Industry Session

Tuesday 01 June 10:40 – 12:40

Making Natural Beauty Happen – performance without compromise

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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

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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

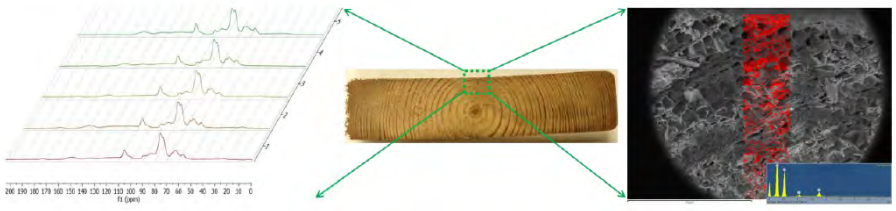

Figure 1: *Graphical abstract of the performed SEM/ EDX and Solid-state 400 MHz NMR spectrometer on the modified wood.*

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

[1] Wikberg, Hanne. PhD thesis *Advanced Solid State NMR Spectroscopic Techniques in the Study of Thermally Modified Wood*, Helsinki, Finland: University of Helsinki, **2004**, 15, ISBN 952-10-2251-5

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

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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.

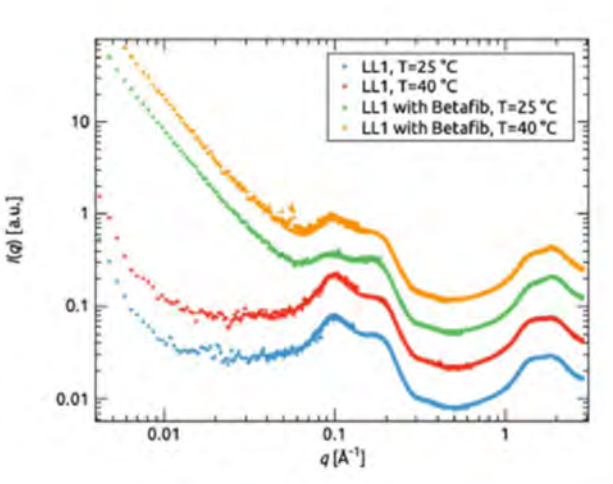

Figure 1: *Example of SAXS data of a Liquid Laundry (LL) composition with and without Betafib® .*

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

[1] https://www/cosunbiobased.com/product-portfolio/betafib-mcf/3

Patient centric Drug Delivery and Manufacturing approaches – Challenges remains

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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

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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.

References

[1]] da Costa Campos, Hornung, Gompper, Elgeti, Caspers: 2021 NeuroImage 231, 117779

Exploring microscopic rearrangements in flowing complex fluids using differential dynamic microscopy

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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.

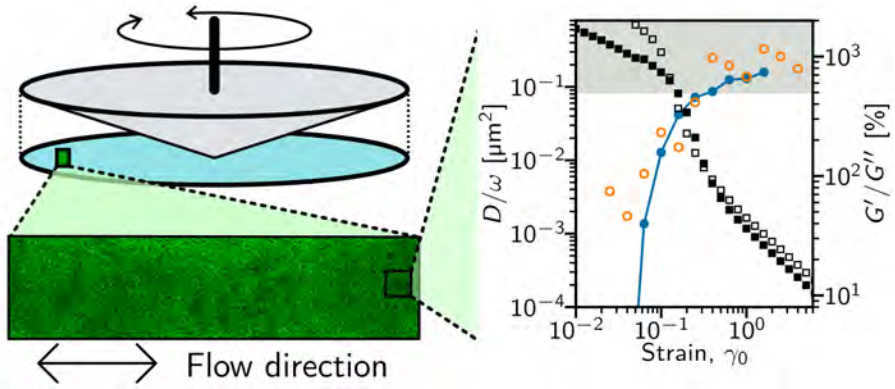

Figure 1: *Left:* Rheo-confocal imaging of a jammed emulsion under oscillatory shear. *Right:* analysis to give microscopic rearrangement rates [D (coloured circles)] compared to bulk rheology [storage modulus to loss modulus ratio, G'/G'' (black squares)]. Filled symbols at 1 Hz and open symbols at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

References

[1] J. A. Richards, V. A. Martinez, J. Arlt *Soft Matter* **2021**, *Advance Article*, . DOI:10.1039/D0SM02255A

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

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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

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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.

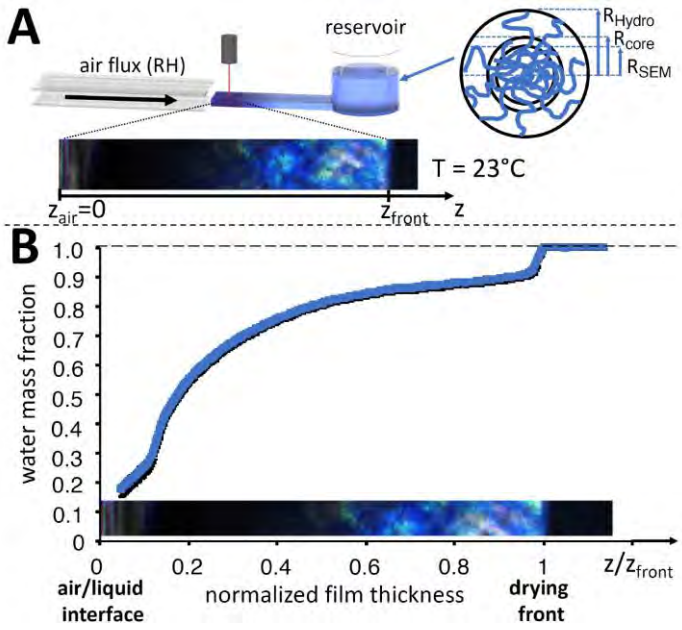

Figure 1: *(**A**) Schematic view of the millifluidic setup, which consists of a rectangular capillary connected on one end to a reservoir containing a 1wt% microgel dispersion and exposed on its other end to an air flux of controlled relative humidity (RH). As water evaporates, microgel particles pack 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

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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.

