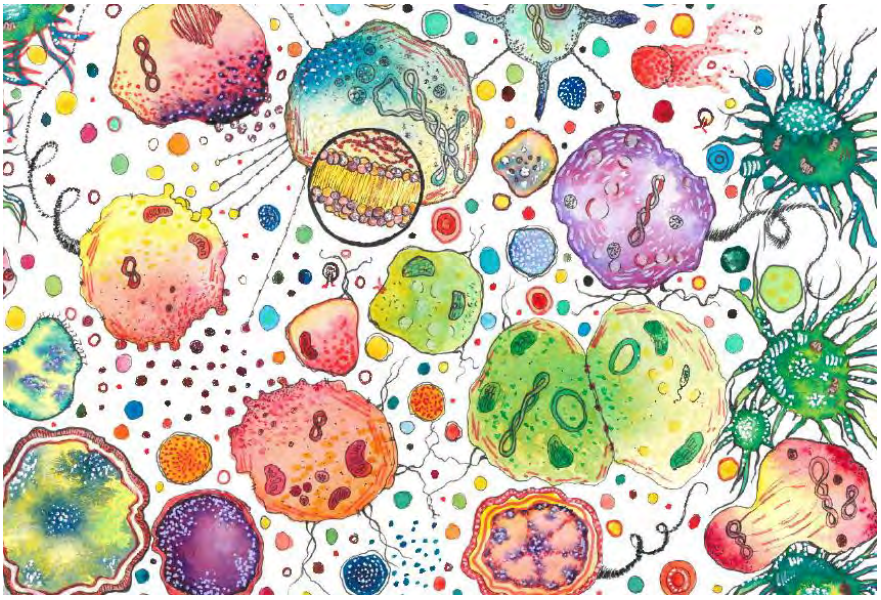
Controlling artificial cell subcompartment spatial organization

Greta Zubaite [1], James W. Hindley [1], Karen Polizzi [2], Oscar Ces *[1,3,4] and Yuval Elani*[1,2,4]

[1] *Department of Chemistry, Molecular Sciences Research Hub, Imperial College London, 82 Wood Lane, London W12 0BZ, UK*
[2] *Department of Chemical Engineering, Exhibition Road, Imperial College London, London SW7 2AZ, UK*
[3] *Institute of Chemical Biology, Molecular Sciences Research Hub, Imperial College London, 82 Wood Lane, London W12 0BZ, UK*
[4] *fabriCELL, Molecular Sciences Research Hub, Imperial College London, 82 Wood Lane, London W12 0BZ, UK*

Corresponding authors: O. C. o.ces@imperial.ac.uk, Y. E. y.elani@imperial.ac.uk) or K. P. k.polizzi@imperial.ac.uk

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



Poster Session 2

Tuesday 01 June 14:00 – 15:30

Smart biomaterials: Exploiting protein mechanics for controlled drug release

C.P. Brown[1]; S.A. Peyman[1], P.L. Coletta[2], S.D. Evans[1], L. Dougan[1,3]

[1]*University of Leeds, School of Physics and Astronomy, Leeds, U.K.*
[2]*St James' University Hospital, Leeds Institute of Medical Research, Leeds, U.K.*
[3]*University of Leeds, Astbury Centre for Structural Molecular Biology, Leeds, U.K.*

Corresponding author: py14cpb@leeds.ac.uk

Folded proteins have a variety of different functions in biological systems: incorporating these functions into rationally designed, folded protein hydrogels [1] provides opportunity for developing responsive drug delivery systems. The inclusion of microbubbles within hydrogels has shown success in controlling the stiffness of the gel to mimic tissues, and release drugs [2,]. Microbubbles have the capability to encapsulate and release drugs via cavitation of the microbubbles under the influence of ultrasound [3]. In this study, we investigate the mechanical properties of a model folded protein hydrogel which we have previously characterized [4], bovine serum albumin (BSA) embedded with phospholipid microbubbles. Initial findings have shown that the inclusion of microbubbles significantly changes the mechanics of the BSA hydrogels (~% reduction in the storage modulus), without significantly changing the folded fraction of protein.

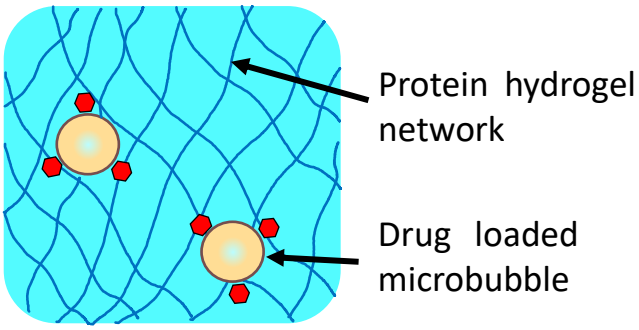


Figure 1: *Schematic of microbubbles encompassed within protein hydrogel.*

The inclusion of microbubbles has the potential to control the mechanical properties of protein hydrogels, potentially allowing for matching the hydrogel stiffness to the appropriate tissue. In addition, the microbubbles provide an on demand method for carrying and releasing drugs without the need for radiative therapy. Further work is required to understand how the use of ultrasound on BSA hydrogels effects the percentage of folded BSA and the mechanics of the hydrogel, before moving on to investigating the system for ultrasound responsive drug release.

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MILD AND SAFE-BY-DESIGN SYNTHESIS OF HYBRID POLYMER-GOLD NANOMATERIALS EXPLOITING SUPRAMOLECULAR INTERACTIONS

G. Calderó[1,2], E. Rosales[3], A. Lalueza[3], M.J. García-Celma[1,2], C. Rodríguez-Abreu[2,3]

[1]*Universitat de Barcelona. Departament de Farmàcia i Tecnologia Farmacèutica i Fisicoquímica, Barcelona, Spain (G. Calderó is currently a Serra-Húnter Fellow)*

[2]*Centro de Investigación Biomédica en Red en Bioingeniería, Biomateriales y Nanomedicina (CIBER-BBN), Barcelona, Spain*

[3] *Institut de Química Avançada de Catalunya (IQAC-CSIC). Barcelona, Spain*

Corresponding author: gcaldero@ub.edu

Hybrid nanomaterials are focusing increased interest in different application fields [1]. Preparation methods based on supramolecular interactions are especially appealing as they imply a low energy consumption for their preparation and they do not need sophisticated equipment. In addition, the prioritization of chemical components of reduced toxicity represents a step forward, making the process of preparation and handling of these materials safer. In this context, as a proof-of-concept, hybrid polymer-gold nanomaterials of controlled features have been synthesized in our group exploiting supramolecular interactions. Firstly, polymeric nanoparticles (150 - 200 nm) were prepared using a low-energy emulsification-solvent evaporation approach [2]. Low toxicity materials were selected for the preparation of these polymeric nanoparticles, including ethylcellulose or poly(lactic-co-glycolic acid) (PLGA) as the polymer material, and ethylacetate as the volatile organic solvent, replacing the most frequently used and more toxic aromatic or halogenated solvents. The surface charge (zeta potential) of these polymeric nanoparticles can be tuned from positive (+39 mV for ethylcellulose) to negative (-40 mV for PLGA) by a proper selection of the template nano-emulsion components. In a second step, the polymeric nanoparticles were decorated with gold (Au) nanospheres or nanorods, which were attached by electrostatic interaction. The positively charged ethylcellulose nanoparticles were decorated with citrate-coated Au nanospheres (33 nm; -22 mV). The hybrid ethylcellulose-Au nanomaterial showed a mean hydrodynamic diameter of about 190 nm and a maximum absorption peak around 598 nm. By contrast, the negatively charged PLGA nanoparticles were successfully decorated with CTAB-coated Au nanorods (length x width of 31 nm x 4 nm, i.e. aspect ratio of 3.35 nm; + 30 mV). The hybrid PLGA-Au nanomaterials showed a mean hydrodynamic diameter around 250 nm and a maximum absorption band at about 800 nm. In summary, the proposed synthesis method is simple, mild and safe, and allows tuning the features of the hybrid polymer-Au nanomaterials.

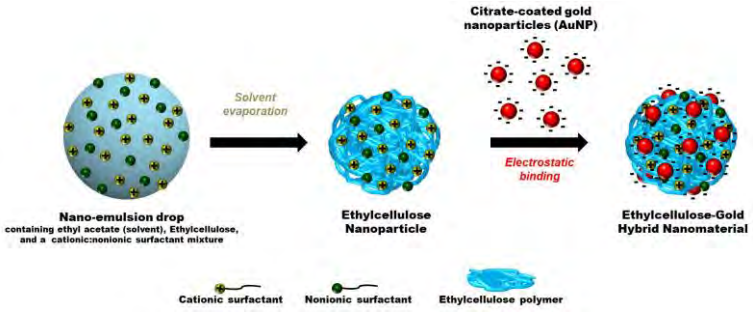

Figure 1: *Scheme of the preparation of ethylcellulose-gold hybrid nanomaterials.*

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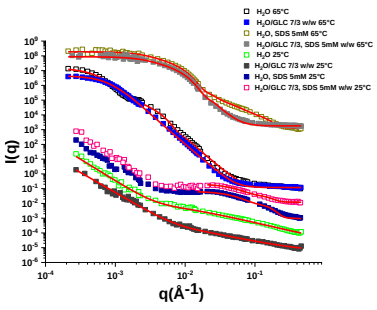
Effect of mixed solvent and temperature on the the phase behavior of hydroxypropyl cellulose in the presence of SDS.

D. Cavasso[1]; A. Radulescu[2], Vitaliy Pipich[2], Bahou Wu[2], L. Paduano[1]
[1]University Federico II, *Department of Chemical Sciences, Naples, Italy*
[2]*Forschungszentrum J lich GmbH, J lich Centre for Neutron Science JCNS, Outstation at Heinz Maier-Leibnitz Zentrum, Lichtenbergstraße 1, Garching, Germany.*

Corresponding author: domenico.cavasso@unina.it

Hydroxypropylcellulose (HPC), one of the most well-known cellulose derivatives, is a surface-active non-ionic polymer. Nowadays HPC is used as emulsifier, stabilizer, thickener and film former in foods, cosmetics and paints. Because of this it is relevant its behaviour in commonly used co-solvent such as glycerol. Indeed one of the most interesting property of this polymer is its thermo-responsivity, HPC can change its solubility as a function of temperature. This feature allows the HPC to be considered for stimuli responsive foams, where macroscopic properties need to be reversibly changed on demand. Thermo-responsivity from HPC is substantially associated to the lower critical solution temperature (LCST) of the polymer in aqueous solutions. The presence of cosolvent can drastically modify this temperature and the size and morphology of the aggregate above the LCST. Furthermore, this kind of polymers typically form complexes with anionic surfactants. Here we have investigated the complexation process between HPC and SDS at different temperature and surfactant concentration in the mixed water/glycerol solvent. The collected experimental data show that the presence of glycerol drastically chances the aggregation process, ruling the morphology and the size of the aggregates and the value of the LCST with respect to that observed in pure water. We investigated the effect of sodium dodecyl sulfate (SDS), a widely used surfactant, on the transition temperature (LCST) of the hydroxypropyl cellulose (HPC) in aqueous solution and in mixed solvent water/glycerol 7/3 w/w by Fluorescence Spectroscopy, Dynamic Light Scattering and Small Angle Neutron Scattering using a temperature gradient. The fluorescence spectroscopy has been conducted using the ANS (8-Anilinonaphthalene-1-sulfonic acid) as a probe. The analysis of the spectra shows a blue signal shift upon formation of polymer-surfactant aggregates and reveals an opposing effect between increasing the SDS concentration and adding glycerol. In particular SDS causes an increase in the LCST value while the presence of glycerol causes a reduction in LCST. This suggests a significant role of glycerol, a nonaqueous hydrogen-bonding solvent, in determining the properties of the system. Furthermore with the Dynamic Light Scattering and SANS experiments, we have studied the change, in morphology and dimension, of the aggregates in solution in the presence of the glycerol and SDS before and after the transition temperature.



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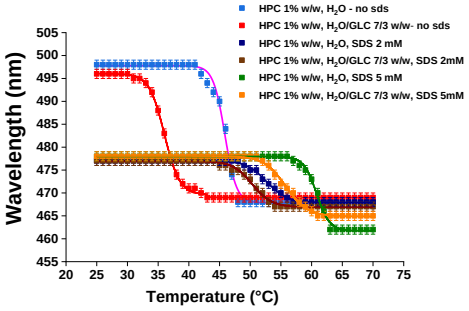

2

Figure1. *SANS scattering profiles at 25 and 65°C.* Figure 2. *The values of the wavelength corresponding to the maximum emission peak reported as a function of temperature*

Competition between shear and biaxial extensional viscous dissipation in the expansion of Newtonian and rheo-thinning fluid drops upon impact on solid targets of different sizes.

C-A. Charles [1], L. Ramos[1], C. Ligoure[1]
[1] *Laboratoire Charles Coulomb (L2C), Université de Montpellier, Montpellier, France*
Corresponding author:christian.ligoure@umontpellier.fr

A drop of fluid hitting a solid surface expands radially until reaching a maximal diameter. When this maximum diameter is larger than the size of the surface, part of the sheet expands in air, free of shear viscous dissipation. The maximal expansion is governed by a competition between baxial extensional (in air) and shear viscous dissipation (on the solid target). In this work, we evaluate the viscous dissipation due to shear and extensional deformations. We investigate Newtonian fluids with viscosity varying over almost three orders of magnitude and shear-thinning polymer solutions. We theoretically show that the maximum expansion factor of the sheet is a function of the relevant Ohnesorge number and of the size of the target to the power four in good quantitative agreement with experimental results. Furthermore, for polymer solutions in the entangled regime, we show that shear thinning at the relevant rate of impact has to be taken into account for the prediction of the maximum expansion factor.

High-pressure small-angle scattering experiments to probe the supramolecular assembly of polysaccharide/surfactant systems

L. Chiappisi [1,2],
[1] *Technische Universität Berlin, Germany*
[2] *Institut Laue Langevin, Grenoble, France*
Corresponding author:chiappisil@ill.eu

The submitted "abstract" was the PDF of a 30 page PowerPoint presentation which cannot be reproduced here. The original is available at the following URL:
`https://eusmi-h2020.eu/uploads/pdf/602900d23ea09/chiappisi-softcomp-6075b8789f412.pdf`

Two-step deswelling in the Volume Phase Transition of thermoresponsive microgels

G. Del Monte [1,2]

[1] *Sapienza University of Rome, Physics Department, Rome, Italy*

[2] *CNR, Institute of Complex Systems, Rome, Italy*

Corresponding author:giovanni.delmonte@uniroma1.it

Soft colloids, thanks to their internal degrees of freedom, often display complex phase behaviour and dynamics. Thermoresponsive pNIPAM microgels are one of the most studied examples of smart soft particles, with highly tunable single-particle and collective properties [1]. Their structural complexity manifests in distinct transition temperatures for individual and collective properties, such as gyration radius, self-diffusion coefficient, electrophoretic mobility and viscosity [2, 3], suggesting an underlying multi-step structural collapse [4]. This can be visualised in the ratio between gyration and hydrodynamic radius, displaying a minimum at the VPT that expresses the inhomogenoeous shrinking of the particles [3].
With this work we aim to explain the microscopic mechanisms underlying their Volume Phase Transition (VPT) combining experiments and numerical simulations. We have studied the VPT of microgels of different sizes, cross-linker and charge content through static and dynamic light scattering, to assess the collapse of both the inner core of the particles and that of the peripheral corona. Concomitantly, we performed Molecular Dynamics simulations of single microgels, using a coarse-grained model of the disordered polymer network explicitly taking into account the presence of charges, stemming from the initiator molecules starting the polymerisation reaction[5]. Indeed, we find that charges, together with the underlying disordered network, are crucial ingredients to reproduce the inhomogeneous deswelling among the core and the surface seen in the experiments [6]. Furthermore, we find in the average screened charge per chain a good indicator to predict the differences in the local swelling, regardless of the amount and distribution of charges on the network, as well as that of cross-linkers.

