

# Talk Abstracts



KOLLOID  
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## 52<sup>nd</sup> Biennial Assembly of the German Colloid Society

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<https://cfaed.tu-dresden.de/kolloidtagung2024>

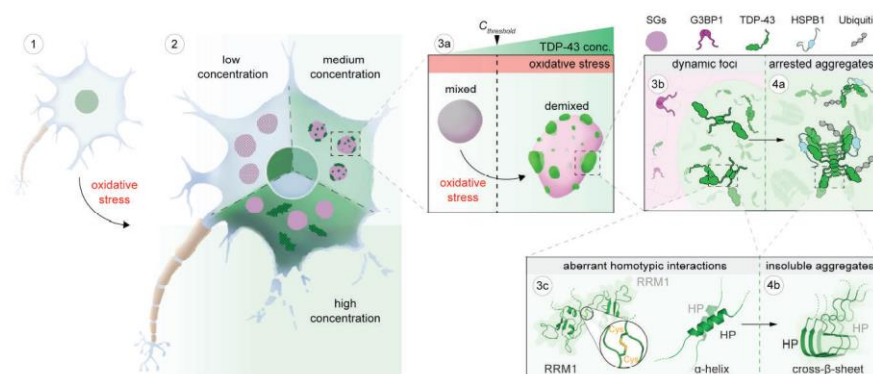
## Plenary Talks

## Intra-condensate demixing of TDP-43 inside stress granules generates pathological aggregates

Xiao Yan, David Kuster, Anthony A. Hyman

Max Planck Institute of Molecular Cell Biology and Genetics; Dresden, Germany

Over the past decade, the application of interface and colloid science to the study of living systems has yielded significant advancements and insights. Biomolecular condensates have hereby proven to play fundamental roles in cellular organization and physiology. Failure to control condensate properties, however, can lead to protein aggregation and often causes diseases. Cytosolic aggregation of the nuclear protein TDP-43, in particular, is associated with many neurodegenerative diseases. However, the triggers for TDP-43 aggregation in the cytosol are still debated. Here, we find stress granule condensates up-concentrate TDP-43, leading to its pathological aggregation. The pathway, giving rise to these aggregates, proceeds via two distinct steps. Initially, intra-condensate demixing of stress granules gives rise to a dynamic, homotypic TDP-43 phase. Subsequently, the demixed TDP-43 phase facilitates a liquid-to-solid transition into aggregates. Mechanistically, intra-condensate demixing is triggered by enhanced homotypic interactions within multicomponent stress granules, potentiated by oxidation of cysteine residues and hydrophobic patch interactions of TDP-43. TDP-43 variants resistant to intra-condensate demixing prevent aggregation in cells. Our findings provide compelling evidence that stress granule condensates can act as crucibles of TDP-43 aggregation via an intra-condensate demixing mechanism and thus as potential sites for disease emergence.



**Figure 1:** Model of intra-condensate demixing of TDP-43 inside stress granules generating pathological aggregates. Depending on TDP-43 expression levels (step 2) in neurons (1), stress granules that form upon oxidative insult (3a) demix into dynamic G3BP1-RNA and TDP-43-rich phases (3b) due to transient homotypic interactions of TDP-43 (3c) inside stress granules. Over time TDP-43 foci harden (4a) as aberrant, irreversible interactions between TDP-43 molecules (4b) are favored in this solvent environment, leading to pathological aggregates.

[1] Yan, X., Kuster, D., Mohanty, P., Nijssen, J., Pombo-García, K., Rizuan, A., et al. & Hyman, A. A., bioRxiv, 2024. 2024-01.

[2] We acknowledge funding made from the Max Planck Society and the European Research Council (PhaseAge, 525 ERC grant agreement number 725836) to S.A. and A.A.H. Funding from Korber Stiftung to A.A.H. Funding by Volkswagen Foundation to D.K. and A.A.H. National Institutes of Health (NIH) National Institute for Neurological Disorders and Stroke (NINDS) and National Institute on Aging (NIA) R01 NS114289, and the Department of Defense CDMRP/ALSRP W81XWH-20-1-0241 to Y.M.A.

## Bio-derived colloids for control of optical appearance

*Silvia Vignolini*<sup>1,2</sup>

<sup>1</sup> *Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Am Mühlenberg 1 14476 Potsdam DE*

<sup>2</sup> *Yusuf Hamied Department of Chemistry, Lensfield Road Cambridge CB2 1EW UK*

Driven by the need to develop sustainable materials, there is an increasing focus on replacing synthetic functional materials with naturally derived alternatives. In the context of colloidal systems, cellulose and chitin nanocrystals have emerged as exceptionally versatile and sustainable building blocks, with potential applications ranging from mechanical reinforcement to stunning structural colouration.

These colloiddally stable nanoparticles have a unique ability to self-organize in water, forming lyotropic cholesteric liquid crystals that can be precisely controlled in terms of periodicity, structure, and geometry. This helicoidal ordering can be preserved in the solid state, providing a straightforward pathway to creating complex nanostructured films, coatings, and particles.

In this talk, I will summarise the process of forming iridescent, structurally coloured films from cellulose nanocrystal (CNCs) suspensions and delve into the chemical and physical mechanisms at each stage [1]. By drawing comparisons with chitin nanocrystals (ChNCs), I will highlight key differences and present strategies for achieving the structural colouration we developed [2-4]. Furthermore, I will discuss the progress made in translating this technology from academia to industry [5], and outline the remaining scientific and technical challenges facing the community [6].

[1] B. Frka-Petecic, *et al* *Chemical Reviews* **2023**, 123, 23, 12595–12756.

[2] C. A. Williams, *et al* *Advanced Materials* **2023** 36, e2307563.

[3] R.M. Parker *et al* *Nature Communications* **2022** 13, 3378

[4] T. Parton *et al* *Nature Communications* **2022** 13, 2657

[5] B. Droguet *et al* *Nature Materials* **2021** 21, 352

[6] M Titirici *et al* *Journal of Physics: Materials* **2022** 5, 032001

## Biophysical insights into protein condensates

*Tuomas P. J. Knowles*

*University of Cambridge, Yusuf Hamied Department of Chemistry, Cambridge, UK*

Proteins are able to access a number of different states, some connected with biological function and others associated with malfunction. This talk explores experimental and theoretical analysis of the rates at which proteins can undergo such transitions, focusing on the liquid condensate and solid amyloid phase of proteins. We will discuss a number of examples where the study of kinetics gives insights into the fundamental molecular mechanisms that underlie protein phase transitions. Many of these mechanisms draw on soft condensed matter concepts and phenomena. Condensate modulation will be discussed both from the point of view of understanding fundamental biological function as well as ameliorating malfunction in disease.

## Memory in Capillary Networks

*Bat-El Pinchasik*

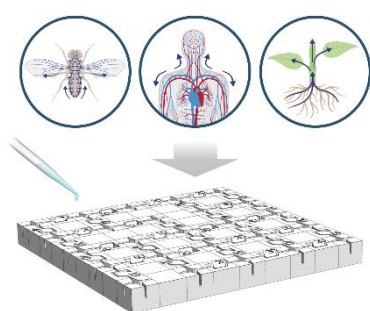
*Tel Aviv University, School of Mechanical Engineering, Faculty of Engineering, Tel Aviv, Israel  
Center for Physics and Chemistry of Living Systems, Tel Aviv University, Israel*

Capillary networks are ubiquitous in nature and biology. Understanding these networks is fundamental to comprehending vascular systems in animals, capillary networks in plants, and has extensive applications in medicine and science. However, many questions remain about how these networks regulate and control flow. While we grasp the general principles of capillary networks and their functions, ongoing research explores how these networks dynamically respond to changes, adapt to varying conditions, and whether they retain memory of past states. Establishing a model system of capillary networks allows us to ask new and exciting questions, such as: "Do capillary networks have memory?"

Creating a model system of capillary networks in nature presents two main challenges. First, the ability to dynamically alter the nature of bonds within the networks and its impact on transport. Second, designing networks that can evolve dynamically in response to external stimuli. Achieving these two aims could revolutionize our ability to reconfigure macroscale flow through the active control of local bonds in capillary networks.

Here, I propose a novel experimental model system of capillary networks, composed of hundreds of interconnected liquid diodes. Analogous to electric diodes, these microscale surface structures guide liquids in specific directions while preventing reverse flow. However, under certain conditions, liquid diodes can fail, allowing bidirectional flow. This introduces bonds of different natures into the capillary networks.

Such a system will enable us to determine whether the wetting state of liquids in the networks depends on the history of actuation—essentially, whether capillary networks can possess memory. This intriguing question opens a new realm of possibilities, such as the potential to encode information within capillary networks, understand how transport responds to external stimuli, explore the interplay between global actuation and local fluid dynamics, investigate the coupling between mechanics and flow, and elucidate how information propagates through capillary networks.



**Figure 1.** Capillary networks in nature and biology (top) and a model system of these networks (bottom).

[1] Sammartino, C.; Rennick, M.; Kusumaatmaja, H.; Pinchasik, B.-E. *Phys. Fluids* **2022**, 34 (11), 112113.

[2] Sammartino, C.; Shokef, Y.; Pinchasik, B.-E. *J. Phys. Chem. Lett.* **2023**, 14 (34), 7697–7702.

[3] The authors acknowledge funding from the Israel Science Foundation (ISF), Grant Number 1323/19.

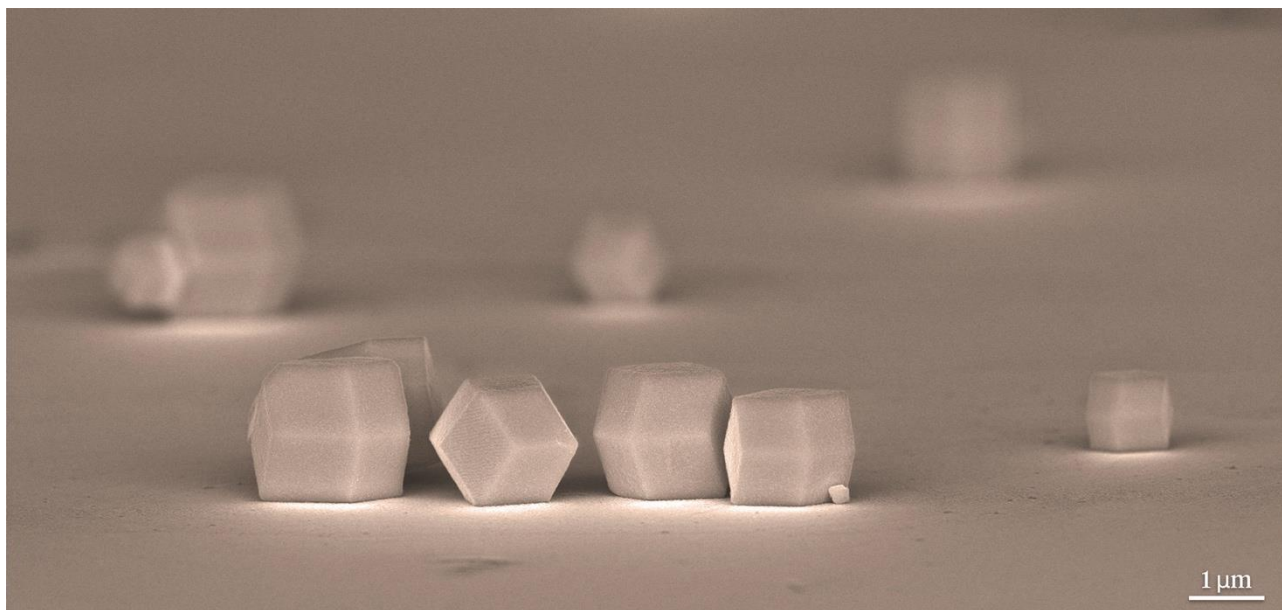
## Harnessing Coulombic interactions to prepare high-quality colloidal crystals

*Rafal Klajn*<sup>1,2</sup>

<sup>1</sup> *Institute of Science and Technology Austria (ISTA), Klosterneuburg, Austria*

<sup>2</sup> *Department of Organic Chemistry, Weizmann Institute of Science, Rehovot, Israel*

Self-assembly of inorganic nanoparticles (NPs) into ordered structures (“superlattices”) has led to a wide range of nanomaterials with unique optical, electronic, and catalytic properties. Various interactions have been employed to direct the crystallization of NPs including van der Waals forces, hydrogen bonding, as well as electric and magnetic dipolar interactions [1]. Among them, Coulombic interactions have remained largely unexplored owing to the rapid charge/ligand exchange between NPs bearing high densities of opposite charges. In this talk, I will describe a new method [2] to assemble these “superionic NPs” under conditions that preserve their native surface charge density. Our methodology was used to assemble oppositely charged NPs into high-quality superlattices exhibiting Catalan shapes [3]. The methodology can be applied to a wide range of charged nanoparticles of various sizes, shapes, and compositions [4]. I will also discuss different ways to employ electrostatic interactions to assemble NPs into transient assemblies [2,5] whose lifetimes depend on and can be controlled by the availability of small-molecule ionic “fuels”.



**Figure 1.** An SEM image of CsCl-type nanoparticle superlattices prepared using our technique.

[1] M. A. Boles, M. Engel, D. V. Talapin, *Chem. Rev.* **2016**, 116 (18), 11220–11289.

[2] T. Bian *et al.*, *Nat. Chem.* **2021**, 13 (10), 940–949.

[3] T. Bian *et al.*, *ChemRxiv* **2022**, 10.26434/chemrxiv-2022-klncg.

[4] Unpublished results.

[5] J. Wang, T. S. Peled, R. Klajn, *J. Am. Chem. Soc.* **2023**, 145 (7), 4098–4108.

## Prize Winner Talks



## The world of nanocapsules

*Katharina Landfester*

*Max Planck Institute for Polymer Research, Mainz, Germany*

Polymeric nanocapsules offer the versatility to cover a wide range of mesoscopic properties for sophisticated applications. By means of the miniemulsion process, custom-made nanocapsule systems for different purposes can be designed. The encapsulation and release of a great variety of payloads, ranging from hydrophobic to hydrophilic substances, have been successfully achieved in a highly controlled manner and with an unmatched high encapsulation efficiency.

The preparation of nanocontainers with a hydrophilic core from water-in-oil emulsions and their subsequent transfer to aqueous medium is of special importance since it enables the efficient encapsulation of hydrophilic payloads in large quantities. However, major challenges are associated with their synthesis include low colloidal stability, leakage of encapsulated payloads due to osmotic pressure, and a demanding transfer of the nanocontainers from non-polar to aqueous media. A general approach for the synthesis of polymer nanocontainers that are colloidally stable is presented, not sensitive to osmotic pressure, and responsive to environmental stimuli that trigger release of the nanocontainer contents. Additionally, the nanocontainers can selectively deliver one or more different payloads. The approach uniquely enables the synthesis of nanocontainers for various (mainly biomedical) applications in which aqueous environments are desired or inevitable. The nanocapsules can also be used as nanoorganelles in natural or synthetic cells.

## The Impact of Cryogenic-Temperature Electron Microscopy on Colloid Science

*Yeshayahu (Ishi) Talmon*

*Department of Chemical Engineering and the Russell Berrie Nanotechnology Institute, Technion-Israel Institute of Technology, Haifa 3200003, Israel*

Direct imaging on the nanometric scale is essential for full nanostructural characterization of any material system. That is true also for nonstructured liquid systems, which we refer to as complex liquids, where the typical domain size is on the supramolecular level. Only electron microscopy provides the required imaging resolution. To make liquid systems compatible with the high vacuum of the microscope, cryogenic-temperature electron microscopy (cryo-EM) must be applied, namely, the specimen is cooled ultra-rapidly to a cryogenic temperature, and kept at such a temperature during imaging in the transmission electron microscope (cryo-TEM) or the scanning electron microscope (cryo-SEM). Cryo-TEM requires very thin specimens, thinner than 300 nm. In cryo-SEM one can image liquids that cannot be made into thin specimens, and where fine, nanometric, details need to be imaged on large, micrometric, objects [1]. Because many complex liquid systems are very sensitive to even small changes of temperature and concentration, care must be taken to control those parameters during specimen preparation [2]. Also, complex liquids are very sensitive to radiolysis by the electron beam, thus minimal-electron-exposure imaging must be employed [3].

Cryo-EM has seen continues evolution in the past 50 years. Main points along this route have been the vitrification of water (rather than freezing that induces crystallization), the introduction of controlled environment chambers for specimen preparation with minimum structural artifacts, for cryo-TEM and cryo-SM, high-pressure cooling for minimizing freezing damage in cryo-SEM, the extension of cryo-EM to non-aqueous systems, introduction of the Volta phase-plate for improved image contrast in cryo-TEM, and the understanding of contrast at low acceleration voltage cryo-SEM. See the suggested references and references therein for more details [4-6]. The continuously evolving tools have made it possible to images a very wide range of nanostructured liquids, e.g., micellar solutions, microemulsions, polyelectrolyte complexes, blood cells and extracellular vesicles, and graphene and carbon nanotubes dispersed in super-acids. That imaging was most important in proving or disproving theories about the nanostructure of complex liquids. It should be emphasized that non-imaging techniques should be used together with the imaging to rule out artifacts and to obtain precise quantitative information.

In my talk I will describe the evolution of cryo-EM, show some most important discoveries that were made using that technique, and demonstrate some possible artifacts associated with cryo-EM, and how to identify and avoid them.

[1] Issman, L., Talmon, Y., *J. Microsc.* **2012**, 246, 60.

[2] Bellare, J. et al., *J. Electron Microsc. Tech.* **1988**,10, 87

[3] Talmon, Y., *J. Molecular Liquids* **2015**, Part A, 2.

[4] Matatyaho Ya'akobi, A., Talmon, Y., *Accounts Chem. Res.* **2021**, 54, 2100.

[5] Gradzielski, M., et al., *Chemical Reviews* **2021**,121, 5671.

[6] Lifshiz-Simon, S., et al., *J. Colloids and Interface Sci.* **2024**, 660, 177.

## Colloidal Hydrogels: Functional Building Block for Interactive Soft Matter

*Andrij Pich<sup>1,2</sup>, Tim Sassmann<sup>2</sup> and Selin Bulut<sup>3</sup>*

<sup>1</sup> *DWI-Leibniz Institute for Interactive Materials, Aachen, Germany*

<sup>2</sup> *Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany*

Colloidal hydrogels are functional polymer colloids exhibiting extraordinary properties like high chemical functionality, surface activity and stimuli-responsiveness. Colloidal hydrogels are considered as interesting candidates for applications in different areas such as catalysis, coatings and sensors. In particular, the application of colloidal hydrogels in drug delivery, food preservation or plant protection require often biocompatibility and programmed degradation without formation of toxic molecules harmful for the biological systems.

This presentation will focus on the development of sustainable synthesis methods and use of biobased building blocks for the synthesis of functional colloidal gels. Mechanochemical synthesis approach based on free-radical polymerisations and crosslinking reactions of functional monomers and polysaccharides was developed. [1] This synthesis methodology does not require the use of solvents and initiators leading to functional nanogels with average sized between 100 nm and 500 nm exhibiting controlled swelling degree and functional surface.

Using polysaccharides as reactive biobased building blocks we synthesized functional microgels with the size ranging from 200 nm to 200  $\mu\text{m}$  using water-in-oil emulsion methodologies. We demonstrated the successful application of polysaccharide-based microgels in delivery of antibiotics, [2] fabrication of microporous scaffolds for tissue engineering, [3,4] and development of plant protection formulations. [5]

[1] C. Hu, P. van Bonn, C. Bolm, A. Pich, *Angew. Chem. Int. Ed.* **2023**, e202305783.

[2] X. Li, N. Wolter, H. Li, X. Shi, A. Pich, *J. Adv. Res.* **2023**, 43, 87-96.

[3] S. Bulut, S-H. Jung, T. Bissing, F. Schmitt, M. Bund, S. Braun, A. Pich, *Small* **2023**, 2303783.

[4] S. Bulut, D. Günther, M. Bund, C. Haats, T. Bissing, C. Bastard, M. Wessling, L. De Laporte, A. Pich, *Adv. Healthcare Mater.* **2023**, 2302957.

[5] S. Braun, G. Dilarri, L. de Lencastre Novaes, P. Huth, A. Töpel, L. Hussmann, A. Boes, A., M. D. da Rocha, F. Jakob, L. O. Regasini, U. Schwaneberg, H. Ferreira, A. Pich, *Adv. Funct. Mater.* **2023**, 2305646.

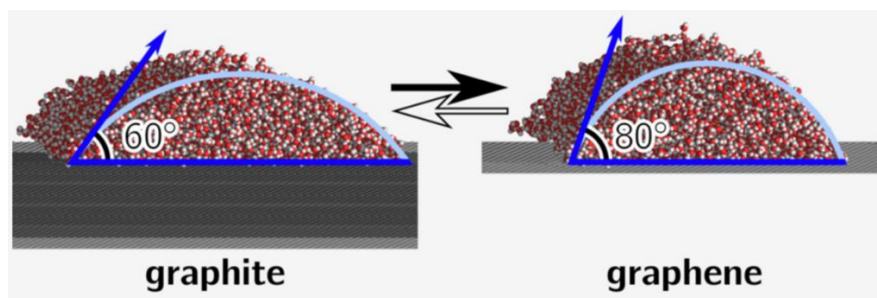
## Wetting behavior and surface potential of water, acids and bases at graphene

Shane Carlson<sup>1</sup>, Otto Schullian<sup>1</sup>, Laura Scalfi<sup>1</sup>, Max Becker<sup>1</sup>, Louis Lehmann<sup>1</sup>, Douwe J. Bonthuis<sup>2</sup> and Roland R. Netz<sup>1</sup>

<sup>1</sup> Fachbereich Physik, Freie Universität Berlin, Germany

<sup>2</sup> Institute of Theoretical and Computational Physics, Graz University of Technology, Austria

Accurate modeling of water interactions with graphene and graphite is important for nanofluidic applications. Experimental water contact angles show extreme variations among reported values for graphene and a clustering into groups for freshly exfoliated ( $60^\circ \pm 13^\circ$ ) and not-freshly exfoliated graphite surfaces. Based on this  $60^\circ$  graphite-water contact angle a contact angle for unsupported graphene of  $80^\circ$  is derived, in agreement with the experimental observation of water entering graphene nanostructures [1]. Based on simulations using quantum-chemical density-functional theory as well as properly optimized water-graphene interaction force fields the propensity of ions (including water ions) to graphene is calculated. Similarly to the interface with air [2], hydronium is attracted to graphene while hydroxide is repelled, thus the surface free energy is predicted to decrease for acids and to increase for bases. The electrostatic surface potential due to the interfacial ion distributions (which is indicative of the electroosmotic Zeta potential [3]) is positive for HCl solutions and close to zero for NaOH solutions at both the air and graphene interface. While graphene substantially changes water structure and dynamics, as shown by predicted linear and non-linear water spectra at graphene, interfacial energies and potentials are rather similar to the interface with air. Thus, graphene is slightly hydrophilic yet exhibits interfacial properties very similar to the air interface.