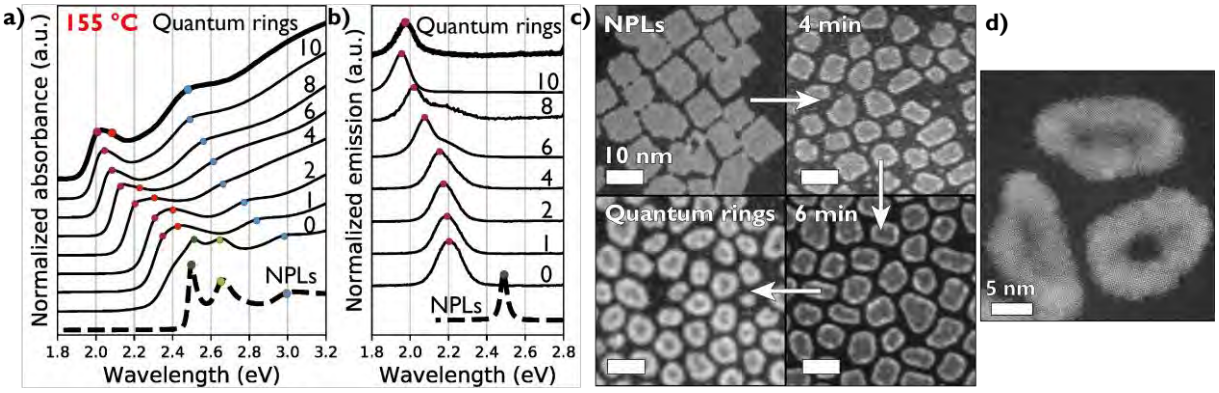

Figure 1: *Characterization of the conversion of CdSe nanoplatelets (NPLs) into quantum rings. Absorption a) and emission spectra b), together with HAADF-STEM images c), showing the gradual conversion. High resolution HAADF-STEM d) shows the single-crystalline nature and (partial) perforation of the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

References

[1] I. Fedin, D.V. Talapin *J Am Chem Soc,* **2016** 138**,** 9771, DOI: 10.1021/jacs.6b05862

[2] I.R. Sellers, V.R. Whiteside, I.L. Kuskovsky, A.O. Govorov, B.D. McCombe, **2008** 100, 136405, DOI: 10.1103/PhysRevLett.100.136405

Topical Session
Responsive Matter

Tuesday 01 June 16:10 – 18:10

Controlling Biological Systems by Ultrasound: Sonopharmacology and Sonogenetics

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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

[1] Haubensak W, Kunwar PS, Cai H, Ciocchi S, Wall NR, Ponnusamy R, Jonathan Biag, Dong H-W, Deisseroth K, Callaway EM, Fanselow MS, Lüthi A, Anderson DJ, Nature (2010) 468: 270.

[2] Kravitz AV, Freeze BS, Parker PR, Kay K, Thwin MT, Deisseroth K, Kreitzer AC, Nature (2010) 466: 622.

[3] Sohal VS, Zhang F, Yizhar O, Deisseroth K, Nature (2009) 459: 698.

[4] Ibsen S, Tong A, Schutt C, Esener S, Chalasani SH, Nat. Commun. (2015) 6:8264.

[5] Zhou Y, Huo S, Loznik M, Göstl R, Boersma AJ, Herrmann A, Angew. Chem. Int. Ed. (2021) 60, 1493.

[6] Shi Z, Wu J, Song Q, Göstl R, Herrmann A, J. Am. Chem. Soc. (2020) 142, 14725.

[7] Shi Z, Song Q, Göstl R, Herrmann A, Chem. Sci. (2021) 12, 1668.

[8] Huo S, Zhao P, Shi Z, Zou M, Yang X, Warszawik E, Loznik M, Göstl G, Herrmann A, Nat. Chem. (2021) 13, 131.

Sculpting hydrogels using advective assembly

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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.

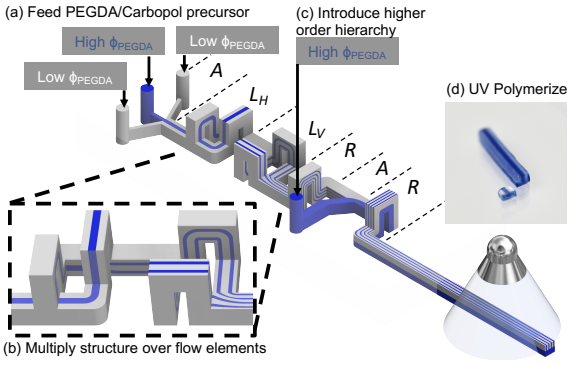

Figure 1: *Advective assemblers sculpt hydrogel crosslinking density along the laminar streamlines of the serpentine device geometry. Here, a 'comb' is produced by (a) feeding disparate hydrogel inks through (b) layer multiplication elements, and (c) adding a second layer perpendicular to the teeth. 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

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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.

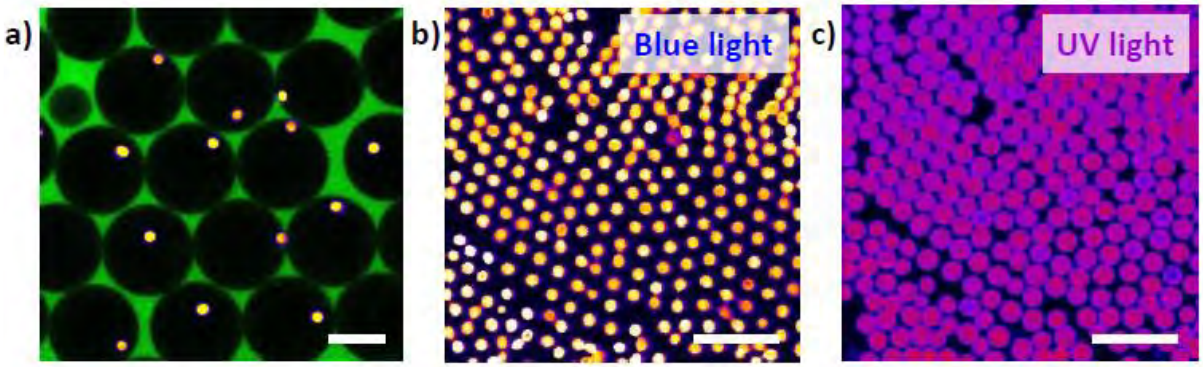

Figure 1: *Confocal laser scanning micrographs (CLSM) showing: a) All-DNA microgels (orange) in the microfluidic emulsion (green) after phase separation. b) Surface immobilized photo-responsive DNA microgels compacted under blue light irradiation and c) swollen under UV light. Scale bars are 20 µm.*

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

[1] A. C. Daly, L. Riley, T. Segura, J. A. Burdick, *Nat. Rev. Mater.* **2020**, *5*, 20.

[2] R. Merindol, S. Loescher, A. Samanta, A. Walther, *Nat. Nanotechnol.* **2018**, 13, 730.