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Cerium oxide-based hybrid nanomaterials: controlling the properties by tuning synthesis and functionalization conditions.

N. Gallucci[1,2]; G. Vitiello[2,3], R. Di Girolamo[1], P. Imbimbo[1], D. M. Monti[1], O. Tarallo[1], A. Vergara[1], I. Russo Krauss[1,2], L. Paduano[1,2]

[1]*University Federico II, Department of Chemical Sciences, Naples, Italy*

[2]*CSGI, Center for Colloid and Surface Science, Sesto Fiorentino, Italy*

[3]*University Federico II, Department of Chemical, Materials and Production Engineering, Naples, Italy*

Corresponding author: noemi.gallucci@unina.it

Owing to the great interest in cerium oxide nanoparticles (CeO_2-NPs), usable in biomedical and technological fields [1-2], we recently synthesized CeO_2-NPs by thermal decomposition of $Ce(NO_3)_3 \cdot 6H_2O$ salt, varying the reaction temperature and using as capping agents two amines with different alkyl chain, namely octylamine and oleylamine, in order to evaluate the role of different chains lengths in modulating the NP surface properties [3]. The NPs thus obtained were extensively characterized by means of several techniques, such as Wide-angle X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Dynamic Light Scattering (DLS), UV-Vis, Fluorescence, Raman, and FTIR spectroscopies. The experimental collected data allowed us to define the role of the synthesis conditions in affecting the shape and size of nanoparticles as well as optical properties. In fact, the use of octylamine, as capping agent, implements the concentration of Ce^{3+} causing absorption throughout the UV-Vis spectrum region. Instead, the use of oleylamine increases the relative quantum yield of NPs. Furthermore, the CeO_2-NPs the most promising characteristics (smaller size and better separation of nanoparticles) were functionalized by using either the ligand exchange or the encapsulation method to disperse them in water. In the first case, the capping agent has been replaced with a derivative of dopamine, in this way you get a hybrid material able to interact with active molecules (such as aptamers, proteins). In the second case, instead, thanks to the interaction between the alkyl chains of the capping agent and another amphiphilic molecule (sodium oleate or oleic acid) a double amphiphilic layer is obtained on the surface of the nanoparticles, thus obtaining orderly hierarchical structures (such as Frank-Kasper phases). In addition, to assess the biocompatibility and the antioxidant activity of selected sample MTT assay on eukaryotic cells were carried out.

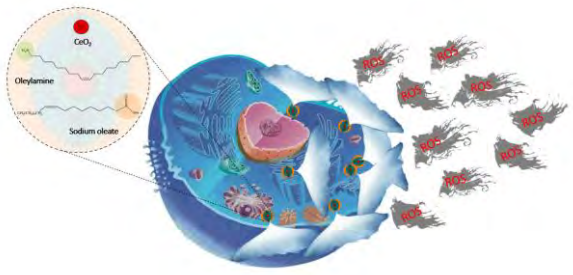

Figure 1: *Antioxidant action of cerium oxide nanoparticles in a eukaryotic cell.*

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Capillary Driven Self-Assembly of Ellipsoidal Composite Microgels at the Air/Water Interface

N. Hazra[1]; J. J. Crassous[2]
[1]*RWTH Aachen University, Institute of Physical Chemistry, Aachen, Germany*

Corresponding author: crassous@pc.rwth-aachen.de

We investigate the spontaneous capillary driven self-assembly of composite prolate shaped microgels. The microgels consist of a polystyrene (PS) core surrounded with a cross-linked fluorescently labelled poly(N-isopropylmethylacrylamide) (PNIPMAM) shell. The aspect ratios of the composite microgels can be finely adjusted upon uniaxial stretching the particles embedded into polyvinyl alcohol films [1]. The fully characterized particles present an aspect ratio ρ varying from 1 to 8.8 as estimated from laser confocal microscopy (CLSM) in their swollen conformation at 20°C. We follow their spontaneous interfacial self-assembly at the air-water interface using bright field and fluorescence microscopy. A transition is observed from an apparently random assembly into compact clusters for ρ=2.1 to a side to side assembly into long chains for ρ=6. The transition occurs between ρ=2.6 and 3.3 for which a trigonal and trigonal/side to side coexistence assembly are respectively identified. The influence of the composite microgel softness and anisotropy on the assembly is discussed as well its influence on the interfacial tension derived from time-resolved pending drop measurements.

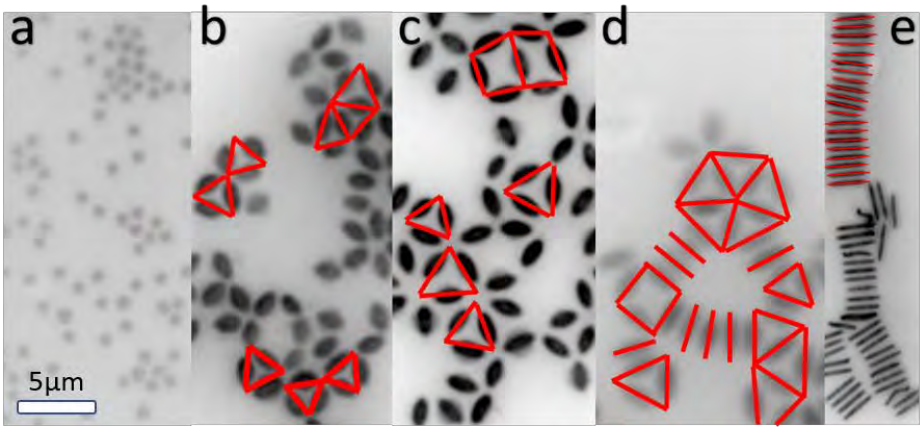

Figure 1: *Colour inverted fluorescence micrographs of spherical composite microgels (a) and ellipsoidal composite microgels with an aspect ratio ρ equal to 2.1 (b), 2.6 (c), 3.3 (d) and 8.8 (e) assembled at the air-water interface at 20°C. Some of the typical assemblies are highlighted with red lines.*

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Diarylethene-crosslinked photoswitchable PNIPAAm microgels

Siyang He[1,2], Robert Göstl[1]
[1]*DWI – Leibniz Institute for Interactive Materials, Aachen, Germany*
[2]Institute of Technical and Macromolecular Chemistry, *RWTH Aachen University, Aachen, Germany*

Corresponding author: goestl@dwi.rwth-aachen.de

Responsive microgels (µgels) are three-dimensional polymer networks which can react to external stimuli such as temperature, pH, and electrical field. These unique properties render µgels eligible for various applications: soft robotics, drug delivery, cancer therapy, and tissue engineering. Within the field of drug delivery, poly(*N*-isopropylacrylamide) (PNIPAAm) has garnered particular attention since it exhibits a lower critical solution temperature (LCST) between 32-35 °C in water, close to human body temperature. Above the LCST, PNIPAAm is hydrophobic and insoluble, whereas it becomes soluble below this value. This property qualifies it as a targeted drug delivery agent capable of reacting to the different temperatures of normal and pathological tissues [1].

However, the reversible modulation of the mechanical properties of such µgels was rarely reported, although it can be assumed that properties, such as stiffness, elasticity, and toughness, contribute to the interaction of µgels with cells or tissues as well as distribution behavior within the blood stream [2]. Through the integration of a photoswitchable diarylethene (DAE), which can reversibly isomerize from the flexible, ring-open form to the stiff, ring-closed form by irradiation with light, as crosslinker into PNIPAAm µgels, we aim to prepare µgels whose mechanical properties can be photomodulated.

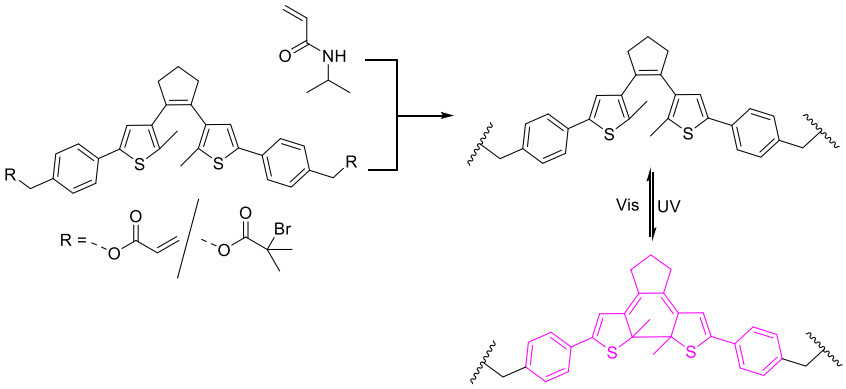

Figure 1: *Reversible photoisomerization of DAE-crosslinked PNIPAAm µgels.*

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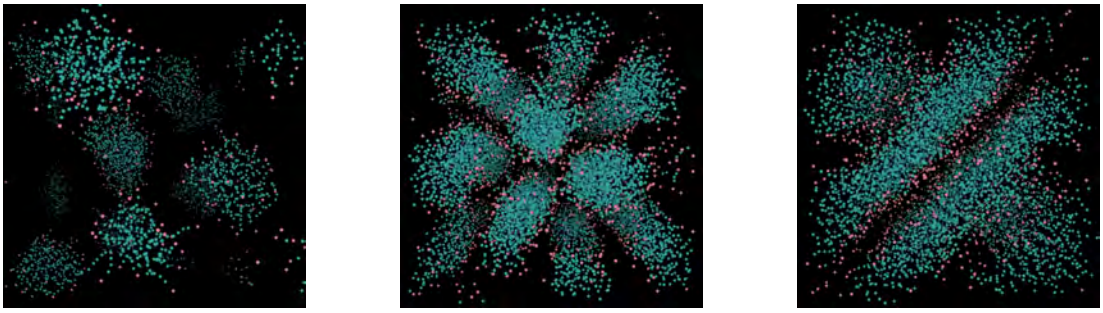
Using Dissipative Particle Dynamics for Investigating Surfactant Solutions Under Shearing

R. Hendrikse [1,2], A. Bayly[1] , P. Jimack[2], X. Lai[1]
[1] *University of Leeds, CDT Fluid Dyanmics, Leeds, UK*
[2] *University of Leeds, School of Chemical and Process Engineering, Leeds, UK*
Corresponding author:scrlh@leeds.ac.uk

Surfactants are present in many everyday products such as detergents and shampoos. Because of the amphiphilic nature of surfactant molecules, they self-assemble into lyotropic liquid crystal structures when in solution. There exists a wide range of possible solution phase structures, e.g. micellar, hexagonal, lamellar, etc, depending on the solution composition. The structure of these phases leads to distinct phase dependent rheologies. The rheology can be very difficult to predict numerically, and therefore is often measured experimentally for such systems. The specific surfactants to be studied in this work are alkyl ethoxysulfates (AES). These anionic surfactants are one of the most common components of personal care products.



(a) Micellar Phase ($c = 15\%$) (b) Hexagonal Phase ($c = 50\%$) (c) Lamellar Phase ($c = 70\%$)

Figure 1: Phase structures found for a variety of AES concentrations c in aqueous solution. Visualisations created using VMD [1]. Coarse graining: hydrophilic (pink) and hydrophobic (green). Water molecules not shown for clarity.

This talk will focus on the use of Dissipative Particle Dynamics (DPD), to understand the effects of phase structure on the rheology of the material. DPD is an off-lattice, mesoscopic simulation technique which involves a set of particles moving in continuous space. While similar, DPD has benefits over Molecular Dynamics (MD) techniques, in particular MD struggles to reach the long time scales involved in the self-assembly process. Most existing DPD research focuses on understanding equilibrium behaviour. However, the complex behaviour of surfactant solutions under shear flow is not well understood. In our research we investigate phase and structural changes that are induced in the fluid, as a result of applied shear. For example, we can show that micelles transform from spheres to worm like micelles under the application of increasing shear. This talk will also present how DPD can be used to calculate the shear viscosity of a fluid, along with the challenges in calculating such properties.

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Investigation of the Dynamics and Dielectric Properties of a Nematic Tripod Liquid Crystal

J. Hobbs[1]; M. Reynolds[1], S. Mallasandra Krishnappa[2]; S. Govindaswamy[2]; J. Mattsson[1]; M. Nagaraj[1]

[1]School of Physics and Astronomy, University of Leeds, Leeds, United Kingdom
[2]Department of Chemistry, Bangalore University, Bengaluru, India

Corresponding author: py14jh@leeds.ac.uk

Although usually associated with rod- and disk-like molecules, liquid crystallinity has been observed in organic molecules with a variety of different and unconventional anisotropic shapes. Amongst these, tripods, tetrapods and octapods pose one of the most fascinating classes as they exhibit unique mesophases including biaxial nematic phase and unusual physical properties compared to conventional liquid crystals.

MKS-6 is a non-symmetric tripod liquid crystal [1] which shows a transition from isotropic to nematic phase at T_{NI} = 135°C before forming a nematic glass at T_g = 21°C. A detailed investigation of MKS-6 using polarizing optical microscopy, Broadband Dielectric Spectroscopy (BDS), Differential Scanning Calorimetry (DSC) and oscillatory and steady-state shear rheology will be presented.

We find evidence for four relaxation processes: a structural α relaxation, a δ relaxation involving the reorientation of the director around the long axis and two secondary relaxations, a β and γ relaxation, which persist within the glassy state. The α relaxation undergoes a change in its T-dependence from Arrhenius to non-Arrhenius at T = 60°C whereas the δ relaxation is non-Arrhenius throughout. The detailed T-dependent behaviour and interpretations of the four relaxation processes will be discussed in detail, based on data from BDS, rate-dependent and modulated DSC, and rheology. Our data will also be compared with data on relevant liquid crystal systems in literature, including those observed for side chain liquid crystal polymers [2-4]. Moreover, we will present results for the T-dependent ionic DC-conductivity and demonstrate how the ion conductivity links to the observed relaxation processes; this is of importance for the potential use of these types of materials as electrolytes for battery applications [5].

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Glyceryl monooleate based lipid liquid crystalline nanoparticles with glyceryl monolaurate additives

J. Jagielski[1]; Ł. Przysiecka[1], D. Flak[1], G. Nowaczyk[1]
1NanoBioMedical Centre, Poznan, Poland

Corresponding author: jakub.jagielski@amu.edu.pl

Lipid liquid crystalline nanoparticles (LLCNPs), cubosomes in particular, are nanoparticles maintaining inner long range order. Owing to the presence of both hydrophilic and hydrophobic regions, huge surface area and low cytotoxicity[1], they emerge as considerable systems for biomedical applications such as drug delivery[2] or contrast carriers[3]. In our studies we focused to obtain enhanced biological, and in turn therapeutical activity, of glyceryl monooleate (GMO) LLCNPs by modification with glyceryl monolaurate (ML).

ML is a lipid chemically similar to GMO, however with a shorter carbon chain and lack of double bond. Variety of biological activities, such as antibacterial activity against gram-positive bacteria[4], modulatory effect on immune cell proliferation[5] or inhibition of production of staphylococcal toxic shock toxin-1[6] was attributed to ML. As a consequence, GMO with ML additives can result in stable nanosystems preserving therapeutic potential.

In presented studies GMO/ML lipid liquid crystalline nanoparticles in different ratios and surfactant amount have been prepared, investigated by means of DLS and cryo-TEM as well as their nanocytotoxicity effect on HeLa cells was verified. Preliminary studies show that GMO/ML creates a stable dispersion with LLCNPs diameter in range of 130-150 nm, depending on GMO/ML ratio. Furthermore the systems exhibit significantly lower cytotoxicity in comparison to the pure GMO LLCNPs.

