Plasmonic Stimulation of Gold Nanorods for the Control of Living Materials

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Composites of living cells in polymer gel matrices are called “Living Materials”. They are useful for the controlled release of drugs that are secreted by the cells while protecting them and their environment. Here, we establish optical control of drug production by introducing gold nanorod composites (GNC) as cores inside Living Materials shells that contain engineered thermoresponsive *Escherichia coli* bacteria. Incident near-infrared light is absorbed by the GNC core, which generates heat that diffuses to shell layer and activates the thermoresponsive bacteria, for example inducing the production of Green Fluorescence Proteins (GFP) (see illustration below). Requirements for this enhanced Living Materials include homogenous GNC distribution and the thermal stability of GNC.

In this contribution, we will introduce the colloidal and physico-chemical properties of the gold nanorods and their composites. The colloidal stability of the GNC was investigated by UV-VIS spectroscopy and cryo-TEM. The photothermal conversion efficiency (PCE) of the Living Material was then determined by Roper´s Method [1]. Heating from an initial 22°C to 45 °C was induced by illumination. Heating rates were analyzed as a function of optical power density and the concentration of the Gold Nanorods in the core layer. Thermography on the shell layer surface indicated the temperature distribution on the surface of the material sample. Finally, the GFP production with and without light stimulation was observed by fluorescence microscopy.
The goal of this project is to develop stimuli-responsive Living Therapeutic Materials, that can be used in biomedical applications and supplement existing schemes for drug delivery (oral, injection, nasal, ocular). The concept profits from the wide range of engineered bacteria that can provide different drugs. The optical stimulus discussed here can be combined with other stimuli.

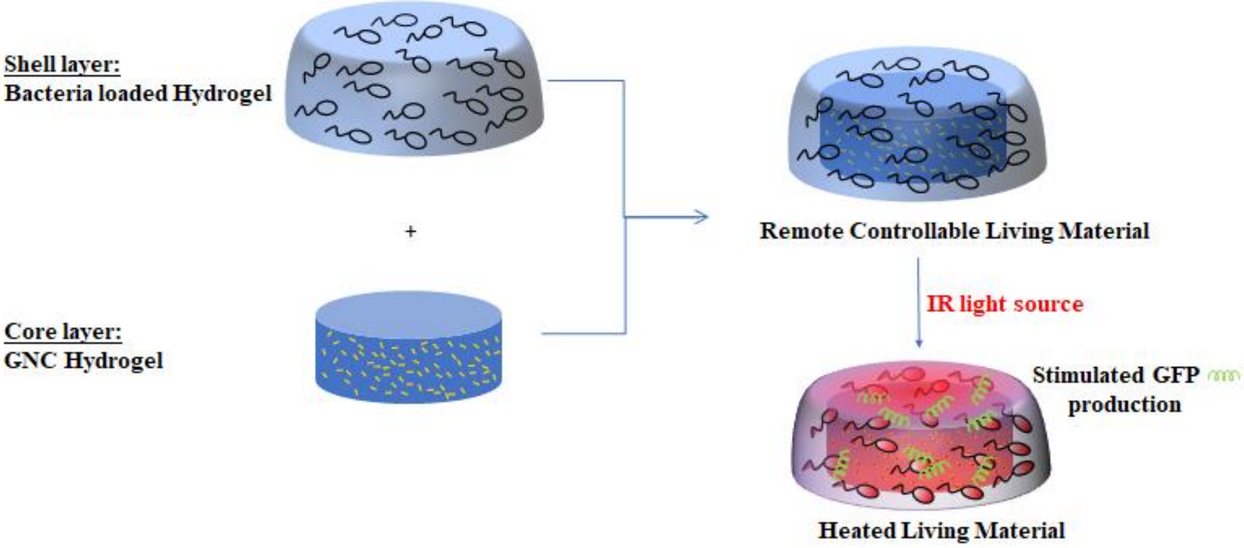

Figure 1. Schematic depiction of the GNC core-shell construct. The shell layer includes bacteria which is externally stimulated to produce GFP.

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Tuning the Magnetic Properties of Hematite Nanospindles

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Hematite nanospindles receive great attention due to their uncommon orientation behavior towards magnetic fields. In contrast to most elongated magnetic nanoparticles that are dominated by shape anisotropy, weakly ferromagnetic hematite nanospindles bear a strong magnetocrystalline anisotropy that drives the alignment of their long axis perpendicular to an applied magnetic field [1-3]. This leads to interesting behavior in static and dynamic magnetic fields [4-6] and makes them relevant for technological applications such as nanoprobes, sensors, active matter, or directional anisotropic materials [7,8]. To further tune their magnetic properties and the associated orientation behavior, we follow the approach to structurally convert hematite nanospindles into a magnetic core-shell morphology.

In this contribution we will present our latest results on the formation of a ferrimagnetic shell surrounding hematite nanospindles. The preparation is based on the seeded growth of synthesized nanospindles with systematically varying amounts of iron oxide. The formation of an iron oxide coating is confirmed by a combination of transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), Mössbauer spectroscopy and field- and temperature dependent magnetization measurements. Mössbauer spectroscopy further reveals a complex magnetic morphology of the coated spindles. The magnetically composite structure is in line with exchange interactions observed by magnetization measurements.

The coexistence of the two different magnetic materials and the corresponding interface promises tunable magnetic properties of the nanospindles, that will be further exploited towards directionally anisotropic materials [9].

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Lyotropic Liquid Crystal Phase Behavior of High Molar Mass Reverse Poloxamers and their Use as Structure-Directing Agents

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Poloxamers, also known as “Pluronics”, are amphiphilic block copolymers composed of poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEO) with the generic structure PEO$_{m/2}$PPO$_{n}$PEO$_{m/2}$ (Figure 1, top). Due to their non-toxicity and their surface-active properties, these polymers find broad use as industrial surfactants, as additives for cosmetics or pharmaceutics and as structure directing agents for the production of mesoporous materials. Unsurprisingly, they have been subject to many fundamental scientific studies, e.g. concerning their micellization or lyotropic liquid crystal (LLC) phase behavior.

In contrast, little is known about the LLC properties and potential applications of their counterpart, the Reverse Poloxamers PPO$_{n/2}$PEO$_{m}$PPO$_{n/2}$. To close this knowledge gap, we synthesized Reverse Poloxamers, with systematically varied block lengths of $n/2 = 32 – 278$ and $m = 90 – 454$, using a recently developed, metal-free polymerization approach [1]. By screening numerous Reverse Poloxamers, we determine the hydrophilic to lipophilic balance range in which LLC phases form and investigate them by polarizing optical microscopy, differential scanning calorimetry and small-angle X-ray scattering. Compared to the few commercially available Reverse Poloxamers [2, 3], we find that our custom-made versions with high-molar masses form a much broader variety of different LLC phases with extraordinary temperature stability (Figure 1, bottom), which makes them excellent candidates for various applications. We verify the latter by subjecting the Reverse Poloxamers to the true liquid crystal templating process, producing ordered mesoporous silica materials with regular structure and narrow pore size distributions. Most impressingly, the accessible pore diameters range from approximately 5 to 20 nm, which has been unprecedented so far with the applied process [4].

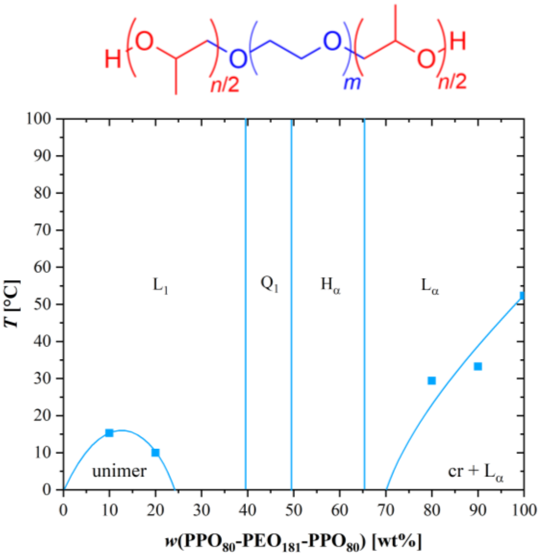

Figure 1. Generic structure of Reverse Poloxamers (top) and phase diagram of a Reverse Poloxamer with water (bottom).

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Defined core-shell particles as the key to complex interfacial self-assembly

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Self-assembly of colloidal particles can yield defined surface patterns over macroscopic areas. However, the prevalence of hexagonal symmetries limits the structural versatility of self-assembling monolayers. In 1998 E. A. Jagla computationally modelled core-shell particles with two interaction length-scales and predicted the formation of complex minimum energy configurations [1]. Despite the elegance of this approach, its experimental realization has remained largely elusive. Here, we use iniferter-type controlled radical polymerization to create core-shell particles consisting of a silica core surface-functionalized with a non-crosslinked polymer shell (figure 1a) [2]. Upon interfacial compression, the resulting core-shell particles arrange in well-defined dimer, trimer and tetramer lattices before transitioning into complex chain and cluster phases. The experimental phase behavior is accurately reproduced by Monte-Carlo simulations and minimum energy calculations, suggesting that the interfacial assembly interacts via a pair-wise additive Jagla-type potential (figure 1b). The possibility to control the interaction potential via the interfacial morphology provides a framework to realize structural features with unprecedented complexity from a simple, one-component system [3].

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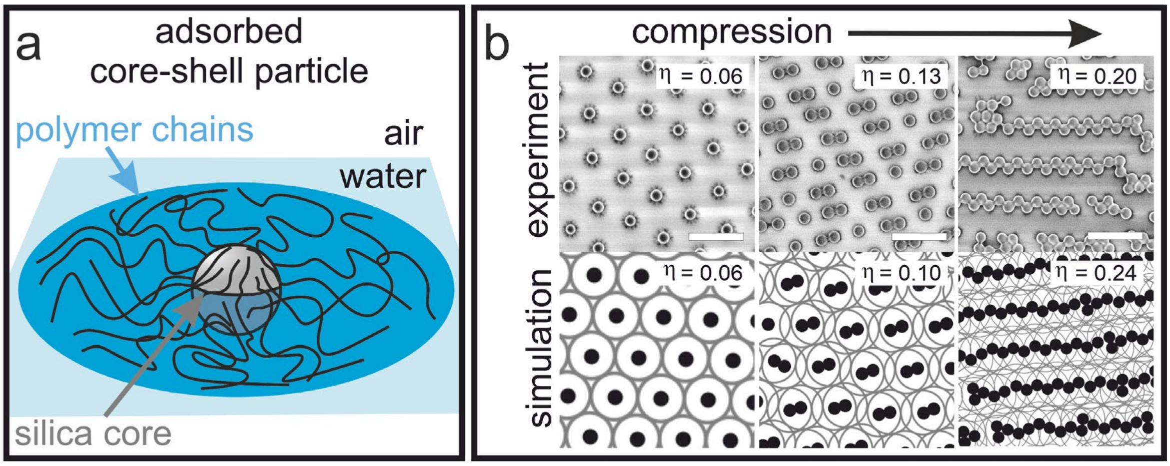

Figure 1. Particle morphology and phase behavior. a) Core-shell particle at the air/water interface. b) Scanning electron micrographs of the particle lattice upon interfacial compression and corresponding Monte-Carlo simulations. Scale bar: 1 µm.