[3] R. Merindol, N. Martin, T. Beneyton, J.-C. Baret, S. Ravaine, *Adv. Funct. Mater.* **2021**, *31*, 2010396.

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

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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.

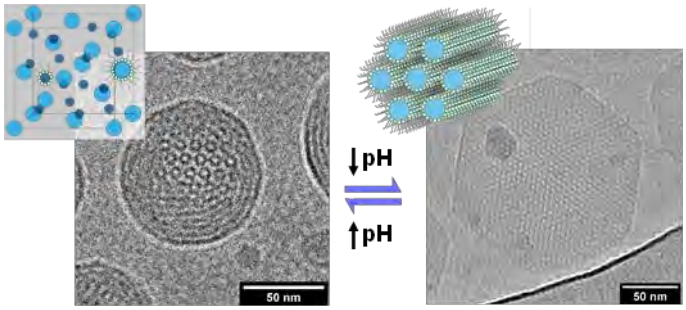

Figure 1: *pH-induced reversible structural transition between Fd3m (left) and H_{II} (right) of LCNPs.*

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

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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.

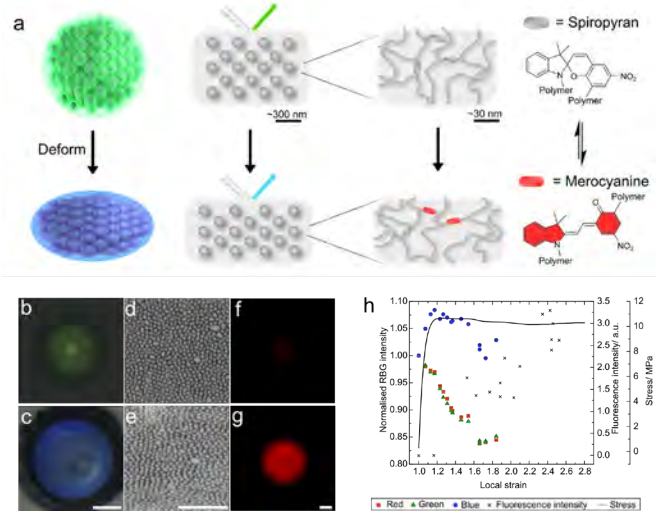

Figure 1: *Mechano-pigments with microstructural and molecular mechanochromism: a) schematic; reflectance images of b) uncompressed and c) compressed sensors (scale-bar 50 µm); d), e) FIB-SEM images of interior colloidal arrangement for sensors in b) and c) (scale-bar 2 µm); fluorescence images of f)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

References

[1] J. M. Clough, C. Weder, S. Schrettl, *Macromol. Rapid Commun.* **2021**, *42*, 1.

[2] R. Göstl, J. M. Clough, R. P. Sijbesma, in *Mechanochemistry Mater.*, The Royal Society Of Chemistry, **2018**, pp. 53–75.

[3] J. M. Clough, J. van der Gucht, T. E. Kodger, J. Sprakel, *Adv. Funct. Mater.* **2020**, *30*, 2002716.

General Session 5

Tuesday 01 June 16:10 – 18:00

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

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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.

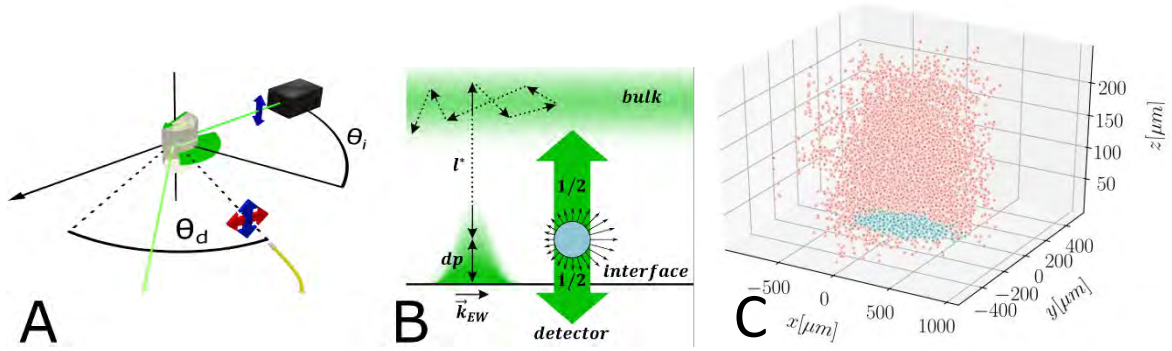

Figure 1 : Geometry of scattering experiment (A,B) and of scattering events (single & multiple) (C)

References

[1] A. Giuliani, R. McKenzie, and B. Loppinet, "Near wall velocimetry on a rheometer," *J. of Rheoogyl.* p 93–104 (63) **2019**, doi/10.1122/1.5047020

[2] A Giuliani, B. Loppinet, **2021** "Evanescent Wave Dynamic Light Scattering of Turbid Samples", submitted

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

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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.

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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.

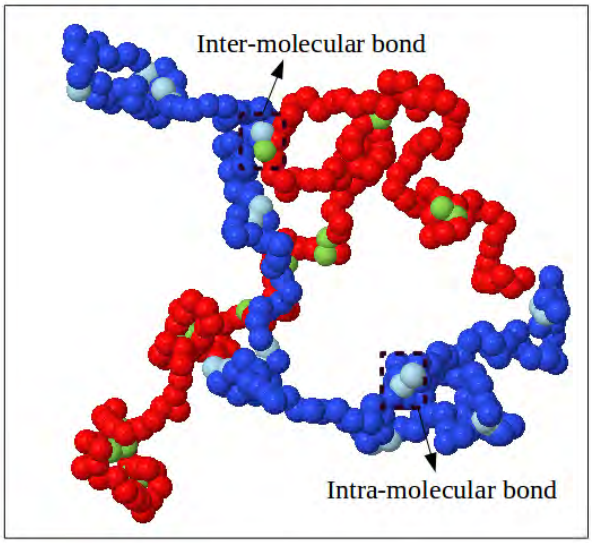

Figure 1: *Representative snapshot from MD simulations for the computation of the effective interactions between linear-SCNPs with reversible bonds.*

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 .

References

[1] M. Gonzalez-Burgos, A. Latorre-Sanchez, J. A. Pomposo, Chemical Society Reviews, 2015, 44, 20 pages, DOI: 10.1039/C5CS00209E .

[2] J. Rubio-Cervilla, H. Frisch, C. Barner-Kowollik and J. A. Pomposo, Macromolecular Rapid Communications, 2019 , 40, 6 pags, DOI: 10.1002/marc.201800491.