The research is financially supported from the National Science Centre under research grant number 2016/22/E/ST3/00458.

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Early crystallization of lipid nanostructures in emulsion evidenced by DSC/SWAXS

D. J. E. Kalnin[1,2]
UR ADI-Suds: "Agro-Développement et Innovations aux Suds" ISTOM, Ecole supérieure d'agrodeveloppement international, Angers, FRANCE
[2]*Moltech d'anjou, UFR Sciences, University of ANGERS, Angers, FRANCE*

Corresponding author: d.kalnin@istom.fr

Lipids are self-assembling molecules, responsible for compartment formation in living cells. Besides real crystals and bilayers, they also form mesophases thanks to their aptitude to modulate interface curvature. Therefore, lipid-based structures such as solid lipid nanoparticles, liposomes, cubosomes, and other hybrids are interesting for drug delivery and are used in food science [1]. Besides, lipids are used in organizing lipid-DNA and lipid-polyelectrolyte mesophases and proved recently to deliver mRNA through lipid nanoparticles [2]. The characterization of the structure of such systems is complex and requires the use of combined techniques for apprehending lipid multiphase systems before applying their properties [3]. This study uses DSC/SWAXS for the monitoring nucleation and phase transitions lipids in emulsion A 20% fat containing emulsion is prepared with cocoa butter in a high-pressure homogenizer (HPV 2000). Crystallization behavior is monitored using microcalix calorimeter [4] at BL 4.2 @ ELETTRA synchrotron. Structural changes are monitored with two independent detectors at SAXS and WAXS simultaneously with the DSC signal. Temperature is decreased from 60°C to -10°C at a rate of 4K/min. In that way phase transitions can be attributed to thermal history. Droplet size, dilution, and complexity prevented any direct identification of the crystalline varieties formed by triacylglycerols inside emulsion droplets in the past. Our research focuses on the structural properties of lipids at a nanometer scale. Triacylglycerols (TAGs), the main constituents of natural fats and oils, exhibit a complex monotropic polymorphism that frequently forecloses the study of thermal and structural properties. Naturally, lipid structures self-organize into complex structures whose periodicity spans from a few nanometers up to hundreds of nanometers [1-3, 5]. As the range of organization is variable, it may affect both molecular and macroscopic properties at the same time. This enables in return, using lipids as molecular building blocks for texturing [6]. Crystal forms and polymorphism can be influenced by different factors. i) The temperature profile of the initial crystallization influence the crystalline form of the crystals' lipid crystals formed inside emulsion droplets.[7] ii) The curvature and composition of the interfaces of the droplets play their role in initial crystallization and then in crystal size and polymorphic changes. iii) Mechanical stress such as shear stress largely influences crystallization kinetics of emulsified and bulk lipids [6]. The polymorphic form and kinetics of polymorphic changes can then be used in reverse as a reporter of these influence factors [7].

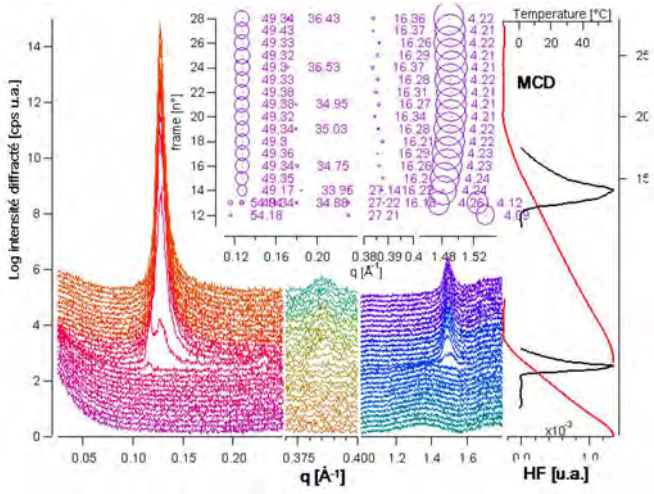

Figure 1: Crystallization of emulsified cocoa butter. Three-dimensional representation of the evolution of the X-ray diffraction patterns recorded at SAXS and WAXS during cooling at v_C=4°C/min from 60°C to -10°C. The diffraction patterns are recorded every 30 seconds simultaneously with the DSC signal from the same sample. The figure shows initial nucleation and further evolution of a $2L_\alpha$ phase (of the cocoa butter triglycerides) during temperature decrease. The temperature is superimposed with the DSC recordings on the right. The position of the peaks is shown as insert. The circles show the intensity, the center the peak position. One can notice that the initial phase at the beginning of nucleation rapidly transforms into $2L_\alpha$

We use small and wide-angle x-ray scattering coupled with DSC to study the initial phase transition of emulsified cocoa butter in **Figure 1**. The initiation phase is sensitive to interface curvature, composition, and cooling rate. In return, this means that all those parameters can be analyzed to a reference. Emulsifiers mainly present at the emulsion interface are also showing bulk properties if they occur in higher concentrations. Gelled mesophases and their transitions strongly influence the textural properties of foodstuff [8, 9].

The molecular structure of lipids, which can dominate the "macroscopic" properties such as rheology, flavor perception, or drug release, can be monitored. The study of lipid phase behavior, which is far behind the study of polymers, will be further strengthened due to the coupling of structural techniques at high brilliance synchrotron radiation workbenches with conventional analytical techniques (such as DSC). Then structure/functionality relationships for soft condensed matter especially in multi-component systems can be established in real systems and under processing conditions using DSC/SWAXS.

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LCST behaviour and structure formation of alternating amphiphilic polymers in water

E. Kostyurina[1]; J. Allgaier[1], H. Frielinghaus[2], R. Biehl[1], M. Kruteva[1], J.U. De Mel[3], G.J. Schneider[3,4], S. Foerster[1,2]

[1]*Forschungszentrum J lich GmbH, JCNS-1/IBI-8, J lich, Germany*
[2]*Forschungszentrum J lich GmbH, JCNS at MLZ, J lich, Germany*
[3]*Louisiana State University, Department of Chemistry, Baton Rouge, Louisiana, United States*
[4]*Louisiana State University, Department of Physics & Astronomy, Baton Rouge, Louisiana, United States*

Corresponding author: e.kostyurina@fz-juelich.de

The alternating amphiphilic polymers (AAPs) with various hydrophobic and hydrophilic segment lengths were synthesized and their properties in water were investigated. The synthesis was performed via alternating copolymerization of hydrophobic dicarboxylic acids (C4 – C20) with hydrophilic ethylene glycol (EG) oligomers (3 – 1000 EG units), e.g. P(C14EG47). The AAPs show a low critical solution temperature (LCST) behavior in water. The transition temperature depends on the polymer composition, molecular weight and concentration, and therefore can be tuned between 0 and 100 °C. The polymer structures were closely investigated by scattering techniques. It was found that depending on the parameters listed above the polymers either dissolve in water as free chains, form micelles or gels (see figure 1).

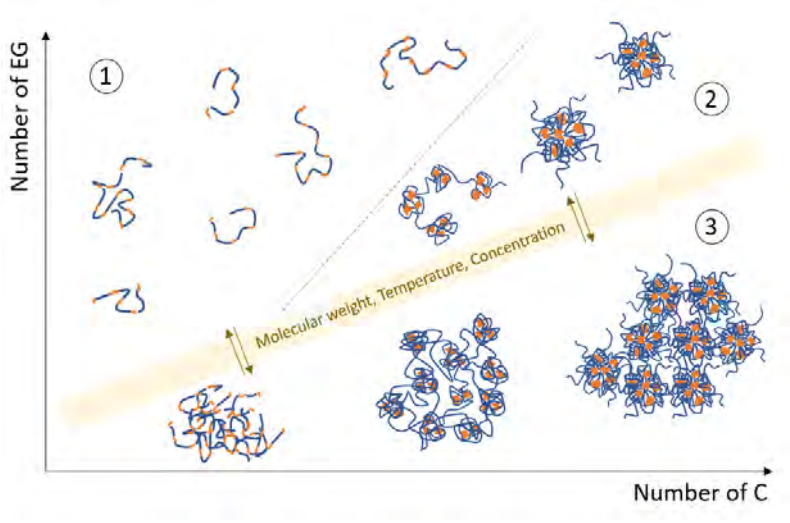

Figure 1: *Qualitative diagram representing the states of the amphiphilic polymers depending on the polymer composition.*

At short hydrocarbon lengths and long enough EG segments (region 1), the polymers solubilize in water as free chains. With increasing the hydrocarbon chain length and still keeping the polymers water-soluble, the polymers form compact objects (region 2). When the PEG length is not long enough to keep the polymers water-soluble, the polymers aggregate into gels (regions 3), which are built from interconnected micellar units.

Relationships between interactions, multi-scale phase separation and viscoelastic properties in elastomer-resin blends

R. Kumar[1,2]; L. Chazeau[1], F. Dalmas[1], N. Malicki[2], C. Gauthier[2] , R. Schach[2]

[1] *Univ Lyon, INSA Lyon, CNRS, MATEIS, UMR 5510, F-69621, Villeurbanne, France*

[2] *Manufacture française des pneumatiques MICHELIN, R&D, Clermont-Ferrand, France*

Corresponding author: robins.kumar@insa-lyon.fr

This study is devoted to new type of elastomer systems, seen as an alternative for conventional nanocomposites widely used in industrial applications such as tire industry. In these systems, low molecular weight and high Tg resins, with various composition, are blended with an SBR (Styrene-Butadiene Rubber) matrix. Several questions are raised: How does these resins incorporation influence the elastomer network structure? Depending on the miscibility of both components and the resin content, what is the resulting morphology, what is its dependance with the temperature, the processing condition and the crosslinking protocol? And of course, how this morphology impacts the macroscopic mechanical properties?

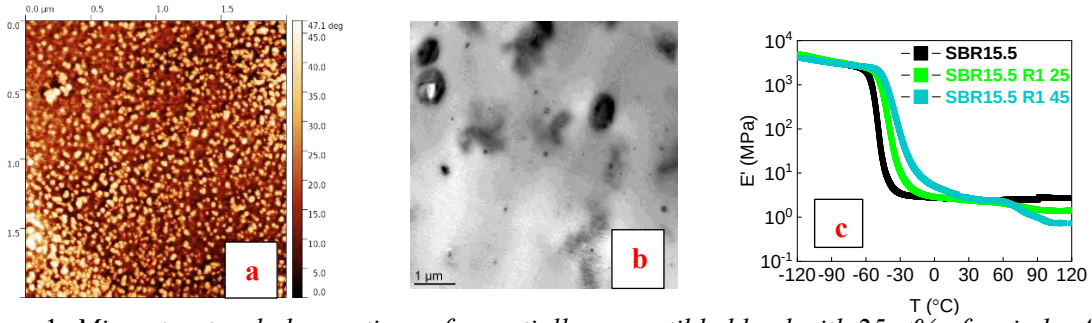

Figure 1: *Microstructural observations of a partially compatible blend with 25wt% of resin by AFM phase imaging (a) and TEM (b); storage modulus as a function of temperature of SBR and its blends with 25% wt or 45% wt of one of the studied resins (c).*

Three different resins have been studied showing different miscibility with the polymer matrix. The multi-scale phase separation (from nano to micrometer scale) and the partial compatibility between SBR and two of these resins were confirmed using DSC analysis, DMA experiments, transmission electron microscopy (TEM) and atomic force microscopy (AFM). Nanocomposite-like morphology (nano-domains of size of 20-35 nm) was highlighted by AFM in the blend and micro-domains whose number and size (<1-2.5 µm) increase with the resin concentration were evidenced by TEM (Figure 1a and 1b). Swelling measurement showed that resin is fully extracted by the solvent and thus do not significantly react with the matrix. This was further confirmed by the DMA and morphological analysis done on the samples after resin extraction. Nevertheless, the presence of resin during the processing of materials leads to a strong decrease of the entanglement/crosslinking density of the network, explained by the swelling of the polymer by part of the resin prior to its crosslinking (Lodge and Mc Leish [1]). The decrease of the topological constraints is partially compensated below the main relaxation of the resin around 60°C (Figure 1c) by the reinforcement generated by the hard resin domains resulting from the phase separation. Ongoing work tries to more deeply understand the composition of the phase, their evolution with temperature, and their mechanical properties.

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How Long Ranged are the Effects of Ions in Solution? Enthalpy of Hydration in Potassium Halides is Dominated by First Hydration Shell

H. Laurent[1]; L. Dougan[1,2]
[1]*University of Leeds, Physics and Astronomy, Leeds, United Kingdom*
[2]*University of Leeds, Astbury Centre for Structural Molecular Biology, Leeds, United Kingdom*

Corresponding author: L.Dougan@leeds.ac.uk

The interactions between water and ions play a vital role to life across multiple length scales. At the molecular level the delicate interplay between ion-water interactions and ion-biomolecule interactions result in perturbations to biomolecular stability fundamental to life as we know it. At the mesoscale ion-water interactions play a key role in the manufacturing of food, textiles, and in the mining industry. Finally, at the macroscale, understanding the ion-water interactions present in clays can help to understand and prepare for environmental processes such as mudslides and help us to understand the properties of recently discovered extra-terrestrial bodies of liquid water.

An important and long-standing question that applies to all these fields concerns the distance over which ions perturb water structure and dynamics. Does the introduction of an ion into water result in a global restructuring of the whole network, or are the perturbations restricted to water molecules in the immediate vicinity of the ion?

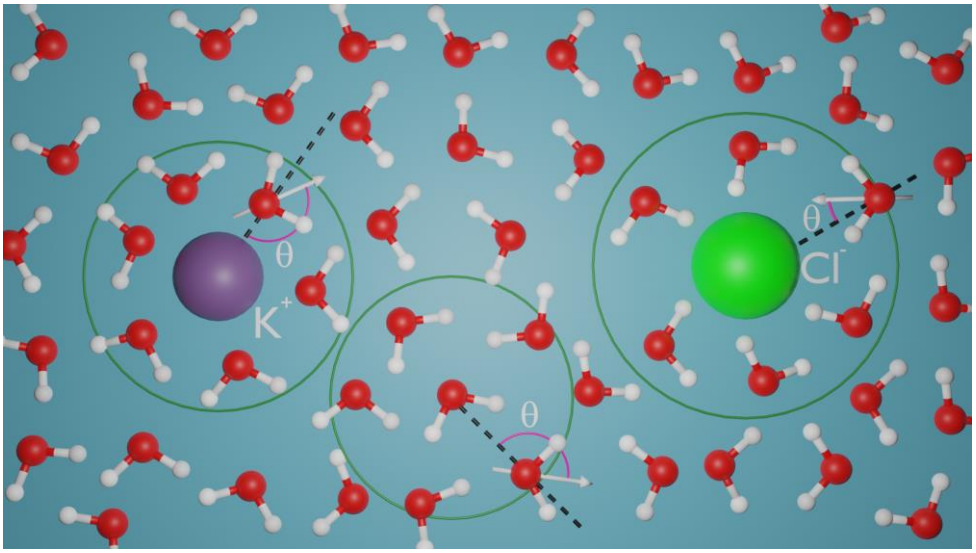

Figure 1: *Schematic representation of aqueous potassium chloride. First hydration shell around a potassium ion, chloride ion, and bulk water molecule shown in green circles and the definition of dipole angle θ is shown in pink arcs.*

In our attempt to address the issue further in this study we choose to investigate aqueous potassium halides. These were chosen as they are simple monovalent ions with large biological relevance that have been previously studied through a variety of techniques including: neutron and x-ray scattering, nuclear magnetic resonance (NMR), dielectric spectroscopy, infrared spectroscopy techniques, simulations and modelling. In this work we employ a novel combination of neutron diffraction with computational modelling with custom-built analysis routines and NMR to obtain a detailed structural and dynamic analysis of the effects of monovalent ions in solution that attempts to bridge the gap between atomistic level information and bulk ensemble information. We observe that structural perturbations are almost entirely limited to the first solvation shell and that these interactions can completely account for bulk experimental measurements such as the enthalpy of hydration.