Structure and stability of DOPG model membranes in the presence of the saponin aescin

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Plasma membranes of procaryotes are represented by a large share of lipids such as phosphatidylglycerols. In this study the role of charged lipids in the plasma membrane is investigated with respect to the interaction with the antiviral saponin aescin in the membrane.

Aescin is a natural surfactant which can be found in the horse chestnut and is known for its anti-inflammatory, anti-exudative, anti-oedematous and venotonic properties.[1-3] Small unilamellar vesicles (SUVs) made of 1,2-dioleoyl-*sn*-glycero-3-phosphoglycerol (DOPG) with different amounts of aescin are analysed by small angle neutron and X-ray scattering (SANS/SAXS) (Fig. 1 left). Furthermore, the chain-chain correlation distance of lipid/saponin mixtures in the SUV structures is studied by wide angle X-ray scattering (WAXS)(Fig. 1 right). Small angle scattering data are evaluated with the Kratky-Porod (KP) and Modified-Kratky-Porod (MKP) method as well as by the Guinier approximation. Afterwards the small angle scattering data is Fourier transformed with the software package *GIFT*.[4] Wide angle scattering data is analyzed by using Lorentzian fits to determine the chain-chain correlation distance. Complete miscibility of DOPG and aescin is found even at a lipid/saponin ration of 1:1.

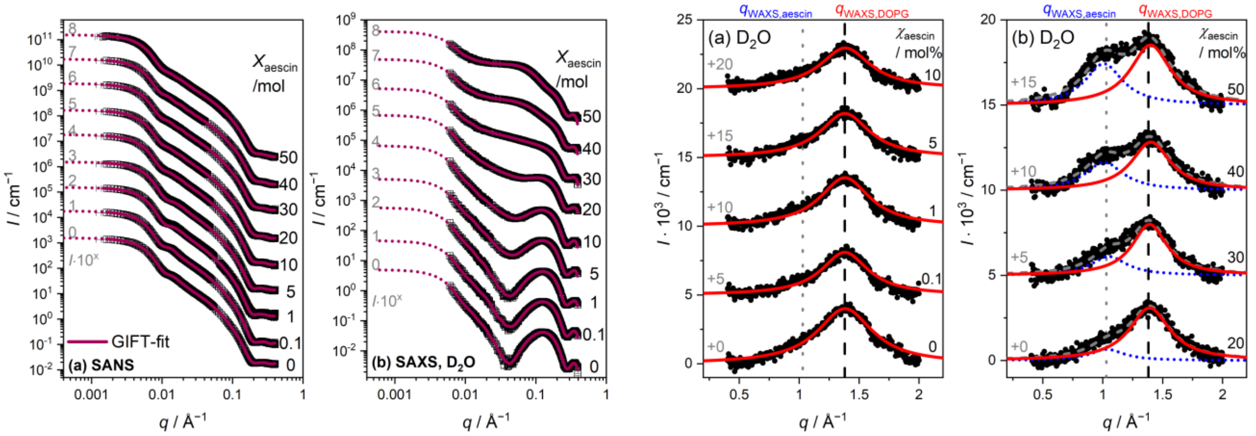

Figure 1. Left: SANS and SAXS scattering curves with fits from the software package *GIFT*. Right. WAXS scattering data with Lorentzian-fits to determine q_{WAXS}.

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Block Copolymers in 3D Confinement: Janus Nano Cups

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Block copolymer nanoparticles with unusual morphologies and complex surface are currently in high demand due to their unique physical properties as non-trivial soft matter.[1] Compared to topologies such as spheres, cylinders and vesicles,[2] the precise formation of patchy polymeric cups with defined surface structure are still rare. Geometrically controlled anisotropic Janus nanoparticles (JNP) have gained considerable interest in the polymer science community. However, currently only a few controlled bottom-up synthesis routes are known that enable JNPs synthesis with high selectivity towards the desired geometries.[3] In the present work, we aim to achieve cup-shaped JNPs and the control of their size and curvature. First, several ABC triblock terpolymers consisting of polystyrene-*b*-polybutadiene-*b*-poly (tert-butyl methacrylate) (SBT) are emulsified in conjunction with high-molecular poly (methyl methacrylate) (PMMA) in varying blending ratios through a SPG membrane, followed by evaporation-induced confinement assembly (EICA) process. This led to the formation of two hemispherical particles, with PMMA forming a hemisphere on its own and SBT instead, arranging in a concentric lamella-lamella morphology. In the second step, the PB microdomain is crosslinked with OsO_4, and the PMMA hemisphere is subsequently removed by washing with THF, whereby dispersed cup shaped JNPs are obtained. The curvature of the JNPs is controlled by the blending ratio of PMMA, as its content increases the more the curvature is decreasing, going from hemispheres to cups to disk like particles. The mechanical stability of the JNPs is controlled by the length of the PB phase through cross-linking, preventing the collapse of the cups. By removing the PMMA phase with THF and redispersing the SBT tulip bulb phase, it is possible to produce Janus nano cups in high yield. Further, the PT nanodomain is hydrolyzed, in order to produce negative charges, that can be paired with cationic species, *e.g.* Au NPs, in order to prove the Janus character. Due to the particular shape, the Janus nano-cups may find application in biotechnology and nanomedicine, as well as templating of inorganic materials and to perform as cargo in biotechnology and nanomedicine due to their cup-like shape.

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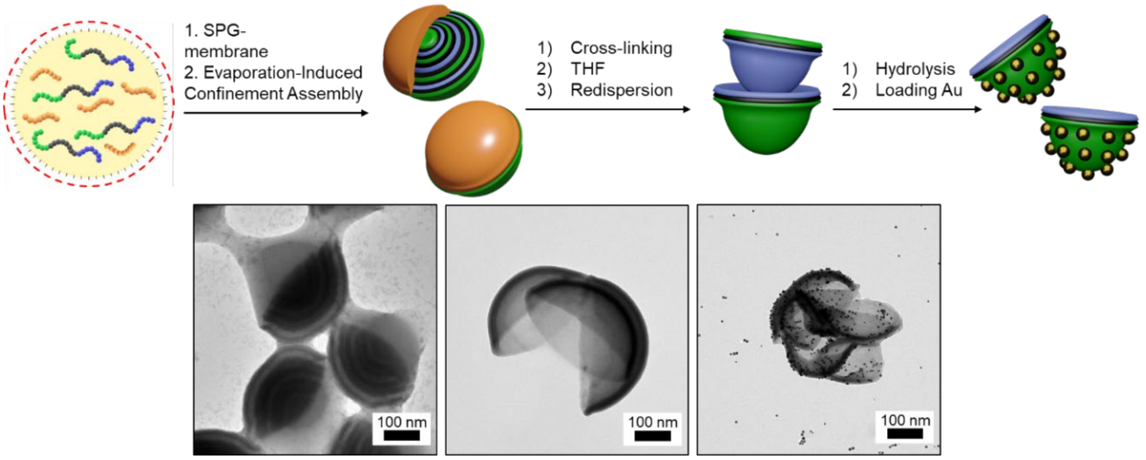

Figure 1. Self-assembly mechanism of Janus Nano Cups.

Chaotropic nano-ion binding as a gelation motif in cellulose ether solutions

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Nanometer-sized ions (nano-ions), such as the polyoxometalate $SiW_{12}O_{40}^{4-}$ (SiW, structure in Fig.1a), interact strongly with non-ionic interfaces, such as polymers[1] and non-ionic surfactants[2], due to a water-mediated driving force, called the chaotropic effect.[3] Due to the drastic effects that these interactions have on the properties of the interface, nano-ions have emerged as promising soft matter additives. In this study, we investigated the effects of chaotropic nano-ions on cellulose ethers, such as hydroxypropylcellulose (HPC, Fig.1a). Cellulose ethers are non-ionic cellulose-based polymers that find ample application as rheology modifiers in cosmetics, foods and drilling fluids in particular due to their molecular stiffness and their intrinsic tendency to aggregate in solution. We find that SiW binds to HPC in the millimolar range and thus induces a drastic increase in viscosity by a factor of 100, see Fig.1b, leading to gelation at higher SiW-concentrations (≈ 50 mM). These rheological effects are unprecedented in comparison to classical additives such as salts, or ionic surfactants as exemplified for SDS, see Fig.1b and appear presumably due to physical nano-ion crosslinking between polymer chains. Small Angle Neutron Scattering further revealed the emergence of a correlation peak at low SiW-concentrations (Fig.1c) that disappears in the presence of an electrolyte like NaCl or at higher SiW-concentrations. This intermittent polyelectrolyte-like behavior relates to the observed rheology trends. Chaotropic nano-ions thus emerge as novel gelation agents and nano-ion/polymer complexes might serve as smart soft materials due to their UV and heat sensitivity.