[3] M. Formanek, L. Rovigatti, E. Zaccarelli, F. Sciortino and Angel J. Moreno, submitted.

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

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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).

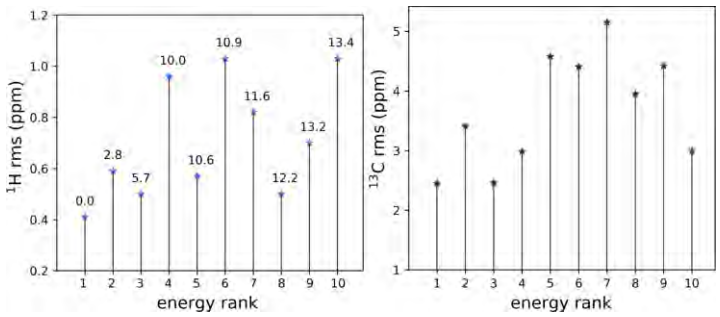

Figure 1: *^{1}H and ^{13}C RMS values obtained after comparison of experimental and theoretical NMR parameters for Z'=2 polymorph of furazidin.*

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

References

[1] M. K. Dudek, P. Paluch, E. Pindelska *Acta Cryst,* **2020**, B76**,** 322

[2] M. K. Dudek, P. Paluch, J. Śniechowska, K. P. Nartowski, G. M. Day, M. J. Potrzebowski *CrystEngComm* **2020**, 22, 4969

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]

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

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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.

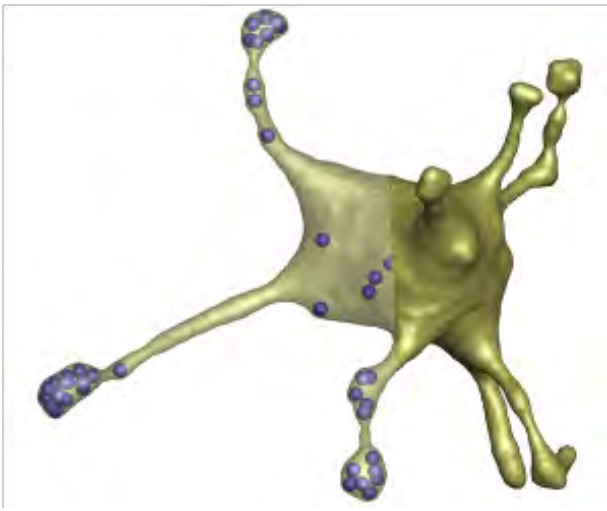

Figure 1: *Dynamic formation of an astrocyte-like shape from a 3D simulation of a vesicle enclosing active particles.*

References

[1] H. R. Vutukuri, M. Hoore, C. Abaurrea-Velasco, L. van Buren, A. Dutto, T. Auth, D. A. Fedosov, G. Gompper, J. Vermant, *Nature* **2020**, *586*, 52-56. DOI:10.1038/s41586-020-2730-x

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]

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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.

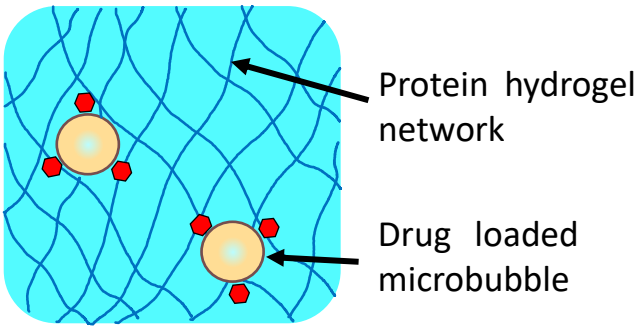

Figure 1: *Schematic of microbubbles encompassed within protein hydrogel.*

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.

References

[1] M.D.H Hughes, S.E. Cussons, N. Mahmoudi, D.J. Brockwell and L. Dougan, Single molecule protein stabilisation translates to macromolecular mechanics of protein network, Soft Matter, 2020, 16: 6389

[2] X. Dong, L. Xiafang, K. Kingston, E. Brewer, B.A. Juliar, O.D. Kripfgans, J.F. Brian, R.T. Francheschi, A.J. Putman, L, Zheng, M.L. Fabiilli. *Acta Biomaterialia,* **2019** 97, 409-419, DOI: 10.1016/j.actbio.2019.08.016

[3] M. Bourn, D.V.B. Batchelor, N. Ingram, J.R. McLaughlan, L. Coletta, S.D. Evans, S.A. Peyman. *Journal of Controlled Release,* **2020** 326, 13-24, DOI: 10.1016/j.jconrel.2020.06.011

[4] A. Aufderhorst-Roberts, M.D.G Hughes, A. Hare, D.A. Head, N. Kapur, D.J. Brockwell and L. Dougan, Reaction Rate Governs the Viscoelasticity and Nanostructure of Folded Protein Hydrogels, Biomacromolecules 2020, 21: 4253

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*

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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.

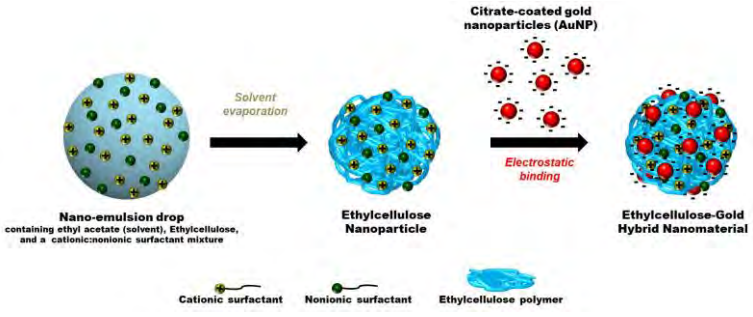

Figure 1: *Scheme of the preparation of ethylcellulose-gold hybrid nanomaterials.*

References

[1] V.P. Ananikov. Organic-inorganic hybrid nanomaterials. Nanomaterials 2019; 9: 1197-2003

[2] G. Calderó, R. Montes, M. Llinàs, M.J. García-Celma, M. Porras, C. Solans. Studies on the formation of polymeric nano-emulsions obtained via low-energy emulsification and their use as templates for drug delivery nanoparticle dispersions. Colloids and Surfaces B: Biointerfaces 2016; 145: 922-931

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]
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[2]*Forschungszentrum J lich GmbH, J lich Centre for Neutron Science JCNS, Outstation at Heinz Maier-Leibnitz Zentrum, Lichtenbergstraße 1, Garching, Germany.*