Role of Particle Shape and Membrane Bending Rigidity in Wrapping

Xiaoyan Liu[1], Thorsten Auth[2], Gerhard Gompper[2], Jérôme Crassous[3], Emma Sparr[1*]

[1]*Division of Physical Chemistry, Department of Chemistry, Lund, Sweden*
[2]*Institute for Biological Information Processing, Forschungszentrum Jülich, Jülich, Germany*
[3]*Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany*

Corresponding author: emma.sparr@fkem1.lu.se

Anisotropic nano and micrometer sized particles have been associated with important processes in phagocytosis and biotechnology applications [1]. In this work, we make soft core-shell microgel particles with spherical and ellipsoidal shapes and study their association with lipid giant unilamellar vesicle. In order to get a mechanistic understanding, we vary the properties of the lipid membrane in terms of its bending rigidity, using model systems composed of either DOPC, DMPC or mixtures of DMPC and cholesterol (DMPC/chol) at temperatures above the lipid melting point. It is shown that the spherical microgels, MG1, adsorb at the surface of the bilayer for all vesicle systems investigated (Figure 1A-C). When the microgels are instead ellipsoidal in shape, MG2 and MG3 (aspect ratio 2, 6), we observe that particles may instead be completely wrapped in the membrane. The overall trend is that wrapping occur for the lipid membranes with the lowest bending rigidity, and for the microgels with the largest aspect ratio. The ellipsoidal MG2 microgel are adsorbed at the surface of vesicles composed of DMPC and DMPC/chol, while they are wrapped in the bilayer composed of DOPC (Figure 1D-F). For MG3 microgels, complete wrapping is observed both for DOPC and DMPC membranes but not for the most rigid DMPC/chol membrane, (Figure 1G-I). Our study brings insights into understanding how particle shape and bending rigidity of lipid bilayer may impact engulfing and endocytosis processes in living cells. The present findings can also provide new strategies to create novel self-assembling structures on fluid templates by employing nonspherical soft particles.

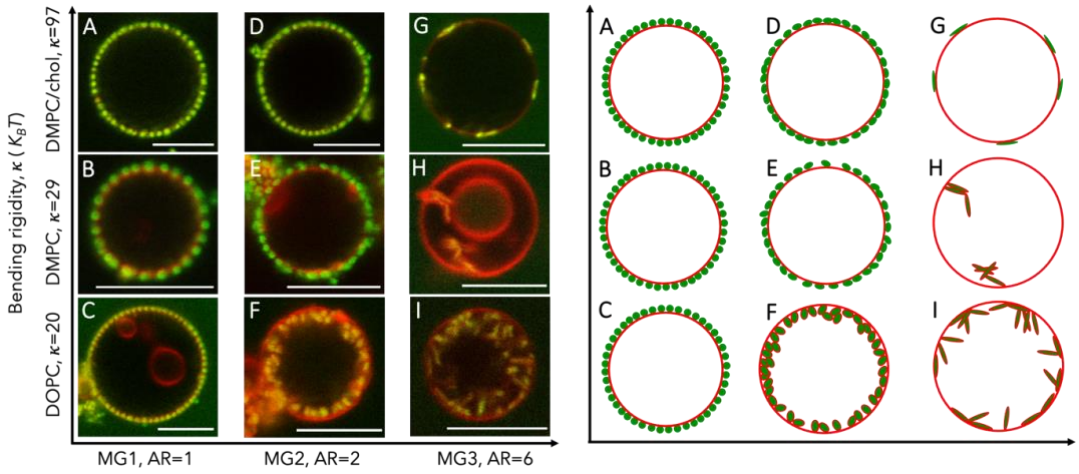

Figure 1: *Left panel: 2D CLSM images of adsorption and wrapping of microgel particles (green) on lipid membrane (red) in GUVs. The lipid composition was DMPC/chol (A, D, G), DMPC (B, E, H) and DOPC (C, F, I), and the microgel particles were either spherical MG1 (A-C), or ellipsoidal with different aspect ratios (AR), MG2 (D-E) and MG3 (G-I). Temperature: 28 °C. The scale bar represents 10 µm. Right panel: sketches to the corresponding CLSM images. A change in microgel shape (aspect ratio of 1, 2 and 6) and bending rigidity of lipid bilayer regulates the balance between surface adsorption and wrapping of microgels on the lipid membranes.*

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Hydrodynamic behavior of ensembles of synchronous microrotors

J. Mecke [1], G. Gompper[1], M. Ripoll[1]
[1] *Forschungszentrum Jülich, Institute of Biological Information Processing, Jülich, Germany*
Corresponding author:j.mecke@fz-juelich.de

The interest in rotating colloidal particles, as a subclass of active matter, has increased in the last years. A prominent example of these microrotors are systems of magnetic colloids in externally imposed rotating magnetic fields [1]. Due to their symmetry, the dynamics of single rotors does not display any directional motion, but approaching rotors have shown strong cooperative effects due to hydrodynamic interactions [2]. We are investigating discs synchronously rotating, *i. e.* with a fixed angular frequency, which interact solely via steric and explicit solvent induced hydrodynamic interactions. We employ a mesoscale solvent model which includes both linear and angular momentum conservation ensuring proper hydrodynamic coupling [3]. Moreover, our code allows us to simulate not only a few rotors, but also large rotors ensembles enabling us to gain insight into the complex dynamics of hydrodynamically interacting rotor materials. In the case of two rotors, the interactions lead to a metastable state with a clear secondary co-rotation of both rotors around their relative centre of mass. In ensembles of rotors, different dynamical behaviors can be observed depending on the system density and frequency of rotation. The system might exhibit long-ranged orientational correlations of the rotor propulsion velocity, which leads to the formation of various vortexes of different sizes, coexisting in the same system, and also interesting swarming effects.

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Wrapping of non-spherical vesicles at lipid-bilayer membranes

J. Midya [1], T. Auth[1], G. Gompper[1]

[1] *Forschungszentrum Jülich, Theoretical Physics of Living Matter, Institute for Biological Information Processing and Institute for Advanced Simulations, 52425 Jülich, Germany*

Corresponding author: j.midya@fz-juelich.de, t.auth@fz-juelich.de, g.gompper@fz-juelich.de

Understanding the interaction of soft particles, including microgels, vesicles, and macromolecular droplets, with biological membranes is of fundamental importance in vivo and in vitro [1]. The wrapping behavior of soft particles at biomembranes can be controlled by systematically varying the particle elasticity and the particle-membrane adhesion strength [2]. Here we investigate how the shape, size, and elastic properties of non-spherical vesicles control wrapping behavior. Analogously to previous work [3], we use triangulated membranes to calculate wrapping energies of non-spherical vesicles at planar membrane patches and predict wrapping states. Systematic variation of membrane-vesicle adhesion strength leads to non-wrapped, partial-wrapped and complete-wrapped states for the vesicles. We observe continuous and discontinuous wrapping transitions and shape transitions of the vesicles. Our findings may allow engineering more efficient vesicles for applications in diagnostics and therapeutics.

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A high-throughput coarse-grained simulation approach for calculating membrane partitioning

T. D. Potter[1]; E. L. Barrett[2], M. A. Miller[1]
[1]*Durham University, Department of Chemistry, Durham, United Kingdom*
[2]*Unilever, Safety and Environmental Assurance Cenre, Bedford, United Kingdom*

Corresponding author: thomas.d.potter@durham.ac.uk

The partition coefficient between a lipid membrane and water, log K_{MW}, is often used in environmental risk assessments to describe the accumulation of molecules within biological tissue.[1] A number of theoretical approaches for calculating log K_{MW} have been developed, which often work well for small neutral organic molecules, but perform less well for large or ionic molecules.[2,3] Here, we a present a high-throughput coarse-grained simulation approach for calculating log K_{MW} using coarse-grained simulations, which addresses many of the issues with other theoretical methods.

A key part of our high-throughput approach is the automated generation of coarse-grained models. We use a graph-theory based method to generate Martini-compatible coarse-grained mappings,[5] which is fast, general and preserves symmetry. Interaction parameters are then assigned based on the *automartini* method of Bereau and Kremer.[6] We have extended this approach to consistently generate stable intramolecular interactions for molecules with extended ring systems, and to generate effective models for charged molecules. Our process also includes a method for building efficient and stable frameworks of constraints for molecules with structural rigidity. This general coarse graining methodology may also be used in many applications of liquid-state simulation besides membrane partitioning.

We have calculated log K_{MW} from probability profiles of CG solutes across a phospholipid bilayer, obtained using umbrella sampling. These simulations have shown good agreement with experimental partitioning data for a large and diverse set of organic solutes, which includes surfactants with charged groups and extended ring systems. We also calculated log KMW for cholesterol-containing membranes, showing a clear trend in log K_{MW} with the addition of cholesterol, which varies according to the structure of the solute.

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The aggregation behaviour of hydrophobically modified thermo-responsive block-polymers in solution

A. Prause[1]; M. Hechenbichler[2], B. von Lospichl[1], A. Laschewsky[2,3], M. Gradzielski[1]
[1]*Technische Universität Berlin, Department of Chemistry, Berlin, Germany*
[2]*Universität Potsdam, Department of Chemistry, Potsdam, Germany*
[3]*Fraunhofer Institute, Applied Polymer Research IAP, Potsdam, Germany*

Corresponding author: albert.prause@tu-berlin.de

Mediation between hydrophilic and hydrophobic phases is necessary for almost every application or process, e.g. cleaning, solubilization, drug delivery, and colloidal stabilization. Best known for this purpose are amphiphilic molecules like surfactants. Very important is usually the ability to control and adjust the rheologic properties of a solution, for which commonly polymers are used. In addition, having the option for a distinct temperature response of the rheological properties for many potential applications. To combine and understand these properties of self-assembly and temperature response, in this work, hydrophobically modified (HM) thermo-responsive (TR) block-polymers were studied with respect to their phase behaviour and structure in solution. In order to have at the same time a relatively high loading with hydrophobic material they were combined with microemulsion droplets.
The HMTR block-polymers are built of a dodecyl (C_{12}) chain as hydrophobic end-cap, a permanently hydrophilic poly(*N*-dimethylacrylamide) block (PDMA) and a hydrophilic/hydrophobic temperature switchable block with a lower critical solution temperature (LCST) such as poly(*N*-isopropylacrylamide) (PNIPAM), poly(*N*,*N*-diethylacrylamide) (PDEA) and poly(*N*-acryloylpyrrolidine) (PNAP) [1]. The PDMA block was kept constant with ~200 units and the responsive block of 20 and 40 units. The aggregation behaviour in pure state and their mixtures with microemulsions was studied for different TR block length and variable LCST. The HMTR block-polymers were investigated in aqueous solution in the range of 20-60°C for concentrations between 0.5 and 5 $\%_{wt}$.

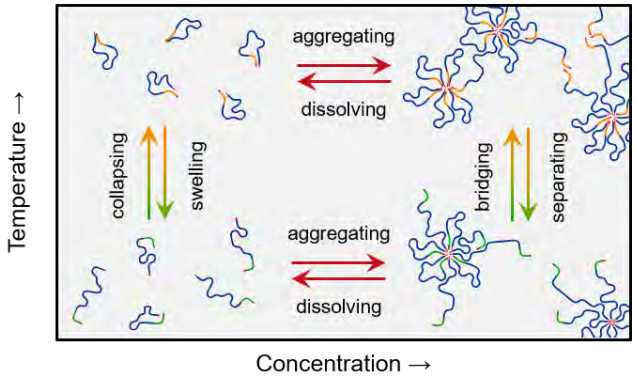

Figure 1: Scheme of interaction and aggregation behaviour of HMTR block-polymers in solution.

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Time control of nanoparticles formation pathways: sub-second composition tuning with a multi-step continuous flow approach

Kevin Roger [1], I. M. Nouha El Amri[1]
[1] *Chemical Engineering Laboratory, CNRS, Toulouse, France*
Corresponding author:kevin.roger@toulouse-inp.fr

Metallic nanoparticles of various shapes and sizes can be synthesized through a diversity of bottom-up pathways. Typically, metal salts are reduced in solution, which triggers precipitation and yields metastable nanoparticles in the presence of an interfacial stabilizer. Varying composition, by adjusting concentrations or adding/replacing species, is the predominant strategy to tune nanoparticles structures. However, controlling time down to the onset of precipitation, nucleation, has not been systematically attempted to control nanoparticles syntheses. Here, we present a millifluidic continuous flow approach that allows multi-step additions down to a millisecond time-resolution. We investigated the synthesis of silver nanoplates stabilized by a polymer, PVP, that is often used to obtain anisotropic nanoparticles. We show that synthesis pathways differing only in the order of sub-second additions lead to drastically different synthetic outcomes. Silver nanoparticles of different shapes and sizes, displaying an array of plasmonic colours, are synthesised at the same final composition by tuning the composition pathways along time. Our results unlock a previously inaccessible portion of the space of parameters, which will lead to an enhanced structural diversity, control and understanding of nanoparticles synthesised in solution.

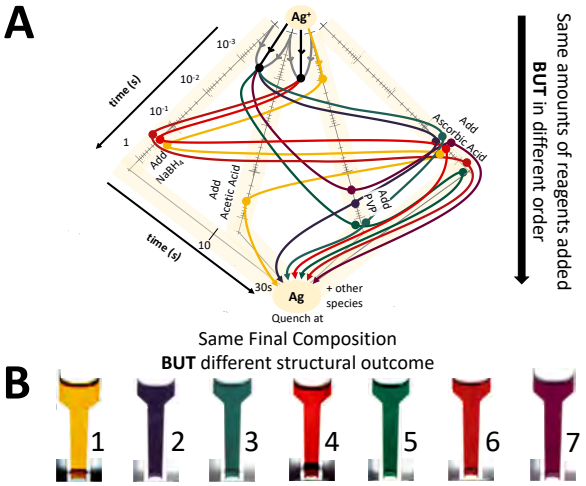

Figure 1: *(A) Seven synthetic pathways differing only by the sub-second sequencing of reagents additions. Silver ions are reduced by $NaBH_4$ and ascorbic acid in the presence of a polymeric stabilizer, PVP, in acidic conditions provided by large concentrations of acetic acid. The final composition in all reagents is the same for all seven pathways. A three-mixer scheme is used and each round symbol along a given pathway corresponds to a mixer (B) Pictures of the resulting seven nanoparticles dispersions, which cover the whole visible spectrum.*

Rheological principles for thickened alcohol-based hand rubs

Andreia F Silva[1], Daniel J M Hodgson[1], Alex Lips[1], John R Royer[1], Tiffany A Wood[1], Job H J Thijssen[1], Wilson C K Poon[1]

[1]*Edinburgh Complex Fluids Partnership (ECFP), SUPA School of Physics & Astronomy, The University of Edinburgh, Peter Guthrie Tait Road, Edinburgh EH9 3FD, United Kingdom*

Corresponding author: andreia.silva@ed.ac.uk

The coronavirus 2019 (COVID-19) pandemic brought sanitising hand rubs to the forefront of public attention. The World Health Organization (WHO) has recommended alcohol-based hand rub (ABHR) formulations, which contain 80% (v/v) ethanol or 75% (v/v) isopropyl alcohol, 1.45% (v/v) glycerol and 0.125% (v/v) hydrogen peroxide in water [1]. However, these formulations are low-viscosity Newtonian liquids making the pouring and rubbing of these formulations on hands difficult due to rapid runoff.