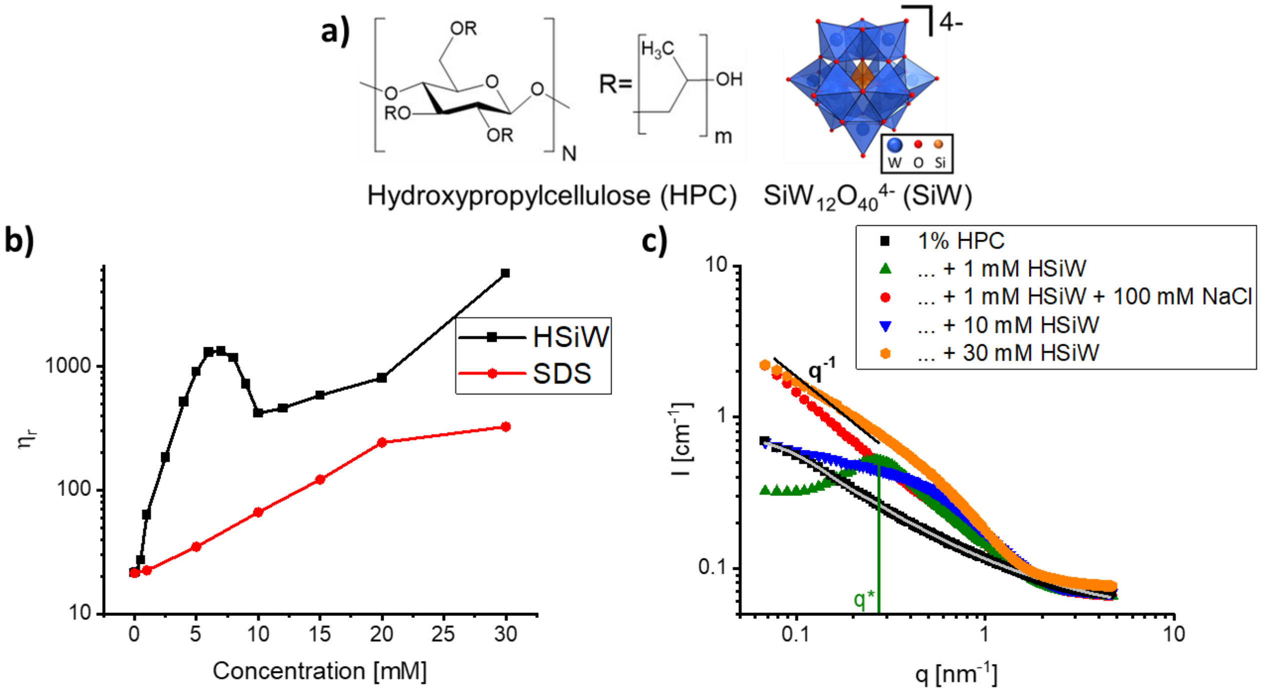

Figure 1. a) Chemical structures of HPC and SiW. b) Relative viscosities η_r of 5% w/w HPC in water upon addition of SiW or the ionic surfactant SDS respectively. c) SANS-spectra of 1% HPC in D_2O at different concentrations of HSiW and with NaCl. The spectra are in absolute scale.

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3D Printing of Photonic Colloidal Glasses into Objects with Isotropic Structural Color

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Structural color is frequently exploited by living organisms for biological functions and has also been translated into synthetic materials as a more durable and less hazardous alternative to conventional pigments. Additive manufacturing approaches were recently exploited for the fabrication of exquisite photonic objects, but the angle-dependence observed limits a broader application of structural color in synthetic systems. Here, we propose a manufacturing platform for the 3D printing of complex-shaped objects that display isotropic structural color generated from photonic colloidal glasses. Structurally colored objects are printed from aqueous colloidal inks containing monodisperse silica particles, carbon black and a gel-forming copolymer. Rheology and Small-Angle-X-Ray-Scattering measurements are performed to identify the processing conditions leading to printed objects with tunable structural colors. Multimaterial printing is eventually used to create complex-shaped objects with multiple structural colors using silica and carbon as abundant and sustainable building blocks.

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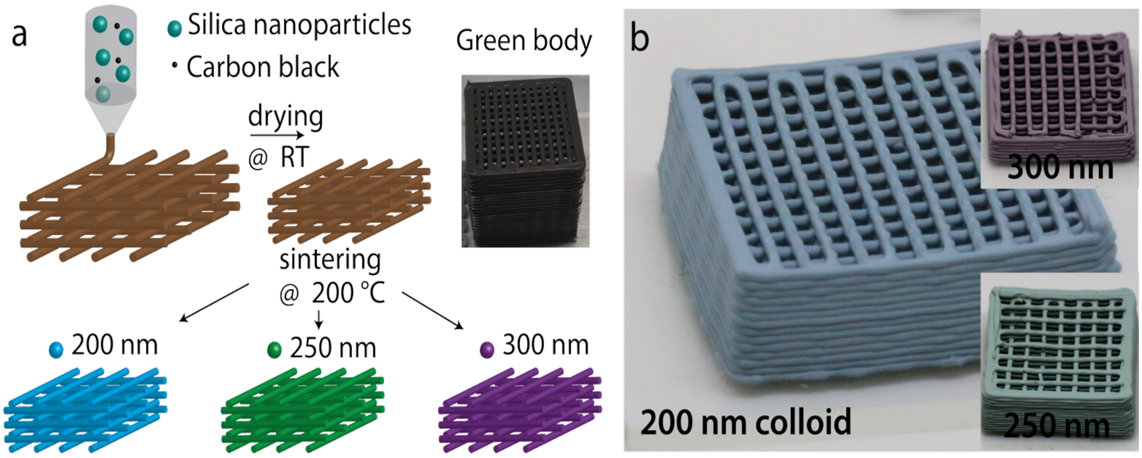

Figure 1. a) Sketch of the DIW 3D printing setup and the procedure of achieving structural color. b) Preliminary results we obtained by 3D printing low-index silica nanocolloids. The size of the nanocolloid dictates the color of the 3D printed object. Printlines of the grids are approximately 0.3 mm thick and the 3D printed grids are 1.2 cm x 1.2 cm.

A Spiropyrane-based dual pH- and Photoswitchable Surfactant for the Targeted Manipulation of Emulsions and Other Colloids

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Stimuli-responsive surface-active molecules may alter their physicochemical characteristics upon the stimulation with an external trigger. Accordingly, their tendency to form micelles in solution, their adsorptive behavior on surfaces or the surface tension of aqueous solutions thereof can be manipulated by external stimulation with light, the pH value or other stimuli.[1, 2] These features render stimuli-responsive surfactants interesting materials for the manipulation of colloidal systems in an aqueous environment.[1] Recently, we demonstrated the synthesis and characterization of a surfactant, which possesses a spiropyrane moiety in its hydrophobic backbone (Figure 1).[3] This molecule, being able to switch from an apolar spiropyrane (SP) form to an ionic merocyanine (MC) counterpart, shows an interesting dual-responsivity to the pH value and light:[4] While under acidic conditions, a pronounced difference of the surface-activities between both forms is found, this behavior is suppressed at an elevated pH level. We exploited this behavior to manipulate the integrity of an oil-in-water emulsion. Furthermore, we are interested to extend the utilization of the surfactant also to other colloids for their targeted manipulation in an aqueous medium.

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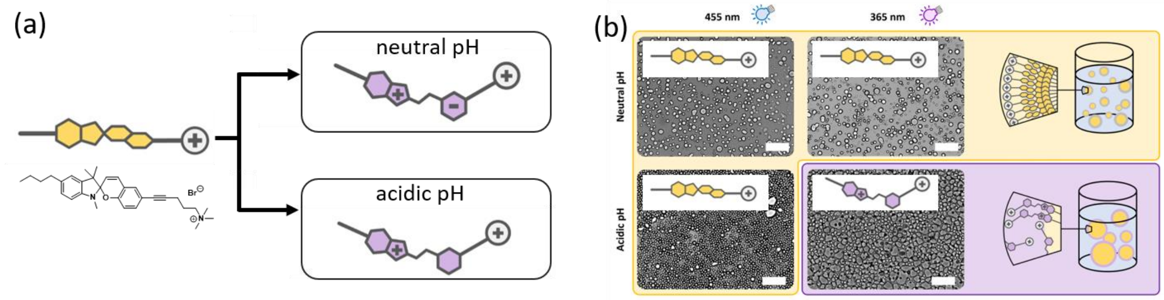

Figure 1: (a) Schematic representation of the prepared surfactant. The surfactant in its spiropyrane form (indicated as yellow) may isomerize to form a zwitterionic merocyanine (MC) under neutral, or a kationic MCH$^+$ form under acidic conditions. (b) The surfactant is used for the manipulation of an oil-in-water emulsion. An emulsion is stable under neutral conditions, while it can be demulsified via light irradiation under an acidic pH value.

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From Single Microgels to Dense Microgel Layers – Investigation by Atomic Force Microscopy

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Microgels are three-dimensionally crosslinked polymer networks that swell in a good solvent. They can change their size and internal structure in response to external stimuli such as temperature, pH or ionic strength. In addition, they are highly interfacial active and possess a rich phase behavior due to their soft and inhomogeneous structure. Based on their interfacial properties, they can be used in various applications, e.g., as emulsion stabilizers or surface coatings. However, there is very little data on the internal structure of microgels in dense layers.

In this study, we used Langmuir-Blodgett type depositions to transfer microgel monolayers at different surface pressures onto solid substrates [1]. These monolayers were then investigated *ex-situ* by atomic force microscopy to investigate (a) their two-dimensional structure and (b) the topography and internal structure of the microgels within the monolayers via force volume measurements.

The results of our measurements show that the confinement of microgels within dense monolayers has a profound impact on their internal structure. Single microgels exhibit an inhomogeneous internal structure at the solid-liquid interface with a stiff core in the center and a decreasing stiffness towards the periphery of the microgels [2]. With increasing compression of the monolayer, the microgels become noticeably stiffer in their core (see fig. 1) [3].

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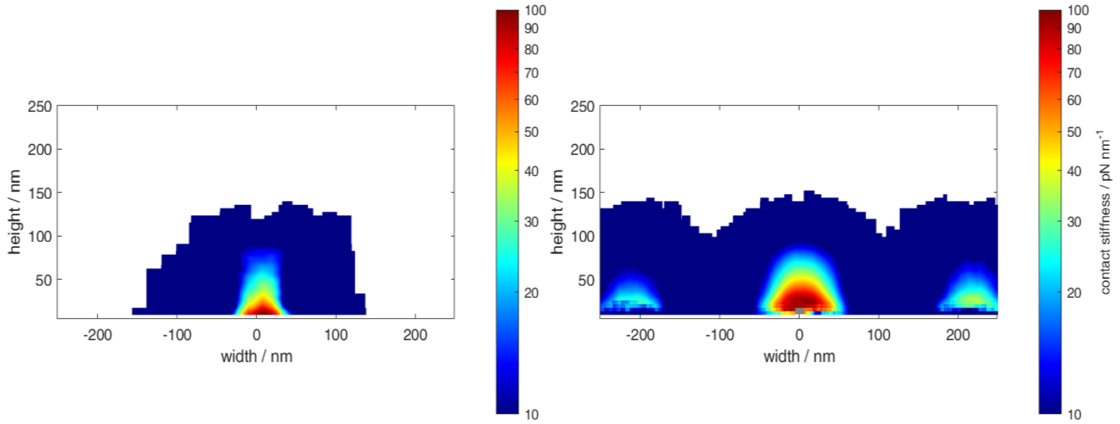

Figure 1. Averaged contact stiffness profile of single microgels (left) and microgels in a dense microgel layer (right) at 27°C at the solid-liquid interface.