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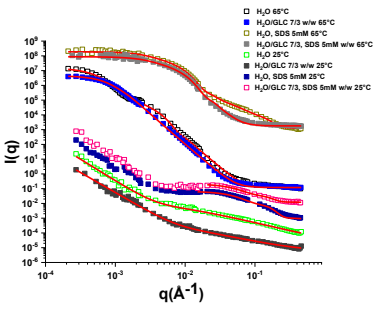
Hydroxypropylcellulose (HPC), one of the most well-known cellulose derivatives, is a surface-active non-ionic polymer. Nowadays HPC is used as emulsifier, stabilizer, thickener and film former in foods, cosmetics and paints. Because of this it is relevant its behaviour in commonly used co-solvent such 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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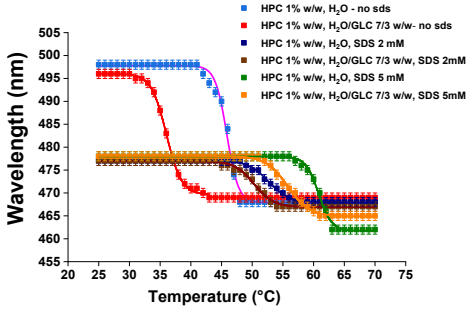

2

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.

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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

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[2] *Institut Laue Langevin, Grenoble, France*
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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

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

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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.

References

[1] M. Karg, A. Pich, T. Hellweg, T. Hoare, L. A. Lyon, J. J. Crassous, D. Suzuki, R. A. Gumerov, S. Schneider, I. I. Potemkin, W. Richtering *Langmuir* **2019**, *35*, 6231-6255. DOI:https://doi.org/10.1021/acs.langmuir.8b04304

[2] A. M. Howe, S. Desrousseaux, L. S. Lunel, J. Tavacoli, H. N. Yow, A. F. Routh *Adv. Colloid Interface Sci.* **2009**, *147-148*, 124-131. DOI:https://doi.org/10.1016/j.cis.2008.07.008

[3] D. Truzzolillo, S. Sennato, S. Sarti, S. Casciardi, C. Bazzoni, F. Bordi *Soft Matter* **2018**, *14*, 4110. DOI:https://doi.org/10.1039/C7SM02357J

[4] E. Daly, B. R. Saunders *Phys. Chem. Chem. Phys.* **2000**, *2*, 3187-3193. DOI:https://doi.org/10.1039/B002678F

[5] G. Del Monte, F. Camerin, A. Ninarello, N. Gnan, L. Rovigatti, E. Zaccarelli *J. Phys.: Condens. Matter* **2021**, *33*, 084001. DOI:https://doi.org/10.1088/1361-648X/abc4cb

[6] G. Del Monte, D. Truzzolillo, F. Camerin, A. Ninarello, E. Chauveau, L. Tavagnacco, N. Gnan, L. Rovigatti, S. Sennato, E. Zaccarelli *submitted* **2021**, , . DOI:

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

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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.

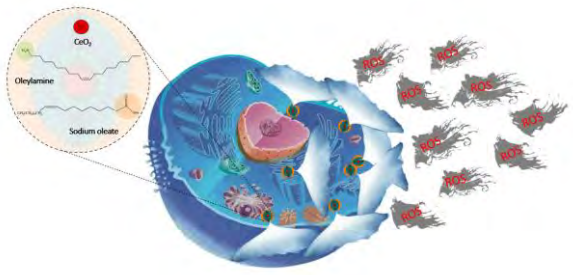

Figure 1: *Antioxidant action of cerium oxide nanoparticles in a eukaryotic cell.*

References

[1] S. Rajeshkumar, P. Naik *Biotechnology Reports,* **2018** 17, 1-5, https://doi.org/10.1016/j.btre.2017.11.008.

[2] T. Montini, M. Melchionna, M. Monai, P. Fornasiero *Chemical Reviews,* **2016** 116, 5987-6041, https://doi.org/10.1021/acs.chemrev.5b00603.

[3] N. Gallucci, G. Vitiello, R. Di Girolamo, P. Imbimbo, D. M. Monti, O. Tarallo, A. Vergara, I. Russo Krauss, L. Paduano *Nanomaterials,* **2021** 11, 542-558, https://doi.org/10.3390/ nano11020542.

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

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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.

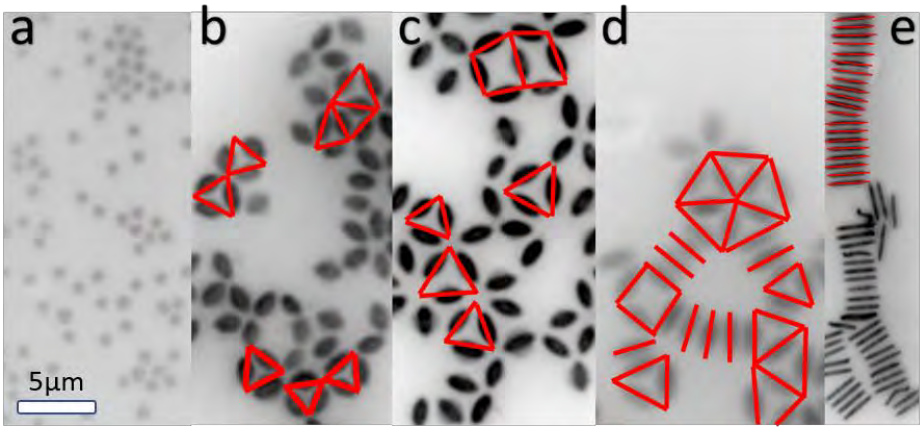

Figure 1: *Colour inverted fluorescence micrographs of spherical composite microgels (a) and ellipsoidal composite microgels with an aspect ratio ρ equal to 2.1 (b), 2.6 (c), 3.3 (d) and 8.8 (e) assembled at the air-water interface at 20°C. Some of the typical assemblies are highlighted with red lines.*

References

[1] J. J. Crassous, A. M. Mihut, E. Wernersson, P. Pfleiderer, J. Vermant, P. Linse, P. Schurtenberger *Nat. Commun.,* **2014** 5**,** 1-7, DOI: 10.1038/ncomms6516

Diarylethene-crosslinked photoswitchable PNIPAAm microgels

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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.