The rheological behaviour of ABHR is key to determine its 'rubbing capacity' and 'hand feel'. In this work we propose several rheological design principles for thickened ABHRs, based on the concepts of runoff, spreadability, smoothness and non-stickiness. We then thicken the WHO formulation using the microgel polymers Carbopol 974P and Sepimax Zen, and also a linear polymer Jaguar HP-120 COS, and investigate if their rheological behaviour fits our proposed design principles.

Our results show that thickening ABHRs with microgels results in a shear thinning and yield flow behaviour that fits most of our design principles. Furthermore, our results suggest that linear polymers can produce gels that have good spreadability, minimal runoff, and additionally offer a smooth feeling during rubbing due to the development of a finite first normal stress difference.

The high demand for thickened ABHRs is predicted to continue post-pandemic. Hence, the development of ABHRs that can offer superior topical application and hand feeling is an ongoing challenge.

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Poster Session 3

Wednesday 02 June 14:00 – 15:30

Kinetics of network formation and heterogeneous dynamics of an egg-white gel revealed by coherent X-ray scattering

Nafisa Begam[1], Anastasia Ragulskaya[1], Anita Girelli[1], Hendrik Rahmann[2], Sivasurender Chandran[3], Fabian Westermeier[4], Mario Reiser[2,5], Michael Sprung[4], Fajun Zhang[1], Christian Gutt[2], and Frank Schreiber[1]

[1] Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany
[2] Department Physik, Universität Siegen, 57072 Siegen, Germany
[3] Department of Physics, Indian Institute of Technology Kanpur, Kanpur, Uttar Pradesh 208016, India
[4] Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, 22607 Hamburg, Germany
[5] European X-ray Free-Electron Laser GmbH, Holzkoppel 4, 22869 Schenefeld, Germany

Corresponding author: nafisa.begam@ifap.uni-tuebingen.de

Gelation of proteins, e.g. egg-white, is a fundamental topic in food chemistry as well as in condensed matter physics [1,2]. Naturally, it draws a lot of attention of the scientific communities. However, our understanding on the kinetics of network formation and the microscopic dynamics, especially at the length scales of the mesh size of the network, is limited due to the experimental difficulties at accessing those length and corresponding time scales. Here, using state-of-the-art X-ray photon correlation spectroscopy [3,4] along with ultra-small angle X-ray scattering, we probe the kinetics of heat-induced gelation and the microscopic dynamics of a hen egg-white gel. Kinetics of structural growth reveals a reaction-limited aggregation process with a gel fractal dimension of ~ 2 and an average network mesh size of ca: 400 nm [5].

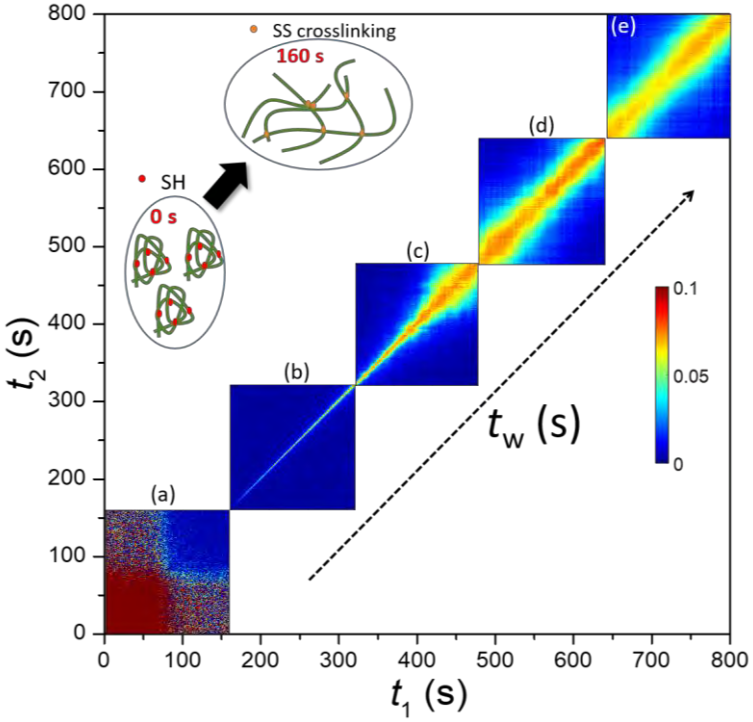

Figure 1: *TTC (CI -1) collected at 80°C (at q = 0.01 nm^{-1}) in the time interval of (a) 0-160 s, (b) 160-320 s, (c) 320-480 s, (d) 480-640 s and (e) 640-800 s after reaching the temperature. Inset schematic shows the native state of the proteins before denaturation (0 s after heating at 80°C) and after unfolding due to heat denaturation (160 s after heating at 80°C).*

Dynamics probed at these length scales reveal two distinct regimes after the establishment of the network structure as can be seen in figure 1. While the first regime of the dynamics is characterized by an exponential growth of the characteristic relaxation times (until t_w = 480 s after heating at 80 ºC), the second regime is characterized by an intriguing steady state and temporally heterogeneous dynamics [5]. The intermediate scattering function changes from an exponential to a compressed exponential decay. We deduce wave vector q-dependent fourth order intensity correlation functions to quantify the observed heterogeneity. The degree of heterogeneity increases with increasing q. We identify the stress-driven dynamics as dynamical rupture events which do not change the structure of the gel. The spatial extension of these decorrelation events decreases from 100 nm to a few nm upon aging accompanied by a lowering of the degree of dynamical heterogeneity. We discuss our results in the broader context of experiments and models describing attractive colloidal gels. Our findings help to understand the transformation of a real protein system to a heat-induced solid-like gel-state and the underlying dynamical transition that dictates the characteristic properties of the gel.

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Linear viscoelasticity of supramolecular bis-urea based polymers at high pressures and temperatures

N. A. Burger[1,2], G. Meier[3], L. Bouteiller[4], B. Loppinet[1], D. Vlassopoulos[1,2]

1 Foundation for Research & Technology Hellas (FORTH), Institute for Electronic Structure & Laser, Heraklion 70013, Greece

2 University of Crete, Department of Materials Science & Technology, Heraklion 70013, Greece

3 Forschungszentrum Jülich, Institute of Complex Systems (ICS-3), 52425 Jülich, Germany

4 Sorbonne Université, CNRS, IPCM, Equipe Chimie des Polymères, 75005 Paris, France

Corresponding author: burker@materials.uoc.gr

The monomer, 2,4-bis(2-ethylhexylureido)toluene (EHUT), self-assembles through hydrogen bonding when immersed in non-polar solvents. Two distinct supramolecular structures have been reported, tubes and filaments (depending on solvent conditions), which are characterized by viscoelastic and viscous behaviour, respectively. Here we report on the effects of high hydrostatic pressure (HHP) on the structures and the (micro)rheology of EHUT solutions in cyclohexane and dodecane. We combine dynamic light scattering (DLS) and passive probe microrheology under HHP. The HHP is obtained by pressurizing a stainless steel chamber by means on an inert gas. The DLS-based probe microrheology provides the linear viscoelastic spectrum over a wide range of frequencies.

The tube to filament transition is identified through strong variation of the viscoelasticity and the scattered intensity. We find that HHP stabilizes the tube structures both in cyclohexane [1] (fig. 1) and in dodecane. We investigate the effect of temperature and concentration on the viscoelastic spectrum, evidencing large variation of the dynamic viscosities. In particular, in dodecane solutions at atmospheric pressure we observe the presence of viscous (unentangled) tube phase at low concentrations (below 3 g/L). The results allow us to build a state diagram in the temperature-concentration space. The influence of the different parameters is discussed including the possible role of dissolved residual water.

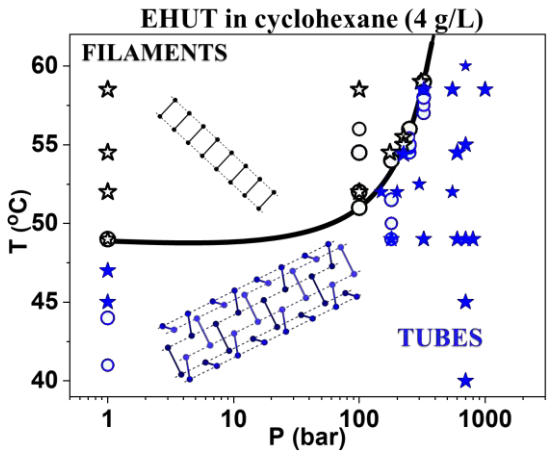

Figure 1: *Phase diagram of a 4 g/L EHUT / cyclohexane solution in the (T, P) space. Star symbols correspond to passive microrheological data. Circles correspond to DLS (without added particles). The black line is drawn to guide the eye. Blue (black) color indicates tubes (filaments).*

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Linear and non-linear rheology of dynamic gels

A. Chaub[1]; M. Cloitre[1]

[1]*ESPCI Paris, Chimie Moléculaire, Macromoléculaire et Matériaux, Paris, Francce*

Corresponding author: arnaud.chaub@espci.psl.eu

Dynamic gels are 3-dimensional networks in solution that rely on short-lived bonds of functional groups, instead of classical chemical crosslinks. They are widely used as additives to control the rheological properties of solutions, exhibit self-healing properties and can transition from liquid to solid state easily with external stimuli such as temperature.

We have studied hydrophobically-modified alkali-swellable emulsions (HASE), one example of polymeric architecture allowing the formation of dynamic gels. HASE polymer chains are composed of a polyelectrolyte backbone on which are grafted hydrophobic macromonomers that associate intra and inter- chains, acting as physical and reversible crosslinks. HASE solutions are viscoelastic liquids and solids depending on the chemistry of the hydrophobic moieties.

We focus on the rheology of aqueous solutions of a HASE polymer with branched alkyl moieties comprising 32 carbon atoms. We perform a systematic investigation of their rheological properties using small and large amplitude oscillatory shear experiments and startup flow tests. Local deformation profiles are measured using in-situ rheofluorescence particle image velocimetry. At polymer concentrations as low as 0.3 wt%, we find a transition between viscoelastic solutions and dynamic gels with yield stress properties (Figure). The nonlinear response of gels strongly depends on the total polymer concentration and several phenomena are detected and analyzed such as wall slip, shear-banding, and fracture.

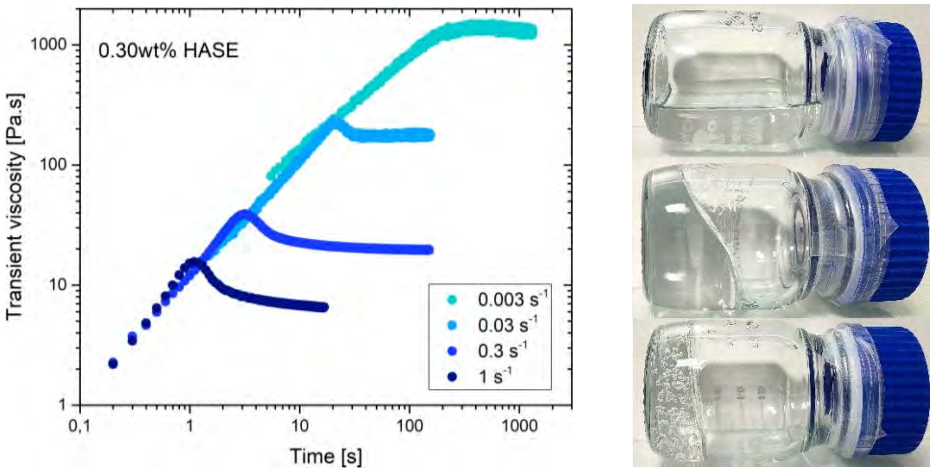

Figure 1: (left) Transient viscosity versus time at different applied shear rates for 0.30wt% HASE. (right) HASE gels at 0.20wt%, 0.30wt%, 1wt% (from top to bottom).

Developing Modelling Tools to Examine Network Formation in Protein Hydrogels

K. R. Cook [1], L. Dougan[1], D. Head[2]
[1] *University of Leeds, School of Physics and Astronomy, Leeds, U.K.*
[2] *University of Leeds, School of Computing, Leeds, U.K.*
Corresponding author: py13kc@leeds.ac.uk

Folded protein-based hydrogels are ideal materials in biomedicine and biomedical engineering because of their inherent biocompatibility, but little is understood about how their bulk properties extend from the single-molecule level. We develop and employ modelling tools to examine how factors, such as protein volume fraction and cross-linking rate, affect network formation and structure in folded protein hydrogels.

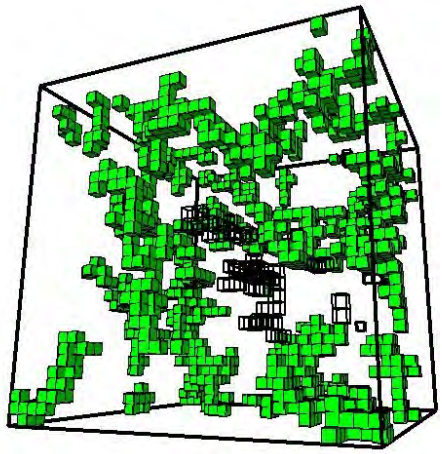

Figure 1: *Gel system at the critical percolation point. Proteins cross-linked in the percolating cluster are represented as green boxes, while non-percolating, intermediate clusters are represented as unfilled boxes.*

We are currently employing a combination of rheology and scattering to study model folded proteins as building blocks in chemically cross-linked hydrogels [1, 2]. Computational modelling offers a powerful way to gain insight into the factors governing protein gelation [3], and using the lattice-based model we have developed, we can efficiently simulate protein clustering and network percolation. Furthermore, we have performed structural analyses on our model gel systems by considering the protein cluster sizes and fractal dimension of the systems at and beyond the precise point of gelation.

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Lipid liquid crystalline nanoparticles loaded with manganese oxide nanoparticles (LLCNPs@MnO) – enhancing Magnetic Resonance Imaging contrast agents

D.K. Flak[1]; T. Zalewski[1], Ł. Przysiecka[1], K. Fiedorowicz[1], G. Nowaczyk[1]
[1]*Adam Mickiewicz University Poznań, NanoBioMedical Centre, Poznań, Poland*

Corresponding author: dorfla@amu.edu.pl

The unique internal structure and morphology of LLCNPs resulting in their higher membrane surface area and hence high loading efficiency, next to their ability to entrap hydrophilic, hydrophobic and amphiphilic molecules, but also their high biocompatibility, makes them potential carriers to be applied in drug and diagnostic agent delivery [1]. In turn, MnO NPs have been recognized as efficient T_1 CAs, particularly as ultrasmall NPs and coated/functionalized with biocompatible molecules [2]. Moreover, taking into account the health risks resulting from the use of Gd-chelates and promising effects of using nanoparticles as CAs, Mn-based NPs are seen in the light of recent research as a highly competitive alternative to Gd-based CAs, but also to withdrawn Teslascan®.
In this work we studied a new class of MRI contrast agents (CAs) based on combined hybrid construct consisting of lipid liquid crystalline nanoparticles loaded with MnO nanoparticles (LLCNPs@MnO and LLCNPs@MnO-DMSA). For this purpose two types of MnO nanoparticles were prepared: (1) oleate-capped MnO NPs as hydrophobic ones, and (2) DMSA (meso-2,3-dimercaptosuccinic acid)-functionalized MnO NPs as hydrophilic ones. These MnO NPs were further embedded into LLCNPs, consisting of glyceryl monooleate (GMO) as a structure-forming lipid and Pluronic F-127 as a the non-ionic copolymer surfactant stabilizing LLCNPs in water-based dispersion. The size of as-prepared constructs, varied depending on composition (175.9 nm for unloaded LLCNPs, 246.0 nm for LLCNPs@MnO and 170.6 nm for LLCNPs@MnO-DMSA, PdI was below 0.2). Moreover, these LLCNPs dispersions exhibited good colloidal stability both in water and human plasma-based dispersions (zeta potential was -19.8 mV for unloaded LLCNPs, -20.2 mV for LLCNPs@MnO, and the lowest -16.2mV for LLCNPs@MnO-DMSA). These two hybrid constructs and bare MnO-DMSA were further compared in terms of their biological safety and MRI contrast enhancing ability. Summarizing, obtained hybrid constructs structurally complex (cryo-TEM), were highly biocompatible towards different cells (*in vitro* studies, IC50 ~130 µg/ml) and efficiently internalized into cells. Studied relaxivity (r_1) for these constructs at 0.4 T in water and human plasma was significantly improved in comparison to bare MnO-DMSA, even when significantly lower Mn^{2+} ions concentration was used in case of LLCNPs@MnO constructs. Above results achieved for these contrast enhancers give a promise for further efficient *in vivo* imaging.