**Figure 1.** The water contact angle at graphene increases slightly compared to graphite yet stays below  $90^\circ$ , indicative of a slightly hydrophilic surface.

[1] Shane R. Carlson, Otto Schullian, Maximilian R. Becker, and Roland R. Netz, *J. Phys. Chem. Lett.* **2024**, 15, 6325–6333.

[2] Shavkat I. Mamatkulov, Christoph Allolio, Roland R. Netz, and Douwe Jan Bonthuis, *Angew. Chem. Int. Ed.* **2017**, 56, 15846–15851.

[3] Maximilian Becker, Philip Loche, Majid Rezaei, Amanuel Wolde-Kidan, Yuki Uematsu, Roland R. Netz, and Douwe Jan Bonthuis, *Chem. Rev.* **2024**, 124, 1–26.

## Shape-morphing of droplets with programmable transience

*Lukas Zeininger*

*Responsive Soft Materials Lab, Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany*

Autonomous chemo-mechanical signal transduction is an inherent feature by which natural systems exert control over complex biological functions. It is therefore essential for the emulation and delineation of complex emergent behaviors in artificial dissipative material systems. Bio-inspired, life-like material platforms focus on the non-equilibrium properties of matter, thereby departing from present-day material design paradigms, which typically emphasize thermodynamic stability to ensure long-term viability in an application context.

Emulsions, composed of liquid droplets dispersed in another immiscible fluid phase, have emerged as fascinating chemically minimal materials for studying such non-equilibrium, life-inspired properties. Surfactant stabilized emulsion droplets intrinsically persist in thermodynamic out-of-equilibrium states and are highly dynamic, with molecules constantly being exchanged between the droplets and their environment. Interface-selective sensitization of droplets allows such systems to exhibit programmed up- and down-regulating capabilities and dynamic and reversible interfacial host-guest complexation can trigger morphological reconfigurations of complex droplets, which resembles cell surface environments. Complex droplets can selectively and dynamically present, hide, or expand liquid-liquid interfaces, and thereby serve as messenger colloids to visualize and report force gradients in temperature, chemistry, and concentration with up to femtomolar sensitivity.

In this presentation, I will explore how studying minimalistic chemical droplet systems that exhibit simple emergent collective behaviors can provide physico-chemical design guidelines for the future design of synthetic active and adaptive material systems. More specifically, the presentation will highlight examples of a kinetic trapping of non-equilibrium droplet shapes as a basis for chemo-mechanical signal transduction. Leveraging the droplets' ability to harness various forms of energies and gradients in parallel and competitively then allows controlling and regulating multiple independent responsive modalities independently. This serves as a basis for designing adaptive droplet ensembles, where a dynamic control over the partitioning yields artificial soft matter systems with self-regulated decision-making skills. Such systems can move chemotactically and reversibly in response to interfacial tension differentials, tilt out of gravitational alignment due to multivalent chemical interactions or intra-droplet thermocapillary fluid convections, and exhibit simple emergent collective behaviors, including a self-regulated ability to communicate, evolve, and organize into patterns or networks, with implications for future soft robotics and sensing technologies.

## Contributed Talks

**Polyelectrolytes**  
**& Polyelectrolyte Coacervates Renaissance**

## T01: Charge effects at liquid interfaces

*Arghya Majee<sup>1</sup>, Christoph A. Weber<sup>2</sup> and Frank Jülicher<sup>3,4,5</sup>*

<sup>1</sup> *Institute Theory of Polymers, Leibniz Institute of Polymer Research Dresden, Germany*

<sup>2</sup> *Institute of Physics, University of Augsburg, Germany*

<sup>3</sup> *Max Planck Institute for the Physics of Complex Systems, Dresden, Germany*

<sup>4</sup> *Center for Systems Biology Dresden, Germany*

<sup>5</sup> *Cluster of Excellence Physics of Life, TU Dresden, Germany*

We present a theory for phase-separated liquid coacervates with salt, taking into account spatial heterogeneities and interfacial profiles [1]. We find that multiple charged layers of alternating sign can form around the interface while the bulk phases remain charge-neutral. We show that the salt concentration regulates the number of layers, the amplitude of the layer's charge density, and the electrostatic potential.

Such charged layers prohibit droplet coalescence if the charge density is sufficiently high. For smaller charge densities, we show that electrostatics can even facilitate droplet coalescence. Moreover, we also observe an electrostatically-mediated delay in the Ostwald ripening process. Our theory could be relevant for artificial systems and biomolecular condensates in cells. Our work suggests that interfaces of biomolecular condensates could mediate charge-specific transport similar to membrane-bound compartments.

[1] A. Majee, C. A. Weber, and F. Jülicher, arXiv:2310.07835 (2023)



## T02: Polyelectrolyte brushes exhibit underscreening in hypersaline environments

*Hayden Robertson*<sup>1,2</sup>, *Geran Dunlop*<sup>1</sup>, *Gareth Elliott*<sup>1</sup>, *Vincent S. J. Craig*<sup>3</sup>, *Andrew R. J. Nelson*<sup>4</sup>, *Stuart W. Prescott*<sup>5</sup>, *Grant B. Webber*<sup>1</sup>, *Erica J. Wanless*<sup>1</sup>

<sup>1</sup> *College of Engineering, Science and Environment, University of Newcastle, Callaghan, Australia*

<sup>2</sup> *Soft Matter at Interfaces, Technische Universität Darmstadt, Darmstadt, Germany*

<sup>3</sup> *Materials Physics, Australian National University, Canberra, Australia*

<sup>4</sup> *Australian Centre for Neutron Scattering, ANSTO, Lucas Heights, Australia*

<sup>5</sup> *School of Chemical Engineering, UNSW Sydney, Sydney, Australia*

Electrostatics plays a fundamental role in a wide range of natural phenomena and is crucial for understanding the interactions between charges in many biological, chemical, and physical systems. Despite being poorly understood, hyper-saline environments are ubiquitous in nature and myriad technological processes. In particular, polymer morphology is critically important in these hyper-saline regimes, with the atomic level interactions between the polymer, solvent and salt determining the overall polymer nanostructure, ultimately governing applications such as lubrication and protein activity.

Recent experiments have revealed that the theory encompassing classical electrostatics (e.g., DLVO theory) breaks down at high salt concentrations [1,2]. For monovalent ions at high concentration regimes, a minimum exists in the electrostatic decay length, beyond which underscreening has been observed, where the range of electrostatic interactions is greater than the anticipated Debye length [1,3,4]. This underscreening phenomenon is enhanced with valency and concentration.

To probe underscreening, we employed a strong cationic and a strong anionic polyelectrolyte brush as exemplars [5]. In the context of polyelectrolyte brushes, underscreening, or re-entrant behaviour, presents itself as a non-monotonic change in brush thickness with increasing salt concentration; an initial decrease in brush thickness at intermediate concentrations followed by a subsequent increase at high concentrations. The influence of both mono- and multivalent ions on the electrostatic decay length at high salt concentrations was examined by probing polyelectrolyte brush conformation in response to electrolyte. Neutron reflectometry (NR) and spectroscopic ellipsometry (SE) revealed that in hypersaline environments, both cationic and anionic polyelectrolyte brushes exhibit re-entrant behaviour. Both NR and SE showed a non-monotonic change in brush thickness as a function of electrolyte concentration. Interestingly, however, NR revealed for the first time that the structure of the swollen polyelectrolyte brush is different in electrolytes of low and high concentration [6].

[1] Elliott, Gregory, Robertson et al., *Chem. Phys. Lett.* **2024**, 843, 141190.

[2] Kontogeorgis et al., *Fluid Phase Equilib.* **2018**, 462, 130.

[3] Smith et al., *J. Phys. Chem. Lett.* **2016**, 7(12), 2157.

[4] Lee et al., *Phys. Rev. Lett.* **2017**, 119(2), 026002.

[5] Robertson et al., *Phys. Chem. Chem. Phys.* **2023**, 25(36), 24770.

[6] Authors acknowledge the Australian Research Council (DP190100788) and ANSTO (PP9789 and PPR13123). AINSE Ltd is thanked for a Post Graduate Research Awards.

## T03: Uptake and release of cationic guest molecules into weak anionic polyelectrolyte microgels: A Monte Carlo study

Christian Strauch and Stefanie Schneider

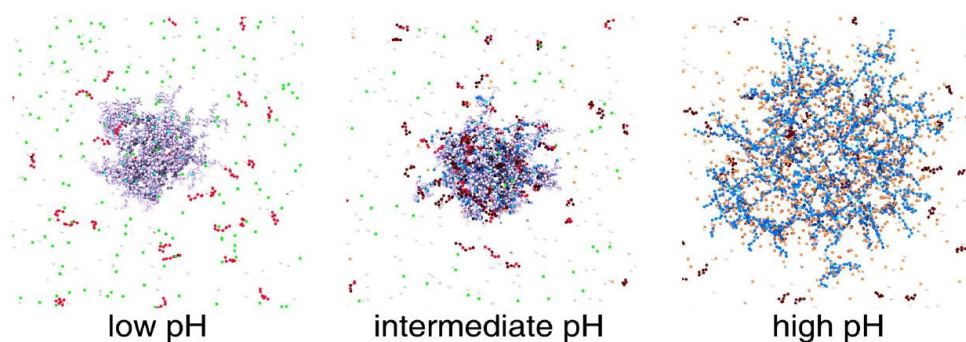
RWTH Aachen University, Institute of Physical Chemistry, Aachen, Germany

Uptake and release of guest molecules in microgels can be triggered by external stimuli. Especially their pH responsiveness makes weak polyelectrolyte (PE) microgels excellent candidates for drug delivery systems. When both microgel and guest molecules are pH-responsive, predicting the electrostatically driven uptake can nevertheless be complex since the ionization depends on many parameters.

We used constant pH Monte Carlo simulations to investigate a microgel/oligomer system at different pH, microgel concentration and oligomer concentration.

In previous studies, we investigated the ionisation and swelling of polyelectrolyte (PE) and polyampholyte (PA) microgels of different architectures and observed a suppression of ionisation for the PE and both enhancement and suppression of ionisation for the PA microgels depending on the pH with respect to the isoelectric point. [1-3]

For both the microgel and the oligomers, the presence of the other species, leads to an enhancement of the degree of ionization over a wide pH range. The uptake of the oligomer into the charged microgel induces a release of counterions and results in complex formation between the oligomers and the network, leading to a microgel collapse. [4] Our results on the uptake of cationic oligomers into anionic networks can help guiding the design of microgels as drug carriers, e.g. for antimicrobial peptides.



**Figure 1.** Snapshots of the uptake behavior of cationic oligomers into a weak polyelectrolyte network at different pH. Charged network beads are depicted in blue, and their counterions are orange, while uncharged network beads are in a light purple. Crosslinks are cyan. Charged monomers of the oligomers are shown in red and their counterions green, while uncharged oligomer beads are brown. White particles have no charges. Reproduced from [4].

[1] C. Hofzumahaus, P. Hebbeker, S. Schneider, *Soft Matter*, **2018**, 14, 4087.

[2] C. Hofzumahaus, C. Strauch, S. Schneider, *Soft Matter*, **2021**, 17, 6029.

[3] C. Strauch, S. Schneider, *Soft Matter*, **2023**, 19, 938.

[4] C. Strauch, S. Schneider, *Soft Matter*, **2024**, 20, 1263.

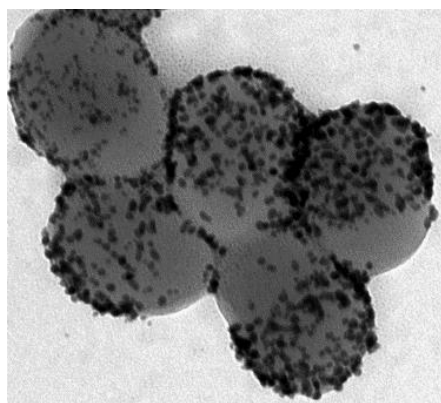
## T04: Synthesis of Janus Dumbbells through Regiospecific Grafting of Polyelectrolyte Brushes

*Gabriel Monteiro<sup>1</sup>, Sara Bäum<sup>1</sup> and Alexander Wittemann<sup>3</sup>*

<sup>1</sup> *Colloid Chemistry, Department of Chemistry, University of Konstanz, Universitaetsstrasse 10, Konstanz, D-78464, Germany*

Polymer dumbbells are anisotropic particles produced through sequential polymerizations, exhibiting great potential in applications such as catalysis, drug delivery systems, self-assembly, membranes, and nanomachines [1, 2]. Their chemical anisotropy is particularly advantageous, allowing the separation of catalytic sites, improving drug delivery targeting, facilitating self-assembly, increasing membrane selectivity, and boosting motion [3]. However, achieving large-scale production of these particles with precise morphological control remains a significant challenge [1]. A promising method to introduce chemical anisotropy in colloidal dumbbells is the asymmetrical functionalization of their surfaces, leveraging their formation mechanism. Since these particles are created through two subsequent polymerizations, functional monomers can be incorporated on either side. Notably, vinyl-containing photopolymerization initiators can be grafted onto the surface of these particles. This allows polymer chains to covalently bind to the surface of the particles, and form polymer brushes [4]. These brushes act as nanoreactors, providing a microenvironment for reactions catalyzed by metal nanoparticles or enzymes, potentially enhancing the motion of the particles [3].

We present synthesis routes for growing regiospecific polymer brushes on the surface of polymer colloidal nanoparticles. Our versatile strategies enable the production of photopolymerization initiator-functionalized dumbbells suitable for various nanoparticles. These particles served as seeds for the photopolymerization of diverse polymer brushes. The resulting brushes were analyzed using various techniques to confirm their regiospecific formation, and demonstrating their effectiveness in uptaking catalysts such as metal nanoparticles (Fig. 1) or enzymes [5].



**Figure 1.** Direct transmission electron microscopy visualization of the regiospecific reduction of metal nanoparticles from metal ion complexes on one specific side of the colloidal dumbbells. The concentration of metal nanoparticles on one side indicates the presence of the brushes selectively on this area of the particles.

[1] Monteiro GAA, Wittemann A, *Colloid Polym Sci*, **2023**, 301, 7, 801-812.

[2] Stuckert R, Plüsch CS, Wittemann A, *Langmuir*, **2018**, 34, 13339–13351.

[3] S. J. Ebbens, D. A. Gregory, *Acc. Chem. Res.*, **2018**, 51, 9, 1931–1939.

[4] A. Wittemann, *et al*, *J. Am. Chem. Soc.*, **2005**, 127, 27, 9688–9689.

[5] This research was co-funded by the Deutsche Forschungsgemeinschaft. Technical support from the Nanostructure Laboratory (nano.lab) and the Particle Analysis Centre (PAC) at the University of Konstanz is gratefully acknowledged

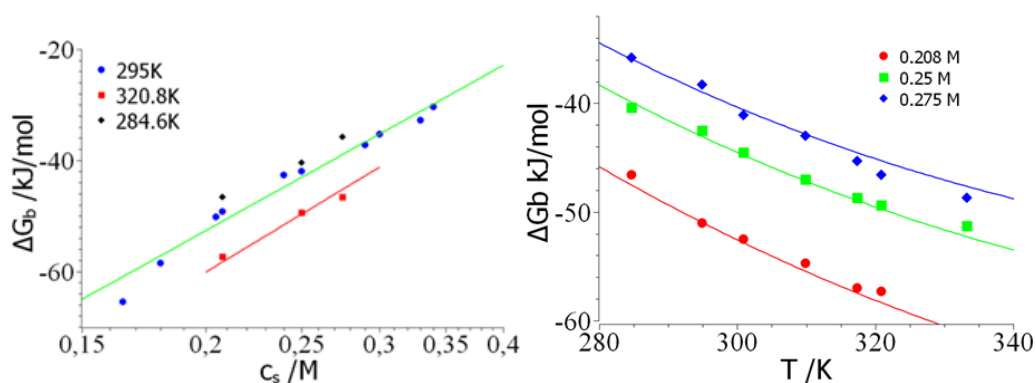
## T05: Driving Forces in the Formation of Biocondensates

*Matthias Ballauff*

*Institut für Chemie und Biochemie, Freie Universität Berlin, Forschungsbau SupraFab, Altensteinstrasse 23a, 14195 Berlin, Germany*

Anionic proteins may form biocondensates with cationic proteins in aqueous solution. Intrinsically disordered proteins (IDP) present an important class of proteins that form such biocondensates. In this contribution, a thermodynamic analysis of the binary complex formation of the highly positively charged linker histone H1 with the highly negatively charged chaperone, prothymosin  $\alpha$  (ProT $\alpha$ ) will be given. ProT $\alpha$  and H1 have large opposite net charges ( $-44$  and  $+53$ , respectively) and form complexes at physiological salt concentrations with picomolar to nanomolar affinity as shown by Chowdhury et al. [1]. Here, data for binary complex formation obtained by Chowdhury et al. [1] are analyzed by a phenomenological model that is based on counterion condensation modulated by hydration effects [2].

The analysis demonstrates that temperature  $T$  and salt concentration  $c_s$  in the system are the decisive variables. Figure 1 displays the free energies of binary complex formation as the function of  $c_s$  and  $T$ . The release of the counterions mainly bound to ProT $\alpha$  is shown to be the main driving force, hydration effects play no role within the limits of error. A release of  $\Delta n_{ci} = 17.5$  counterions per binary complex can be derived. It is shown that  $\Delta n_{ci}$  is independent from temperature which is in full agreement with data obtained on comparable systems. Complex formation is characterized by a large additional entropic term which is most probably due to water reorientation. Moreover, a strongly negative change of the specific heat  $\Delta c_p$  ( $-0.87$  kJ/(K mol)) is found which is due to the loss of conformational degrees of freedom. Full agreement of the model with the measured free energies can be achieved as shown in Figure 1. The entire analysis demonstrates that a thermodynamic analysis proceeding virtually without model assumptions is capable of identifying the main driving forces of complex formation by IDPs [3].



**Figure 1.** Free energy  $\Delta G_b$  for the formation of binary complexes between ProT $\alpha$  and H1 as the function of the two decisive variables, namely salt concentration  $c_s$  (left panel) and temperature (right panel). The symbols display the experimental data taken from ref.[1] whereas the solid lines present the fit by the model.

[1] A. Chowdhury et al., *Proc Natl Acad Sci U S A* **2023**, 120 (41), e2304036120.

[2] J. J. Walkowiak, M. Ballauff, *Adv. Sci.* **2021**, 8 (12), 2100661.

[3] The author acknowledges funding by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – 434130070, GRK 2662.

## T06: Complexation of Humic Acid by Polycations as Model System for Water Treatment – Phase Behaviour and Aggregate Structures

Yuan Mingyu<sup>1</sup>, Bin Dai<sup>1</sup>, Heriberto Bustamante<sup>2</sup>, Long D. Nghiem<sup>3</sup>, and Michael Gradzielski<sup>1</sup>

<sup>1</sup> Stranski-Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany

<sup>2</sup> Sydney Water, Parramatta NSW 2125, Australia

<sup>3</sup> Centre for Technology in Water and Wastewater, University of Technology Sydney (UTS), Sydney Australia

Humic acid (HA) is a major component of natural organic matter (NOM) in raw water, which negatively affects the quality of drinking water and therefore should be removed from it during the process of water treatment. As HA is a negatively charged mix of macromolecules one option for removal is complexation by a polycation and subsequent precipitation of the formed complexes. Conventionally this involves addition of poly(diallyldimethylammonium chloride) (pDADMAC) but NOM removal is rather incomplete. Therefore we synthesized novel chitosan polymers to maximise NOM removal, as the chemistry of chitosan allows for a wide range of derivatization that should lead to improved structures for polyelectrolytes for water treatment[1].

The degree of quaternisation (and thereby the charge density of the chitosan) was varied over a larger range, and its behaviour was compared to that of pDADMAC. In our experiments we kept the HA concentration constant and varied the concentration of the polycation as well as the pH value. For these systems we studied the macroscopic phase behaviour and the structure of the formed complexes in solution by static and dynamic light scattering, as well as by laser light diffraction. Small-angle x-ray scattering (SAXS) showed formation of hydrophobic domains in the size range of ~20 nm for qCs, which is not observed for PDADMAC. The initial formation process of the complexes was followed with time-resolved SAXS, showing marked differences of the structural evolution in this process, depending on the charge density of the qCs employed. Finally, we also addressed the effect of the presence of different ions on the precipitation process, where we found a marked effect of rather small amounts of Ca<sup>2+</sup> [2].

In order to generalise our findings on the model system HA, we extended then our work to study the behaviour of our different polycations with natural raw water. Here we observed that NOM removal was particularly good for intermediate charge density of the qCs and interestingly the precise extent of charge neutralisation was not so important for NOM flocculation.

In conclusion, we did a fundamental investigation of one of the key steps in water treatment, the flocculation by polycation. The combination of different experimental techniques allows to discern the structures formed with HA and how they and their evolution depend on the type of complexing polycation and pH. This insight then can be used for understanding the interaction of the different polycations with raw water, which constitutes an interesting contribution to improve water treatment based on fundamental principles of colloid science.