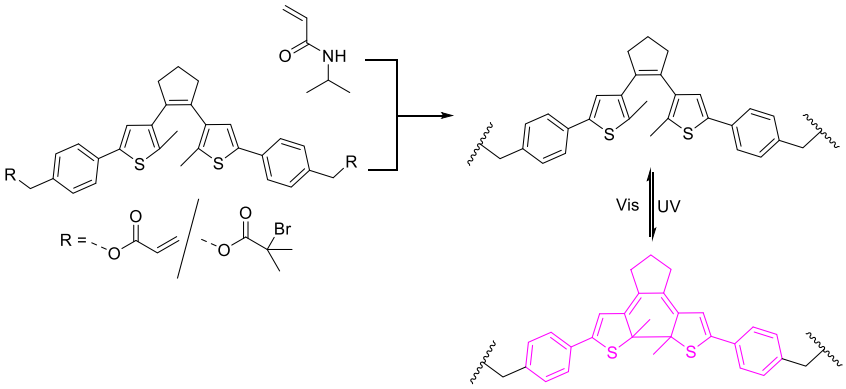

Figure 1: *Reversible photoisomerization of DAE-crosslinked PNIPAAm µgels.*

References

[1] Maxim Dirksen, Carina Dargel, Lukas Meier, Timo Brändel and Thomas Hellweg *Colloid Polym. Sci*, **2020** 298, 505–518. DOI: https://doi.org/10.1007/s00396-020-04632-5

[2] Victoria K Switacz, Sarah K. Wypysek, Rudolf Degen, Jérôme J. Crassous, Marc Spehr and Walter Richtering *Biomacromolecules*, **2020** 21, 4532–4544, DOI: https://doi.org/10.1021/acs.biomac.0c00478

Using Dissipative Particle Dynamics for Investigating Surfactant Solutions Under Shearing

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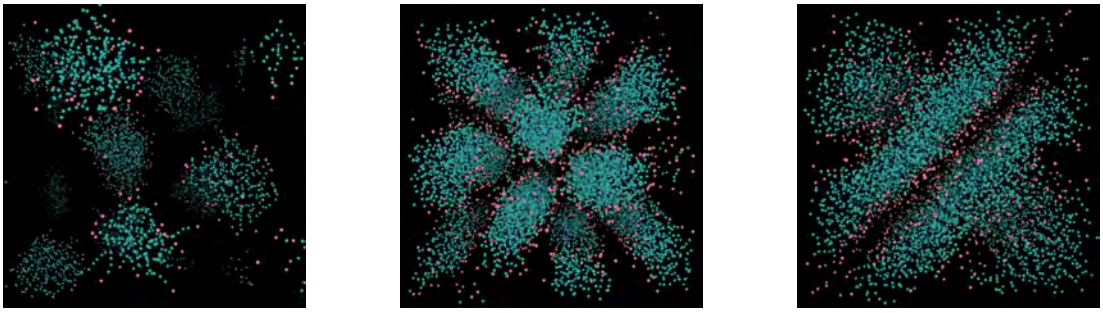
Surfactants are present in many everyday products such as detergents and shampoos. Because of the amphiphilic nature of surfactant molecules, they self-assemble into lyotropic liquid crystal structures when in solution. There exists a wide range of possible solution phase structures, e.g. micellar, hexagonal, 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.

References

[1] W. Humphrey, A. Dalke, K. Schulten, 'VMD - Visual Molecular Dynamics', *J. Molec. Graphics* **1996**, *14*, 33-38. DOI:10.1016/0263-7855(96)00018-5

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

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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].

References:

[1] S. Mallasandra Krishnappa, et. al. *Journal of Molecular Liquids,* (2020), **317**, 114244

[2] R. Zentel, et al, *Macromolecules*, (1985), **18**, 960.

[3] A. Schönhals, et al., *Macromolecules*, (1998), **31**, 9019.

[4] C. Shick, et al, *Macromolecular Chemistry and Physics*, (2001). **202**, 1398.

[5] A. L. Agapov, A. P. Sokolov, *Macromolecules*, (2011) **44**, 4410.

Glyceryl monooleate based lipid liquid crystalline nanoparticles with glyceryl monolaurate additives

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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.

References

[1] G. Garg, S. Saraf, S. Saraf, *Biological and Pharmaceutical Bulletin*, **2007**, Vol. 30, 350-353, DOI: 10.1248/bpb.30.350

[2] N.M. Lakshmi, P.R. Yalavarthi, H.C. Vadlamudi, J. Thanniru, G. Yaga, *Current drug discovery technologies*, **2014**, Vol. 11, 181-188, DOI: 10.2174/1570163811666140505125923

[3] N. Alcaraz, B.J. Boyd, *Current medicinal chemistry*,2017, Vol. 24, 470-482, DOI:10.2174/0929867323666160817141556

[4] A. Krislee, C. Fadly, D.A.A. Nugrahaningsih, T. Nuryastuti, F.O. Nitbani, E.N. Sholikhah, *BMC proceedings,* **2019**, Vol. 13, 1-6, DOI: 10.1186/s12919-019-0174-9

[5] E. Subroto, R. Indiarto, *Food Research*, **2020**, Vol. 4, 2355-2365, DOI: 10.26656/fr.2017.4(6).324

[6] H.G. Preuss, B. Echard, M. Enig, I. Brook, T.B. Elliott, *Molecular and cellular biochemistry*,

2005, Vol. 272, 29-34, DOI: 10.1007/s11010-005-6604-1

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

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Lipids are self-assembling molecules, responsible for compartment formation in living cells. Besides real crystals and bilayers, they also form mesophases thanks to their aptitude to modulate interface curvature. Therefore, lipid-based structures such as solid lipid nanoparticles, liposomes, cubosomes, and other hybrids are interesting for 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].

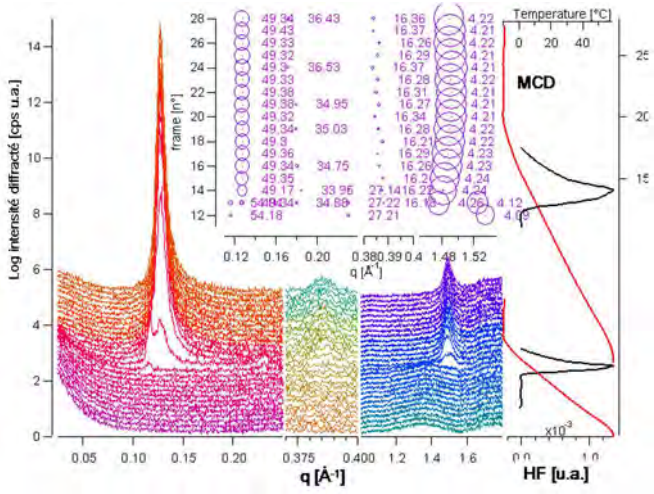

Figure 1: Crystallization of emulsified cocoa butter. Three-dimensional representation of the evolution of the X-ray diffraction patterns recorded at SAXS and WAXS during cooling at v_C=4°C/min from 60°C to -10°C. The diffraction patterns are recorded every 30 seconds simultaneously with the DSC signal 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.