Interface Driven Atomically Oriented 2D Assembly of Colloidal Gold Nanodisks Leads to Tunable Plasmonic Resonance

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Colloidal Nanoparticles (NPs) are broadly used to produce self-assembled superstructures, however, a little have been achieved on the 2D assembly of NPs with anisotropic shapes[1]. A key challenge with the anisotropic NPs is to assemble them into long-range positional and orientational order. We synthesize disk-shaped colloidal gold nanocrystals (AuNDs) and assemble them into two-dimensional iso-oriented ordered superlattices at the air-liquid interface using Langmuir method[2-3]. *In-situ* structural and optical properties of the ND assemblies have been monitored using grazing incidence small-angle X-ray scattering (GISAXS), X-ray reflectivity (XRR), grazing incidence X-ray diffraction (GIXD) and UV-vis spectroscopy. Au NDs assemble into a highly ordered 2D hexagonal superlattice and align preferentially with a specific atomic orientation at the air-liquid interface. A continuous blue shift of the plasmonic peak has been observed from the coherent ND assembles with increasing surface pressure[4]. Such preferentially oriented anisotropic NCs is expected to lead to novel optoelectronic properties, which have promising prospects for future applications.

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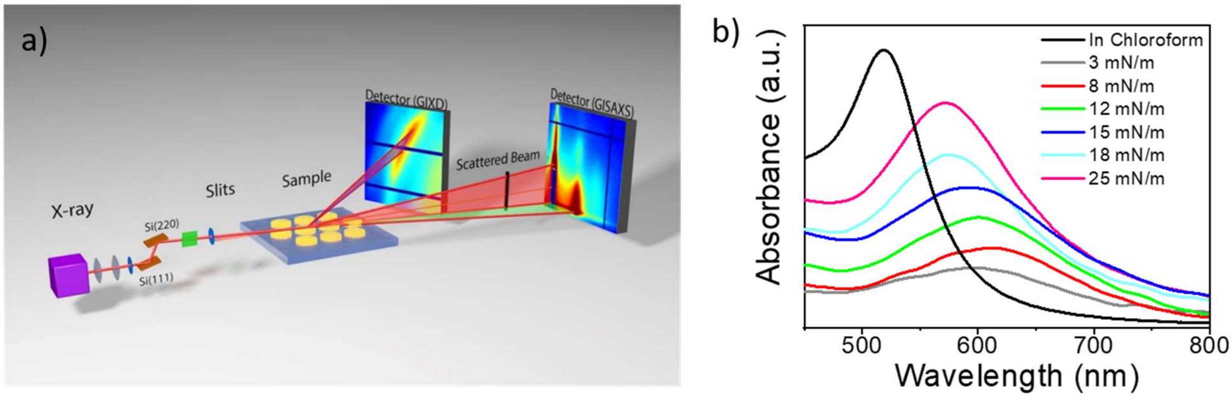

Figure 1. a) A schematic of simultaneous GISAXS, GIXD geometry to study *in-situ* self-assembly at the air-water interface. b) UV-vis absorption spectra of AuND superstructure films.

Phase behavior of super soft spheres in two- and three dimensions

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In our recent publications [1-4], we explored the phase behavior of super-soft spheres using solutions of ultra-low crosslinked poly(N -isopropylacrylamide) based microgels as a model system.

We used SANS with contrast variation to directly access the microgel bulk modulus showing that is one order of magnitude smaller than for regular microgels. In bulk, the samples show a liquid-to-crystal transition at higher volume fraction with respect to both hard spheres and stiffer microgels. Furthermore, stable body centered cubic (bcc) crystals are observed in addition to the expected face centered cubic (fcc) crystals. Small-angle X-ray and neutron scattering with contrast variation allow the characterization of both the microgel-to-microgel distance, and the architecture of single microgels in crowded solutions. The measurements reveal that the stable bcc crystals depend on the interplay between the collapse and the interpenetration of the external shell of the ultra-low crosslinked microgels [1]. This peculiar phase behavior is due to strong defomations of the particles that we determine combining small-angle neutron scattering with contrast variation data and computer simulations [2,3].

Then we confine them at liquid-liquid interface [4]. Atomic force measurements are used to study their phase behavior. In addition, neutron reflectivity and interfacial rheology are used to both their vertical extension and the visco-elastic properties of the monolayer. Once confined at interfaces, these ultra-soft spheres show a behavior in between flexible macromolecules and hard particle.

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Modification of Interfacial Block Copolymer Structures: Electrochemical Switching of Interfacial Tension and Interfacial Viscoelasticity

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Block copolymers can be crucial for several industrial or pharmaceutical products due to versatile and adaptable properties in solution. We investigated the properties of poly(ethylene oxide)$_{110}$-*b*-poly{[2-(methacryloyloxy)ethyl]diisopropylmethylammonium chloride}$_{170}$ in the bulk phase and at the interface. Potassium hexacyanoferrates (HCF), added as counterions, showed the ability to change the water-solubility of the polycationic block. The “charge compensation” in presence of ferrocyanide $[Fe(CN)_6]^{4-}$ is weaker compared to ferricyanide $[Fe(CN)_6]^{3-}$. Utilizing their electrochemical addressability, the ratio between ferro- and ferricyanide was changed, while interfacial tension was traced. A chemical oxidation/reduction was feasible, but also an electrochemical oxidation leads to a significant change in the interfacial tension. The corresponding reduction showed only a mild response under the same conditions. Micelles in the bulk phase were detected by dynamic light scattering in presence of ferricyanide ions. [1] Further, it was possible to detect a prolonged rearrangement of the block copolymer/ferricyanide mixture at the water/*n*-decane interface from adsorbed micelles to layers of connected unimers by interfacial shear rheology. This was discernible due to the formation of viscoelastic “gel-like” structures at the interface, since the interfacial viscosity increased drastically and the storage modulus G´ approached the loss modulus G´´. Atomic force microscopy, dynamic light scattering, and small angle X-ray scattering accompanied the measurements. The gel formation at the interface was reversible by reducing ferricyanide ions or enhanced by generating Prussian Blue nanoparticles at the interface. [2, 3]

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Structure and dynamics of polyelectrolytes in water solution

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Proteins are biological macromolecules built from a sequence of amino acids with varying characteristics as hydrophobicity, charge and side-group that determine their biological and physical properties. Unfolded proteins, like intrinsically disordered proteins (IDPs), share similarities with polymers in structure and dynamics. For thermal unfolded Ribonuclease A or the IDP myelin basic protein we showed already similarities to polymer dynamics reflected by Zimm-like dynamics with internal friction [1-3]. Also normal mode analysis based on explicit configurations resulted in improved description of the dynamics. Here we explore the dynamics of polystyrene sulfonic acid (PSS-H) and salt (PSS-Na) as a well-known polyelectrolyte well below the overlap concentration to examine the single chain conformation and dynamics. The aim is to observe the influence of the large charged sidechain onto the chain dynamics and to find similarities to the molecular dynamics of IDP that deviates from standard polymer dynamic models.

The structure of PSS-H can be described by a wormlike chain model with a finite thickness. A disclike cross-section indicating the extended side chains can be observed by SAXS due to the specific contrast conditions (Figure 1, left). Neutron Spin Echo (NSE) experiments, observing the molecular dynamics, clearly indicate a change of chain dynamics as a function of salt concentration and temperature. The dynamics shows a crossover between rigid body like behavior (stiff chains) to Zimm-like dynamics as expected for flexible polymer chains (Figure 1, right)..

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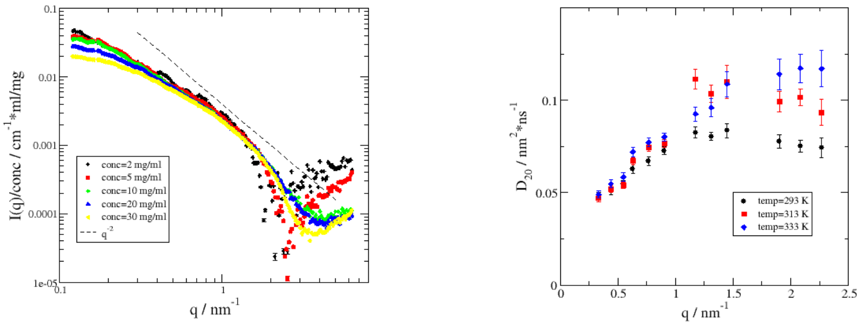

Figure 1. Left: SAXS data for PSS-H 39kDa 500mM NaCl for different polymer concentrations. Right: Effective diffusion coefficient from single exponential fits to NSE intermediate scattering function for 3 temperatures for PSS-H 39kDa at 500mM NaCl in D_2O. The diffusion coefficients are scaled by the D_2O viscosity to represent the effective diffusion at 20°C.

Optimization and fabrication of silica-coated nanoemulsion as reservoir for essential oils

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Essential oil-based nanoemulsions have garnered significant attention in the past few decades in the field of nanomedicine, food, and agriculture) [1]. However, they suffer from major shortcomings such as ageing (Ostwald ripening, coalescence), leakage of the encapsulated agent over time, burst release, or rapid degradation under harsh environmental conditions (pH and temperature change) [2]. Moreover, controlling the release of the encapsulated agent from the nanoemulsion matrix is a tedious task.

Coating the surface of the nanoemulsion droplet with some low-cost and biocompatible material like silica (US-FDA approved food additive) can enhance the nanoemulsion performance and can prevent premature degradation of the encapsulated agent. Moreover, silica-coated nanoemulsions can open up the window for functionalization of nanoemulsion to tune the release of encapsulated agents [3].