Acknowledgements
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Co-administration of polyol coated Inorganic Nanoparticles and Antibiotics for enhanced antimicrobial properties.

K. Giannousi[1], I. Eleftheriadou[2], C. Dendrinou-Samara[1]

[1]*Aristotle University of Thessaloniki, Laboratory of Inorganic Chemistry, Department of Chemistry, Thessaloniki, 54124, Greece*
[2] *Aristotle University of Thessaloniki, Department of Genetics, Development and Molecular Biology, School of Biology, , 54124, Thessaloniki, Greece*
Corresponding author: klegia@chem.auth.gr

The abuse of antimicrobial drugs has led to the upsurge of multidrug-resistant bacteria, representing an extremely serious public health concern. The nanomaterials could be used as innovative tools to combat the ongoing crisis of antimicrobial resistance due to the higher surface to volume ratio enabling high synergy for antimicrobial action. A plethora of inorganic nanoparticles (NPs) has been used as antimicrobial agents. However, their clinical application demands high effective dosages, which induce colloidal dispersion and cytotoxicity problems. Herein, the synthesis of polyol coated CuO, ZnO and bimetallic CuZn NPs is reported.[1,3] The structural and morphological characterization of the NPs was accomplished in the solid and liquid phase. The capped NPs were evaluated in terms of cytotoxicity and antibacterial activity, while their potential role as efflux pump inhibitors has been also investigated against multidrug resistant clinical strains.[2] Drug extrusion by the multidrug efflux pumps represents an important mechanism of multidrug resistance. The co-administration of low dosages of the as-prepared NPs with the antibiotics meropenem and ciprofloxacin towards multi-resistant *Pseudomonas aeruginosa* has led to efflux inhibition and synergistic activity was recorded. The biocompatible-coated NPs are suggested as adjuvant therapy to extend the lifetime of currently used antibiotics, overcoming the costly need for construction of new organic drug formulations and antibiotic scaffolds.

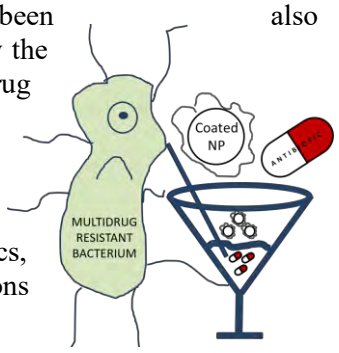

Figure 1: Cocktail of coated NPs and Antibiotics for addressing multidrug

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Stretching Liquid Bridges on Liquid Infused Surfaces

S. J. Goodband[1], H. Kusumaatmaja[1], K. Voitchovsky[1]
[1]*Durham University, Department of Physics, Durham, UK*

Corresponding author: s.j.goodband@durham.ac.uk

Liquid infused surfaces (LIS) have been shown to exhibit highly desirable anti-fouling properties which can lead to surfaces that are anti-icing, antibacterial, self-healing and anticorrosive. Although their self-cleaning abilities are well known, more work is needed to understand the complex relationship between the oil layer and any attached fouling droplets that form liquid bridges with the surface. While there has been theoretical studies of bridge stretching on LIS surfaces in the quasi-static limit [1], experimental studies, especially those that shed light on the bridge dynamics, are sparse.

In this work, a model LIS system [2] is used to experimentally investigate aqueous capillary bridges formed between two LIS and stretched at different velocities. The force exerted by the bridge and its geometry (contact angle, height and curvature radii) are recorded as a function of the LIS separation. The force profiles can be quantitatively explained with a simple liquid bridge model [3] at low stretching velocities (< 0.01 mm/s). However, significant deviations occur at higher velocities suggesting that mechanisms not captured by the model are at play. Interestingly, the force exerted by the bridge on the LIS decreases with increasing velocity. Additionally, a hysteresis loop opens up over a stretching/recovery cycle indicating previously not considered dissipation mechanisms, possibly in the oil layer [4].

Our experiments provide novel insights into the dynamic behaviour of capillary bridges on LIS and may help inform a functionality-lead development of future LIS. **References**

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CO_2 incorporation into the head groups of nonionic surfactants – effects on structure and thermodynamics

M. Gradzielski[1]; V.J. Spiering[1], R. Marschall[1], A. Ciapetti[1], L. Noirez[2], M.-S. Appavou[3]
[1]*Stranski Laboratorium für Physikalische Chemie, Institut für Chemie, Technische Universität Berlin, Berlin, Germany*
[2]*Laboratoire L8on Brillouin (CEA-CNRS), C.E.-Saclay, 91191 Gif sur Yvette Cedex, France*
[3]*Jülich Centre for Neutron Science (JCNS) at MLZ. 1, 85747 Garching, Germany*

Corresponding author: e-mail address of corresponding author

In this work we present an investigation of nonionic surfactants of the C_iE_j type, which were modified by incorporating different amounts of CO_2 units into their hydrophilic head groups. This modifies their HLB value and lowers their cmc. Most interestingly the phase behavior of such CO_2 modified surfactants differs largely from their conventional analogues by the fact that for high concentration no gel-like liquid crystalline phases are formed [1]. Instead up to the highest concentrations simple Newtonian liquids are present and this behavior was characterized by rheological measurements. This unexpected phase behavior was studied by means of comprehensive static and dynamic light scattering and small-angle neutron scattering experiments (SLS, DLS, SANS). In addition, the thermodynamics of self-assembly were determined from temperature-dependent cmc measurements and more directly from isothermal titration calorimetry (ITC) [2]. These experiments showed that the incorporation of CO_2 units imparts a marked hydrophobic character to the surfactants and reduces the repulsive interaction between the aggregates to such an extent that no longer liquid crystalline phases with their unfavorable flow properties are formed. This behavior is highly interesting for the use of nonionic surfactants in formulations at high concentration and can be fully understood based on the aggregate structure and their interactions.

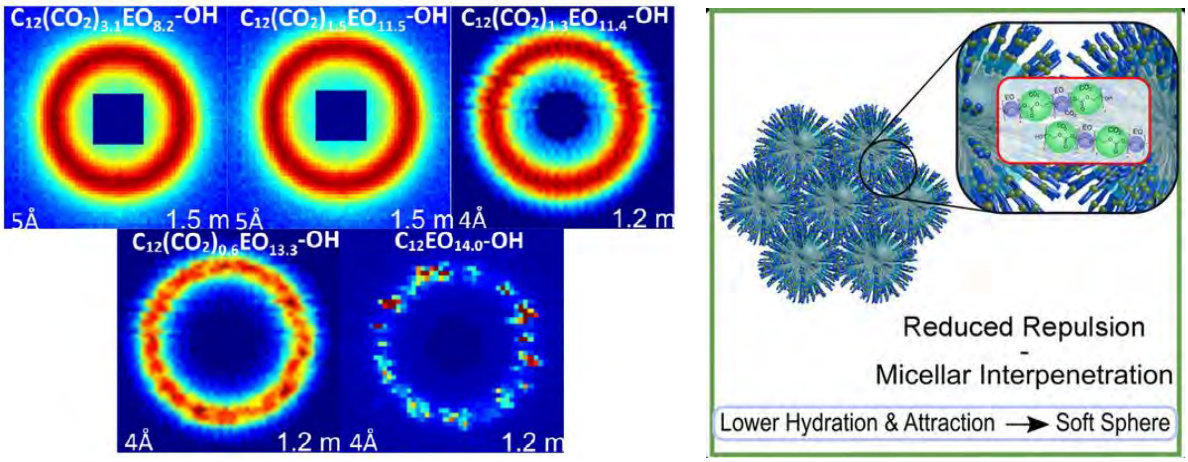

Figure 1: *2D-SANS curves for 50 wt% surfactant samples with different content of CO_2 in the head group and scheme of the effect of CO_2 incorporation on surfactant aggregation and micellar interactions.*

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Quantifying molecular diffusion in thin solvated bio-polymer films

Saikat Jana[1]; Rickard Frost[1], Delphine Débarre[2], Ralf P. Richter[1]
[1]*University of Leeds, School of Biomedical Sciences, Faculty of Biological Sciences, School of Physics and Astronomy, Faculty of Engineering and Physical Sciences, Astbury Centre of Structural Molecular Biology, and Bragg Centre for Materials Research, Leeds, United Kingdom*
[2]*Universite Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, France*

Corresponding author: S.Jana1@leeds.ac.uk

Solvated biopolymer coatings are ubiquitous in biomaterials, biosensors, antifouling coatings and separation membranes. These coatings often tens of nanometers thick, occupy much smaller volumes when compared to the illumination volume of a confocal microscope. As a result, while measuring diffusion using microscopy techniques like fluorescence recovery after photobleaching (FRAP) one captures molecular diffusion in bulk solvent rather than in film diffusivity. To overcome this limitation, we confine the polymer films in between a planar and spherical glass surface thereby physically excluding the excess solvent. The resulting plane-sphere contact creates a gap of nanoscale dimensions which allows visualization of molecular diffusion within the solvated films. In addition, by controlling the contact forces one can compress the polymer film to varying amounts within the nanoscale gap. The technique which we call as plane sphere confinement microscopy (PSCM) is used to investigate mechanisms of protein transport through films of end grafted FG Nucleoporins. The FG Nucleoporin films are model systems for studying nuclear pore permeability barrier and allows understanding of mechanisms behind the selective nucleo-cytoplasmic transport of macromolecules in eukaryotic cells. The PSCM technique is employed to gain insights into the in-film diffusivity and partitioning of protein molecules (of different functionalities) as function of compression of the nucleoporin films[1]. We also present the details of a stage insert that implements the PSCM technique and can be installed on fluorescence and/or confocal microscope. The insert is able to engage the plane sphere contact position with sub-micron precision and exerts constant forces in the sub millinewton range, thereby allowing the user flexibility and a greater control over experimental variables. The technique has the potential to enable new investigations in area of functional films and coatings, for example, in understanding the diffusivity of viruses through extracellular matrices or visualizing the assembly of cytoskeletal proteins on cell membranes.

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Studies of emulsion droplet distribution in case of hemp seed oil nanoemulsion system

Maciej Jarzębski[1]; Wojciech Smułek[2], Farahnaz Fathordoobady[3]; Anubhav Pratap-Singh[3]
[1] *Poznań University of Life Sciences, Department of Physics and Biophysics, Faculty of Food Science and Nutrition, Poznań, Poland*
[2] *Poznan University of Technology, Institute of Chemical Technology and Engineering, Poznań, Poland*
[3] *The University of British Columbia, Faculty of Land and Food Systems, Vancouver, Canada*
Corresponding author: maciej.jarzebski@up.poznan.pl

Nanoemulsion systems are one of the most investigated systems due to their possible application for biomedical application and their promising implementation into food technology. Various systems based on oil in water (O/W) and water in oil (W/O) have been studies in case of their stability behavior. Nevertheless, one of the key facto of the emulsion stability is their droplet size. One of the most popular and applied techniques for droplet size distribution is dynamic light scattering (DLS). Here we would like to discuss the way of droplet size distribution in the case of hemp seed oil O/W nanoemulsion systems. Base on our results previous results [1]–[3] we stated that not only z-ave and peak maximum should be discussed in the case of high polydispersity samples. In the presentation, it is recommended to show particle (droplet) size distribution versus scattered light intensity as well as particle number [4]. As a final recommendation, we strongly encourage a minimum of two different techniques for particle size determination or verification homogeneity of the nanoemulsion systems i.e. DLS and microscopic imaging [5].

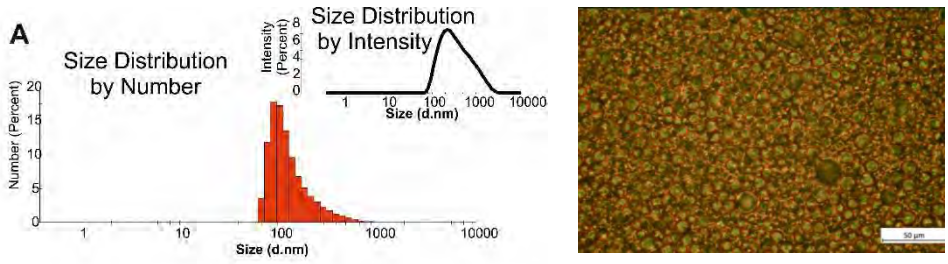

Figure 1: *Nanoemulsion droplet size distribution obtained by DLS and image from the reversed optical microscope (results taken from* [1]*)*

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Self-diffusion and microstructure of ammonium ionic liquids

A. Klimaszyk [1,2], R. Markiewicz[1], M. Jarek[1], S. Jurga[1]
[1]*Adam Mickiewicz University, NanoBioMedical Centre, Poznań, Poland*
[2] *Adam Mickiewicz University, Faculty of Physics, Poznań, Poland*

Corresponding author: adakli@amu.edu.pl

Ionic liquids (ILs), organic/inorganic salts with a melting point below 100 °C are usually characterized with variety of features, from which common to great group of ILs are low vapor pressure, wide range of liquid state, high thermal, electrochemical and chemical stability, and the ability to dissolve many organic and inorganic compounds, including some polymers. These are properties that conventional solvents do not have, and this is the reason ILs are often considered as green solvents used in laboratory and industrial processes. The specific properties its use, and these depend exclusively on the construction of the anion and cation (changing these two elements, it is possible to design an ionic liquid with the desired physical and chemical properties).

The small differences between ionic liquids (alkyl chain length, type of anion etc.) can have a large effect on their properties. For example, by changing from an ionic liquid with tetrafluoroborate anion, to an ionic liquid with the same cation but a bis(trifluoro-methylsufonyl)imide anion, there is a decrease in the viscosity of the ionic liquid and change from hydrophilic to hydrophobic behaviour, due the nature of the anion.

Physical properties of bulk ILs are affected by different factors, such as chemical structure of the ions, the intra-molecular and inter-molecular interactions, temperature, and the presence of gaseous, liquid or solid impurities.

Diffusion (self-diffusion) coefficient is a parameter, which is not dependent on time and, therefore, can be used to characterise the translational mobility (diffusivity) of a certain type of molecule under certain conditions (temperature, pressure, molecular interactions). As the external conditions change, diffusion coefficient obligatorily also change. For example, an increase in temperature (and, therefore, mean thermal energy of molecules) leads to an increase of D. To describe the temperature dependence of D is not a trivial task. In a simplified assumption it has been described as an activation process of the type of an Arrhenius function.

The aim of this work is the evaluation of microscopic and macroscopic structure of two ammonium ILs' families (with varied cation) solutions as well as the exact characterization of their microscopic interactions by terms of self-diffusion coefficient. In this way, we prepared alkyltriethylammonium and alkylcyclohexyldimethylammonium-based ionic liquids with varied alkyl chain length and bis(trifluoromethylsufonyl)imide anion. After structure confirmation by means of NMR and FTIR, phase transition temperatures were determined by means of differential scanning calorimetry technique. Finally, self-diffusion coefficients were determined for series of the prepared ILs measurements at 14,4 T Agilent NMR spectrometer techniques (DOTY DSI-1372, g_z=28 T/m, VnmrJ 4.2; Pulse sequence: PGSE (Pulsed Gradient Spin-Echo).