References

[1] Couvreur et al. Small 2008;4(2):247–253
[2] Artzner F et al, Cell Mol Biol 2000;46(5):967-978;Novakowski S et al, Sci Rep 2019;9, 552
[4] Ollivon et al. J. Therm. Anal. Cal. 2006;85, 219-224
[5] Kalnin et al. Food Res. Int. 2002;35, 927-934
[6] Michon et al. ISFRS proceedings 2003; 235-239
[7] Kalnin et al. Crystal Growth & Design 2004;4(6):1283-1293
[8] Pernetti et al. Current Opinion in Colloid & Interface Science 2007;12, 221-231
Pernetti et al. Food Hydrocolloids 2007;21, 855-861.

LCST behaviour and structure formation of alternating amphiphilic polymers in water

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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).

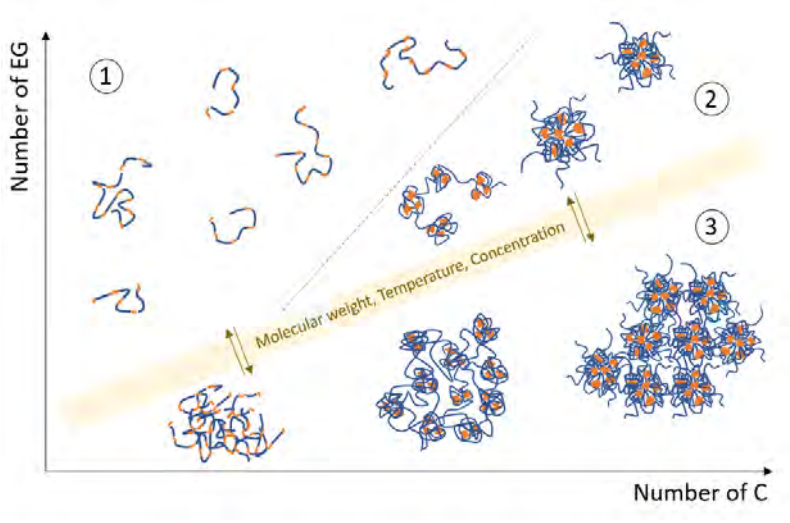

Figure 1: *Qualitative diagram representing the states of the amphiphilic polymers depending on the polymer composition.*

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

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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?

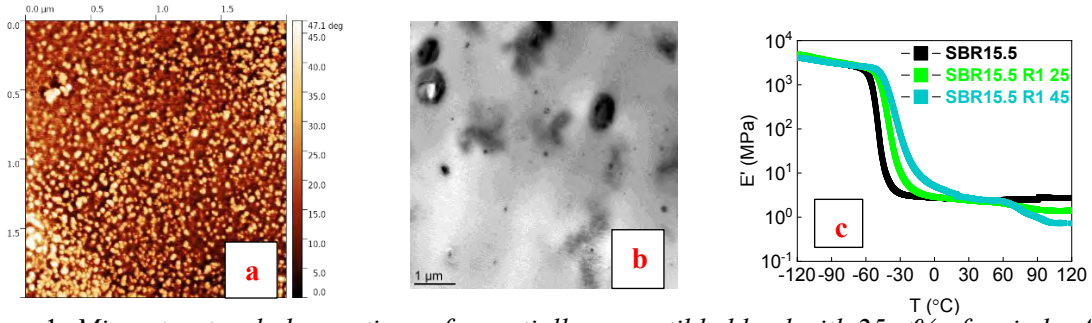

Figure 1: *Microstructural observations of a partially compatible blend with 25wt% of resin by AFM phase imaging (a) and TEM (b); storage modulus as a function of temperature of SBR and its blends with 25% wt or 45% wt of one of the studied resins (c).*

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.

References

[1] T.P. Lodge, T. McLeish *Macromolecules,* **2000** 33**,** 5278-5284, DOI: 10.1021/ma9921706

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

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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?

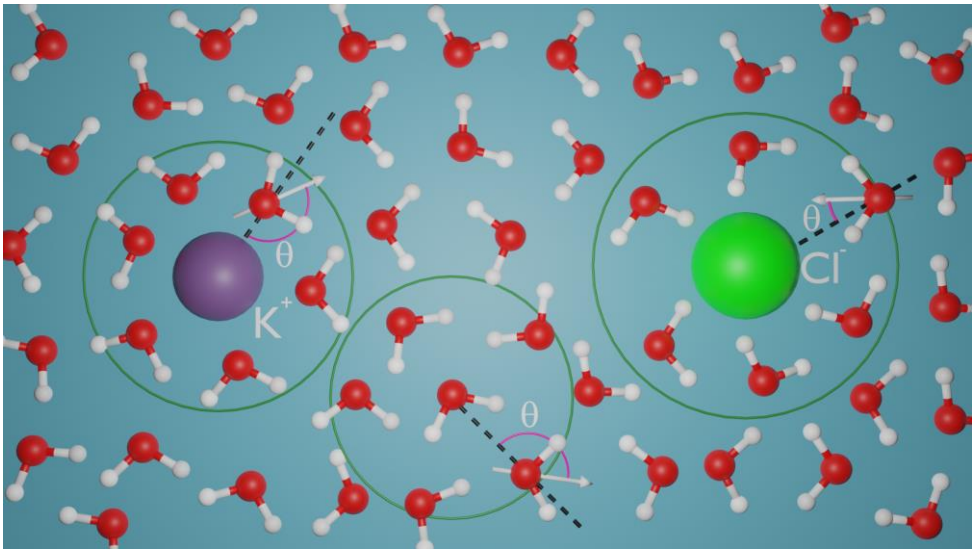

Figure 1: *Schematic representation of aqueous potassium chloride. First hydration shell around a potassium ion, chloride ion, and bulk water molecule shown in green circles and the definition of dipole angle θ is shown in pink arcs.*

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

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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.