[1] Loganathan P, Gradzielski M, Bustamante H, Vigneswaran S., *Env. Sci.: Water Res. Tech.* **2020**, 6, 45-61.

[2] Yuan M, Bustamante H, Mahmoudi N, Gradzielski M. *Langmuir* **2024**, 40, 4108-4121.

[3] The authors acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG), Grant Number GR1030/26-1.

**Surfactant Science, Membranes, Foams,  
Microemulsions, Emulsions & Amphiphilic  
Copolymers**

## T 07: Degradability of surfactants containing Ester groups

*Abdulhamid Hejazi Almidani*<sup>1</sup>, *Christian Bittner*<sup>2</sup>, and *Thomas Sottmann*<sup>1</sup>

<sup>1</sup>*Institute of Physical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany*

<sup>2</sup>*BASF SE, 67056 Ludwigshafen am Rhein, Germany*

Due to their wide range of applications, large amounts of surfactants are released into the environment, where their accumulation and non-degradability can have ecological ramifications [1]. An obvious approach to reduce this accumulation is to use surfactants that are stable during application, but degrade afterwards. We therefore investigated the stability of surfactants with cleavable bonds, e.g. with ester groups that can be degraded by hydrolysis, complementing the studies by Holmberg and others [2]. For these studies, we selected one of the most commonly used anionic surfactants, di(*n*-hexyl)sulfosuccinate sodium salt (SDHSS) and the biosurfactant di-rhamnolipid (Rha<sub>2</sub>-C<sub>10</sub>-C<sub>10</sub>) produced by microorganisms [2]. The chemical stability of these two surfactants was studied recording time-resolved (TR) <sup>1</sup>H-NMR spectra of surfactant/D<sub>2</sub>O/NaOD solutions as a function of temperature, *pD* and surfactant concentration. We found that the degradation often follows first-order kinetics. Thus, for SDHSS at *pD* = 12, 20 °C and a concentration below the critical micelle concentration (CMC), a half-life of 4 days was determined. Recording the TR-<sup>1</sup>H-NMR spectra at 45 °C and 60 °C revealed an exponential growth of the rate constant, with an activation energy of  $E_A = 55 \pm 21$  kJ/mol typical for chemical compounds containing ester groups [3]. When the concentration was increased above the CMC, the SDHSS molecules were only partially degraded, which may suggest that surfactant molecules forming the micelle are protected from hydrolysis [4]. This explanation, which neglects the fast micelle kinetics, could be disproved through measurements at *pD* = 13, demonstrating a complete degradation of the SDHSS molecules even at concentrations above the CMC with even shorter times (half-life of 7 hours). Additional studies of the degradation of SDHSS at *pD* = 11 enabled a better understanding of the decomposition mechanism, which takes place in two steps that depend on the OD/SDHSS ratio. In the first step, SDHSS decomposes into the intermediate mono(*n*-hexyl)sulfosuccinate sodium salt and 1-hexanol, which in the second step is further hydrolysed to sodium sulfosuccinate and 1-hexanol. For the di-rhamnolipid (Rha<sub>2</sub>-C<sub>10</sub>-C<sub>10</sub>), the same activation energy  $E_A = 56 \pm 14$  kJ/mol was found in comparable TR-<sup>1</sup>H-NMR studies (*pD* = 12 and a below the CMC) performed at 20 °C, 45 °C and 60 °C. The comparison of the kinetic data of SDHSS and Rha<sub>2</sub>-C<sub>10</sub>-C<sub>10</sub>, e.g. at *pD* = 13, 20 °C and above the CMC, shows that Rha<sub>2</sub>-C<sub>10</sub>-C<sub>10</sub> degrades 2.5 times slower than SDHSS, probably due to steric hindrance of the two rhamnose units.

[1] E. Olkowska, M. Ruman, Z. Polkowska, *Journal of analytical methods in chemistry* **2014**, 2014, 769708.

[2] T. Hellweg, T. Sottmann, J. Oberdisse, *Front. Soft. Matter* **2023**, 2.

[3] M. L. Bender, R. D. Ginger, J. P. Unik, *J. Am. Chem. Soc.* **1958**, 80, 1044.

[4] M. Stjerndahl, K. Holmberg, *J Surfact Deterg* **2003**, 6, 311.

## T08: Self-assembled Peptides Structure Mediated by Solid Interfaces

*Leila Sahebmoammadi<sup>1</sup>, Oliver Stach<sup>2</sup>, Pol Besenius<sup>2</sup>, Markus Mezger<sup>3</sup> and Regine von Klitzing<sup>1</sup>,*

<sup>1</sup> *Soft Matter at Interfaces, Department of Physics, Technical University of Darmstadt, Germany*

<sup>2</sup> *Department of Chemistry, Johannes Gutenberg-Universität Mainz, Germany*

<sup>3</sup> *Faculty of Physics, Universität Wien, Austria*

The molecule's self-assembly arises from non-covalent interactions, steric limitations, and excluded volume effects. This study investigates the self-assembly dynamics of amphiphilic, C3-symmetric dendritic peptides, both with and without thermosensitive moieties. The oppositely charged dendritic peptide amphiphiles supramolecular are self-assembled into the 1D nanorod-like pattern in the aqueous buffer [1]. Circular dichroism spectroscopy results approve that the nanorod pattern was following  $\beta$ -sheet structure [2,3]. The question arises what structures are formed at solid interfaces.

Using Quartz Crystal Microbalance with Dissipation (QCM-D) show that layer-by-layer adsorption process of charged peptides leads to the formation of multilayers, which is strongly temperature dependent. The comonomer based on lysin (cationic comonomer) emerges as the optimal grafting layer, exhibiting heightened adsorption on both gold (Au) and silicon (Si) surfaces. The study indicates that the thermosensitive moiety enhances the amount of adsorbed material, improves adsorption kinetics, and increases the homogeneity of the coating. In addition the process is very pH sensitive. Notably, exposure to extreme pH conditions (2 or 12) induces the removal of multilayers, indicative of a pH-responsive behavior driven by reduced electrostatic interaction.

Atomic Force Microscopy (AFM) is used to study the structure at the surface. This approach enhances our understanding of peptide self-assembly and provides insights for customizing surface properties through the integration of self-assembly and surface confinement.

[1] Ahlers, Patrick, et al., *Macromolecules* 50.19 (2017): 7712-7720.

[2] Engel, Sabrina, et al., *Faraday discussions* 204 (2017): 53-67.

[3] Frisch, Hendrik, et al., *Angewandte Chemie International Edition* 55.25 (2016): 7242-7246.



## T09: Dynamic and Equilibrium Self-Assembly of Volatile Amphiphiles, Surfactants and Polymers

*Larisa Tsarkova*<sup>1,2</sup>, *Oxana A. Soboleva*<sup>3</sup>

<sup>1</sup> German Textile Research Center North West (DTNW), Krefeld, Germany

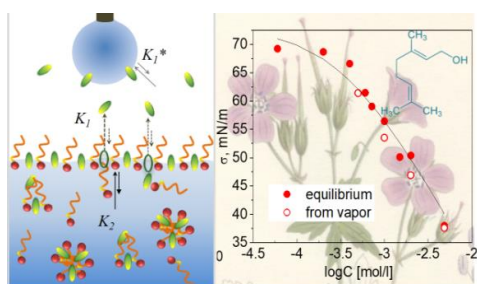
<sup>2</sup> University of Duisburg-Essen, Essen, Germany

<sup>3</sup> Department of Chemistry, Moscow State University, Moscow, Russia

Molecular aggregation in multicomponent systems, which contain amphiphiles of different nature, polymers, inorganic salts is often defines the targeted functioning of such mixtures. The ability to manage self-assembly on different time scales in bulk and at interfaces is an important task. Two examples of application of dynamic surface tension measurements and of sensing tensiometry in understanding the aggregation behavior will be presented.

A complex multicomponent system, containing ethoxylated anionic surfactants, anionic polyelectrolytes and enzymes, is discussed. A key contribution to the characterization of the macroscopic effect of enhanced solubilisation performance of immobilized proteins was gained by the analysis of dynamic processes at interfaces and of competitive binding interactions with  $\text{Ca}^{2+}$  ions with the components, resulting in bridging interactions between like-charged polyanions and surfactants [1].

Second, we evaluate interfacial adsorption-evaporation behavior of a volatile amphiphile geraniol at both sides of the interface in mixed solutions with micelle-forming surfactants of different nature under variation of the concentration and composition of the mixtures. Additionally, pending drop sensing tensiometry proved to be a sensitive method in assessing the concentration of geraniol in the vapors above mixed solutions (Figure 1). Differences in the release of the fragrance from the mixed interfacial layers are explained by competitive contributions of specific barrier mechanisms and concentration-dependent aggregation in bulk solutions [2,3,4].



**Figure 1.** Left: Schematic of the sensing tensiometry. Right: Comparison of the equilibrium surface tension isotherm (from bulk solution), with the isotherm resulting from the adsorption of geraniol on a surface of a water drop in the head-space volume above solutions with indicated concentrations.

[1] Thiele, M. J. et al. *Angew. Chem., Int. Ed.* **2018**, 57, 9402-9407.

[2] Soboleva, O. A. et al. *Langmuir* **2022**, 38, 2793-2803.

[3] Soboleva, O. A. et al. *Colloids and Surfaces A* **2023**, 676, 132119.

[4] LT acknowledges funding from IGF project No. 22921 N of Forschungskuratorium Textil e.V., Reinhardtstraße 12-14, 10117 Berlin, Germany the German Federal Ministry for Economic Affairs and Climate Action.

## T10: Shifting Polymeric Micelles from/into Kinetically-Trapped Nonequilibrium States

*Felix Plamper and Quirin Prasser*

*TU Bergakademie Freiberg, Institute of Physical Chemistry, Freiberg, Germany*

Non-equilibrium self-assembled nanostructures hold promise for stimulated transitions at otherwise constant conditions. They can be also used for sensing. However, the reliable formation of these structures can be a challenge.[1,2] This is true when considering the delicate balance between kinetic trapping of micelles for long term stability and otherwise implementing the possibility to induce morphological transitions toward the equilibrium structure by applying minute deflections from metastability.

We have introduced an adjustable temperature-responsive polymer-based system, which meets both demands, allowing considerable changes of the material properties upon triggering the non-equilibrium micelles by help of various stimuli.[3] Low viscosity dispersions of spherical micelles can be transformed on their way toward equilibrium to a network of worm-like micelles forming a gel. This transformation takes place at constant conditions upon application of a temporary trigger. Hence, the system remembers the history of the sample, like a past cold wave. As a further advancement, the non-equilibrium nature of interpolyelectrolyte complex micelles can be recycled after approaching equilibrium.[4] Here, the interplay between addition/removal of salt as plasticizer and a temperature-responsive polymer gives a handle to modulate the hydrophilic/hydrophobic balance while freezing and melting the internal micellar structures. Hence, micellar morphologies obtained at certain conditions can be conserved for other conditions, where the morphology of these micelles is not the equilibrium one. Finally, we present a micellar system, which memorizes any heat above a certain threshold temperature, as it turns irreversibly turbid upon suffering high temperatures.[5] Smoluchowski-type aggregation kinetics were observed. Besides the history monitoring of exceeding such a temperature, it can also be switched to a system that only senses the current temperature.

In summary, we present different systems, where minute changes in the conditions lead either to irreversible or sometimes reversible changes in the colloidal properties.[6] In the latter case, certain measures need to be taken to shift the system back...

[1] H. Cui, Z. Chen, S. Zhong, K. L. Wooley, D. J. Pochan, *Science* **2007**, 317, 647.

[2] K. Kim, M. W. Schulze, A. Arora, R. M. Lewis, M. A. Hillmyer, K. D. Dorfman, F. S. Bates, *Science* **2017**, 356, 520.

[3] A. A. Steinschulte, A. Scotti, K. Rahimi, O. Nevskyi, A. Oppermann, S. Schneider, S. Bochenek, M. F. Schulte, K. Geisel, F. Jansen, A. Jung, S. Mallmann, R. Winter, W. Richtering, D. Wöll, R. Schweins, N. J. Warren and F. A. Plamper, *Adv. Mater.* **2017**, 29, 1703495.

[4] C. Dähling, J. E. Houston, A. Radulescu, M. Drechsler, M. Brugnioni, H. Mori, D. V. Pergushov, F. A. Plamper, *ACS Macro Lett.* **2018**, 7, 341.

[5] Q. Prasser, T. Fuhs, B. Torger, R. Neubert, E. Brendler, C. Vogt, F. Mertens and F. A. Plamper, *ACS Appl. Mater. Interfaces* **2023**, 15, 57950.

[6] The authors acknowledge funding from the DFG, Grant Number PL 571/5-1.

## T11: Transition from a Sponge-Like to a Foam-Like Nanostructure in Water-Rich $L_3$ Phases

Philipp Menold<sup>1</sup>, Reinhard Strey<sup>2</sup>, Ulf Olsson<sup>3</sup>, Zoltan Takacs<sup>4</sup>, Daniel Topgaard<sup>3</sup>, Natalie Preisig<sup>1</sup> and Cosima Stubenrauch<sup>1</sup>

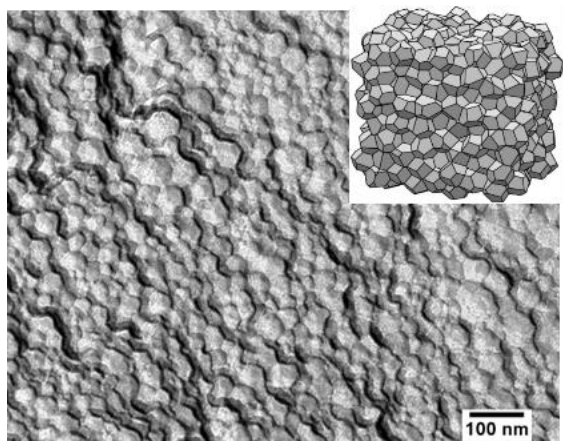
<sup>1</sup> Institute of Physical Chemistry, University of Stuttgart, Germany

<sup>2</sup> Institute of Physical Chemistry, University of Cologne, Germany

<sup>3</sup> Physical Chemistry, Lund University, Sweden

<sup>4</sup> Centre for Analysis and Synthesis, Lund University, Sweden

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<sub>6</sub>MA) - 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<sub>6</sub>MA) 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. Already upon addition of small amounts of oil to the  $L_3$  phase the conductivities become very low and the viscosities very high [5]. 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. [6] for a related system with a technical grade nonionic / anionic surfactant mixture. Subsequently, we investigated the structural transition in the  $L_3$  channel by NMR self-diffusion measurements (FTPGSE).



**Figure 1:** Freeze fracture electron microscopy (FFEM) image of an oil-continuous microemulsion H<sub>2</sub>O/NaCl - C<sub>6</sub>MA - AOT with AOT mass fraction  $\gamma = 0.15$  and C<sub>6</sub>MA mass fraction  $\alpha = 0.04$ . Scale bar = 100 nm. The inset illustrates the polyhedral foam like structure taken from [7].

[1] D.F. Evans, D.J. Mitchell, B.W. Ninham, *J. Phys. Chem.*, **1986**, 90, 2817.

[2] W. Jahn, R. Strey, *J. Phys. Chem.*, **1988**, 92, 2294.

[3] S.H. Chen, S.L. Chang, R. Strey, P.Thiyagarajan, *J. Phys.: Condens. Matter*, **1991**, 3, F91.

[4] M. Skouri, J. Marignan, R. May, *Colloid Polym Sci*, **1991**, 269, 929.

[5] P. Menold, R. Strey, N. Preisig and C. Stubenrauch, *JCIS*, **2021**, 601, 133.

[6] L. Wolf, H. Hoffmann, W. Richter, T. Teshigawara, T. Okamoto, *J. Phys. Chem. B*, **2011**, 115, 11081.

[7] A. M. Kraynik, *Adv. Eng. Mater.*, **2006**, 8, 900.

## T12: Liquid foams: new insights from neutron scattering experiments

Julien Lamolinarie<sup>1</sup>, Olivier Diat<sup>2</sup>, Leonardo Chiappisi<sup>1</sup>

<sup>1</sup> Institut Max von Laue - Paul Langevin, 71 avenue des Martyrs 38042 Grenoble Cedex 9, France,

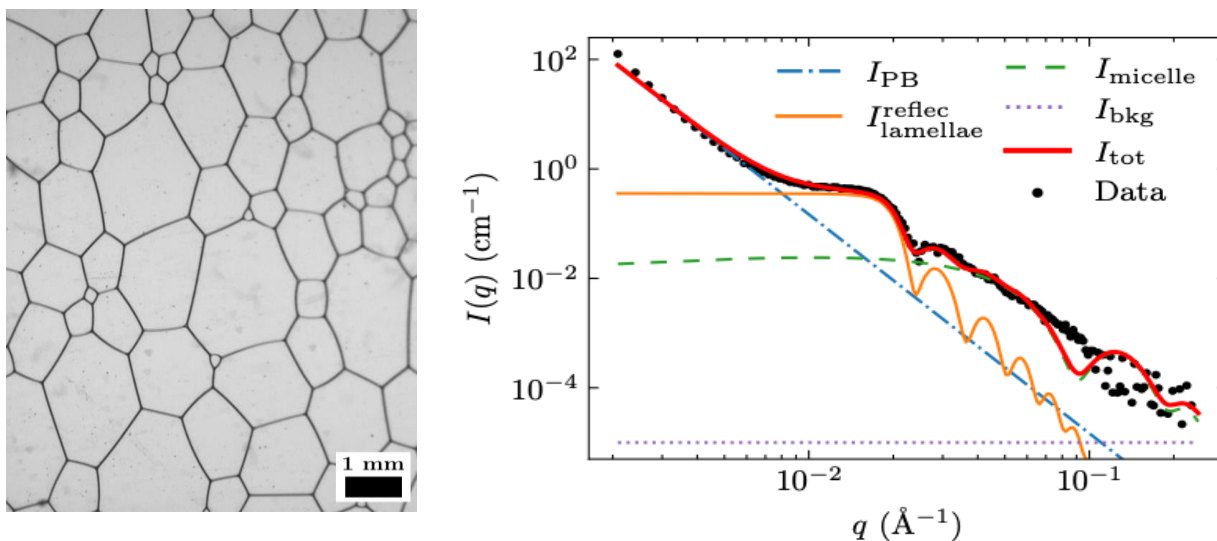
<sup>2</sup> Institut de Chimie Séparative de Marcoule, France

Soft, light, and aesthetically captivating, yet often enigmatic, liquid foams represent highly complex and intriguing systems. Their intrinsic multi-scale structure requires the integration of multiple techniques to fully unveil their properties.

In this contribution, we present a new experimental device that couples small-angle neutron scattering, electrical conductivity measurements, and macrophotography. This device allows for the characterization of foam and its aging from the nanometer to the centimeter scale in a single experiment.

An improved, fully quantitative analysis method enables the extraction of structural parameters, such as the liquid fraction, bubble size distribution, specific surface area of the Plateau borders and inter-bubble films, and thin film thickness, covering all relevant structural length scales.

The simultaneous analysis of nano- and macroscopic information allows us to better understand the correlation between the mechanisms of drainage, ripening, and coalescence involved at different scales in the aging of foam, with significant implications for both fundamental and applied research.



**Figure 1:** Left - Picture of a foam obtained for a 65 min aging time (free drainage mode). Right - Various contributions of the total scattering simulation (red curve) to adjust small-angle scattering data from a foam as photographed in left picture:  $I_{\text{PB}}$  from Plateau Borders,  $I_{\text{micelle}}$  from micelles present within the foam,  $I^{\text{reflec}}$  from lamellae.

[1] Lamolinarie, Dollet, et al., *Soft Matter*, **2022**, 18, 8733-8747

[2] Chiappisi, *Current Opinion in Colloid & Interface Science*, 2024, [10.1016/j.cocis.2024.101823](https://doi.org/10.1016/j.cocis.2024.101823)

## T13: Amphiphilic nanogels as versatile stabilizers for Pickering Emulsions

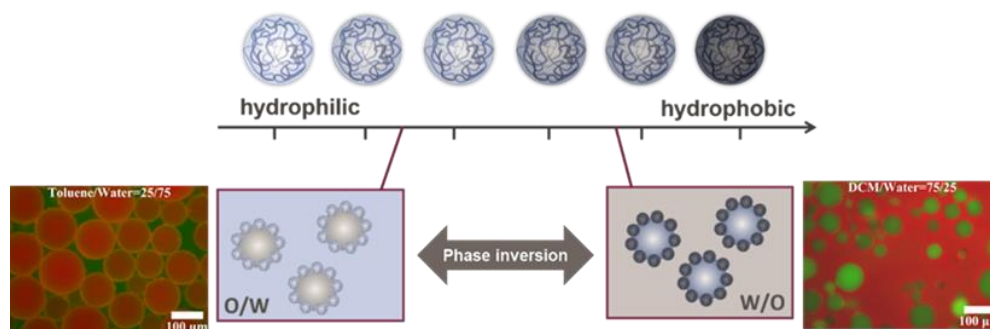
*Daniel Klinger*

*Freie Universität Berlin, Department of Biology, Chemistry, Pharmacy, Berlin, Germany*

Pickering emulsions (PEs) are stabilized by particles at the water/oil interface and exhibit superior long-term stability compared to emulsions with molecular surfactants. Among colloidal stabilizers, nano-/microgels facilitate emulsification and can introduce advanced features, like stimuli-responsiveness. In such systems, emulsion type and stability are governed by the stabilizers' network swelling and deformation at the oil/water interface. It is observed that increasing nano-/microgel hydrophobicity can cause phase inversion from oil-in-water (O/W) to water-in-oil (W/O) emulsions. However, a predictive model to relate this phase inversion to the molecular structure of the colloidal network remains missing. This can be attributed to the synthetic difficulties in accurately controlling the network hydrophobicity of such water swollen colloidal stabilizers.