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Transient rheology of model gluten gel in water

Ameur Louhichi[1], Marie-Hélène Morel[2], Laurence Ramos[1] and Amélie Banc[1]

[1]*Laboratoire Charles Coulomb (L2C), Univ.Montpellier, CNRS, Montpellier, France*
[2]*I nierie des Agro-Polym res et Technologies Emergentes (IATE), Univ. Montpellier, CIRAD, INRAE, Montpellier, France*

Corresponding author: amelie.banc@umontpellier.fr

We investigate the transient viscoelasticity of model gluten gel in water. We used the start-up shear at various rates, from $0.1\ s^{-1}$ to $10\ s^{-1}$, and with different total deformations: 100 SU, 500 SU, 1000 SU and 2000 SU. Thus, transient responses are obtained for the same shear rate window but with changing the mechanical history of samples. The ratio between the maximum and steady stress ($\frac{\sigma_{Max}}{\sigma_{Steady}}$) and strain at the maximum stress (γ_{Max}) are analyzed for the above experimental conditions.

The transient regime reveals that the gluten gel behaves as a branched polymeric system, with noticeable wakening as a function of the mechanical history.

The ratio $\frac{\sigma_{Max}}{\sigma_{Steady}}$ as a function of shear rate, for the different total deformations, increases with higher total deformation and the data has a shear rate power law dependence that become stronger with total strain, suggesting the weakening of system. Concomitantly, we found that $\gamma_{Max} \geq 10$ for the different experimental conditions, suggesting a strong stretching.

Moreover, the shear rate dependence of both quantities exhibits the presence of two regimes (transition at $\dot{\gamma} \cong 2s^{-1}$) only with higher total strains (1000 SU and 2000 SU), suggesting the appearance of new local dynamics in relation with structural changes in the system.

Additional experiments were performed by using supramolecular blockers: urea to disturb hydrogen bonding and N-ethylmaleimide to compete with the thiol/disulfide exchange. The transient data reveals that the effect of supramolecular blockers on the nonlinear transient rheology is comparable to that of the mechanical history, suggesting a common physics driving the mechanical properties of gluten gels under large deformation.

Temperature-induced structural changes of PNIPAM- from milliseconds to minutes

J. Michalska[1]; M. Dulle[1], S. Hauschild[1], S. Förster[1]
[1] *Jülich Centre for Neutron Science (JCNS-1/IBI-8), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany*

Corresponding author: j.michalska@fz-juelich.de

Structural changes at the intra- and interchain level induced by the phase transition of poly(N-isopropylacryl amide) (PNIPAM) can be tracked in real-time by time-resolved small-angle neutron scattering (tr-SANS). PNIPAM is one of the most commonly and extensively studied thermoresponsive polymer due to lower critical solution temperature (LCST) in water that occurs at the physiologically relevant temperature. Block copolymer micelles and polymer microgels have been used as drug carriers and as microreactors for enzymatic reactions. For drug release and enzyme reactions, the kinetics of the transport across the micellar core and shell region depends on the local mobility of the core-shell region. The control of time-response is of critical importance for applications of responsive polymers. A general and fundamental understanding of the volume phase transition kinetics is still lacking. The aim of the present study is investigation of the collapse kinetics of PS-PNIPAM micelles by temperature jump above LCST using TR-SANS, light scattering and cryo-electron microscopy. The thermal responsiveness was followed over a broad timescale from the early-stage collapse of polymer in milliseconds to slow growth of aggregates in minutes. Using different experimental methods for homopolymers or micellar block copolymers we got comparable results indicating a common multistep scheme. Thus we concluded a general mechanism for PNIPAM polymers behavior depending on the temperature.

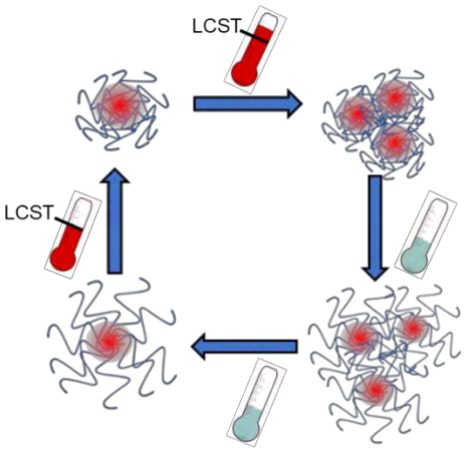

Figure 1: *Temperature-dependence of the multistep behavior of polymer in water.*

Changing the flow profile and resulting drying pattern of dispersion droplets via contact angle modification

Carmen Morcillo Perez[1], Marcel Rey[1], Benjamin D. Goddard[2], and Job H. J. Thijssen[1]

[1]*The University of Edinburgh, SUPA School of Physics and Astronomy, Edinburgh, United Kingdom*
[2]*The University of Edinburgh, School of Mathematics, Edinburgh, United Kingdom*

Corresponding author: carmen.morcillo.perez@ed.ac.uk

Prediction and control over particle deposit patterns obtained from sessile droplet evaporation are essential for many industrial processes, such as inkjet printing and crop protection. Numerous formulations have been studied in order to understand how the different components affect the final dried deposit. Yet, the testing substrates used are generally far from similar to those in the real application. Thus, a key challenge resides in understanding how the substrate properties can affect the drying process. We present a systematic investigation on the effect of surface wettability on the evaporation dynamics of a particle-laden droplet and the final distribution of the particles after evaporation. We tuned the wettability of glass slides using silanisation reactions; and measured the flow inside the drying droplets using fluorescent tracer particles and particle tracking algorithms. We found that the internal flows shift from predominantly outwards flow for low contact angles to predominantly inward flow for large contact angles. Upon increasing the substrates hydrophobicity, the dried deposit gradually changes from the typical coffee-ring to a central stain, as the evaporation is no longer fastest at the contact line. On the basis of the results obtained, we conclude that the substrate plays an essential role on the drying process and supports the need for improved procedures during formulation design.

Rheological and structural properties of polyacrylamide microgels designed by two different synthesis strategies

A. Mungroo[1]
IMP Laboratory, Jean Monnet University of Saint-Etienne, France

Corresponding author: ashley.mungroo@univ-st-etienne.fr

Unveiled by Baker[1] in 1949 microgels are remarkable materials describing a colloidal dispersion of cross-linked polymers micro-network with the ability to swell in good solvent. Nowadays, we are able to tailor-made their ability to swell depending on the stimuli applied such as the temperature, pH or ionic strength. In this work, we focused our attention on crosslinked polyacrylamide microgels which have attracted a lot of attention this past decade thanks to their water solubility, extremely valuable for bioapplications as biosensors[2], [3] and for oil recovery applications[4]. We compared two different types of synthesis procedures: inverse microemulsion polymerization (IMEP) and precipitation polymerization (PP) using light scattering and rheological measurements. We investigated the influence of solvent and crosslinking on microgels architecture and on their rheological properties. We shed lights on the use of a co- solvent in PP which allowed to control the hydrodynamic radius (R_H) of PAAm microgels and the reduction of the amount of crosslinker drastically decreased the turbidity of the PAAm microgels aqueous solution. We compared the shear rheological responses pointing out that PAAm microgels prepared via PP are soften (and so have lesser density of crosslinking) than those prepared via IMEP.

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Revealing the origin of the specificity of calcium and sodium cations binding to adsorption monolayers of two anionic surfactants

F. Mustan,[1] A. Ivanova,[2] S. Tcholakova,[1] N. Denkov[2]

[1]*University of Sofia, Department of Chemical and Pharmaceutical Engineering, Sofia, Bulgaria*

[2]*University of Sofia, Department of Physical Chemistry, Sofia, Bulgaria*

Corresponding author: fm@lcpe.uni-sofia.bg

The studied anionic surfactants linear alkyl benzene sulfonate (LAS) and sodium lauryl ether sulfate (SLES) are widely used key ingredients in many home and personal care products. These two surfactants are known to react very differently with multivalent counter-ions, including Ca^{2+}. This is explained by a stronger interaction of the calcium cation with the LAS molecules, when compared to SLES. The molecular origin of this difference in the interactions remains unclear. In the current study, we conduct classical atomistic molecular dynamics simulations to compare the ion interactions with the adsorption layers of these two surfactants, formed at the vacuum-water interface. Trajectories of 150 ns are generated to characterize the adsorption layer structure and the binding of Na^+ and Ca^{2+} ions. We found that both surfactants behave similarly in the presence of Na^+ ions. However, when Ca^{2+} is added, Na^+ ions are completely displaced from the surface with adsorbed LAS molecules, while this displacement occurs only partially for SLES. The simulations show that the preference of Ca^{2+} to the LAS molecules is due to a strong specific attraction with the sulfonate head-group, beside the electrostatic one. This specific attraction involves significant reduction of the hydration shells of the interacting calcium cation and sulfonate group, which couple directly and form surface clusters of LAS molecules, coordinated around adsorbed Ca^{2+} ions. In contrast, SLES molecules do not exhibit such specific interaction, because the hydration shell around the sulfate anion is more stable, due to the extra oxygen atom in the sulfate group, thus precluding substantial dehydration and direct coupling with any of the cations studied.

Multiresponsive starPEG-hydrogels crosslinked with pyrene-functionalized copolymers

Dustin Rasch[1,2], Robert Göstl[1]
[1]*DWI – Leibniz-Institute for Interactive Materials, Aachen, Germany*
[2]*Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany*

Corresponding author: goestl@dwi.rwth-aachen.de

Pyrene is widely used as fluorescent, distance-sensitive sensor powered by its excimer formation and emission. Yet, distance sensing based on pyrene relies on the interplay of multiple intricate spectroscopic phenomena. Especially in aqueous solution, the hydrophobic character of pyrene leads to the interference of different effects rendering the reproducible collection and meaningful analysis of the obtained spectral data non-trivial.

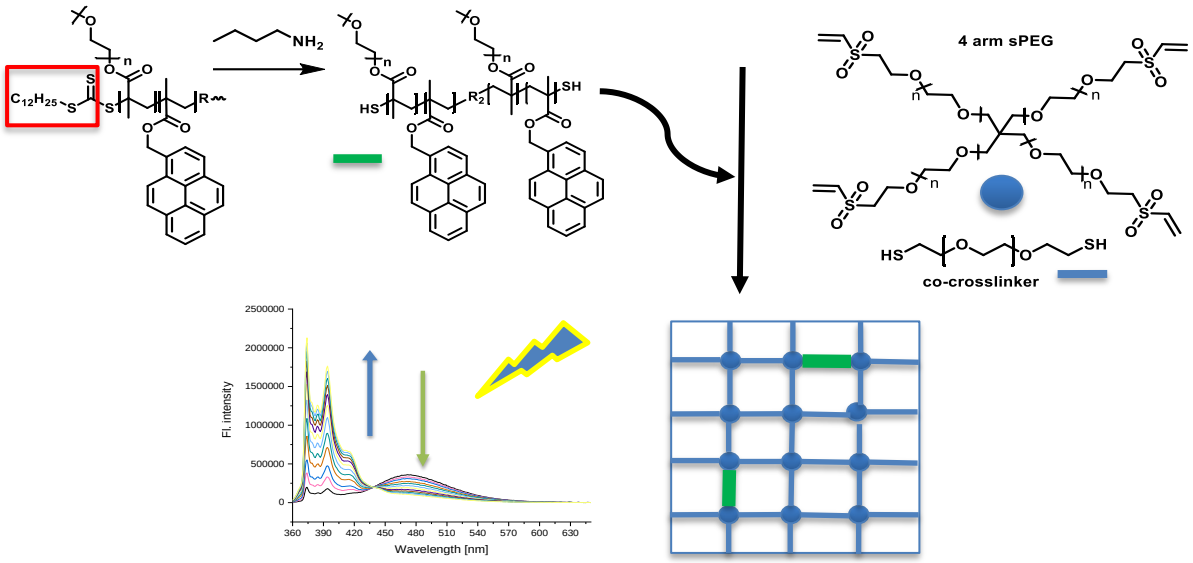

Figure 1: *Synthesis strategy for multiresponsive starPEG hydrogels and photoinduced pyrene cleavage from the macromolecules.*

We investigated a series of well-defined statistical copolymers composed of pyrenylmethyl methacrylate (PyMA) and oligo(ethylene glycol) methyl ether methacrylate (OEGMEMA) with varying pyrene content (Figure 1). By chemical modification of the end-groups, these were incorporated as covalent macrocrosslinkers into starPEG hydrogels. The emissive properties of the obtained materials was strongly dominated by intra- and intermolecular effects depending on the pyrene concentration within each chain and the overall macrocrosslinker concentration. We show that static excimer formation, which we clearly distinguish from dynamic pyrene excimer emission, is a major contributor to these observed effects.

The resulting hydrogels were shown to be multi-responsive and photoinduced pyrene cleavage was used for irreversible photolithography in these materials. In addition, the controlled swelling of the hydrogels with discrete amounts of water revealed a novel counterintuitive chromatic effect, which was used to control the lithographic process.

Innovative microfluidic platforms for biomedical applications. Novel technologies for the obtaining of functionalized bioceramics and hybrid hydrogel microparticles production.

Ramón Rial[1*]; Juan M. Ruso[1]

[1]*University of Santiago de Compostela, Soft Matter and Molecular Biophysics Group, Department of Applied Physics, Santiago de Compostela, Spain*

**Corresponding author: ramon.rial@usc.es*

This work focuses on the production of new sophisticated biomaterials for their use in modern tissue regeneration approaches. New strategies [1, 2] and novel synthetic routes [3] were successfully developed. The resultant biomaterials are economically feasible and their refined attributes help them becoming a great solution in numerous applications in tissue regeneration and biomedical engineering.

Particularly, bioceramic nanoparticles attract a lot of attention within the biomedical device industry. Nevertheless, most of their potential uses are conditioned by their shapes and morphologies, so controlling their synthesis is a more than efficient way of enhancing their properties. In this regard, microfluidic techniques are a highly helpful tool which allows a great precision on the management of flows and concentrations. In particular, one of the innovations of this work is the conception and the effective development of a new procedure for the obtaining of hydroxyapatite nanorods (HAp). This novel methodology, apart from notably reducing the production costs, also enables the manipulation of the synthesis conditions, allowing to fine tune the structure of the resulting nanorods by simple engineering, just varying inlet flow velocities and ratios.

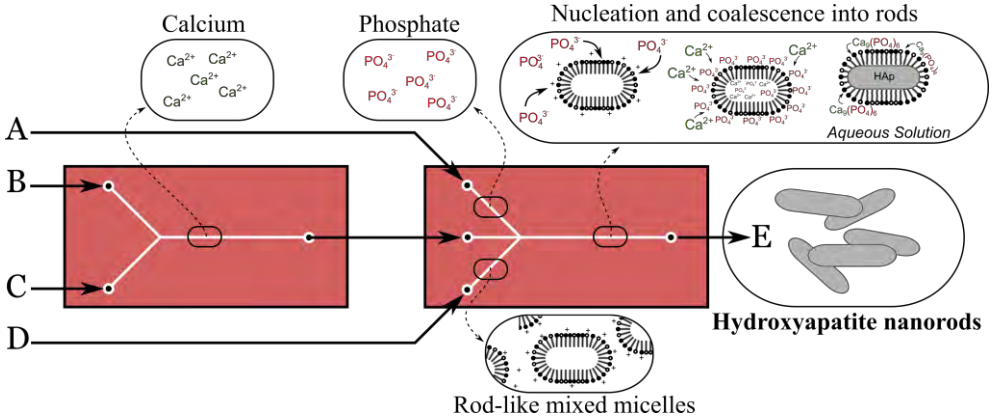

Figure 1: Schematic representation of the microfluidic system operation.