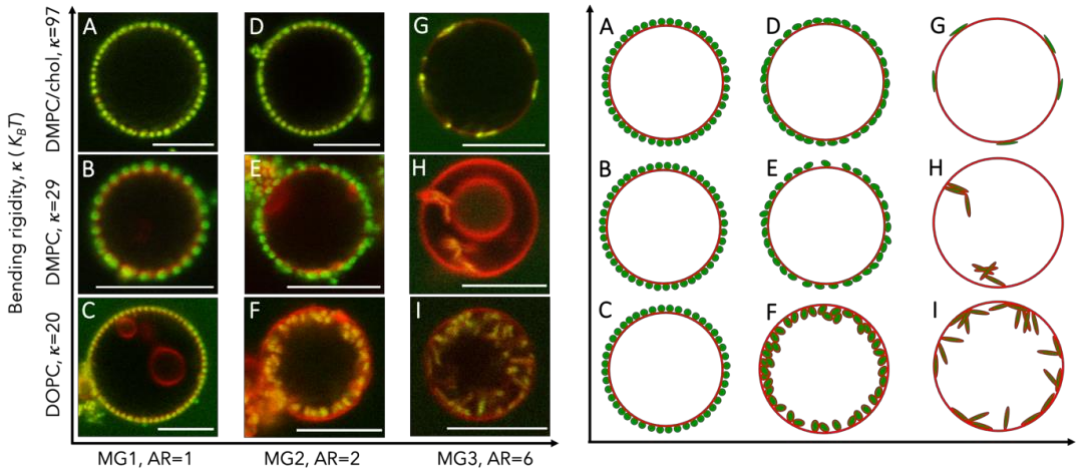

Figure 1: *Left panel: 2D CLSM images of adsorption and wrapping of microgel particles (green) on lipid membrane (red) in GUVs. The lipid composition was DMPC/chol (A, D, G), DMPC (B, E, H) and DOPC (C, F, I), and the microgel particles were either spherical MG1 (A-C), or ellipsoidal with different aspect 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.*

References

[1] Mitragotri, S., In Drug Delivery, Shape Does Matter. Pharmaceutical Research 2009, 26 (1), 232-234.

Hydrodynamic behavior of ensembles of synchronous microrotors

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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.

References

[1] B A Grzybowski, H A Stone, and G M Whitesides, Nature **405**, 6790 (2000);
B Kavčič, D Babič, N Osterman, B Podobnik, and I Poberaj, Appl. Phys. Lett. **95**, 2 (2009);
K Han, G Kokot, S Das, R G Winkler, G Gompper, and A Snezhko, Sci. Adv. **6**, 12 (2020)

[2] Y Fily, A Baskaran, and M C Marchetti, Soft Matter **8**, 10 (2012)

[3] Anatoly Malevanets and Raymond Kapral, J. Chem. Phys. **110**, 17 (1999);
I O Götze, and G Gompper, EPL **92**, 6 (2011);
I O Götze, and G Gompper, Phys. Rev. E **84**, 3 (2011)

Wrapping of non-spherical vesicles at lipid-bilayer membranes

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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.

References

[1] S. Dasgupta, T. Auth and G. Gompper *J. Phys. Condens. Matter* **2017**, *29*, 373003. DOI:10.1088/1361-648X/aa7933

[2] X. Yi, X. Shi, and H. Gao *Phys. Rev. Lett.* **2011**, *107*, 098101. DOI:10.1103/PhysRevLett.121.199902

[3] Q. Yu, S. Othman, S. Dasgupta, T. Auth and G. Gompper *Nanoscale* **2018**, *10*, 6445. DOI:10.1039/C7NR08856F

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

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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.

References

[1] J. Seydel, Drug-Membrane Interactions: Analysis, Drug Distribution, Modeling, Wiley-VCH, 2003.

[2] K. Bittermann, S. Spycher and K.U. Goss, Chemosphere, 144, 382 (2016).

[3] S. Jakobtorweihen, T. Ingram and I. Smirnova, J. Comput. Chem., 34, 1332 (2013).

[4] S. Marrink, H. Risselada, S. Yefimov, D. Tieleman and A. de Vries, J. Phys. Chem B, 111, 7812 (2007).

[5] M. Webb, J. Delannoy and J. de Pablo, J. Chem. Theory Comput., 15, 1199, (2019).

[6] T. Bereau and K. Kremer, J. Chem. Theory Comput., 11, 2783 (2015).

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

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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 $\%_{wt}$.

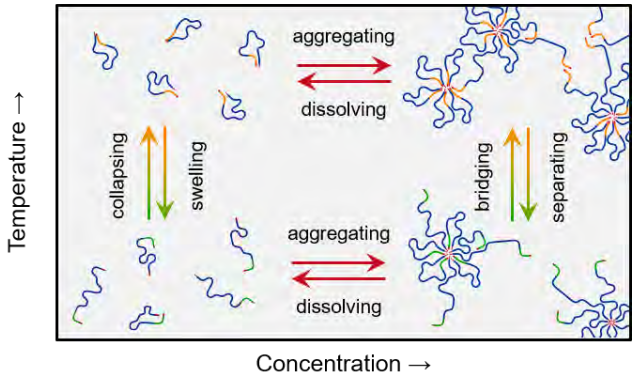

Figure 1: Scheme of interaction and aggregation behaviour of HMTR block-polymers in solution.

References

[1] M. Hechenbichler, A. Laschewsky, and M. Gradzielski, Colloid Polym. Sci. **299**, 205 (2021), DOI: 10.1007/s00396-020-04701-9.

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

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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.

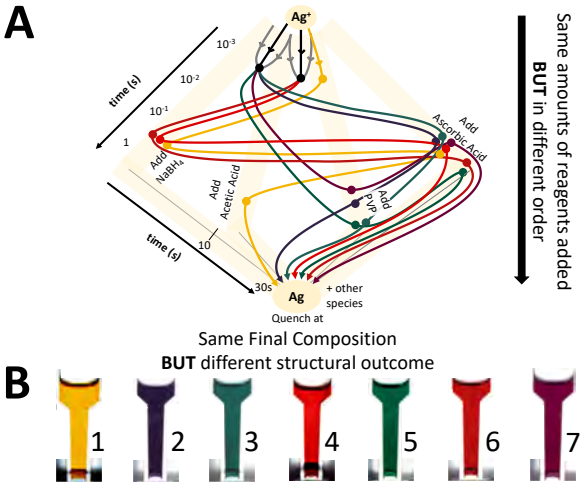

Figure 1: *(A) Seven synthetic pathways differing only by the sub-second sequencing of reagents additions. Silver ions are reduced by $NaBH_4$ and ascorbic acid in the presence of a polymeric stabilizer, PVP, in acidic conditions provided by large concentrations of acetic acid. The final composition 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

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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.

References

[1] The World Health Organisation, https://tinyurl.com/wojctpy, last accessed 11 April 2021.