To address this challenge, we have developed a versatile synthetic platform that allows preparing a library of amphiphilic nanogels (ANGs) with accurately tuned network hydrophobicity but similar colloidal features.[1-4] Our synthetic approach is based on network functionalization of reactive polymethacrylate-based nanogel precursors with various ratios of hydrophilic (2-hydroxypropyl amine – HPA) and hydrophobic (dodecyl amine - DODA) moieties.

For a library of ANGs with DODA contents from 0 – 50 mol%, the influence of network hydrophobicity on emulsion stabilization was systematically examined (Figure 1). We found that W/O emulsions are preferred with increasing ANG hydrophobicity, oil polarity, and oil/water ratio. For non-polar oils, increasing emulsification temperature enabled the formation of W/O PEs that are metastable at room temperature. We connected this behavior to interfacial ANG adsorption kinetics and quantified ANG deformation and swelling in both phases via atomic force microscopy. Importantly, we developed a quantitative method to predict phase inversion by the difference in Flory-Huggins parameters between ANGs with water and oil ( $\chi_{\text{water}} - \chi_{\text{oil}}$ ). Overall, this study provides crucial structure-property relations to assist the design of new nano-/microgels for advanced PEs.



**Figure 1.** Network hydrophobicity in amphiphilic nanogels controls the type of Pickering emulsion.

[1] A. Gruber, D. Isik, B. B. Fontanezi, C. Bottcher, M. Schafer-Korting, D. Klinger, *Polym. Chem.* **2018**, *9*, 5553.

[2] A. F. Thunemann, A. Gruber, D. Klinger, *Langmuir* **2020**, *36*, 10979.

[3] A. Gruber, A. A. Joshi, P. Graff, J. L. Cuéllar- Camacho, S. Hedtrich, D. Klinger *Biomacromolecules* **2022**, *23*, 112.

## T14: Writing polymer images into mesoporous silica films using visible light induced polymerizations

Annette Andrieu-Brunsen

*Technische Universität Darmstadt, Macromolecular Chemistry – Smart Membranes, Peter-Grünberg-Str. 8, 64287 Darmstadt, Germany*

Biological pores and channels demonstrate a transport performance which is unreached by technical materials. One key factor for this performance is their nanoscale structure and their arrangement of functional components. Fascinated by this performance and nanoscale precision we aim to advance control and precision of polymer functionalization of technological porous materials. Thereby, automated polymer writing as well as precise local placement of multiple polymers into porous materials is an important aspect.

This talk will highlight our recent advances related to automated polymer writing and local polymer functionalization in nanopores. This includes polymerization control and re-initiation of polymerization to graft block co-oligomers in silica mesopores mainly focusing on iniferter-initiated RAFT polymerizations.[1] The effect of this chain architecture control on ionic mesopore accessibility will be discussed. Furthermore, visible-light- and surface plasmon induced nanopore polymer functionalization[2, 3] as well as automated polymer writing of polymers, including block-copolymers, using a high-resolution fluorescence microscope will be presented.[4-6] Interestingly, we were able to demonstrate polymer writing using iniferter initiation even at visible light wavelengths outside the absorption wavelength of the respective initiator. Using this approach of polymer writing, we achieved writing of block copolymer images with polymerization times of 1 second per pixel, polymer spot sizes on the micrometer scale resulting in images sizes on the millimeter length scale. We expect this approach of automated local polymer writing to be of general interest for miniaturized design of polymer functionalized surfaces and porous materials.

[1] R. Brilmayer, C. Hess, A. Andrieu-Brunsen, Influence of Chain Architecture on Nanopore Accessibility in Polyelectrolyte Block-Co-Oligomer Functionalized Mesopores, *Small*, 2019, 15, 1902710.

[2] N. Herzog, J. Kind, C. Hess, A. Andrieu-Brunsen, Surface Plasmons & Visible Light For Polymer Functionalization of Mesopores and Manipulation of Ionic Permselectivity, *Chem. Commun.*, 2015, 51, 11697.

[3] D. John, M. Stanzel, A. Andrieu-Brunsen, Surface Plasmons and Visible Light Iniferter Initiated Polymerization for Nanolocal Functionalization of Mesoporous Separation Layers, *Adv. Funct. Mater.*, 2021, 2009732.

[4] C. Förster, R. Lehn, E. M. Saritas, A. Andrieu-Brunsen, Laser Writing of Block-Copolymer Images into Mesopores Using SBDC-Initiated Visible-Light-Induced Polymerization *Angew. Chem.* 2023, e202217806.

[5] C. Förster, R. Lehn, A. Andrieu-Brunsen, Automated Multi- and Block-Copolymer Writing in Mesoporous Films Using Visible-Light PET-RAFT and a Microscope, *Small*, 2023, 2207762.

[6] C. Förster, L. Veith, A. Andrieu-Brunsen, Visible light induced RAFT for asymmetric functionalization of silica mesopores, *RSC Adv.*, 2022, 12, 27109-27113.

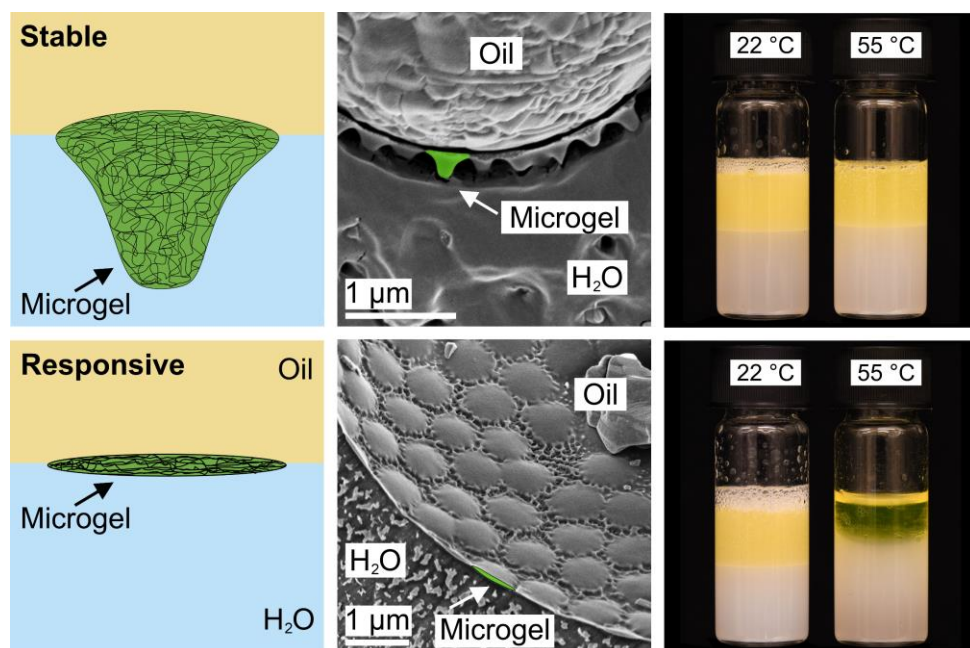
## T15: Interactions between interfaces dictate stimuli-responsive emulsion behaviour

*Marcel Rey*

*Institute for Physical Chemistry, University of Münster, D-48149 Münster, Germany.*

Stimuli-responsive emulsions offer a dual advantage, combining long-term storage with controlled release triggered by external cues such as pH or temperature changes. The destabilisation mechanism was previously primarily attributed to the shrinkage or desorption of the temperature-responsive microgels, leading to a lower surface coverage inducing coalescence [1].

This study [2] establishes that thermo-responsive emulsion behaviour is primarily determined by interactions between, rather than within, interfaces. Consequently, the stability of these emulsions is intricately tied to the nature of the stabilizing microgel particles - whether they are more polymeric or colloidal, and the morphology they assume at the liquid interface (Fig. 1). The colloidal properties of the microgels provide the foundation for the long-term stability of Pickering emulsions. However, limited deformability can lead to non-responsive emulsions (Fig. 1 top). Conversely, the polymeric properties of the microgels enable them to spread and flatten at the liquid interface, enabling stimuli-responsive behaviour (Fig. 1 bottom). Furthermore, microgels shared between two emulsion droplets in flocculated emulsions facilitate stimuli-responsiveness, regardless of their internal architecture. This underscores the pivotal role of microgel morphology and the forces they exert on liquid interfaces in the control and design of stimuli-responsive emulsions and interfaces.



**Figure 1.** Stimuli-responsive emulsion behaviour is linked to the morphology the stabilizing microgels. [2].

[1] T. Ngai, S. H. Behrens, H. Auweter, *Chem. Commun.* **2005**, 331–333.

[2] M. Rey, J. Kolker, J. A. Richards, I. Malhotra, T. S. Glen, N. Y. D. Li, F. H. J. Laidlaw, D. Renggli, J. Vermant, A. B. Schofield, S. Fujii, H. Löwen, P. S. Clegg, *Nature Communications*, **2023**, 14(1), 6723 .

## T16: Interaction of DOPG model membranes with the saponin aescins

Carina Dargel<sup>2</sup>, Paul Wenk<sup>2</sup>, Friederike Gräbitz-Bräuer<sup>1</sup>, Thomas Hellweg<sup>1</sup>

<sup>1</sup> Fakultät für Chemie, Physikalische und Biophysikalische Chemie, Universität Bielefeld, Universitätsstr. 25, 33615 Bielefeld, Germany

<sup>2</sup> Institute of Physical Chemistry, University of Münster, Corrensstraße 28/30, 48149 Münster, Germany

Saponins are usually plant derived amphiphiles which exhibit strong physiological effects. In the present contribution we discuss the saponin  $\beta$ -aescin with respect to its interaction with model membranes made of the negatively charged lipid 1,2-dioleoyl-sn-glycero-3-phosphoglycerol (DOPG). The study is conducted at a pH value at which aescin is negatively charged as well, and mixtures up to an aescin content of 50 mol% (equivalent to a molecular ratio of 1:1) were investigated, so that the cmc of aescin is exceeded by far. Analysis of the system by scattering and NMR methods was performed with respect to two reference systems made of the bare components: DOPG SUVs and aescin micelles. Wide-angle X-ray scattering (WAXS) was used to determine molecular correlation distances for both kinds of molecules, and small-angle neutron and X-ray scattering (SANS and SAXS) revealed a structural picture of the system, which was further confirmed by diffusion-ordered nuclear magnetic resonance spectroscopy (DOSY-NMR).

Contrary to the expected solubilization of the DOPG membrane, most probably none- or only weakly-interacting, separated DOPG SUVs and aescin micelles were found [1]. This is in line with preliminary results from neutron spin-echo (NSE). The study highlights the importance of using independent methods to characterize a rather complex colloidal system in order to obtain a complete picture of the structures formed.

[1] F. Gräbitz-Bräuer et al.; Colloid and Polymer Science (2023) 301:1499–1512



**Functional Interfaces**  
**& Bio-Interfaces**

## T17: Eco-corona driven heteroaggregation of microplastic and sand particles can induce microplastic sedimentation

*Thomas Witzmann<sup>1</sup>, Anja F. R. M. Ramsperger<sup>2,3</sup>, Simon Wieland<sup>2,3</sup>, Christian Laforsch<sup>2</sup>, Holger Kress<sup>3</sup>, Andreas Fery<sup>1,4</sup>, and Günter K. Auernhammer<sup>1</sup>*

<sup>1</sup> *Leibniz-Institute of Polymer Research Dresden, 01069 Dresden, Germany*

<sup>2</sup> *Animal Ecology I and BayCEER, University of Bayreuth, 95447 Bayreuth, Germany*

<sup>3</sup> *Biological Physics Group, University of Bayreuth, 95447 Bayreuth, Germany*

<sup>4</sup> *Physical Chemistry and Polymer Physics, Technical University Dresden, , 01069 Dresden Germany*

Microplastic (MP) particles in the environment are covered by a so-called eco-corona. The eco-corona is made up of natural organic matter (NOM) like biomolecules, humic substances and other natural molecules. NOM substantially changes the surface properties of MP particles and therefore the interaction with other surfaces in the aqueous environment influencing their aggregation behaviour.

Using Colloidal Probe-AFM we studied the interactions of eco-corona covered MP particles on the nanoscale. Measurements were performed in different ionic concentrations to mimic changing environmental conditions. We found that the eco-corona is able to \*pull\* at the silica colloidal probe by polymer bridging. This mechanism will lead to aggregation and consequently sedimentation in the environment. With simple MP-silica sand aggregation experiments and following Raman- and ESEM-Imaging we verified the presence and stability of these aggregates on the microscale.

In conclusion, we show that the eco-corona is able to form polymer bridges and \*pull\* surfaces towards itself to form aggregates on two different length scales. This mechanism may contribute substantially to MP particle aggregation in the aqueous environment and explains why MPs sediment.

## T18: What defines softness in soft nanogels, and how can it be quantified using atomic force microscopy?

*M. Friederike Schulte<sup>1</sup>, Steffen Bochenek<sup>1</sup>, Simon Schog<sup>1</sup>, Timon Kratzenberg<sup>1</sup>, Andrea Scotti<sup>2</sup>, Walter Richtering<sup>1</sup>*

<sup>1</sup> *Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany*

<sup>2</sup> *Department of Biomedical Science, Malmö University, Malmö, Sweden.*

Softness plays a major role when trying to understand the macroscopic properties of colloidal systems. However, in the nanoscience community we are lacking in a definition of 'softness'. One way in determining the mechanical properties of a colloid at the solid/fluid interface are compression experiments performed with an atomic force microscope (AFM). AFMs visualize the surface topography and quantify mechanical properties down to atomic resolution. But how to quantify softness for a sample not having a surface in a classical sense - namely nanogels?

Nanogels are three-dimensional intramolecularly cross-linked polymeric networks swollen by a good solvent. The poly(*N*-isopropylamide) (PNIPAM)-based nanogels own a unique architecture: Their polymer density profile decays from the center towards their periphery, caused by a heterogeneous distribution of cross-links. These nanogels do not exhibit a clear boundary but an open structure with dangling polymeric chains at their periphery. Nanogels rapidly adsorbed at solid interfaces. Still, their interfacial behavior is not entirely understood.

In this work, we shed light on PNIPAM nanogels adsorbed to solid/liquid interfaces. An AFM equipped with a sharp tip was employed to investigate the softness. While a classical measure of the softness in terms of the Young's modulus is not accessible in these experiments, here, we propose two different ways how to quantify softness for soft nanostructures. This is done in terms of deformation and contact stiffness.

Force volume measurements create three-dimensional maps of the network density, i.e., their topography and internal network density combined. A particular focus was on the variation in softness: Nanogels of various architecture were examined at different temperature-induced swelling states. This gives us new insights into nanogels - beyond their surface - relevant for all porous and soft materials. [1-4]

[1] M. F. Schulte, S. Bochenek, M. Brugnoli, A. Scotti, A. Mourran, W. Richtering, *Angew. Chem. Int. Ed. Engl.* **2021** (60), 2280.

[2] M. F. Schulte, E. Izak-Nau, S. Braun, A. Pich, W. Richtering, R. Göstl, *Chem. Soc. Rev.* **2022** (51), 2939.

[3] A. Scotti, M. F. Schulte, C. G. Lopez, J. J. Crassous, S. Bochenek, W. Richtering, *Chem. Soc. Rev.* **2022** (122), 11675.

[4] We thank the Deutsche Forschungsgemeinschaft for financial support within the Sonderforschungsbereich SFB 985 'Functional Microgels and Microgel Systems' (Projects A3 and B8).

## T19: Atomic force microscopy adhesion measurements between soft polymeric materials

*Dmitrii Sychev*<sup>1, 2</sup>, *Doreen Hofmann*<sup>1, 3</sup>, *Zlata Zagradska-Paromova*<sup>1, 3</sup>, *Simon Schubotz*<sup>1, 4</sup>, *Quinn A. Besford*<sup>1</sup>, *Eva Bittrich*<sup>1</sup>, *Jens Gaitzsch*<sup>1</sup>, *Andreas Fery*<sup>1, 2</sup>, and *Gunter K. Auernhammer*<sup>1</sup>.

<sup>1</sup> *Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany*

<sup>2</sup> *Chair of Physical Chemistry of Polymeric Materials, Technische Universität Dresden, 01069 Dresden, Germany*

<sup>3</sup> *Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, 01069 Dresden, Germany*

<sup>4</sup> *Technische Universität Dresden, Helmholtzstraße 10, Dresden 01062*

The adhesion properties of the material can be quantified using the work of adhesion. The analysis of the work of adhesion can reveal the peculiarities of the interacting surfaces on the microscale when the colloidal probe atomic force microscopy (c-AFM) is utilized. However, the choice of the material and size of the probe is crucial in c-AFM. Here, we used polymeric soft particle as a colloidal probe to investigate the adhesion of the poly-N-isopropylacrylamide (PNIPAM) in collapsed and swollen states and the main aspects of the adhesion mechanism.

The setup used allowed the simultaneous use of two different methods of the calculation of the work of adhesion. The first one is the use of the theoretical contact geometry and the calculation of the work of adhesion from force curves. The second approach is based on the optical measurement of the contact radius. The latter approach resulted in values closer to thermodynamic equilibrium. The PNIPAM brush adhesion study revealed that the swollen state is more adhesive than collapsed state[1]. The swelling/deswelling of PNIPAM was triggered by changing the solvent due to co-nonsolvency effect. At first, the adhesion properties of PNIPAM brush were investigated. The higher adhesion of the PNIPAM brush in swollen state was attributed to the higher degree of freedom of the polymer in the swollen state. To verify this explanation the adhesion measurements on the PNIPAM-based Redox responsive hydrogel were carried out. The adhesion decreased with an increase of the cross-linking degree of the hydrogel proving the initial hypothesis[2, 3].

[1] Dmitrii Sychev, Simon Schubotz, Quinn A. Besford, Andreas Fery, Günter K. Auernhammer. *J. Colloid Interface Sci.* **2023**, 642, 216-226.

[2] Doreen Hofmann, Dmitrii Sychev, Zlata Zagradska-Paromova, Eva Bittrich, Günter Auernhammer, Jens Gaitzsch. *Macromol. Rapid Commun.* **2024**, 2400049

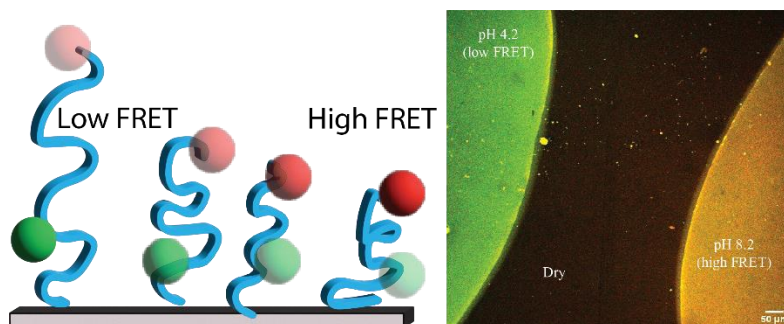
[3] The authors acknowledge funding from the DFG (project number 211944370 (RTG 1865), project number 496201730 (BE7737/2-1), project number 422852551 (AU321/10-1 and FE600/32-1), and project number 456180046, Dr. M. Seuss is thanked for the IGOR Pro evaluation procedure and O.D. Veleev and L. Okelo (NCSU) are thanked for the polymeric colloidal probes synthesis.

## T20: Leveraging Conformationally-Fluorescent Polymers for In Situ Sensing of Interfacial Phenomena

Jyoti Yada<sup>1</sup>, Khrystyna Rymsha, Andreas Fery, and Quinn A. Besford

Leibniz-Institut für Polymerforschung e.V., Dresden, Germany

Spatially resolving interfacial stimuli, such as pH, solvent, pressure, as examples, can allow us to better understand physicochemical processes on surfaces [1]. Towards this goal, we develop ways of integrating Förster resonance energy transfer (FRET) chemistry into stimuli-responsive polymer brush architectures, such that FRET output (i.e., spectral shift in output fluorescence intensities) reflects polymer chain conformations both with and without applied stimuli [2]. Stimuli-responsive polymer brushes provide rapid and dramatic changes in chain conformation in response to stimuli, therefore integrating FRET chemistry into such functional interfaces can allow for a real-time identification of conformational transitions in response to stimuli that is spatially resolved [3]. We leverage confocal laser scanning microscopy to identify these transitions in real-time. In this talk, we will discuss strategies to integrate FRET into grafting-to and grafting-from polymer brushes, and into solvent- and pH-responsive polymers. These systems are used to study 1) surface wettability processes, 2) localised changes in pH, and 3) flow processes through polymer brushes. Our systems provide a non-invasive optical measure of changing surface conditions, which holds great promise for identifying processes in real-time. [4]



**Figure 1.** Schematic of a FRET polymer brush (left) along with a confocal laser scanning microscopy image of a FRET-integrated polyelectrolyte polymer brush that spatially reveals changes in pH on a surface (right).

[1] Q. A. Besford, C. Rossner, A. Fery, *Adv. Funct. Mater.* **2023**, 2214915.

[2] Q. A. Besford, H., Yong, H., Merlitz, A. J., Christofferson, J. U., Sommer, P., Uhlmann, A., Fery, *Angewandte Chemie*, **2021**, 60, 16600-16606.

[3] Q. A. Besford, P. Uhlmann, A. Fery, *Macromol. Chem. Phys.* **2023**, 224, 2200180.

[4] The authors gratefully acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG) for funding projects 496201730 (BE 7737/2-1) (Q.A.B.), and the Alexander von Humboldt foundation (J.Y.).