In this work, we fabricated eugenol nanoemulsions *via* the ultrasonication method using a mixed surfactant system of a non-ionic and cationic surfactant. Obtained nanoemulsions were stable with droplet size < 100 nm and zeta potential of ~-40 mV. The effect of coating the nanoemulsion surface with silica using different silica precursors was then studied. The effect of ageing time on the thickness of silica shells under different pH conditions was investigated using FESEM and SAXS. A comparison between non-coated and silica-coated nanoemulsions in terms of encapsulation efficiency, sustained-release, stability against different pH, temperature, and storage conditions was drawn [4]. Results obtained from the investigation may have invaluable implications for fabrication of such silica coated formulations in the agri-food, pharmaceutical and cosmeceutical products

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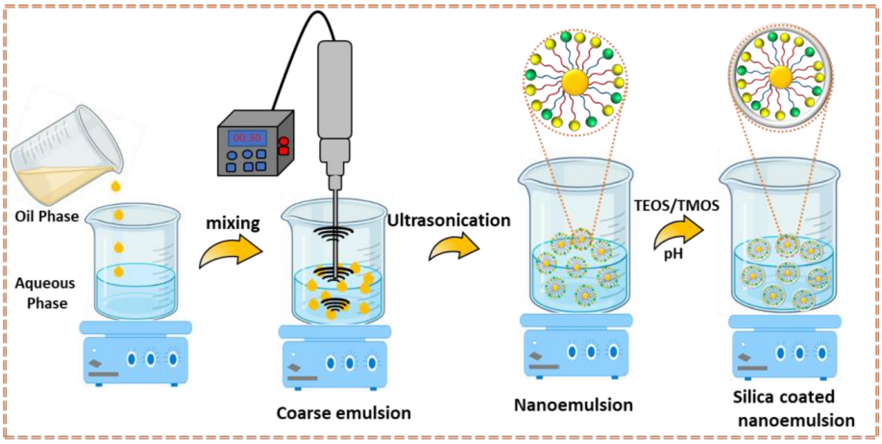

Figure 1. Schematic presentation for fabrication of silica-coated essential oil nanoemulsion

Surface topography quantification of DNA-functionalized colloids via super resolution microscopy

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Microparticles have wide range of applications in materials and sensing. In a quest for programmable materials, DNA coated colloids are of great interest because they can self assemble and form crystal. However, if the DNA coatings are not synthesized correctly and/or homogeneously the self-organization can fail. Therefore, the quantification of the details of surface coating is necessary to understand the mechanisms of interactions between particles and how to control their synthesis in our favor. The aim of this work is to characterize the colloids' surface on a single particle level through single molecule microscopy and by developing quantitative analysis methods.

By employing STED and DNA-PAINT microscopy, we visualize the surface of DNA coated colloids on a nanoscale level [1]. Via DNA-PAINT and qPAINT we can quantify the amount of surface DNAs and correlate these numbers to bulk measurements with Flowcytometry, while STED microscopy enable us to identify the heterogeneity of the DNA groups, figure 1 [2,3]. These methods ultimately pave the path to modify synthesis protocols and produce programmable materials.

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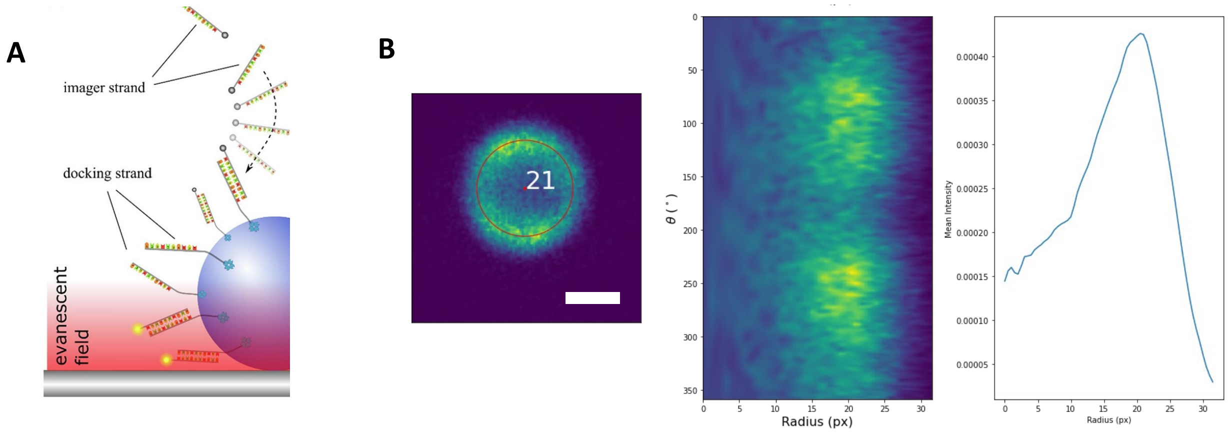

Figure 1. Image A, demonstration of DNA-PAINT method for streptavidin coated micron particles[1]. Image B, DNA distribution heterogeneity on the surface of 1μm polystyrene particle, imaged and analyzed with STED microscopy, scale bar: 500 nm.

A core-shell model describing the deformation behavior of microgels in crowded environment

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Microgels, cross-linked polymer networks swollen by a solvent, are a well-studied model system for soft deformable spheres. In response to increasing the volume fraction of microgels in a suspension, they start to isotropically deswell or facet. Traditionally, small deformations of elastic spheres are modelled through the Hertz pair potential. However, recent simulation studies revealed that in highly concentrated suspensions, the approximation of small deformations is no longer valid. Additionally, microgels are intrinsically heterogeneous, with higher numbers of cross-links near their core. Thus, a more accurate description of microgel deformation was proposed in the form of the multi-Hertzian potential. Hertz-like terms with varying amplitudes are summed up for differently strong cross-linked microgel regions [1].

This study aims to additionally incorporate the free energy of swelling in that model, to enable the simultaneous description of deswelling and faceting of microgels in concentrated suspensions. A Flory-Hertz model for a homogeneous microgels is already known and will be extended to a heterogeneous distribution of cross-links [2]. The simple case of a concentrated system containing core-shell microgels – meaning two regions in a microgel – is simulated. We find that mainly parameters related to microgel softness influence the deformation behaviour in crowded environment. At medium volume fractions the interactions are mainly governed through the properties of the microgel shell. Less cross-linked shells are more inclined to be faceted, while vice versa highly cross-linked shells preferably deswell. The highest investigated volume fractions lead to deformations of the microgel core, depending on its size and softness. In those systems the shell is completely collapsed, which aligns with the experimental observations of core-shell microgels.

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All-natural Pickering emulsion gels for high-fidelity direct ink-writing

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Direct ink writing (DIW) is especially interesting for biomedical applications due to gentle conditions and the possibility to create customized objects on-demand. Natural abundant polymers arise as sustainable and biocompatible alternatives to synthetic and bio-accumulating polymers. The printing of pure nanocellulose suspensions has proven difficult due to low loadings and high shrinkage, as well as unfit rheology. At the same time, emulsion gels have gained attention for their favorable viscoelastic properties [1].

Our novel sulfur-free cellulose nanocrystals (CNCs) with a low degree of substitution and a low positive surface charge [2] enable the straightforward employment of CNCs as Pickering emulsifiers. We present an emulsion gel ink co-stabilized by this new type of CNCs and α-cyclodextrin (α-CD) interfacial inclusion complexes, composed of entirely natural and biodegradable compounds. The produced inks are shear-thinning and exhibit a high storage modulus up to 70 kPa, allowing for the high fidelity and low shrinkage printing of even complex overhanging structures without requiring a support structure. A low yield stress of only 230 – 270 Pa should facilitate the inclusion of cells for biomedical applications into the formulation, as it was shown that a high shear stress in the nozzle has a negative impact on cell viability [3]. The gel can be tuned to desired rheological properties and equipped with both polar and apolar compounds due to the biphasic system, making it a promising platform for biocompatible additive manufacturing.

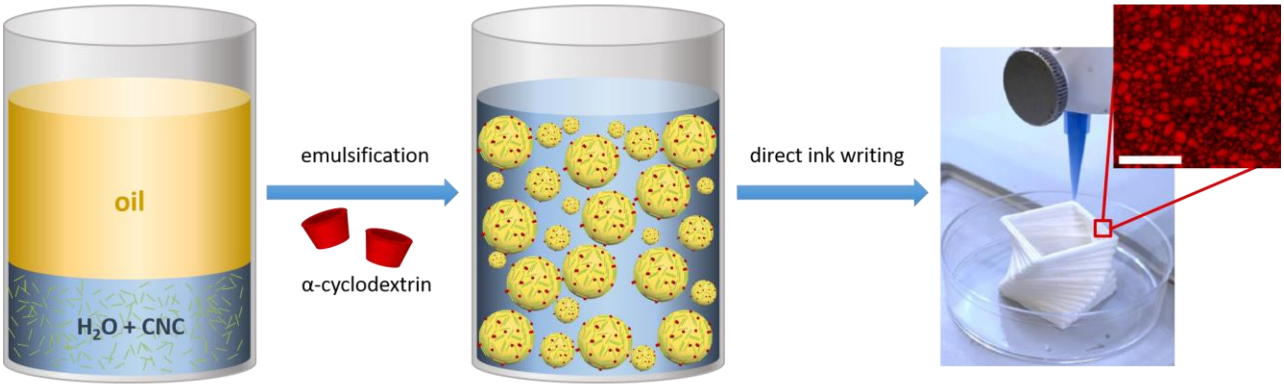

Figure 1. Schematic for the fabrication of an emulsion gel 3D printing ink from oil (sunflower), an aqueous CNC dispersion, and α-cyclodextrin with a picture of a support-free rotating square object printed with one of the inks. Scale bar: 50 µm.

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pH dependent Foam Film Properties of β-lactoglobulin Foams in comparison to Silica Sphere stabilized Foam Films

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The properties of foams are of interest in many applications such as food technology, firefighting and in personal care products. For understanding macroscopic foam properties, it is important to investigate its single building blocks – the so-called foam films, which separate the air bubbles from each other. A widely known foam-stabilizing protein is β-lactoglobulin which appears naturally in milk and is responsible for milk froth. This protein shows an interesting pH dependent behavior.

Engelhardt et al. [1] found maxima of yield stress, storage modulus, dilatational storage modulus and foam film thickness of β-lactoglobulin foams at the isoelectric point around pH 5. These findings are explained by agglomerated β-lactoglobulin multilayers. At pH 3 and pH 7 significant discrepancies in terms of dilatational storage modulus appear despite the same distance to the isoelectric point. To ensure the reason for the discrepancies, more insights in the foam film properties are needed.

Therefore, we use a camera based thin film pressure balance to study protein and particle stabilized foam films in terms of disjoining pressure inside the foam films, drainage kinetics, and foam film stability. Film thickness profiles give insights into bridging, agglomerate and network distributions. Comparison with hydrophobized silica nano particle stabilized foam films helps to distinguish between steric stabilization effects affected by the spherical shape of the particles and protein specific stabilization effects [2].