Similarly, a new method for the synthesis of crosslinked hydrogel microparticles (HMPs) was also developed. Typically, hydrogels are made as solid materials with macroscale external dimensions and nanoscale internal mesh sizes. However, for certain uses, such as injection or extruded-based 3D printing, bulk hydrogels have inherent drawbacks[4]. To address this problem, hydrogel microparticles (HMPs) are emerging as a promising solution in this field, due to their modular nature, the adjustability of the level of porosity and their ability to flow through small needles or catheters[5][6]. This work describes the procedure for obtaining hydrogel microspheres for doped-hydroxyapatite encapsulation and controlled drug delivery. Combining external and internal gelation, it is possible to obtain Calcium-Alginate microparticles (Ca-ALG) and core-shell Calcium-Alginate-Chitosan microspheres (Ca-ALG-CHI) with homogeneous sizes and morphologies and load them with doped HA. The study of this kind of micro-hydrogels with advanced functionalities is crucial for the

construction of granular hydrogels, which are a very promising solution for a great array of modern therapies in regenerative medicine areas.

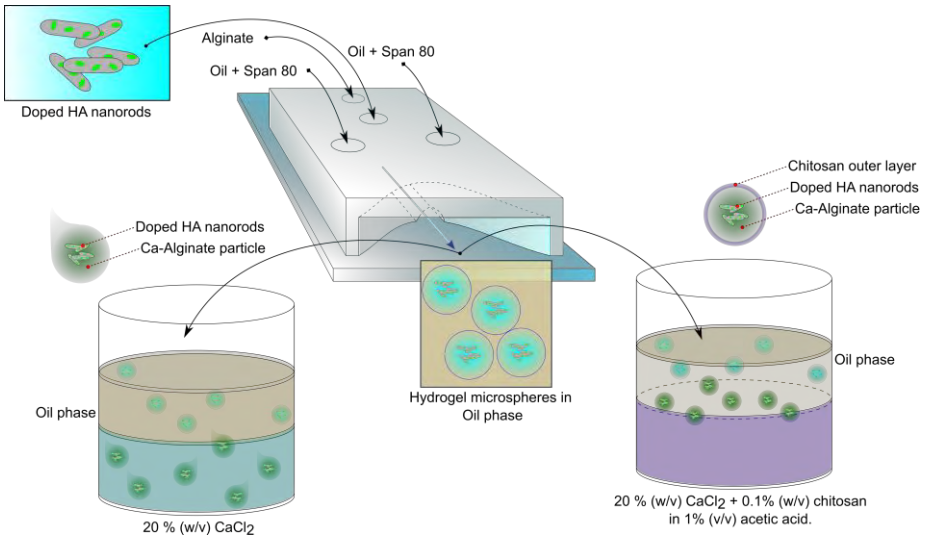

Figure 2: Microfluidic set-up for the hybrid hydrogel microparticles production. Spherical droplets are created inside the microchanels of the chip. After the collection in the gelation baths, two different microparticles are obtained: teardrop-shaped Ca-Alg microparticles and spherical core-shell ALG-CHI microgels.

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On the effect of particle morphology and interaction on near wall dynamics

J. A. Rivera Morán [1], Y. Liu[1], S. Monter[1,2], M. Lisicki[3], C.-P. Hsu[4], P, R. Lang[1]
[1] *Forschungszentrum Jülich GmbH, IBI-4, Jülich, Germany*
[2] *Universität Konstanz, Germany*
[3] *University of Warsaw, Physics Department, Warsaw, Poland*
[4] *Eidgenössische Technische Hochschule , Department of Materials, Zürich, Switzerland*
Corresponding author: j.rivera.moran@fz-juelich.de, p.lang@fz-juelich.de

We employed evanescent wave dynamic light scattering[1] to study the near wall dynamics of different types of silica particles, i. e. full spheres, spherical shells and spheres with surface roughness, with the objective to investigate the effect of particle morphology on their near wall dynamics.

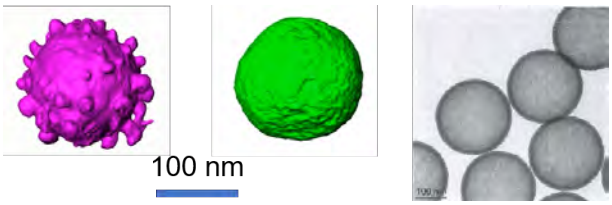

Figure 1: *Investigated particle types: 3D-reconstructions of a rough (left) and of a smooth (middle) silica particle from cryo-TEM. TEM-image of silica-shells (right)*

While the dynamics of spherical particles and hollow shells is in agreement with theoretical predictions for hard sphere colloids[2] within experimental error, the rough particles show slower dynamics than expected for spheres. As the latter finding is at conflict with hydrodynamic theory, we further investigated the influence of static particle wall interaction on the dynamics. Our results indicate that the rough particles experience stronger van der Waals attraction than particles with a smooth surface, which may contribute to settle an open question in literature concerning the effect of particle roughens on interaction and adhesion[3, 4].

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Role of the environment in tuning the dynamical transition of PNIPAM: a neutron scattering study

B. P. Rosi [1], A. D'Angelo[2], M. Zanatta[3], A. Paciaroni[1], S. Corezzi[1], L. Comez[4], C. Petrillo[1], F. Sacchetti[1], A. Orecchini[1,4]

[1] *Università di Perugia, Dipartimento di Fisica e Geologia, Perugia, Italy*

[2] *CNRS c/o Université Paris-Saclay, Laboratoire de Physique des Solides, Paris, France*

[3] *Università di Trento, Dipartimento di Fisica, Trento, Italy*

[4] *CNR-IOM c/o Università di Perugia, Dipartimento di Fisica e Geologia, Perugia, Italy*

Corresponding author:benedettapetra.rosi@unipg.it

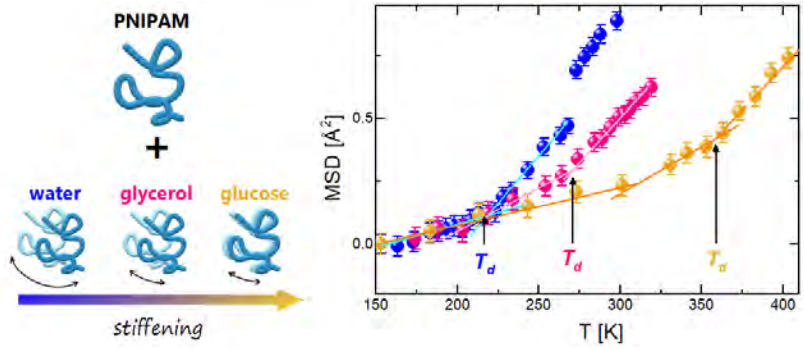

Figure 1: *Mean square displacements (MSD) of PNIPAM samples in the presence of different environments. The MSD are obtained by the EINS intensities collected at the IN13 neutron spectrometer that samples motions on a time scale of about 150 ps. Black arrows indicate the dynamical transition temperature T_d for each sample.*

Hydrated proteins undergo a dynamical transition (DT) at $T_d \approx 200$ K that is associated with the activation of protein dynamics on the ps to ns time scales, that are made accessible by Elastic Incoherent Neutron Scattering (EINS) experiments. The transition is accompanied with an increased flexibility that is ascribed to a plasticizing action exerted by water, thanks to the tight coupling between protein and solvent. This aspect has attracted the widest interest, since flexibility is deemed as necessary to perform biological functions. The impact of the environment on protein flexibility and dynamics has been further explored by substituting water with *stabilizing* compounds usually employed for storage of proteins, in order to preserve them from degradation. Several studies have shown that stabilizers stiffen protein motions and shift T_d toward higher values, suggesting a connection between preservative action and inhibition of fast dynamics. Quite surprisingly, a DT has also been recently observed in a hydrated synthetic polymer, i.e. poly(*N*-isopropylacrylamide) or PNIPAM [1], making it an excellent case study for investigating the connection between solvent characteristics, macromolecular flexibility and activation of the DT. By means of EINS techniques we studied the impact of stabilizers on the fast dynamics of PNIPAM, revealing strong analogies with protein behaviour.

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TRACKING COLLOIDAL PARTICLES TO EVALUATE THEIR DISPERSION UNDER SHEAR APPLICATIONS

M. Saeed[1]; A. Otsuki[1,2].
[1]*University of Lorraine, ENSG, GeoRessources, Vandoeuvre-les-Nancy, France*
[2]*Luleå University of Technology, Waste Science Technology, Luleå, Sweden*

Corresponding author: akira.otsuki@univ-lorraine.fr

We studied the effect of shear rate (0-500 s^{-1}) and solution pH (6, 10) on the dispersion degree of colloidal silica particles via the determination and comparison of interparticle distances. Silica particle suspensions prepared at desired pH and solid concentrations were monitored using a confocal rhescope with the shear rates from 0 to 500 s^{-1} and then decreased back to 0 s^{-1}. Images corresponding different shear rates (0, 0.005, 0.05, 0.5, 5, 50, 500 s^{-1}) were treated with Fiji / image J software and coordinates of the particles were identified. These coordinates were then treated in Visual studio to calculate the distance among the particles. It was found that population of the particles under different shear rates varied and less number of particles per unit area of the image were identified with the increasing shear rate.

One-Component DNA Mechanoprobes for Facile Mechanosensing in Photopolymerized Hydrogels and Elastomers

R.S. Schmidt[1]; G. Creusen[1], A. Walther[1,2*]
[1]*A³BMS Lab, Department of Chemistry, University of Mainz, 55128 Mainz, Germany*
[2]*DFG Cluster of Excellence "Living, Adaptive and Energy-Autonomous Materials Systems" (liv*MatS*), 79110 Freiburg, Germany*

**Corresponding author: andreas.walther@uni-mainz.de*

The combination of mechanical sensory functions with easily detectable visual output is a key feature towards fundamental understanding of e.g. cell behavior and the design of responsive materials systems e.g. in tissue engineering. The translation of a mechanical force into an optical readout is accessible via DNA nanotechnology, providing a toolbox living up to multiple requests in today's materials systems. The programmability of DNA-based motifs enables bond directionality, control over the force range, and orthogonality in the use of multiple force sensors.

We herein describe the development of a new approach towards an all-in-one DNA-based fluorescent mechanosensing macro-monomer easily implementable into hydrogel networks by free radical polymerization (**Figure 1**). In contrast to previous designs of DNA mechanoprobes that contain multiple individual strands, we herein merge all relevant components synthetically into a single and highly robust entity. The mechanosensing feature relies on hybridization of single stranded DNA (ssDNA) folding into a hairpin loop, immobilizing the fluorophore-quencher pair (added as in strand modifications) for the optical force sensor readout at the root of the motif. Both termini of the mechanoprobe are modified with methacrylamide functionalities, assuring simple incorporation into the polymer network of hydrogels by free radical polymerization. We demonstrate mechanoactivation in hydrogels and in solvent-free elastomers.

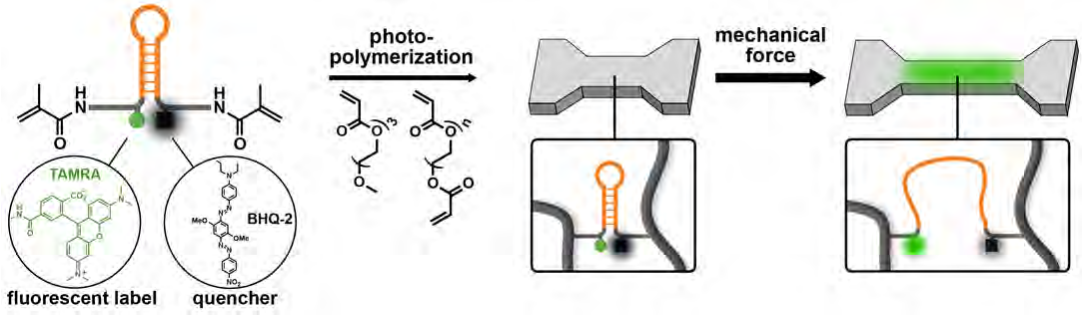

Figure 1: *All-in-one DNA mechanoprobes and their incorporation into the hydrogel network via photopolymerization. Mechanical stress is visualized by the DNA force sensor via an increase in fluorescence upon spatial separation of the dye-quencher pair.*

Our simplified all-in-one design overcomes two major bottlenecks currently limiting wider application of DNA-based mechanofluorescent probes in (bio)materials research: (1) reliable correct folding of the mechanoprobe by a single-component hairpin design with internal dye-quencher modifications for the optical readout without the requirement of a complex annealing protocol including multiple components, and (2) reliable implementation of the force sensing motif by direct incorporation of the DNA mechanoprobe into the polymer network of the hydrogel via free radical polymerization without requiring further DNA interfaces.

Building blocks of protein structures

T. Škrbić [1,2], J. R. Banavar[1], A. Giacometti[2], T. X. Hoang[3],A. Maritan[4],G. Rose[5]

[1] *University of Oregon, Department of Physics and Institute for Fundamental Science, Eugene, Oregon, USA*

[2] *Università Ca Foscari, Dipartimento di Scienze Molecolari e Nanosistemi, Venezia, Italy*

[3] *Vietnam Academy of Science and Technology, Institute of Physics, Hanoi, Vietnam*

[4] *Università di Padova, Dipartimento di Fisica e Astronomia, Padova, Italy*

[5] *Johns Hopkins University, T. C. Jenkins Department of Biophysics, Baltimore, Maryland, USA*

Corresponding author:tskrbic@uoregon.edu

We present a prediction of the building blocks of protein structures with no chemistry and no adjustable parameters. Our predictions arise from one hypothesis that the dominant folding mechanism of a protein is the drive to maximize its self-interaction, thereby attaining a space-filling folded state. Our results are in good accord with experimental data on more than four thousand protein structures and they underscore the consilience in the fit of chemistry and biology to the dictates of mathematics and physics. Our work has consequences for the energy landscape of proteins and the role of evolution in shaping sequences and functionalities.

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Structure of dense adsorption layers of escin at the air-water interface studied by molecular dynamics simulations

S. Tsibranska[1]; A. Ivanova[2], S. Tcholakova[1], N. Denkov[1]
[1]*Faculty of Chemistry and Pharmacy, University of Sofia, Department of Chemical and Pharmaceutical Engineering, Sofia, Bulgaria*
[2]*Faculty of Chemistry and Pharmacy, University of Sofia, Department of Physical Chemistry, Sofia, Bulgaria*

Corresponding author: st@lcpe.uni-sofia.bg

Saponins are abundant natural surfactants applied in pharmaceutical, food and beverage industries, due to their strong surface activity. Saponins have also various types of useful bioactivity. One of the saponins with very interesting properties is escin, extracted from horse chestnut. The escin adsorption layers, formed at the air-water interface, have unusually high surface visco-elasticity and relatively low permittivity to gas molecules [1,2]. In a previous study [3], using molecular dynamics simulations, we investigated the molecular origin of this behavior with diluted adsorption layers. We found that the escin molecules rapidly self-assemble in clusters on the air-water interface, due to the combined action of several attractive interactions [3]. Here we present a continuation of our previous study with atomistic molecular simulations of dense escin adsorption layers. The major aim is to obtain deeper insight into the alignment and the interactions between the escin molecules in such dense layers. The molecular orientation at the interface is determined in two models, with different areas per escin molecule in the adsorption layer. The results show that the high flexibility of the hydrophilic sugar groups in the escin molecule, combined with the attractive molecular interactions, lead to fast molecular rearrangement into densely packed adsorption layers. The layer thickness and the surface tension calculated from the computer simulations agree with the experimental data [1,2], thus confirming the reliability of the model used. The new simulations confirm our previous conclusion [3] that a specific interaction, which appears as an intermediate between the classical short-range hydrogen bonding and the conventional dipole-dipole attraction, is the key to explain the substantial surface visco-elasticity of the escin adsorption layers.

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