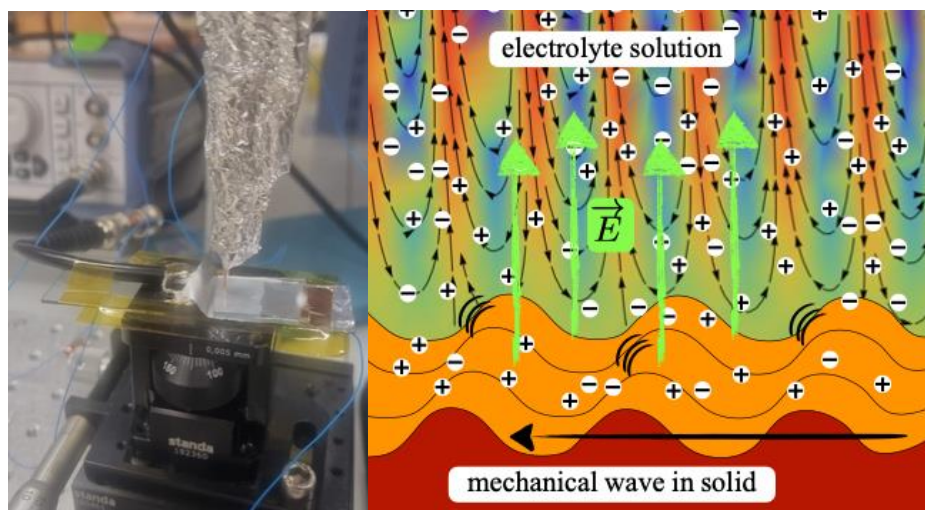
## T21: Electrokinetic spectroscopy of ion dynamics near charged surfaces using modulated surface acoustic waves

*Ofer Manor, Sudeepthi Aremanda, Yifan Li*

*Chemical Engineering, Technion – Israel Institute of Technology, Haifa 3200003*

We use MHz-level modulated surface acoustic waves (SAWs) to study the dynamics of ions near charged solid/solution interfaces in the electrical double layer (EDL). The SAW travels in the solid, and the EDL exists in the electrolyte solution; both phenomena are entangled through a field effect, an evanescent wave, which is invoked in the solution by the SAW [1] and vibrates ions in the EDL [2]; see figure 1. This is a new MHz-level spectroscopy for studying ion dynamics near surfaces.

Electrical double layers (EDLs) are a surface phenomenon. These are nanometer-thick clouds of ions that appear at the charged interface between a substrate and an electrolyte solution. They support the complexity of biology and countless industrial processes and products from water desalination and electrochemistry to shampoo and super-capacitors. Ions diffuse and migrate through the thickness of EDLs as individuals or as groups of ions and counter-ions (coupled diffusion) in micro-to nano-seconds: These are ion-specific times for charging and discharging the EDL, which are a product of the EDL structure and the ion size and charge and are known as the EDL relaxation-times. Individual and coupled ion relaxation-times similar to the SAW periodic time result in an ion electro-mechanical resonance, which maximizes ion vibration and the leakage of electrical fields off the out-of-equilibrium EDL. The leakage identifies the relaxation-time spectrum of individual ions [3] and coupled groups of ions and the intrinsic rate by which they charge and discharge EDLs. [4]



**Figure 1.** Figure 1: (right) Illustration of a surface acoustic wave (SAW) in solid, interacting with ions in an electrical double layer (EDL) via a mechanical evanescent wave in the neighboring electrolyte. This results in an electrical field leakage,  $\vec{E}$ , that we measure (left).

[1] O. Manor, L. Y. Yeo, J. R. Friend, *J. Fluid Mech.* 2012, 707, 482–495

[2] O. Dubrovski and O. Manor, *Langmuir* **2021**, 37, 14679–14687

[3] S. Aremanda and O. Manor, **2023**, *J. Phys. Chem. C*, 127, 20911–20918

[4] We are grateful for support from the Israel Science Foundation=

## T22: Rod Rolls: self-driven motion of active micro rods on active surfaces

*Martin Wittmann*<sup>1,2</sup>

<sup>1</sup> Physical Chemistry, TU Dresden, Dresden, Germany

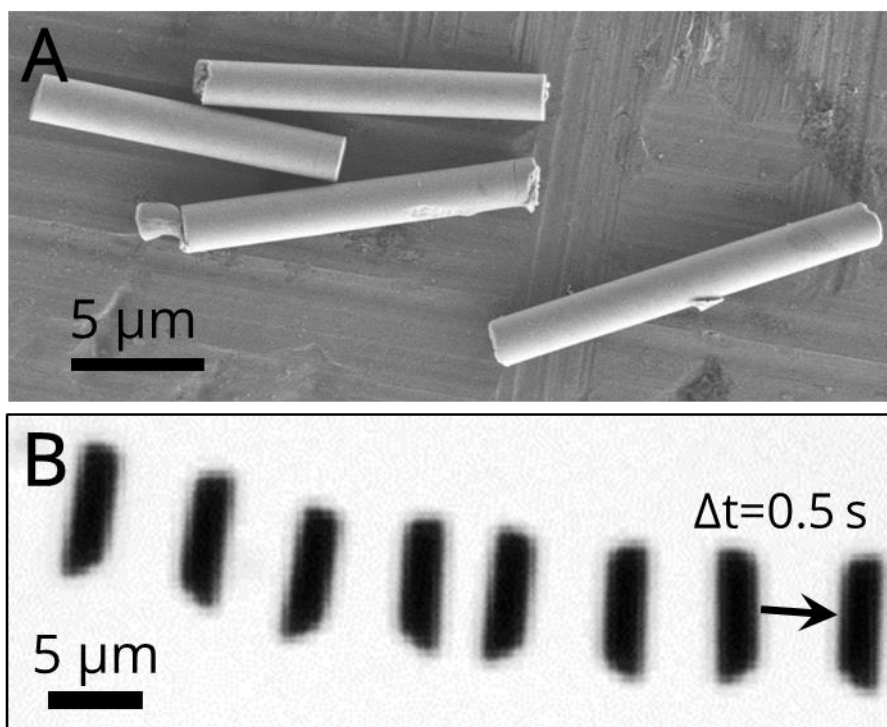
<sup>2</sup> Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK

Rolling is a broad concept in everyday life, and the wheel, considered one of mankind's greatest inventions and the basis of modern mobility, has enabled many economic and technological developments. However, on the microscale this kind of behavior is much more scarce.

In this work we develop and analyze a new way of self-driven active motion on the micro scale: self-propelled rolling microrods.[1]

For that, catalytically active MnO<sub>2</sub> micro rods without any apparent asymmetric structure are used (Figure 1A). However, when placed near an active surface in H<sub>2</sub>O<sub>2</sub> solution, they break symmetry and show an active motion perpendicular to their long axis. In addition to that translational motion, they perform rotations around their long axis, which seems to correspond to a rolling motion on the micro scale. This rotation can be observed by looking at asymmetries at the tips of some rods (Figure 1C).

Finally, interactions between individual rods are analyzed and compared to our earlier work on polar Janus microswimmers.[2,3]



**Figure 1.** (A) SEM image of the MnO<sub>2</sub> micro rods, (B) scheme showing the required “ingredients” for the active motion: MnO<sub>2</sub> micro rod in H<sub>2</sub>O<sub>2</sub> solution on oxidized Pt, (C) overlaid microscope images of a rod moving while undergoing rotations around its long axis.

[1] Martin Wittmann et al. *Colloid and Polymer science*, **2023**, 301, 783–799.

[2] Priyanka Sharan et al. *Small*, **2023**, 19, 36, 2300817.

[3] The author acknowledges funding from the DFG for the DFG-ANR project RODROLLS SI 2141/3-1

## T23: Biocompatible Poly(2-oxazoline) Nanorods as Tuneable Drug Delivery Platform

*Kristian Kempe*<sup>1,2</sup>

<sup>1</sup> *Materials Science and Engineering, Monash University, Melbourne, Australia*

<sup>2</sup> *Monash Institute of Pharmaceutical Sciences, Monash University, Melbourne, Australia*

The morphology of polymer nanoparticles critically influences their biological interactions contributing to the determination of their in vivo fate [1]. However, currently there is a lack of robust methods for the preparation of non-spherical particles from biocompatible materials. Recently, we developed a promising drug delivery platform through the combination of 'living' crystallization-driven self-assembly (CDSA), a seeded growth method that enables the preparation of rod-like polymer nanoparticles of controlled length, with poly(2-oxazoline)s (POx), a polymer class that exhibits high structural versatility, 'stealth' behavior, and excellent biocompatibility [2-4].

In this presentation the potential to modulate the interaction of POx nanorods with biological entities through variation of size, shape and surface modifications will be discussed. Specifically, we carefully optimized the assembly and disassembly of the nanorods and studied their interaction with white blood cells in a human blood assay [5, 6]. Variation of the nanorod corona and their surface modification with nanobodies allowed to fine-tune their cellular interactions [7, 8]. Moreover, first insights into their drug delivery potential will be given [9].

[1] Kinnear, C.; Moore, T.L.; Rodriguez-Lorenzo, L.; Rothen-Rutishauser, B.; Petri-Fink, A. *Chem. Rev.* **2017**, 117, 11476–11521.

[2] Ganda, S.; Stenzel, M. H. *Prog. Polym. Sci.* **2019**, 101, 101195.

[3] Wilson, P.; Ke, P. C.; Davis, T. P.; Kempe, K. *Eur. Polym. J.* **2017**, 88, 486–515.

[4] Leiske, M. N.; Lai, M.; Amarasena, T.; Davis, T. P.; Thurecht, K. J.; Kent, S. J.; Kempe, K. *Biomaterials* **2021**, 274, 120843.

[5] Finnegan, J. R.; Pilkington, E. H.; Alt, K.; Rahim, Md. A.; Kent, S. J.; Davis, T. P.; Kempe, K. *Chem. Sci.* **2021**, 12, 7350-7360.

[6] Finnegan, J. R.; Davis, T. P.; Kempe, K. *Macromolecules* **2022**, 55, 3650-3660.

[7] Warne, N. M.; Elbourne, A.; Tran, M. P.; Finnegan, J. R.; Feeney, O. M.; Kempe, K. *Polym. Chem.* **2023**, 14, 2916-2929.

[8] Finnegan, J. P.; FitzGerald, L. I.; Chen, M. Z.; Warne, N. M.; Yuen, D.; Davis, T. P.; Johnston, A. P. R.; Kempe, K. *Nano Lett.* **2024**, 24, 89-96.

[9] The author acknowledges the award of an ARC Future Fellowship (FT190100572) from the Australian Research Council (ARC).



## T24: Targeting bacterial biofilms with multi enzyme functionalized antibiotic-loaded nanogel particles

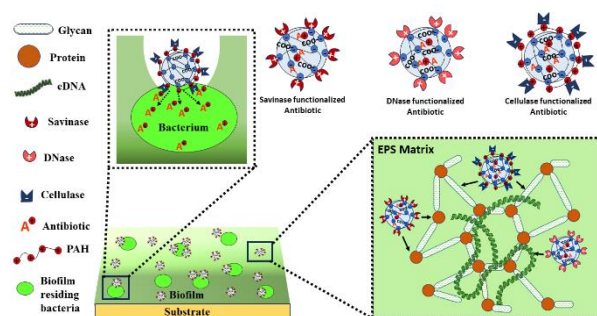
*Evans Asare,<sup>1</sup> Aruzhan Seidakanova,<sup>2</sup> Dana Amangeldinova<sup>1</sup> Enrico Marsili<sup>3</sup> and Vesselin Paunov<sup>1</sup>*

<sup>1</sup>Department of Chemistry, School of Sciences and Humanities, Nazarbayev University, Astana, Kazakhstan

<sup>2</sup>Department of Biology, School of Sciences and Humanities, Nazarbayev University, Astana, Kazakhstan

<sup>3</sup>University of Nottingham Ningbo, Faculty of Science and Engineering, China.

Infections of pathogenic bacteria are causing hundreds of thousands of deaths annually worldwide due to antimicrobial resistance and their biofilm formation capabilities. Among these bacteria is *Staphylococcus epidermidis*, commonly found on skin and mucous membranes of humans and animals. Its virulence depends on biofilm formed in medical devices-related infections and chronic wounds causing severe health complications and impeding wound healing while resisting traditional antibiotic treatments [1-3]. To overcome *S. epidermidis* biofilm-based resistance to antibiotics, three types of active nano-formulations were developed based on surface functionalizing antibiotic-encapsulated nanoparticles with enzymes that can degrade the extracellular polymeric substance (EPS) matrix components of the biofilm [1-6]. This approach allows the enzyme-coated NPs-loaded with antibiotic to penetrate the bacterial biofilm where they can reach the residing bacterial cells and deliver therapeutic concentration of antibiotic directly onto the cell walls, hence killing them (See figure). In this study, polysaccharide, protein and eDNA hydrolytic enzymes were used to functionalize antibiotic-loaded polyacrylic acid copolymer NPs separately, their biofilm clearing, and bactericidal effect were investigated and compared. Generally, the three enzyme-coated NPs loaded with antibiotic were found to be more effective against *S. epidermidis* biofilm than the equivalent concentration of free antibiotic when compared to untreated biofilms. We examined the cytotoxic effect of these formulations using HeLa human cell line and found that they have low-to-moderate cytotoxicity. These smart antibiotic nanocarriers are promising nano-formulations for overcoming biofilm based antibiotic resistance as well as other bacterial biofilms resistant mechanisms and may find potential applications in chronic wound treatment.



**Figure 1.** Action of the various enzyme-functionalized formulated antibiotics against bacterial biofilm and its viable cells. Savinase, Cellulase and DNase enzyme-functionalized antibiotics hydrolyze the proteins, glycans and eDNAs respectively to degrade the EPS matrix, that allow the antibiotics to be directly delivered to the residing bacterial cells and ensure a high efficacy treatment [2].

[1] Asare, E.O., Mun, E.A., Marsili, E., Paunov, V.N., *J. Mater. Chem. B*, **2022**, 14, 5129 – 5153

[2] Asare, O. E., Seidakanova, A., Amangeldinova, D., Marsili, E., Paunov, N. V. *ACS Appl. Nano Mater.* **2023**, 6, 22792-22806.

[3] Weldrick, P.J., Wang, A., Halbus, A.F., Paunov, V.N., *Nanoscale* **2022**, 14, 4018 – 4041.

[4] Weldrick, P.J., San, S., Paunov, V.N., *ACS Appl. Nano Mater.* **2021**, 4, 1187–1201.

[5] Weldrick, P.J., Hardman, M.J., Paunov, V.N., *Mater. Chem. Front.*, **2021**, 5, 961–972.

[6] Weldrick, P.J., Hardman, M.J., Paunov, V.N., *ACS Appl. Mater. Interf.*, **2019**, 11, 43902–43919

[7] The authors acknowledge funding from the Faculty Development Competitive Research Grant, Grant Number SSHM/SSH2022005.

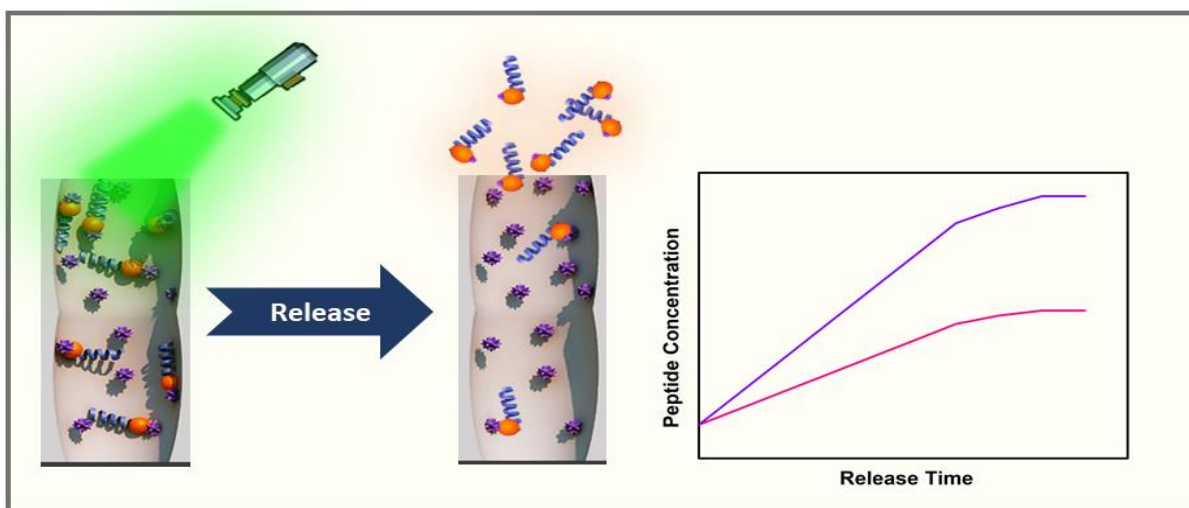
## T25: Controlled Release of Antimicrobial Peptides from Mesoporous Silica to Improve Wound Healing

*Mohadeseh Bagherabadi, Annette Andrieu-Brunsen*

*Technische Universität Darmstadt, Darmstadt, Germany*

Wound healing materials, for example in the context of burn injuries, would profit from the precise delivery of biomolecules and medications, especially when activated by particular triggers. Stimuli-triggered, on-demand medication holds promise for decreasing the necessary therapeutic dose, enhancing effectiveness, and mitigating unintended side effects. Implementing controlled-release systems sensitive to stimuli could notably enhance wound therapy, particularly in instances of infection, by enabling the focused distribution of therapeutic substances directly to the affected area.

We present a strategy for on-demand controlled release and delivery of bacterial-killing antimicrobial peptide C14R from mesoporous silica, employing BODIPY-N3 as a photo-cleavable linker release triggered by visible green light. Mesoporous coatings are synthesized through sol-gel chemistry and evaporation-induced self-assembly. Conjugation of peptides to the mesoporous materials is achieved via the covalently grafted and light-sensitive BODIPY-N3 linker. The peptide's release mechanism is confirmed through ATR-IR, BCA assay, and fluorescence analysis, shedding light on how different peptide sequences influence the optical properties and fluorescence intensity of the coatings. The customization of the release profile is achieved by adjusting the intensity and duration of irradiation. Following the release, the antimicrobial effectiveness against *E. coli* BL21(DE3) is demonstrated, suggesting potential advancements in targeted wound healing therapies. Additionally, the integration of the C14R coating into different wound-dressing relevant fabrics is accomplished, marking a significant stride towards future wound treatment technologies.



**Figure 1.** The photo-triggered release of antimicrobial peptides from mesoporous silica, enabling tailored concentration-time profiles in release media.

## T26: A polymer brush-supported microcontact printing ( $\mu$ CP) routine: Towards (sub-) microscale patterning of capillary-active and superhydrophilic substrates

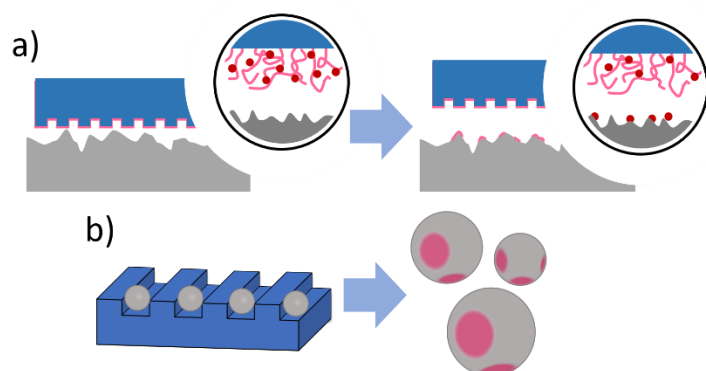
*Martin Reifarth, Nazim Pallab, Pinar Akarsu*

<sup>1</sup> University of Potsdam, Institute of Chemistry, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany

<sup>2</sup> Fraunhofer Institute for Applied Polymer Research, Geiselbergstr. 69, 14476 Potsdam, Germany

We present a modified microcontact printing routine, which enables the precise patterning of capillary-active and superhydrophilic surfaces, combining a high printing precision with a defined chemical functionality of the printed areas. The protocol enables the fabrication of highly anisotropic colloids. The process is based on a polymer-supported printing routine, during which polymer brushes, bound to an elastomeric polydimethylsiloxane (PDMS), stamp are used for the transfer of the reactive ink (Figure 1a).[1] The ink is first immobilized at the brush matrix, from where it is transferred to the substrate exclusively during the physical contact of stamp and substrate. During the printing process, thus, the ink is locally precisely transferred, rather than being distributed over the substrate.

The method is applicable to different substrates, which may be patterned at a microscale. As such, we demonstrated the transfer of small patterns on inorganic substrate, using reactive silanes as ink.[1,2] The printing procedure is also adapted to other substrates, such as cellulose surfaces, or glycan interfaces. Accordingly, we were able to address capillary-active and superhydrophilic surfaces, and the protocol can also be implemented to address curved surfaces. As such, we could structure the surface of SiO<sub>2</sub> microspheres, resulting in the fabrication of patchy particles with an intricate surface pattern (Figure 1b).[3] Moreover, anisotropically functionalized microgels could be prepared.



**Figure 1.** Principle of  $\mu$ CP. a) Schematic representation of the printing routine. b)  $\mu$ CP for the preparation of patchy particles.

[1] P. Akarsu, R. Grobe, J. Nowaczyk, M. Hartlieb, S. Reinicke, A. Böker, M. Sperling, M. Reifarth, *ACS Appl. Polym. Mater.* **2021**, *3*, 2420–2431.

[2] N. Pallab, S. Reinicke, J. Gurke, R. Rihm, S. Kogikoski Jr., M. Hartlieb, M. Reifarth, *Polym. Chem.* **2024**, *15*, 853–867.

[3] P. Akarsu, S. Reinicke, A.-C. Lehnen, M. Bekir, A. Böker, M. Hartlieb, M. Reifarth, *Small* **2023**, *19*, 2301761.