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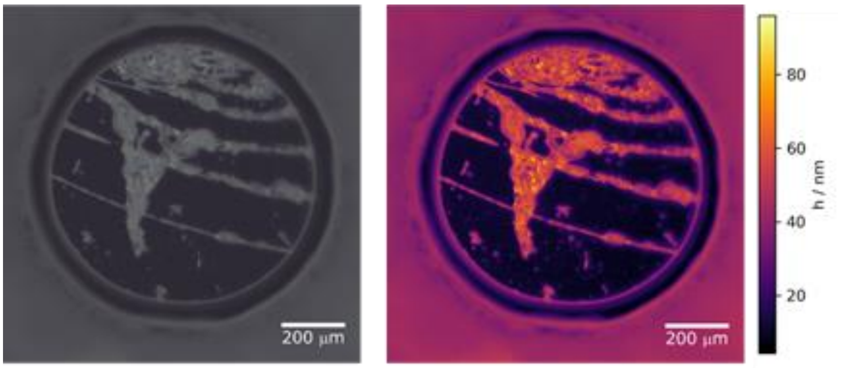

Figure 1. Thin foam film of β-lactoglobulin (c = 10^{-6} M, pH = 5.0) in natural color representation (left) and false color representation indicating the film thickness (right)

Self-Assembly of Sugar Surfactants in Deep Eutectic Solvents and Their Solubilization of Terpenoids

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Amphiphilic self-assembly of surfactants in aqueous solutions is a well-studied phenomenon. Self-assembly of surfactants is also possible in deep eutectic solvents (DES), a novel class of polar solvents that has the potential to become a non-toxic and cheap alternative to conventional organic solvents, ionic liquids or even water[1]. Structure formation by surfactants in DES has been studied only to some extent, as their solubility in DES is often very limited[2]. The DES based on choline chloride and urea, known as "reline", has been reported to dissolve only a few anionic surfactants, e.g. SDS[2].

As a result of our experiments, we were able to widen the limited scope of reline-soluble surfactants with sugar surfactants. They can be easily produced from biomass and are readily biodegradable[3]. Interestingly, alkyl glucopyranoside solutions in "reline" could furthermore solubilize monoterpenoid compounds as limonene, menthol, pinene, eucalyptol and borneol, which are otherwise insoluble in neat "reline" or water.

All components were chosen thoroughly with the stress on biocompatibility, biodegradability and their potential use in medicine and cosmetics. Upon addition of menthol, the microemulsions exhibit remarkable viscoelastic properties, such as shear-thinning. The viscosity of such mixtures changes dramatically with the increase of menthol content. Such property could find application in creams and topical drug delivery.[4].

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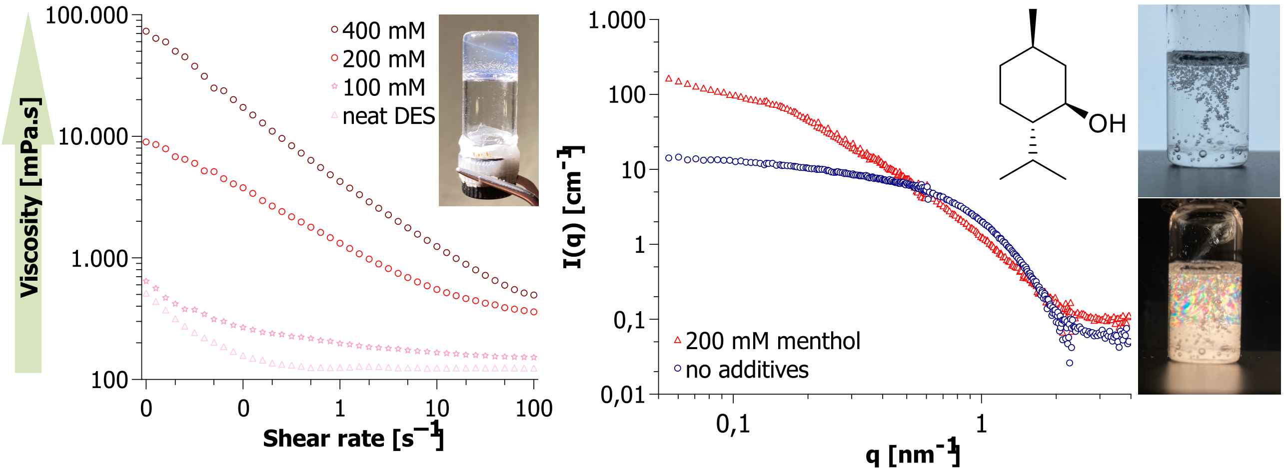

Figure 1. **(Left)** The viscosities of equimolar solutions of dodecyl-β-glucopyranoside and menthol in reline at 50°C as a function of the shear rate. Photo of the 400 mM sample upside down demonstrating its high viscosity. **(Right)** Small-angle neutron scattering (SANS) curves of the 200 mM samples with (red) and without menthol (blue) demonstrating major structural changes as supported by cross-polarized image of the sample.

Method to simultaneously probe the bulk modulus and structure of soft compressible objects using small-angle neutron scattering with contrast variation

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An object's bulk modulus quantifies its resistance to an isotropic compression. For soft deformable colloids the bulk modulus must be known to predict their response to crowding. Here, we will present a new approach to obtain partially-deuterated, high molecular weight polyethylene glycol (dPEG), which is used to exert osmotic stress on soft objects. In this study, microgels were used as a model system for soft compressible spheres and their bulk modulus is determined by means of small-angle neutron scattering with contrast matching. By partial deuteration the scattering length density of the dPEG was matched in pure heavy water. Consequently, no contribution of the osmotic stress polymer is measured during the scattering experiments, and the form factor of the microgels was directly measured. Furthermore, in addition to the total radius, the variation of the different parts of the microgels can be also measured as a function of the external osmotic stress. Therefore, using this method the different elasticity along a single particle, such as proteins or viruses, can be determined directly.

Building mechanism and controlled synthesis of eumelanin particles

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The biological pigment eumelanin protects various organisms from harmful UV radiation and shows interesting material properties like radical scavenging, paramagnetism and broadband absorption combined with low fluorescence. It can be synthesized biomimetically in aqueous solution starting with L-Dopa and catalyzed by tyrosinase, leading to oligomeric sheets. These undergo a subsequent particle formation, which is not yet fully understood [1]. A 3-step self-assembly process is suggested by previous findings. First, oligomeric sheets are formed which may stack to so-called protoparticles with a size of a few nm. In the second step, the protoparticles form type-A particles, which have a radius close to 20 nm. Finally, spherical particles with a diameter of 200 nm are formed, denoted as type-B particles [2]. The mechanism and the controllability of this supramolecular buildup has been investigated by us. Time-resolved combined static and dynamic light scattering (SLS/DLS) made possible to follow the formation of the final type-B particles from type-A particles under various conditions and indicated a monomer addition mechanism. The adjustment of the pH value enabled us to inhibit the formation of the final type-B particles at the level of type-A particles, characterized by SLS/DLS, scanning electron microscopy (SEM) [3] and Small Angle X-Ray Scattering (SAXS). Subsequent decreasing of the pH value of such type-A particle dispersions triggered the spontaneous formation of type-B particles even 24 h after completion of the formation of the type-A particles [3]. We could demonstrate that the formation of type-B particles is reversible during an initial period by re-inceasing the pH value. The loss of the reversibility with time indicates a consolidation of the type-B particles after their formation by aggregation of type-A particles. [5]

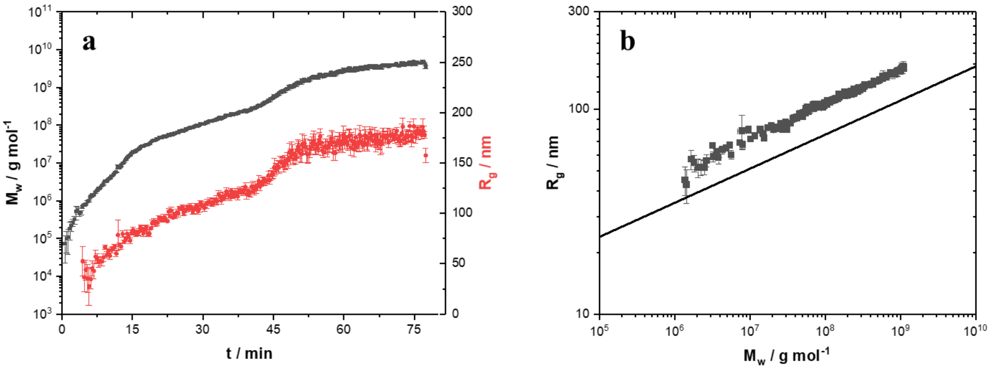

Figure 1: Weight averaged molar mass M_w and radius of gyration R_g of growing eumelanin particles followed by SLS (**a**) and respective correlation of M_w and R_g (**b**). The solid line indicates a slope of 1/6 which corresponds to a monomer addition mechanism [4].

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Elasticity vs. capillarity: How soft is a substrate soft?

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Placing a small liquid droplet on a soft substrate deforms the substrate. The surface tension of the droplet rises a wetting ridge along the three-phase contact line and the Laplace pressure inside the droplet creates a depression (i.e., dimple) underneath the droplet [1,2] (Figure 1A). The deformation of the substrate is determined by the capillary and elastic energies, which is characterized by the softness ratio γ_S/Gr (where γ_S and G are the surface tension and shear modulus of the substrate, respectively, and r is the contact radius of the nanodroplet).

Using atomic force microscopy (AFM), we have probed the three-dimensional interfacial configuration of nanodroplets (with different r) and the deformed soft substrates (with different G). This allows measuring the ridge height and the dimple depth (Figure 1B) in a range of softness ratios. With increasing the softness ratio, the normalized ridge height increases and then decreases, while the normalized dimple depth increases and approaches to a limiting value. The substrate capillarity overcomes the substrate elasticity in dominating the substrate deformation when $\gamma_S/Gr \gtrsim 1$ (Figure 1C), illustrating that a substrate becomes soft when $\gamma_S/Gr \gtrsim 1$. Our results show a direct experimental observation of the elasticity-to-capillarity transition [3].

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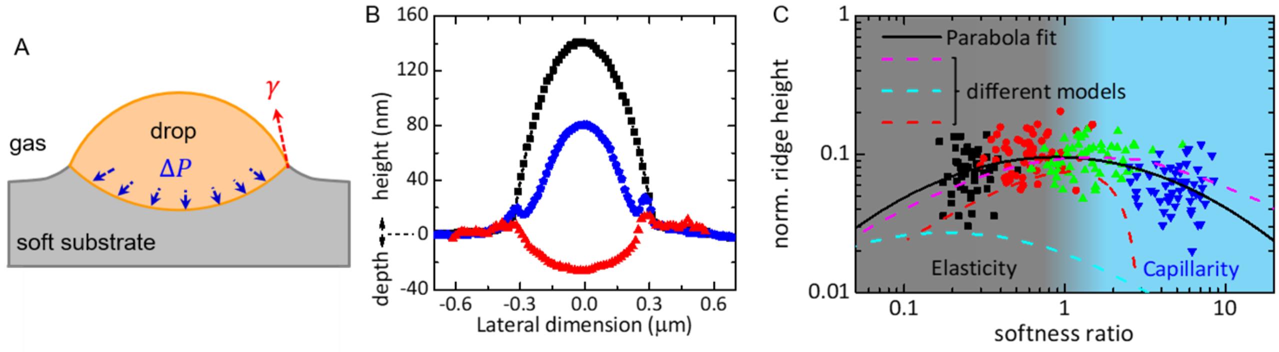

Figure 1. (A) Schematic illustration of the substrate deformation. (B) Profiles of nanodroplet, wetting ridge and dimple probed by AFM. (C) Normalized ridge height versus softness ratio showing the elasticity-to-capillarity transition.