## T27: Amphiphilic zwitterionic low fouling coatings

A. Rosenhahn<sup>1</sup>, L. Schardt<sup>1</sup>, A.M. Guajardo<sup>2</sup>, A. Laschewsky<sup>2,3</sup>

<sup>1</sup> Analytical Chemistry - Biointerfaces, Ruhr University Bochum, 44801 Bochum, Germany

<sup>2</sup> Institute of Chemistry, University Potsdam, 14476 Potsdam, Germany

<sup>3</sup> Fraunhofer Institute of Applied Polymer Research IAP, 14476 Potsdam, Germany

Manmade materials in contact with water become rapidly colonized by living matter like bacteria, diatoms, barnacles, or mussels, which can seriously affect their function. As the historical paradigm to combat fouling by biocide releasing coatings is increasingly challenged by legal restrictions, environmentally benign low-fouling materials are intensively explored [1]. While several hydrophilic and hydrophobic materials show promising properties, their combination into amphiphilic coatings unites the best of the two worlds [2]. As hydrophilic compound, zwitterionic materials with different molecular architectures were developed and their structure-function relationship against different fouling organisms have been studied [3]. Amphiphilic coatings based on zwitterionic polymers have been designed and their anti-polyelectrolyte properties have been characterized by several methods including AFM and SPR. Their antifouling properties against a range of freshwater and marine fouling species and in short term field exposures have been assessed and the results will be discussed under consideration of the interaction of the organic coatings with inorganic particulate matter [4,5,6]. Based on the obtained data, design criteria for optimized zwitterionic building blocks for fouling-release technologies will be discussed.

[1] M. Callow, J. Callow, *Nature Communications* **2011**, 2, 244

[2] S. Krishnan, C. Weiman, C. Ober, *J. Materials Chemistry* **2008**, 18, 3405

[3] A. Laschewsky, A. Rosenhahn, *Langmuir* **2018**, 35, 1056

[4] F. Koschitzki, R. Wanka, L. Sobota, J. Koc, H. Gardner, K.Z. Hunsucker, G.W. Swain, A. Rosenhahn, *ACS Applied Materials & Interfaces* **2020**, 12(30), 34148

[5] J. Koc, E. Schönemann, R. Wanka, N. Aldred, A.S. Clare, H. Gardner, G.W. Swain, K. Hunsucker, A. Laschewsky, A. Rosenhahn, *Biofouling* **2020**, 36(6), 646

[6] L. Schardt, A.M. Guajardo, J. Koc, J.L. Clarke, J.A. Finlay, A.S. Clare, H. Gardner, G.W. Swain, K. Hunsucker, A. Laschewsky, A. Rosenhahn, *Macromolecular Rapid Communications* **2021**, 43(12), 2100589

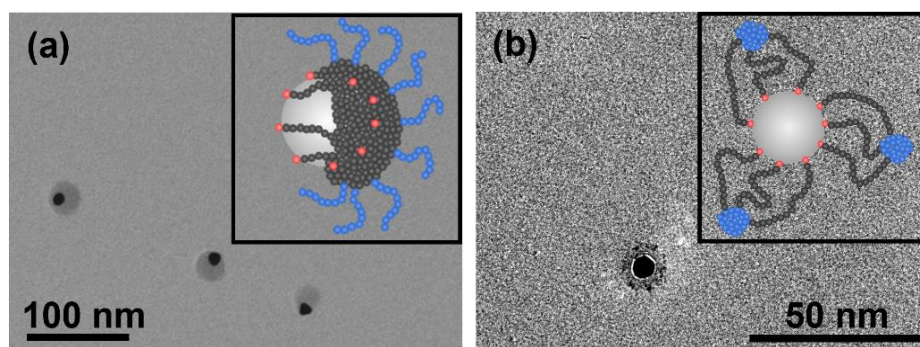
## Nanoparticles

## T28: “Hairy” metallic nanoparticles: from structural complexity at the single-particle level to dynamic supracolloidal assembly structures

*Christian Rossner,<sup>1</sup> Shayan Vazirieh Lenjani,<sup>1</sup> and Sophie Jancke,<sup>1</sup> Marina Sebastian,<sup>1</sup> Olga Kuharenko<sup>1</sup>*

<sup>1</sup>*Leibniz-Institut für Polymerforschung Dresden e.V., Institut für Physikalische Chemie und Physik der Polymere, D-01069 Dresden, Germany.*

Metallic nanoparticles grafted with polymer-molecule ligands combine distinct properties in a single, nanosized entity: While the metallic part may provide plasmonic functionality, the polymer ligand shell determines interactions with the environment, like for example responsivity toward external cues. Thus, the polymer ligand shell architecture is of critical importance. Against this background, we recently presented a new approach which allows – for the first time – to quantify the number of “hairy” ligands at the single-particle level, and also at distinct sites of anisotropic nanoparticles.[1] For nanoparticles with well-defined numbers of “hairy” ligands, structural plasticity of the polymeric shell can lead to unique single-particle structures, like pinned-micelle decorated nanoparticles,[2] as well as multicompartmentalized, core–satellite-type structures (Figure 1).[3] The latter can also be realized by directed assembly of distinct metal nanoparticles into supracolloids, exploiting polymer molecules as stimulus-responsive linker and spacer. Dynamic re-configuration of such structures gives rise messenger materials and associated sensing concepts, which are based e.g. on surface-enhanced vibrational spectroscopies.[4,5]



**Figure 1.** (Bright-field) transmission electron micrographs of gold nanoparticles grafted with diblock-copolymer ligands. Segregating inner blocks lead to surface-pinned micelle formation (a), while segregating outer blocks

lead to multicompartmentalized (core-satellite-type) structures (b).

[1] S. Vazirieh Lenjani, M. Mayer, R. Wang, Y. Dong, A. Fery, J.-U. Sommer, C. Rossner, *J. Phys. Chem. C* **2022**, 126 (32), 14017.

[2] C. Rossner, E. B. Zhulina, E. Kumacheva, *Angew. Chem. Int. Ed.* **2019**, 58 (27), 9269.

[3] *unpublished*.

[4] S. Jancke, C. Liu, R. Wang, S. Sarkar, Q.A. Besford, T.A.F. König, J. Popp, D.-C. May, C. Rossner, *Nanoscale* **2023**, 15 (46), 18687.

[5] Support was by a Liebig fellowship (Fonds der Chemischen Industrie) and Deutsche Forschungsgemeinschaft (project number: 466182523).

## T29: Colloidal Self-Assembly of Plasmonic Molecules via Hydrogen Bonding

*Yingying Cai<sup>1</sup>, Swagato Sarkar<sup>2</sup>, Yuwen Peng<sup>1</sup>, Tobias A.F. König<sup>2</sup>, and Philipp Vana<sup>1</sup>*

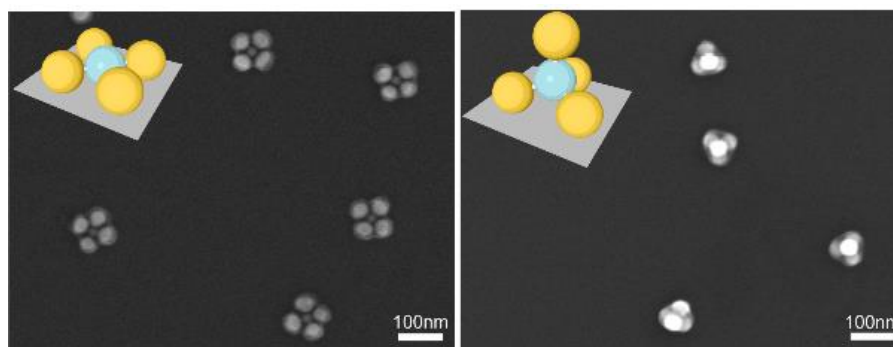
<sup>1</sup> *Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Göttingen, Germany.*

<sup>2</sup> *Institut für Physikalische Chemie und Physik der Polymere, Leibniz-Institut für Polymerforschung Dresden e.V. Dresden, Germany.*

Plasmonic nanostructures, such as those made from gold and silver, with precise geometry and high symmetry, exhibit collective optical properties that surpass those of individual nanoparticles (NPs). These properties make them of great potential for sensing and nano-optics applications. [1] While the lithographic method often requires costly templates, the colloidal self-assembly approaches enhance fabrication efficiency. In the latter approach, the structural precision and fidelity are highly dependent on fine-tuning the interactions between the individual building blocks. [1-2]

To this end, we introduced hydrogen bond (HB) interaction to guide the colloidal self-assembly process. This approach allowed us to tailor various geometries, including plasmonic molecules [3] and ring [4] nanostructures, using polymer-grafted AuNPs as building blocks. At the core of this concept, the interaction between donor/acceptor pairs must be optimized by polymer selection and colloidal conditions to simultaneously ensure effective interparticle binding and structural arrangement. The solvent-competition model is applied to assist the experimental design and provide thermodynamic insights. [3]

The resulting plasmonic molecules can be analogous to their molecular counterparts. The “bond length” (interparticle distance) can be further reduced, and “bond stiffness” can be enhanced by strengthening the polymer linkages. [5] This adjustment can enable 2D-to-3D isomerization (Figure 1), similar to molecular behavior.



**Figure 1.** Structural isomerization between square planar and tetrahedral configurations of plasmonic molecules  $AB_4$ , assembled from A-type (acceptor) and B-type (donor) of polymer-grafted AuNPs. [5]

[1] G. Haran, L. Chuntonov, *Chem. Rev.* **2018**, 118, 5539–5580.

[2] W. Peng, Y. Cai, L. Fanslau, P. Vana, *Polym. Chem.* **2021**, 12, 6198–6229.

[3] Y. Cai, P. Vana, *Angew. Chem. Int. Ed.* **2023**, e202309798.

[4] Y. Cai, W. Peng, P. Vana, *Nanoscale Adv.* **2022**, 4, 2787–2793.

[5] Y. Cai, S. Sarkar, Y. Peng, T. A.F. König, P. Vana, *Manuscript in Preparation*.

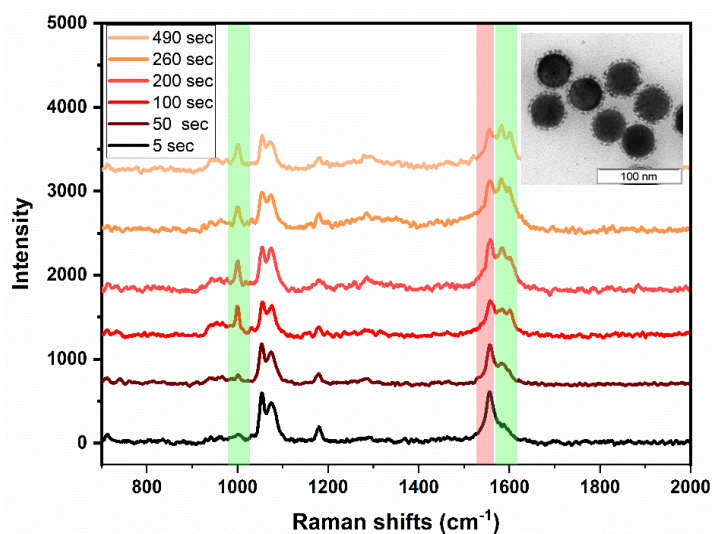
## T30: Bifunctional gold-palladium nanoparticles for plasmon-assisted C-C coupling reactions

Radwan M. Sarhan,<sup>1</sup> Shivani kesarwani,<sup>2</sup> Holger Lange,<sup>2</sup> and Ilko Bald<sup>1</sup>

<sup>1</sup> Institute of Chemistry, University of Potsdam, 14467 Potsdam, Germany

<sup>2</sup> Institute of Physics and Astronomy, University of Potsdam, 14476 Potsdam, Germany

Bimetallic nanostructures have been recently introduced as a promising route to develop new photo-induced nanoreactors, owing to the synergistic combination of their monometallic components. Bifunctional nanoparticles have been applied to many fields such as plasmonic nanocatalysis, where new chemical reactions can be driven by the interaction of light with plasmonic nanoparticles (e.g., Au and Ag) [1]. In our work, we aim at extending the applicability of plasmonic nanocatalysis to include more complex Pd-catalysed reactions [2]. Therefore, bifunctional Au-Pd nanoparticles of different morphologies as well as different optical properties (i.e., surface plasmon resonance) have been developed and used for driving C-C Suzuki coupling reaction at room temperature via the resonant excitation of the surface plasmon. In my talk, I am going to show the synthesis, characterization and the optical properties of several plasmonic nanoparticles including hybrid Au-Pd nanoparticles. In addition, I will present how we used surface-enhanced Raman scattering (SERS) on these Au-Pd nanoparticles to drive and in-situ monitor C-C coupling reaction at different and controlled conditions.



**Figure 1.** shows SERS spectra of 4-iodothiophenol (ITP) adsorbed on the Au-Pd nanoparticles (inset), the new peaks appear at 1585 and 1000  $\text{cm}^{-1}$  are due to the interaction of ITP molecules with phenyl boronic acid upon light irradiation, leading to a successful C-C Suzuki coupling reaction.

[1] Radwan M. Sarhan et al., *J. Phys. Chem. C* **2023**, 127, 21, 10051–10061.

[2] Yuhang Zhao, Radwan M. Sarhan, Alberto Eljarrat, *ACS Appl. Mater. Interfaces* **2022**, 14, 15, 17259–17272.

[3] Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – CRC 1636 – Project ID 510943930 - Project No. A02.



## T31: Control of magnetic dipole-dipole interactions in iron oxide-based supraparticles

Stephan Müssig<sup>1</sup>, Andreas Wolf<sup>1, 2</sup> and Karl Mandel<sup>1, 2</sup>

<sup>1</sup>Friedrich-Alexander-Universität Erlangen-Nürnberg, Professorship for Inorganic Chemistry, 91058 Erlangen, Germany

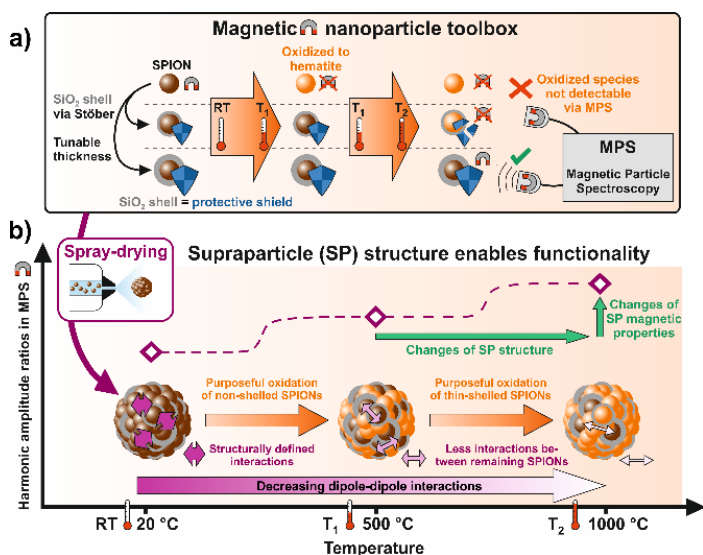
<sup>2</sup>Fraunhofer-Institute for Silicate Research ISC, 97082 Würzburg, Germany

The size, shape and composition of superparamagnetic (SPIONs) or ferrimagnetic magnetite/maghemite nanoparticles determines their magnetic and colloidal properties. Their defined assembly into micron-scaled powders (so called supraparticles) by spray-drying facilitates their defined arrangement and their combination with various other materials (polymers, silica, ...). Due to the close proximity of the nanoparticles within supraparticles, interaction phenomena arise and novel functionalities can be obtained [1].

It has recently been shown that magnetic particle spectroscopy (MPS) [2] is very sensitive towards dipole-dipole interaction changes of iron oxide nanoparticles within such supraparticles.

In this contribution, it is shown how different supraparticle architectures are synthesized in order to exploit the interaction (changes) within iron oxide-based supraparticles for novel applications such as magnetic recording of elapsed temperature events. Specific examples for control of the interactions are shown. For instance, how a silica shell with various thicknesses around iron oxide nanoparticles affects the temperature-dependent oxidation and thus represents a tool to control the high-temperature (up to 1000 °C) behavior of magnetic supraparticles (Figure 1) [3].

The presentation will introduce the concepts of magnetic supraparticles, the readout technique magnetic particle spectroscopy and give several examples of material combinations and their functionalities in hierarchically structured supraparticles from a material chemistry perspective.



**Figure 1.** Schematic working principle of high-temperature event recording magnetic supraparticles (SPs). a) Magnetic nanoparticle toolbox containing SPIONs with silica ( $\text{SiO}_2$ ) shells that protect SPIONs from oxidation at higher temperatures (400–1000°C). b) Structurally emerging functionality of SPs to record elapsed temperature events based on the purposeful oxidation of non-shelled and thin-shelled SPIONs to decrease dipole-dipole interactions. The resulting structure-property relation is resolved in MPS. Reprinted from [3].

[1] S. Wintzheimer, L. Luthardt, K. A. Le Cao, I. Imaz, D. Maspoch, T. Ogi, A. Bück, D. P. Debecker, M. Faustini, K. Mandel, *Adv. Mater.* **2023**, 35, e2306648.

[2] S. Biederer, T. Knopp, T. F. Sattel, K. Lütke-Buzug, B. Gleich, J. Weizenecker, J. Borgert, T. M. Buzug, *J. Phys. D: Appl. Phys.* **2009**, 42, 205007.

[3] A. Wolf, J. Sauer, K. Hurle, S. Müssig, K. Mandel, *Adv. Funct. Mater.* **2024**, 2316212.

## T32: Characterization of Transport Properties of Colloidal Dispersions by Photon Correlation Spectroscopy and Conventional Techniques

*Wenchang Wu*<sup>1</sup>, *Francisco E. Berger Bioucas*<sup>1</sup>, *Michael H. Rausch*<sup>1</sup>, *Thomas M. Koller*<sup>1</sup>, *Nicolas Vogel*<sup>2</sup>, *Wolfgang Peukert*<sup>2</sup>, and *Andreas P. Fröba*<sup>1</sup>

<sup>1</sup> *Institute of Advanced Optical Technologies – Thermophysical Properties (AOT-TP), Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Paul-Gordan-Straße 8, 91052 Erlangen, Germany*

<sup>2</sup> *Institute of Particle Technology (LFG), FAU, Egerlandstraße 3, 91058 Erlangen, Germany*

To characterize heat and mass transfer in colloidal dispersions in the field of process and energy technology, their thermal conductivity  $\lambda$  and diffusion coefficients are of great importance. For a colloidal dispersion as a heterogeneous system, the heat transfer is described by an effective thermal conductivity  $\lambda_{\text{eff}}$ . It is a function of size, shape, and volume fraction of the dispersed particles as well as the  $\lambda$  of both the dispersed and the continuous phase. In connection with nanofluids, often discussed as heat transfer fluids,  $\lambda_{\text{eff}}$  is expected to be larger in comparison to the base fluid. The debate on the extraordinary increase in  $\lambda_{\text{eff}}$ , which could be found in the literature over more than two decades, could be ended by recent critical reviews of models and experimental methods including sample handling and preparation, where research activities at AOT-TP contributed significantly. In colloidal dispersions, a single translational particle diffusion coefficient  $D_P$  is sufficient to describe mass transfer in unimodal systems. In bimodal and multimodal systems, the overall diffusive mass transport is described by a diffusion matrix. Here, the diffusive mass transport of an individual particle fraction depends on the concentration gradients of itself and of all other particle fractions. In anisotropic colloidal dispersions, the rotational diffusion coefficient  $D_R$  of the particles can additionally be considered. Within the Collaborative Research Center 1411 – “Design of Particulate Products”, the knowledge of diffusive mass transport is of special interest as it is often a prerequisite for the design and optimization of particulate products. For example, the design of classification processes by particle chromatography requires  $D_P$  data under confinement.

This contribution highlights research activities at AOT-TP for the determination of  $\lambda_{\text{eff}}$  by a steady-state guarded parallel-plate instrument and of  $D_P$  and  $D_R$  by photon correlation spectroscopy (PCS) for colloid dispersions. The former research part aims to understand how relevant parameters and phenomena affect  $\lambda_{\text{eff}}$  by studying nanofluids with the dispersed phase consisting of CuO, TiO<sub>2</sub>, SiO<sub>2</sub>, or polystyrene nanoparticles (NPs) and the continuous liquid phase being based on water, 1-pentanol, ethylene glycol, or glycerol as well as microemulsions containing water, *n*-decane, and a surfactant. The obtained results contributed to the development of a prediction model for  $\lambda_{\text{eff}}$  of dispersions. For the determination of  $D_P$ , the two PCS techniques dynamic light scattering and differential dynamic microscopy were further developed and selectively applied to dispersions containing isotropic or anisotropic NPs in free media, to microemulsions, and to dispersions comprising isotropic NPs under confinement. For bimodal dispersions, two  $D_P$  associated with the particle fractions were accessed by PCS. By applying PCS combined with its depolarized configuration,  $D_P$  and  $D_R$  of nanorods were determined simultaneously. For a polyol-based microemulsion containing micelles swollen with CO<sub>2</sub>, the micelle size was analyzed by PCS via the determination of the micelle diffusivity. Moreover, the applicability of PCS for studying  $D_P$  under confinement in porous media without using a refractive index matching fluid is demonstrated [1].

[1] The authors acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation), Grant Number Grant FR 1709/20-1 and Project-ID 416229255 – SFB 1411.

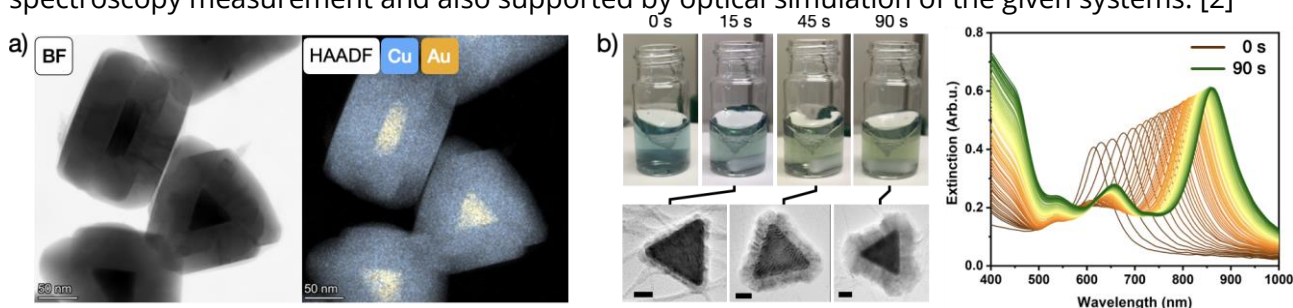
### T33: Cuprous oxide shell growth on gold nanoprisms

Dániel Zámbo<sup>1</sup>, Dávid Kovács<sup>1</sup> and András Deák<sup>1</sup>

<sup>1</sup> HUN-REN Centre for Energy Research, Konkoly-Thege M. út 29–33, 1121, Budapest, Hungary

Multicomponent nanoparticles that combine plasmonic and semiconductor domains show interesting optoelectronic properties that can be utilized in catalysis and energy harvesting. Nanoscale heterostructures prepared from gold and cuprous oxide are especially interesting, as for the given combination the excellent stability of the plasmonic nanoparticle is combined with the earth abundance of the p-type semiconductor. Expanding on our recent results on gold/cuprous oxide heteroparticles,[1] in the present work we investigate the formation of gold nanoprism/Cu<sub>2</sub>O nanoparticles, with the aim to clarify whether the largely anisometric shape of the metal nanoparticle translates to any site-selective deposition of the cuprous oxide. In general, this would be expected, as that nanoparticle surface curvature related ligand layer inhomogeneities is believed to influence molecule or material deposition to a great extent. Another interesting aspect of the investigations is that despite the well-known compatibility between gold and cuprous oxide, the triangular geometry of the present gold core does not match the favored crystalline symmetry of Cu<sub>2</sub>O.

During the experiments, the role of the reducing agent type was investigated and the time-evolution of the Cu<sub>2</sub>O coating studied using electron microscopy, ensemble as well as single-nanoparticle spectroscopy. Both time dependent electron microscopy and optical spectroscopy indicate that presumably due to the different kinetics of the cuprous oxide shell deposition process, the heteroparticle formation proceeds differently when hydrazine or hydroxylamine is used. For hydrazine the deposited shell is prism-face determined and multiple parallel slabs try to encapsulate the core particle. For hydroxylamine in contrast, a multicrystalline cuprous oxide shell is first deposited at the tips and edges in the initial phase of the growth, and hence is in line with the general expectations. At later stages, the metal core gets engulfed by the shell, which transforms to a polyhedral coating due to the symmetry and overall size of the particles. The structural evolution of the shell was further confirmed by correlative electron microscopy / single nanoparticle spectroscopy measurement and also supported by optical simulation of the given systems. [2]



**Figure 1.** Electron microscopy images of the Au nanoprism/ Cu<sub>2</sub>O heteroparticles prepared using hydrazine (a) and hydroxylamine (b). For the latter the time evolution of the extinction spectrum is shown in the right panel (scale bar: 20 nm).

[1] Kovács, D.; Deák, A.; Radnóczy, G. Z.; Horváth, Z. E.; Sulyok, A.; Schiller, R.; Czömpöly, O.; Zámbo, D. Position of Gold Dictates the Photophysical and Photocatalytic Properties of Cu<sub>2</sub>O in Cu<sub>2</sub>O/Au Multicomponent Nanoparticles. *J. Mater. Chem. C* **2023**, 11 (26), 8796–8807.

[2] The work received funding from the National Research, Development and Innovation Fund (NRDI) Fund of Hungary under the grants FK 142148, FK 128327 and TKP2021-NKTA-05.

## T34: Insights into the semi-continuous synthesis of magnetic iron oxide nanoparticles *via* thermal decomposition of iron oleate

*Egon G. Höfgen and Sulalit Bandyopadhyay*

*Partilce Engineering Centre, Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), Trondheim-7491, Norway*

Magnetic iron oxide nanoparticles (IONPs) have advanced from a subject of fundamental research to extensive everyday application in biomedical labs, such as in diagnostics based on nucleic acid extraction or size-selective DNA fragment separation,[1] and in treatment through magnetic field-induced drug release or hypothermia.

The increasing demand for IONPs in nanomedicine necessitates efficient and scalable production methods. Thermal decomposition synthesis offers excellent tailoring of the IONP's properties but its present batch-operation is restricting scale-up and commercial applications. To overcome these challenges, we show the successful translation of thermal decomposition into a semi-continuous process by slowly injecting the iron precursor. The set of semi-continuous reaction conditions chosen as standard, yield IONPs with properties ( $10.7 \pm 1.2$  nm,  $60 \text{ Am}^2\text{kg}^{-1}$ ) matching those obtained via the conventional heat-up method, 9.5 – 16 nm and  $55 \text{ Am}^2\text{kg}^{-1}$ . Starting from this standard condition, we explored the impact precursor addition speed, precursor amount, amount of oleic acid (stabilizing and shape directing ligand), reaction temperature and dwell time have on particle size, monodispersity and magnetic saturation of the IONPs, to address the research gap of a comprehensive mapping of the physico-chemical properties to reaction conditions. Available studies on semi-continuous thermal decomposition are limited, often focusing on single synthesis variables and few use iron oleate precursors. Our iron oleate precursor obtained from salt exchange was employed without pretreatment or dilution thereby facilitating a streamlined synthesis process. We found that, the reaction temperature has the strongest effect on the particles, by halving their magnetic saturation and altering sizes and size distributions, an important finding that has not been reported earlier. Within moderate addition rates in our system, seemingly, the dwell time has a stronger effect on particle sizes and magnetic saturation values than the addition speed. Furthermore, an increased precursor amount led to larger IONPs ( $16.4 \pm 2.2$  nm), consistent with existing literature. In conclusion, we produced different batches of IONPs in a size range of 5 – 20 nm with magnetic saturations between 30 to  $60 \text{ Am}^2\text{kg}^{-1}$ , depending on the conditions investigated. An oxidative phase transfer was used to mitigate the key challenge of hydrophobicity of oleate-capped IONPs, enabling their potential use in biomedical applications. The obtained hydrophilic particles show a high colloidal stability in water due to their high negative zeta potential of -33 mV.

Our work advances the understanding of synthesis-property relationships of IONPs by demonstrating the translation of an established synthesis protocol into more efficient and scalable processes through which it provides insights for developing and optimizing future IONP production protocols for various applications [2].

[1] Ravlo, E., et al., *Scientific Reports* **2023**, 13(1), 11714.

[2] The authors acknowledge the Research Council of Norway for funding this project (project number 327917) and the support of the Norwegian Micro- and Nano-Fabrication Facility, NorFab (project number 295864).

## T35: Application of microwave-assisted hydrothermal treatment for the modification of electro- and photocatalytic properties of MXenes

*Anton S. Zverev<sup>1</sup>, Christina Günter<sup>2</sup>, Sibylle Rüstig<sup>1</sup>, Claudia Prietzel<sup>1</sup>, Radwan M. Sarhan<sup>1</sup>, and Ilko Bald<sup>1</sup>*

<sup>1</sup> *Institute of Chemistry, University of Potsdam, Potsdam, Germany*

<sup>2</sup> *Institute of Geosciences, University of Potsdam, Potsdam, Germany*

The 2D transition metal carbides (MXenes) are one of the most discussed materials [1], which find their application in many of the most important processes from electrocatalysis and energy storage to photochemical processes and biomedical sensing. The high electrical conductivity, plasmonic activity, water solubility, and ability of surface functionalization are MXene's advantages, making them a universal basis for applied 2D nanomaterials [2]. But for achieving the required properties, a simple, express, and reliable method of MXene nanoflake modification or decoration by specific terminal groups, metal single-atoms, or other nanosized crystalline phases is needed.

In this work, the microwave-assisted hydrothermal method was applied for MXene nano-flakes decoration by both single-atom (SA) and nanoparticles. Ti<sub>3</sub>C<sub>2</sub> nanoflakes, synthesized by the MILD method [3], were modified by solvothermal treatment in the Microwave Synthesis Reactor (Discover, CEM). Acetonitrile and DMF were used as media. Acetates and acetylacetonates of Rh, Pd, Ni, Co, Cu, and Fe were used as precursors for SAs and crystalline particles decorating the MXene surface. The obtained samples of modified MXenes were studied by XRD, HR-TEM, EDS, and UV-Vis-NIR and Raman spectroscopy methods. It was shown that microwave treatment decreases the number of MXene layers in the package and increases the distance between the layers. The variety of the concentration of metal in the initial solution allows for control of the form of metal: nanoparticles or subcrystalline (single-atoms or clusters).

The obtained materials were tested as catalysts in the hydrogen evolution electrochemical process and Suzuki cross-coupling reaction. It was shown that the decoration of titanium carbide nanoflakes by Rh single-atoms can significantly (several times) increase HER electrocatalytic activity concerning pristine MXene nanoflakes. It was also shown that the Ti<sub>3</sub>C<sub>2</sub> nanoflakes decorated by Pd nanoparticles can be used as a catalyst for photoinduced room temperature Suzuki reaction. The formation of biphenyl product from p-iodothiophenol and phenylboronic acid on the Ti<sub>3</sub>C<sub>2</sub>@Pd surface was registered by Operando surface-enhanced Raman spectroscopy measurements.

[1] Li, Xinliang, et al., *Nature Reviews Chemistry* 2022, 6 (6) (2022), 389-404.

[2] Vahid Mohammadi, Armin, Johanna Rosen, Yury Gogotsi, *Science* 2021, 372 (6547), eabf1581

[3] Zhang, Jizhen, et al. *Advanced Materials* 2020 32(23) (2020), 2001093

[4] This work was supported by the European Research Executive Agency (Marie Skłodowska-Curie Actions HORIZON-MSCA-2022-PF-01-01) grant 101108465 (P2XSACat Project).

## T36: Additive-induced coalescence of apolar gold nanoparticles

*Tobias Valentin Knapp<sup>1</sup>, Bart-Jan Niebuur<sup>1</sup> and Tobias Kraus<sup>1,2</sup>*

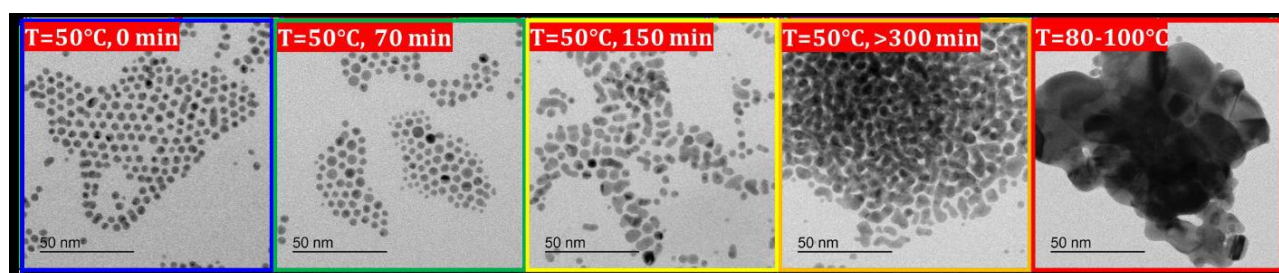
<sup>1</sup> INM – Leibniz Institute for New Material, Saarbrücken, Germany

<sup>2</sup> Saarland University, Colloid and Interface Chemistry, Saarbrücken, Germany

Gold nanoparticles (AuNPs) with apolar ligand shells are promising building blocks for materials with well-defined structures and properties. Modification of the shells can improve colloidal stability or control self-assembly [1]. If the shell is strongly bound (e.g. by thiols on gold), it can prevent irreversible aggregation and coalescence [2]. Molecular additives such as cyclic sulfides, for example, improve the colloidal stability of AuNPs by replacing a small number of hexadecanethiol ligands on the AuNP surfaces [3]. In this work we want to study how a stronger replacement of ligands by additive molecules influences the shape stability of gold nanoparticles, and how it depends on temperature.

Hexadecanethiol (HDT)-coated AuNPs with a diameter of 4 nm were dispersed in decane exposed to the molecular additive tetrahydrothiophene (R5S). Temperature-dependent small-angle X-ray scattering and transmission electron microscopy indicated the onset of stepwise R5S-induced irreversible agglomeration and coalescence of the cores at more than 40°C. Thermogravimetric analysis showed, that this is due to a gradual replacement of HDT by R5S.

To investigate this further, time-dependent structural characterization was performed at 40°C, 50°C and 60°C, and indicated a specific sequence shown in Figure 1: First, Ostwald ripening increased the size distribution of the AuNPs, and second, the AuNPs agglomerate and partially coalesce. When the reaction was performed at a temperature of 80°C and above, a third step involving merging of the agglomerates into microparticles with diameters between 0.1-5 µm followed. We identified temperature, degree of exchange, and the excess of unbound sulfur species as key parameters for the duration of the individual processes. The picture that emerges is the following: The replacement of HDT by R5S decreases the density of the shell, impeding their stabilizing effect. As a result, diffusion or fragmentation processes can occur more frequently, causing Ostwald ripening. The combination of increasing particle size and shrinking shell leads to agglomeration and coalescence of the particles.



**Figure 1.** Transmission electron micrographs of the reaction sequence of AuNPs with a R5S concentration of 128 mM during time-dependent heating at 50°C and stronger heating above 80°C.

[1] Monego, D.; Kister, T.; Kirkwood, N.; Doblaz, D.; Mulvaney, P.; Kraus, T.; Widmer-Cooper, A. *ACS Nano* **2020**, 14 (5), 5278–5287.

[2] Sahu, P.; Prasad, B. L. V. *Nanoscale* **2013**, 5 (5), 1768–1771.

[3] Knapp, T. V.; Hasan, M. R.; Niebuur, B.; Widmer-Cooper, A.; Kraus, T. *Langmuir* **2024**, accepted.

## T37: Multielemental synergy in symmetry breaking tetrametallic nanoparticles

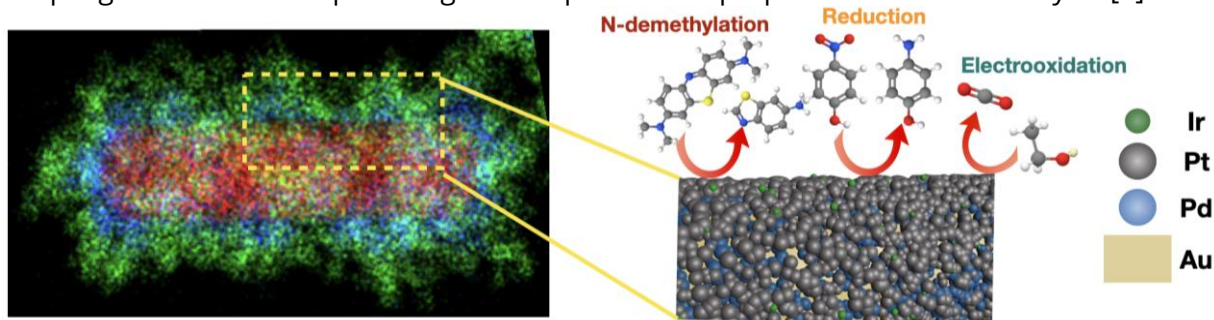
Omondi S. Apoko,<sup>1,2</sup> Dávid Kovács,<sup>1,2</sup> György Z. Radnóczy,<sup>1</sup> Zsolt E. Horváth,<sup>1</sup> Attila Sulyok,<sup>1</sup> István Tolnai,<sup>1</sup> András Deák<sup>1</sup> and Dániel Zámbo<sup>1</sup>

<sup>1</sup> HUN-REN Centre for Energy Research, Konkoly-Thege M. út 29–33, 1121, Budapest, Hungary

<sup>2</sup> Budapest University of Technology and Economics, Budapest, Hungary

Noble metal nanoparticles have already demonstrated their outstanding optical and catalytic properties in diverse applications. Despite the high surface-to-volume ratio of nanoparticles in general, the ultimate use of monometallic NPs as heterogeneous and electrocatalyst is limited by stability issues and cost effectiveness. Two main approaches became popular in the recent decade to address these issues and to further enhance their specific activity: (i) preparation of porous nanoparticles and (ii) integration of more than one noble metal into well-designed particles. Bi- and trimetallic noble metal NPs have already proven the synergism between the metals enabling improved structural and operational properties. Integration of four different metallic species in the form of engineered, porous NPs remained challenging, whereas such multimetallic porous particles might combine the advantageous electronic and structural properties of the elements and dramatically enhance the availability of the active sites at the same time.

In this study, tetrametallic nanoparticles were synthesized in consecutive synthetic steps to form a trimetallic, meso- and microporous PdPtIr shell on symmetry breaking gold cores.[1] Investigating the effect of acidity, temperature and core morphology enabled the robust and reliable preparation of porous Au@PdPtIr NPs with excellent uniformity. Multielemental synergy allows outstanding colloidal stability due to the quasi ligand-free and extensively charged NP surface making these particles active in various catalytic reactions. Excluding any illumination-related plasmonic effects, the NPs are demonstrated to be active in heterogeneous reduction reactions, dye degradation and alcohol electrooxidation with structural stability and recyclability. In-depth structural investigations imply that these properties can be attributed to the overall morphology of the particles, namely that symmetry breaking core particles are superior in terms of catalytic activity. Moreover, the multifunctionality of the particles is related to the intraparticle charge transfer and electronic coupling of the elements providing a novel platform to prepare robust nanocatalysts.[2]



**Figure 1.** TEM elemental map, schematic surface composition and the catalytic reactions of NPs.

[1] Zámbo, D.; Kovács, D.; Radnóczy, G. Z.; Horváth, Z. E.; Sulyok, A.; Tolnai, I.; Deák, A. Structural Control Enables Catalytic and Electrocatalytic Activity of Porous Tetrametallic Nanorods. *Small* **2024**, 2400421.

[2] The work received funding from the National Research, Development and Innovation Fund (NRDI Fund) of Hungary under the grants FK 142148 and TKP2021-NKTA-05.

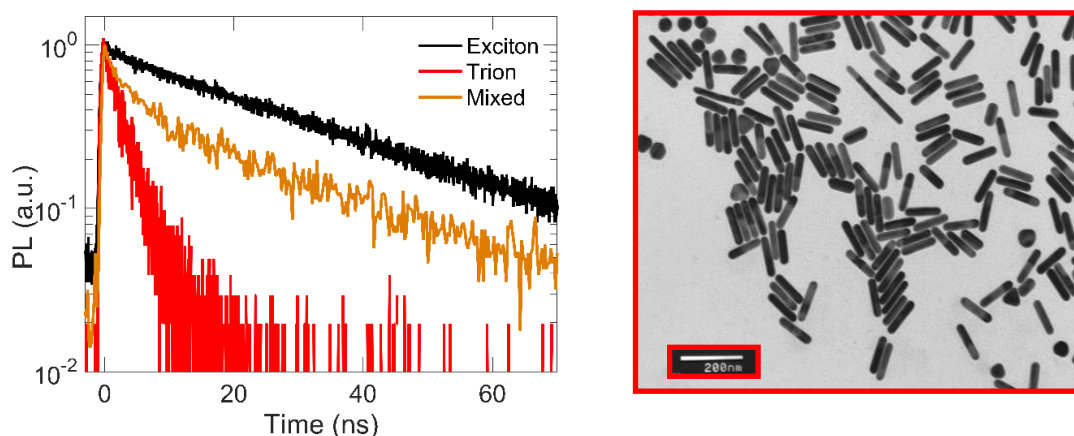
## T38: Spectroscopy of Gold Nanocrystals and Quantum Dots

*Paul Mulvaney*

*ARC Centre of Excellence in Exciton Science, School of Chemistry, University of Melbourne, Parkville, VIC., 3010, Australia*

Nanocrystals have remarkable size dependent optical properties. But to exploit these materials we also need to consider the role of chemistry, especially surface chemistry. In this talk I will discuss three cases where nanocrystal surface chemistry is critical for understanding optical experiments.

- Nanoscale assembly – can we ever create arbitrary structures from colloids through chemical or directed assembly? [1], [2].
- The mechanical properties of nanoscale materials – are they really stronger than bulk materials? We look at gold nanocrystals under pressure.[3]
- Why aren't quantum dots (QDs) in all of our electronic devices? We use single QD spectroscopy to understand blinking in semiconductor nanocrystals.[4]



**Figure 2.** (Left): Single QDs exhibit blinking which limits their applications in optoelectronics. (Right): Gold nanorods exhibit unusual size and shape dependent properties. How can we assemble them? Are they as strong as bulk gold metal?

[1] Growth of Gold Nanorods: A SAXS Study; S Seibt, H Zhang, S Mudie, S Förster, P Mulvaney  
The Journal of Physical Chemistry C 125, 19947-19960 (2021).

[2] A General Method for Directed Assembly of Single Nanocrystals, H Zhang, Y Liu, A Ashokan, C Gao, Y Dong, C Kinnear, N Kirkwood et al. Advanced Optical Materials, 2200179 (2022).

[3] Effects of Hydrostatic Pressure on the Surface Plasmon resonance of Gold Nanocrystals  
C Martín-Sánchez, JA Barrada-Argüeso, S Seibt, P Mulvaney et al., ACS Nano 13, 498-504 (2018).

[4] Two mechanisms determine quantum dot blinking, G Yuan, DE Gómez, N Kirkwood, K Boldt, P Mulvaney, ACS Nano 12, 3397-3405 (2018).



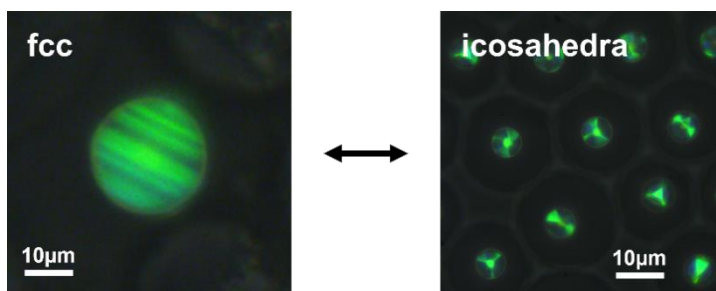
## T39: Seeing the invisible: Using structural color to analyze structure and dynamics of self-assembling colloids

*Nicolas Vogel*

*Institute of Particle Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*

Colloidal particles are interesting model systems to study self-assembly processes, as they can be synthesized with high control of sizes and shapes. If their size is within the range of the wavelength of visible light, such materials can also recreate the vivid structural coloration found in the natural world. Confining elements imposed upon the self-organizing particles can significantly alter the assembly process and may lead to crystal structures not observed in the bulk. However, the small size prevents the direct experimental observation of such crystallization processes. While the final structure of the assembly can be imaged using electron or X-Ray tomography, such processes are experimentally demanding and thus do not allow for the accumulation of statistically relevant data.