Hybrid soft magnetic micro-actuators with thermo-programmable response to external magnetic field

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Hybrid materials that can respond to multiple stimuli are promising materials with the potential to be employed as carrier materials in biological systems [1]. Poly(N-isopropylacrylamide) PNIPAm hydrogels are an excellent option to achieve such systems. Their thermo-responsive nature allows a reversible switch from a swollen to a shrunken state. By adding maghemite nanoparticles and pre-programing their alignment in the matrix of those hydrogels, thermo- and magneto-responsive systems can be designed.

Different microgel shapes with embedded maghemites were synthesized using Particle Replication in non-wetting template (PRINT). Their thermo-and magneto- responsivity were determined through swelling experiments and through the investigation of their response under rotating magnetic fields of different strengths. These systems were characterized by a maximum rotation speed ω_c marking their transition from a synchronous to an asynchronous rotation. ω_c showed to be strongly varying with the temperature (Figure 1a).

When the hydrogels were additionally coated with a metal layer, the restricted swelling of the soft layer enabled the creation of more complex shapes [2-3]. The conformations and polarizability to the applied magnetic field of such shapes can be controlled with the temperature (Figure 1 b). These properties were further utilized to create diverse actuations combining the response to temperature, magnetic field, and light. Additionally, active micro-swimmers made from such system can be designed and their swimming can be directed when an external magnetic field is applied [4].

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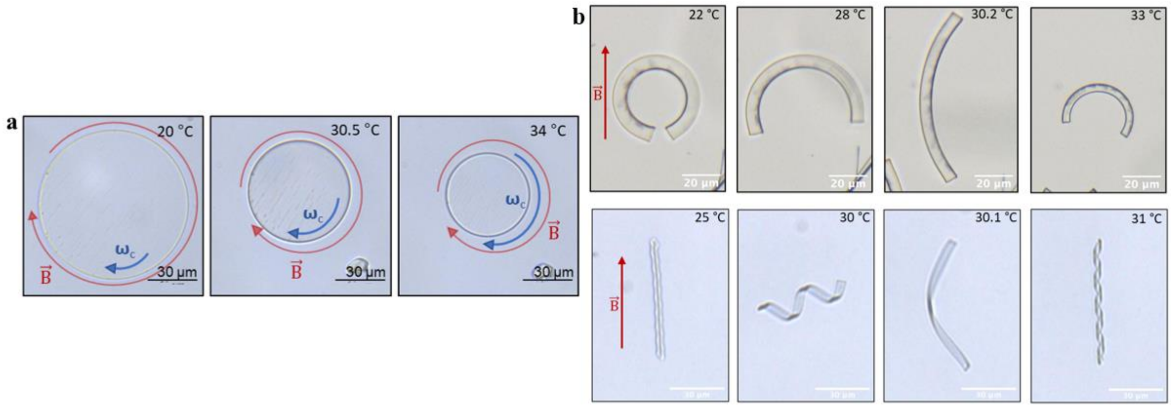

Figure 1. *Thermo-responsive and magnetic microgels a) Hybrid disks with tunable response under an applied rotating field b) Arc and helix bilayer structures that change their alignment to the field when the temperature is varied.*

Janus emulsions as adaptive material platform for the transduction of (bio-)chemical information

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Autonomous regulation of chemical reactivity represents a fundamental ability of living organisms. Chemical information can be processed with high fidelity and highest substrate specificities are achieved as multiple individual or combinations of independent chemical equilibrium-driven non-covalent interactions and covalent chemical transformations are translated into a specific response. This cross-check capability and self-regulation behavior forms the basis for the high complexity and specificity achieved within biological systems and is further fundamental for the complex emergent behavior observed in multibody systems, for instance their self-regulated ability to communicate, move, evolve, and self-organize into patterns or networks.

An emulation of these individual capabilities within a synthetically minimal, biomimetic model system may help to better understand the underlying complex cascade mechanisms and pave the way towards artificial dynamic and self-regulatory adaptive materials that display unprecedented autonomous capabilities. In my group, we are interested in the bioinspired generation of artificial soft matter systems that exhibit chemo-intelligence in that they are capable to autonomously operate in response to (bio-) chemical cues. Guided by basic scientific questions we explore the creation of new, transformative application concepts with the goal to generate artificial chemo-intelligent microreactors that can ultimately rival the regulatory and motile behavior observed in Nature. Our complex colloidal microreactors (complex emulsions, hydrogel capsules, intricate polymer particles) usually comprise two or more phases, and multiple exquisitely sensitive interfaces. As a result, they can, for instance, selectively change morphology in response to a variety of external stimuli, including the presence of specific chemical and biological entities, small pH changes, light or high-energy irradiation, as well as an external electric or magnetic field. Such structures can also be designed to undergo programmed assembly or disassembly, and as a result of the density and refractive index contrast of the individual phases, manipulate the pathway of light. Demonstrations on how an associated understanding of the unique chemical-morphological-optical coupling inside these chemically active functionalized active soft colloids can be used in new and improved soft matter applications, including in biomimicry, droplet-based imaging platforms, as structural templates for the generation of functional precision objects, and as chemo-intelligent transducers in chemo- and biosensing applications will be presented.

Charging of dielectric surfaces in contact with aqueous electrolyte – the influence of CO_2

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ABSTRACT

The charge state of dielectric surfaces in aqueous environments is of fundamental and technological importance. We use super-heterodyne light scattering in a custom-made cell to study the influence of dissolved CO_2 on the charging of three, chemically different surfaces. We compare an ideal, CO_2-free reference state to ambient CO_2 conditions. Systems are conditioned under conductometric control at different low concentrations of NaCl. As expected for constant charge densities, ζ-potentials drop upon increasing the salt concentration in the reference state. Presence of CO_2 leads to an overall lowering of ζ-potentials. Moreover, for the inorganic dielectric, the salt dependent drop is significantly weakened, and it is inversed for the organic dielectrics. We suggest that at ambient conditions, the charge state of dielectric surfaces is related to dielectric charge regulation caused by the salt concentration dependent adsorption/desorption of CO_2.

Repulsive interactions of eco-corona covered microplastic particles quantitatively follow modelling of polymer brushes

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Environmental fate and toxicity of microplastic particles is dominated by their surface properties. In the environment an adsorbed layer of biomolecules and natural organic matter forms the so-called eco-corona [1]. A quantitative description of how this eco-corona changes the particles' colloidal interactions is still missing. Here, we demonstrate with colloidal probe-atomic force microscopy that the formation of the eco-corona on microplastic particles introduces a soft film on the surface which changes the mechanical behaviour. We measure single particle-particle interactions and find a pronounced increase of long-range repulsive interactions upon eco-corona formation. These force distance characteristics follow well the polymer brush model by Alexander and de Gennes. The foundation of the eco-corona interacting like a polymer brush with its surrounding may help understand microplastic transport and aggregation in the environment [2, 3].

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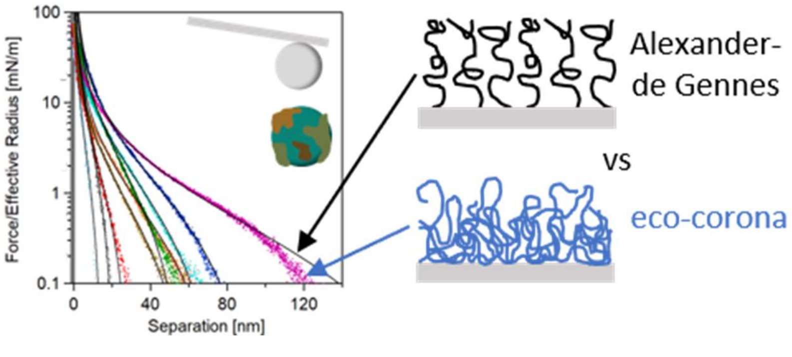

Figure 1. Interaction forces of the eco-corona quantitatively follow polymer brush theory of Alexander-de Gennes although its structure is different as outlined right.

Effect of polymer chain stiffness on depletion layers in colloid–polymer mixtures

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Mixtures of colloidal particles with non-adsorbing polymers are ubiquitous both in science and in industry. The non-adsorbing polymers induce an effective attraction between the colloidal particles, known as the depletion interaction, and as a result colloid–polymer mixtures display rich physics. Theoretical descriptions of such systems historically assumed the polymer chains to be fully flexible coils, while in reality many polymers have a certain degree of chain stiffness. The effect of this stiffness on the depletion interaction and the resulting phase behavior of these mixtures is as of yet poorly understood, even though it is highly relevant for describing realistic systems.

We present a new analytical theory [1] that describes the concentration profile and depletion thickness of a solution of non-adsorbing semiflexible polymers next to a flat surface. Our theory covers both the dilute and semidilute regime. For fixed polymer radius of gyration, increasing the chain stiffness leads to a monotonic decrease in the depletion thickness in dilute conditions. However, in the semidilute regime, remarkably there is a maximum in the depletion thickness as a function of the chain stiffness. Furthermore, we present an extension of the theory towards semiflexible polymer solutions around spherical colloids, yielding insights into the phase stability of colloid–polymer mixtures. The analytical expressions are in quantitative agreement with numerical self-consistent field calculations [2].

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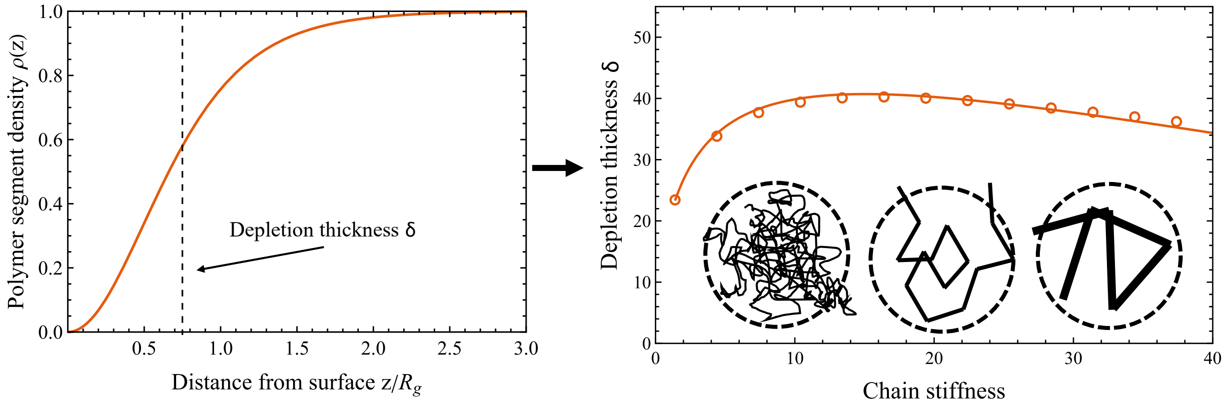

Figure 1. (left) Sketch of the normalized segment density of a non-adsorbing polymer near a hard wall. (right) The depletion thickness in the semidilute concentration regime at constant polymer radius of gyration has a maximum as a function of chain stiffness. Points: numerical self-consistent field lattice computations; curve: our new analytical theory.

Effect of Red Blood Cell Shape Changes on Haemoglobin Interactions and Dynamics: A Neutron Scattering Study

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By using a combination of experimental neutron scattering techniques, it is possible to obtain a statistical perspective on red blood cell (RBC) shape in suspensions, and the inter-relationship with protein interactions and dynamics inside the confinement of the cell membrane. In this study [1], we examined the ultrastructure of RBC and protein-protein interactions of haemoglobin (Hb) in them using ultra-small-angle neutron scattering (USANS) and small-angle neutron scattering (SANS). In addition, we used the neutron backscattering method to access Hb motion on the ns time scale and Å length scale. Quasielastic neutron scattering (QENS) experiments were performed to measure diffusive motion of Hb in RBCs and in an RBC lysate. By using QENS, we probed both internal Hb dynamics as well as global protein diffusion, on the accessible time scale and length scale by QENS. Shape changes of RBCs and variation of intracellular Hb concentration were induced by addition of the Na^+-selective ionophore monensin and the K^+-selective one, valinomycin. The experimental SANS and QENS results are discussed within the framework of crowded protein solutions, where free motion of Hb is obstructed by mutual interactions [2].

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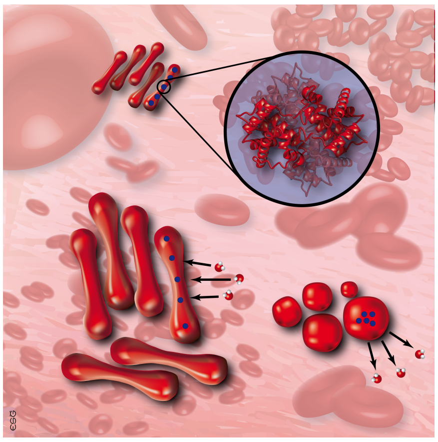

Figure 1. Neutron scattering experiments show the influence of the shape of red blood cells on the colloidal properties of the oxygen transport protein haemoglobin.

Experimental Evidence of a Transition from a Sponge-Like to a Foam-Like Nanostructure in Water-Rich L_3 Phases

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Early studies [1-3] on water – *n*-alkane – ionic surfactant microemulsions provide first hints for the possible existence of a foam-like nanostructure, *i.e.* a dense packing of polyhedral nanometer-sized water droplets separated by a thin layer of a continuous oil phase. We chose the system water/NaCl – hexyl methacrylate (C_6MA) - dioctyl sulfosuccinate sodium salt (AOT) for two reasons. First, because AOT is a single, pure surfactant known to form inverse structures and, secondly, our ultimate goal is to polymerize the continuous oil (C_6MA) phase, *i.e.* to synthesize genuine nanoporous polymer foams. Inspired by the pioneering work of *Skouri* et al. [4] we were able to locate an isotropic one-phase channel, the L_3 phase, emanating from the pseudo-binary system water/NaCl - AOT at ambient temperature. In addition, there is an isotropic oil-in-water microemulsion found at high temperatures [5]. Already upon addition of small amounts of oil to the L_3 Phase the conductivities become very low and the viscosities very high [6]. Freeze fracture electron microscopy allows us to actually see the anticipated foam-like nanostructure (see Fig.1).
The structure is reminiscent of that of *Wolf* et al. [7] for a related system with a technical grade nonionic / anionic surfactant mixture. Currently, we are studying the kinetics of the oil (C_6MA) polymerisation. Subsequently, the structural transition in the L_3 channel will be investigated by small angle neutron scattering (SANS) and NMR self-diffusion (FTPGSE).

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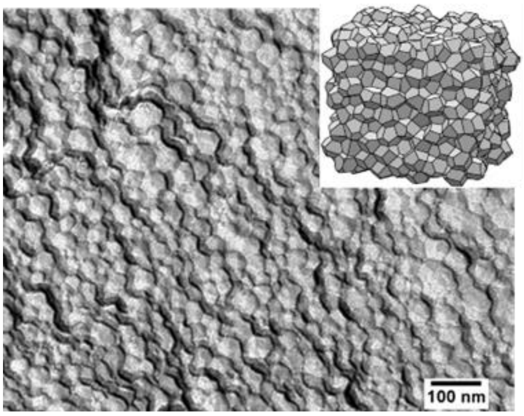

Figure 1. Freeze fracture electron microscopy (FFEM) image of an oil-continuous microemulsion H_2O/NaCl – C_6MA – AOT with AOT mass fraction $\gamma = 0.15$ and C_6MA mass fraction $\alpha = 0.037$. Scale bar = 100 nm [6]. The inset illustrates the polyhedral foam-like structure taken from [8].

Supraparticles as identification taggants with spectral magnetic readout

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Complex global supply chains, counterfeit products or quality control demand the identification of arbitrary objects. Smart additives in form of (sub)micron sized particles that carry a unique code, provide a promising approach to overcome the drawbacks of RFID and barcode labels. [1] Going beyond optical signal carriers, magnetic signals can be transmitted through many materials that would not allow optical information to pass. The possibility to read out the magnetic signals out of a certain depth even when covert within dark solid objects, enables an easy incorporation of the marker during production of the materials and additionally protects the marker against environmental harm or easy reveal. Thereby, objects in different application fields could be equipped with such a smart additive (Fig. 1). [2]

Figure 1. A magnetic particle with a spectrally resolved magnetic code equips arbitrary objects with information. The readout independent of optical constraints, enables a vast variety of unexploited marking applications. Reprinted from [2].

In this work it is presented that nanostructured micron-sized particles (so called supraparticles [3]) have the potential to be *spectrally* encoded with more than 77 billion magnetic codes as resolved by magnetic particle spectroscopy (MPS). [2] Thereby, a magnetic identification taggant, that does not rely on the spatial arrangement of magnetic particles, is established. A chemical synthesis strategy was developed that enabled the control of nanoparticle-nanoparticle interactions within multi-hierarchical supraparticles in order to obtain a large number of different magnetic codes. This principle will be vividly demonstrated in analogy to a musical ensemble in order to explain the readout technique MPS. Additionally, it is shown that a luminescent code can be united within such supraparticles, yielding dual-*spectrally* encoded supraparticles. [4]

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Phase Behaviour of a Biocompatible Microemulsion based on Tween 20, Ethylhexylglycerin and Isopropyl Palmitate

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A novel biocompatible microemulsion system based on Tween 20 (Tw20), ethylhexylglycerin (EHG) and isopropyl palmitate (IPP) as surfactant/co-surfactant, and oil is introduced. We show that a high solubilization capacity can be obtained by employing EHG as co-surfactant, a glycerol ether frequently employed in cosmetic applications [1]. The solubilization capacity is maximized for a Tw20 to EHG ratio of 1:5, i.e., for large excess of the co-surfactant. The phase behaviour is discussed as a function of co-surfactant and oil concentration. Monophasic samples are found for Tw20 to EHG molar ratios of up to 1:7. With increasing EHG concentration, the phase sequence: L_1, L_a, L_3 is reported. At even higher EHG concentrations, bi- and triphasic samples are formed.

The various phases were characterized by means of static and dynamic light scattering (SLS/DLS), small-angle neutron scattering (SANS), rheology, and conductivity measurements. The measurements confirm the formation of oil-in-water (O/W) droplets at lower Tw20 to EHG ratios. Without the addition of oil, the Tw20/EHG system first shows significant elongation with increasing EHG concentration before the aggregates become converted to bilayer structures. Here birefringent lamellar phases and finally a sponge phase are formed. When IPP is added this diverse phase behavior is lost in exchange for larger O/W droplets, which in size increase systematically with increasing EHG content. The structural evolution could in particular be followed in detail by the scattering experiments and this is a system that can structurally be controlled over a wide range and has potential for applications in the field of cosmetic or pharmaceutical formulations.

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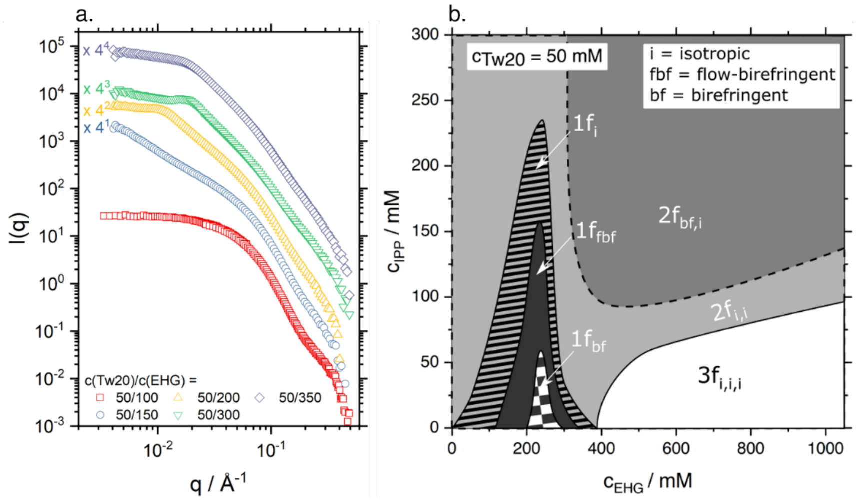

Figure 1. a. SANS intensities for samples are higher EHG concentrations. The spherical droplets first elongate before forming birefringent bilayer structures. b. Section of the phase diagram.