Here, we show that the structural coloration of such materials provides a convenient experimental access to both structure and crystallization pathway of confined colloidal self-assemblies. We first establish how the structure of colloidal clusters that can assemble within the confinement of emulsion droplets produces characteristic, anisotropic structural color patterns (Figure 1). These arise from the reflection of light at crystal planes oriented perpendicular to the optical axis of the microscope. As a result, the color patterns allow us to unambiguously assign icosahedral, decahedral, and fcc crystal structures without having to see individual particles. The ability to identify the resultant symmetry enables us to create phase diagrams connecting the cluster symmetry as a function of system size. Furthermore, following the evolution of structural color during the crystallization and melting process gives us experimental access to the dynamics and formation pathways. These experimental pathways corroborate event-driven molecular dynamics simulations and thus provide a full understanding of confined self-assembling systems.



**Figure 1.** Structural color patterns of a colloidal cluster with fcc- and icosahedral symmetry, respectively.

- [1] J. Wang, U. Sultan, E.S.A. Goerlitzer, C. F. Mbah, M. Engel, N. Vogel, Structural Color of Colloidal Clusters as a Tool to Investigate Structure and Dynamics, *Adv. Funct. Mater.* **2020**, 30, 1907730.
- [2] C. Mbah, J. Wang, S. Englisch, P. Bommineni, E. Spiecker, N. Vogel, M. Engel, Early-Stage Bifurcation of Crystallization in a Sphere, *Nature Communications* **2023**, 14, 5299.
- [3] J. Wang, S. Hahn, E. Amstad, N. Vogel, Tailored Double Emulsions Made Simple, *Adv. Mater* **2022**, 34, 5, 2107338.

## T40: Stretched or Wrinkled? On the Conformation of Amphiphilic Block-Copolymers in Polymersome Membranes

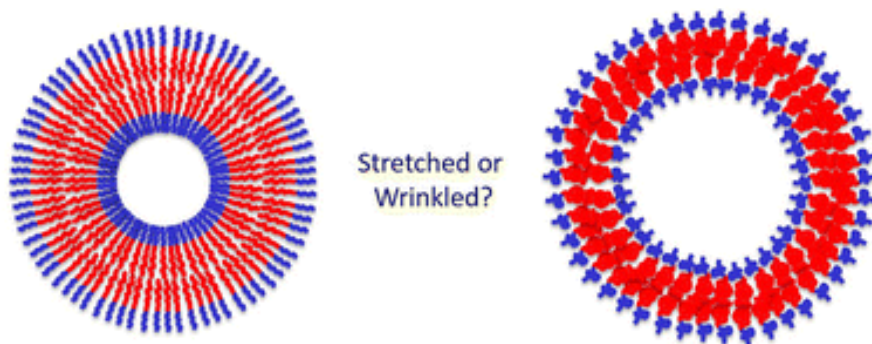
Christiane Effenberg and Jens Gaitzsch

Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany

Ever since the first report of polymersomes as polymeric analogues to the well-known liposomes, these polymeric nanoparticles have been studied intensively with numerous examples of polymers across the board. One main advantage of polymersomes is their improved mechanical stability over liposomes and this is usually associated to polymer entanglements within the polymersome membrane. This raises the question: How entangled are they and are there general tendencies?

Looking at literature, polymersome depictions sometimes contain highly coiled (e.g. “wrinkled”) hydrophobic parts of the amphiphilic block-copolymers, and sometimes more stretched versions (Figure 1). While these graphical representations are more or less a matter of taste of the authors, there is actually a way to look into this aspect from a physical chemical point of view. All polymers have maximum length in their stretched conformation and a suspected minimum when there are present as an ideal random coil. The dimensions of both conformations can be calculated. Since the real length of the hydrophobic part of the block-polymer within the membrane can be estimated by the membrane thickness of the polymersome (which effectively comprises the hydrophobic part of the block-copolymers), one can calculate how stretched and how coiled the polymers actually are.

<sup>[1,2]</sup> While we started looking into this for derivatives of poly(ethylene glycol) (PEG), this has now been massively expanded. Looking at over 90 amphiphilic block-copolymers across literature allowed to note general tendencies for longer or shorter polymers, ones with bulky side chains and also on how crystalline they are.<sup>[3]</sup> On top of this, the presentation will also offer a differentiated view for AB diblock as well as ABA/ABC triblock-copolymers.



**Figure 1.** Typical depictions of polymersomes show the amphiphilic block-copolymer either in a stretched (left) or wrinkled (i.e. coiled, right) conformation.

Shedding light onto this questions will allow to purposely design less and more stable polymersomes and aid researchers to pre-determine the conformation of their block-copolymers. It may also lead to a more unified depiction of polymersomes across literature.

[1] Davy Daubian, Jens Gaitzsch\* and Wolfgang Meier\*, *Polym. Chem.*, **2020**, 11, 1237-1248

[2] Riccardo Wehr, Elena C. dos Santos, Moritz S. Muthwill, Vittoria Chimisso, Jens Gaitzsch\* and Wolfgang Meier\*, *Polym. Chem.*, **2021**, 12, 5377-5389

[3] Christiane Effenberg, Jens Gaitzsch\*, *Soft Matter*, **2024**, 20, 4127-4135

## T41: Selective adjustment of non-densely packed arrangements of nanoparticles on planar and concave-structured surfaces

*Christina Graf<sup>1</sup>, Melike Barak<sup>1</sup>, Florian Wolf<sup>1</sup>, Paolo Scharmman<sup>1</sup>, Patrick Diel<sup>1</sup>, Madlen Schmudde<sup>2</sup>, Christian Grunewald<sup>2</sup>, Christian Goroncy<sup>2</sup>, and Thomas Risse<sup>2</sup>*

<sup>1</sup> *Fachbereich Chemie- und Biotechnologie, University of Applied Sciences Darmstadt, Germany*

<sup>2</sup> *Institut für Chemie und Biochemie, Freie Universität Berlin, Germany*

Non-close-packed two-dimensional arrays of colloidal particles are needed for applications such as anti-reflective coatings, superhydrophobic surfaces, and plasmonic devices. Most approaches for such arrays are multi-step procedures. We have developed a method for preparing well-ordered, non-close-packed colloidal monolayers directly from the dispersion by self-assembling amino-functionalized silica nanoparticles (SiNPs) on gold surfaces [1]. Aggregation is suppressed by electrostatic repulsion and frictional forces between the rough nanoparticles and the rough gold surfaces during drying. Enhanced chemical binding between nanoparticles and gold yields extended, well-ordered arrays. Increasing the ionic strength of the dispersion medium decreases the nearest-neighbor distance distribution of the SiNPs, indicating stronger shielding of electrostatic interaction [2]. The observed saturation coverages are well explained with an effective hard-sphere model in which the saturation coverage is limited by Coulomb repulsion.

The nearest neighbor distance and the suppression of possible aggregation at small interparticle distances can be further tuned by exploiting specific ion effects (Hofmeister effects), i.e., varying the polarizability, hydrophilicity, and charge of the ions in the dispersion medium. Multivalent counter-ions led to the highest aggregation in the dried non-close-packed nanoparticle arrays because multivalent counter-ions adsorb more strongly than monovalent counter-ions, thereby reducing the colloidal stability of the nanoparticles. In contrast, the least aggregation was found in non-close-packed nanoparticle arrays prepared with multivalent co-ions. Additionally, co- and counter-ions with the same valence influence the ordering in the nanoparticle arrays due to variations in their polarizability and hydrophilicity. Until now, specific ion effects on critical coagulation concentration have been only determined in dispersion, which makes it feasible to quantify strong aggregation. Our study offers a sensitive approach to determining minor aggregation in dried structures.

The effect of particle and substrate roughness on nearest neighbor distance and aggregation state was also systematically investigated. For this purpose, rough silica particles were synthesized using n-octadecyltrimethoxysilane, and virus-like silica particles were prepared using an approach utilizing cetyltrimethylammonium bromide. Both particle types were also amino-functionalized.

Plasmonic interactions can be tuned when concave-structured surfaces consisting of gold nanobowls serve as substrates. Arranging silica nanoparticles on such substrates is challenging, even if their diameter matches the gold bowls, since electrostatic interactions between silica nanoparticles determine the interparticle distances, not the gold bowl geometry. However, the distance between the silica nanoparticles on the concave surface can be adjusted by the ionic strength of the medium. Silica nanoparticles outside the gold nanobowls are removed using ultrasound, and ordered arrays of silica nanoparticles result.

[1] M. Schmudde, C. Grunewald, C. Goroncy, C. Njiki Noufele, B. Stein, T. Risse, C. Graf, *ACS Nano* **2016**, 10 (3), 3525–3535.

[2] M. Schmudde, C. Grunewald, T. Risse, C. Graf, *Langmuir* **2020**, 36 (17), 4827-4834.

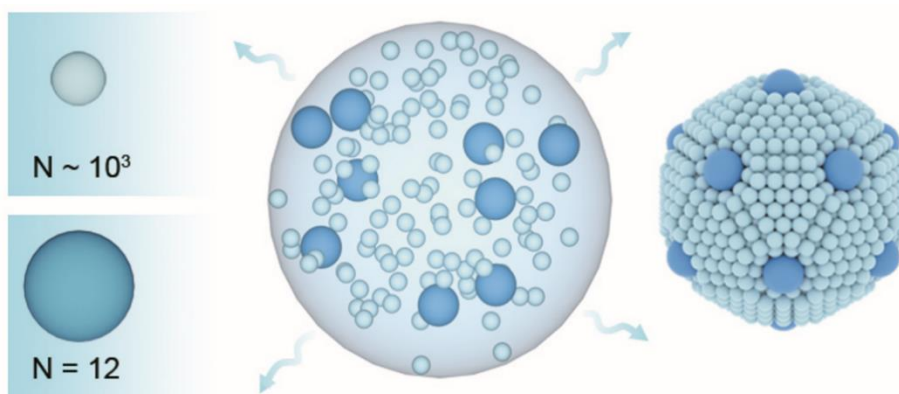
## T42: Entropic Trapping in Icosahedral Colloidal Supraparticles by Spherical Confinement

*Jonathan Martín González, Lukas Roemling, Nicolas Vogel*

*Institute of Particle Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany*

Entropy-driven self-assembly has been fundamental for the exploration of colloidal structures ever since discovered. A particularly interesting system appears when colloidal particles are constrained under spherical confinement, where the curvature alters the self-assembly process. For clusters ranging from  $10^2$  to  $10^4$  particles and sufficiently low drying rates, icosahedral supraparticles are the thermodynamically stable structures [1]. Icosahedral symmetry emerges from the balance between maximizing the packing fraction while conforming to the spherical constraints. However, this balance requires the exposure of various crystalline planes at the surface, with different packing densities, being the lowest in the vertex positions [2]. The surface packing density map can be explored through the inclusion of impurity particles, which should accommodate where they have the lowest entropy penalty, i.e. at the vertex side. These impurities can be described as being entropically trapped within these regions.

Event-driven molecular dynamics simulations of hard spheres in a hard spherical confinement demonstrate the trapping of large impurity particles at the vertex positions. Expanding from these findings, we design an experimental system, where icosahedral supraparticles are assembled from a large population of small particles and a few larger impurity particles. We have investigated the phase diagram of the system, exploring the behavior for different particle size ratios of small and impurity particles, and multiple supraparticles sizes. We find that under specific size ratios, large impurity particles self-assemble in the predicted low entropy penalty positions, experimentally proving the entropic trapping mechanism.



**Figure 1.** Schematic representation of the synthesis of icosahedral supraparticles with entropically trapped large impurity particles.

[1] De Nijs, B. et al. Entropy-driven formation of large icosahedral colloidal clusters by spherical confinement. *Nat. Mater.* **2015**, 14, 56–60.

[2] Wang, J. et al. Magic number colloidal clusters as minimum free energy structures. *Nat. Commun.* **2018**, 9.

## T43: Insights into Self-Assembly Mechanisms of Polymer-Grafted Gold Nanoparticles in Colloidal Solution

*Shayan Vazirieh Lenjani,<sup>1</sup> Cheng-Wu Li,<sup>2</sup> Sezer Seçkin,<sup>1</sup> Tobias A. F. König,<sup>1,3,4,5</sup> Holger Merlitz,<sup>2</sup> Jens-Uwe Sommer,<sup>2</sup> and Christian Rossner<sup>1,3,4</sup>*

<sup>1</sup>*Institut für Physikalische Chemie und Physik der Polymere, Leibniz-Institut für Polymerforschung Dresden e.V., D-01069 Dresden, Germany.*

<sup>2</sup>*Institut für Theorie der Polymere, Leibniz-Institut für Polymerforschung Dresden e.V., D-01069 Dresden, Germany.*

<sup>3</sup>*Dresden Center for Intelligent Materials (DCIM), Technische Universität Dresden, D-01069 Dresden, Germany.*

<sup>4</sup>*Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, Bergstraße 66, 01069 Dresden, Germany.*

<sup>5</sup>*Center for Advancing Electronics Dresden (cfaed), Technische Universität Dresden, Helmholtzstraße 18, 01069 Dresden, Germany.*

Triggered self-assembly of hybrid polymer-functionalized gold nanoparticles (AuNPs) in colloidal solutions has been applied in sensors, imaging and therapeutics [1, 2]. However, to enhance control over the self-assembly process, the interplay of attractive solvophobic and repulsive electrostatic forces which govern the interaction between these hybrid NPs need to be understood. In this study, the importance of electrostatic forces in directional self-assembly of polystyrene-grafted gold nanorods (AuNRs) [3] and kinetics of their self-assembly in solution [4] have been revealed. The important role of surface charges in directing the self-assembly of polystyrene-grafted AuNRs was revealed by new structural insights obtained using energy-filtered transmission electron microscopy (EFTEM) and kelvin probe atomic force microscopy (KPAFM) [3]. In addition, combination of time-resolved vis/NIR extinction spectroscopy with simulations run within the finite-difference time-domain (FDTD) theory framework allowed to deduce conversion profiles for NP assembly [4]. Comparison with diffusion-controlled rates revealed the presence of free-energy barriers, the origin of which could be traced back to surface charges of NPs. Coarse-grained molecular dynamic simulations aligned with the experimental results and helped to rationalize the observed tip-to-tip self-assembly mode.[4] These results demonstrate that the intrinsic properties of colloidal particles such as their surface charge can be used to promote site-selective self-assembly, which can additionally be tailored by changing the nanoparticle dimension, the polymer's macromolecular architecture and its molar mass.

[1] Marek Grzelczak et al., Chem Soc Rev **2019**, 48, 1342.

[2] Anish Rao et al., ACS Appl. Mater. Interfaces **2023**, 15, 21, 25248–25274

[3] Shayan Vazirieh Lenjani et al., J. Phys. Chem. C **2022**, 126, 32, 14017–14025

[4] Shayan Vazirieh Lenjani et al., Langmuir **2024**, 40, 5, 2487–2499

The authors acknowledge funding from the Fonds der Chemischen Industrie.

## **Applications & Sustainable Formulations of Colloidal Systems**

## T44: Biosurfactants – Greenwashing or Green Washing?

*Joachim Venzmer*

*Evonik Operations GmbH, Research Interfacial Technology, Essen/Germany*

Biosurfactants are not only based on sustainable feedstocks, but are also produced by microorganisms. After showing the biosynthesis by fermentation, the phys-chem properties of Rhamnolipids and Sophorolipids will be discussed. The necessary requirements of a surfactant such as surface activity or micelle formation, however, are not sufficient to predict the suitability of biosurfactants for specific applications. The same applies to the elucidation of the aggregate structures of biosurfactants by scattering methods. The most relevant features of biosurfactants – related to their application performance – are the combination of solubilization and mildness as well as their lack of interaction with cationic groups. The latter is the reason why the deposition of cationic polymers on hair is greatly improved, in case the classical anionic surfactant in a conditioning shampoo was completely replaced by Rhamnolipids. Another example is laundry detergents: Substituting a small portion of the classical surfactants by biosurfactants is more or less only greenwashing. It will be shown that in well-established application fields such as laundry detergents and cosmetics, the full potential of biosurfactants can only be unleashed by using completely new formulation concepts – and then, there is the opportunity for really green washing.

## **T45: Selective and reversible electrostatic surface monolayer of citric acid-coated magnetic nanoparticles on the fluorescent powder Y<sub>2</sub>O<sub>3</sub>:Eu**

*Peter Boelens<sup>1</sup>, Mélody Perret<sup>2</sup>, Emma Pustlauk<sup>1</sup>, Elsayed Gadelrab<sup>1</sup>, Sirine El Mousli<sup>2</sup>, Jean-Michel Siaugue<sup>2</sup>, Emilie Secret<sup>2</sup> and Franziska Lederer<sup>1</sup>*

<sup>1</sup> *Helmholtz-Zentrum Dresden-Rossendorf, Helmholtz Institute Freiberg for Resource Technology, Freiberg, Germany*

<sup>2</sup> *Physicochimie des Electrolytes et Nanosystèmes Interfaciaux PHENIX, Sorbonne Université CNRS UMR 8234 Paris, France*

Electronic waste contains high amounts of valuable metals in the form of ultrafine (<10 µm) inorganic powders. Currently, only a minor fraction of these metals is economically recycled, whereas the vast majority ends up in landfill. Separation of the inorganic powders would significantly enhance the recyclability of these secondary resources. However, the most prominent particle separation (froth flotation, gravity, magnetic and electric separation) processes were developed by the mining industry for primary resources. These processes are only partially suitable for electronic waste recycling because they face challenges related to the ultrafine particle sizes and the complex waste composition (typically >60 elements in electronic waste).

In a novel approach, we propose the use of magnetic nanoparticles (MNPs) as carriers for the magnetic separation of critical raw materials from electronic waste. MNPs can be synthesized cost-effectively with a broad variety of surface functionalization possibilities and exhibit unique superparamagnetic properties. We present a case study for the recycling of rare-earth elements from ultrafine fluorescent lamp powders by separation based on the selective attachment of MNPs. First, we obtained a Massart ferrofluid with monodisperse maghemite nanoparticles, electrostatically stabilized with a negatively charged citric acid coating. These MNPs form an electrostatically driven selective monolayer on the surface of the red fluorescent powder Y<sub>2</sub>O<sub>3</sub>:Eu (YOX). Subsequently, a gradient magnetic field is used to selectively purify YOX from other fluorescent powders. After magnetic separation, the pH is increased beyond the isoelectric point of YOX, the MNPs detach from the surface, the two types of particles are then separated based on their size difference and the MNPs are successfully reused in new rounds of magnetic carrier separation. The presented study represents a significant advancement in the utilization of MNPs for the recycling of ultrafine inorganic powders from electronic waste and has been submitted for a European patent application. In coming work, we will collaborate with a lamp recycling company to scale up this process by means of high-gradient magnetic separation.

[1] Acknowledgements: The MAGSEL project is co-financed by tax revenue on the basis of the budget adopted by the Saxon state parliament and the European Union.



## T46: Biomolecules as green flotation reagents in bioionflotation process

*Mital Chakankar<sup>1</sup>, Katrin Pollmann<sup>1</sup>, Sabine Kutschke<sup>1</sup> and Martin Rudolph<sup>2</sup>*

<sup>1</sup> *Department of Biotechnology, Helmholtz Institute Freiberg for Resource Technology, Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstraße 400, 01328 Dresden, Germany*

<sup>2</sup> *Department of Processing, Helmholtz Institute Freiberg for Resource Technology, Helmholtz-Zentrum Dresden-Rossendorf, Chemnitz Straße 40, Freiberg, Germany*

Industrial wastewaters are secondary sources of many critical and base metals. Recovering these metals from such waste streams helps in resource recycling and reduce the environmental burden. Low concentration of target metals and high concentration of unwanted metals makes such a recovery challenging. Ion flotation is a promising separation and recovery process in this regards. The use of various flotation agents is well documented, yet there is a high demand for new flotation agents. The new ion flotation agents need to be highly selective, efficient, and environmentally friendly. Microbial biomolecules are an attractive alternative and we are exploring various biomolecules in this regards. The critical metal complexing ability and interfacial properties of these biomolecules are unknown, which needs to be deciphered to fill the knowledge gap and develop the fundamental understanding required to develop the process and improve efficiency. This perception will allow to fully embrace the potential of novel bio-ion collectors in developing a highly synergistic process of bioionflotation for recovery of critical metals.

In this study, we provide an insight on the use of biosurfactants and amphiphilic siderophores as green flotation reagents with a focus on the dynamic surface tension, foamability and foam characterization as well as influence of metal ions on these properties followed by flotation studies for selective separation of metals. The results provide the basis for application of these biomolecules as green flotation reagents in bioionflotation for recovery of critical metals from wide range of secondary sources such as industrial wastewaters, leachates, mine waters, etc. Moreover, the resulting eco-friendly technology will boost resource efficiency, increase recycling rate, reduce waste, reduce critical metal dependency on non-EU countries and proliferate circular economy in EU [1].

[1] The authors thankfully acknowledge the European Commission for the Marie Skłodowska-Curie Individual fellowship on 'BioFlot' project (Project number 841437).

## T47 Scottish Heritage from a colloidal perspective

*Khalifa Mohamed and Juliane Simmchen*

*University of Strathclyde, Pure and Applied Chemistry, Glasgow, United Kingdom*

Aspects of Scottish heritage are known worldwide, and specifically for the colloidal chemist the legacy of Thomas Graham is omnipresent.[1] But colloidal aspects are also pivotal for the characteristics of some well-known Scottish products, including whisky and shortbread.

As there is a wide breadth of different whiskys produced in Scotland, their taste and smell are the main distinguishing marks. Each distillery uses their own procedure, which leads to a different distribution of congeners, by-products of fermentation, which lend the whisky its final taste and smell. Sulfides, thiols, thiophene, thiazoles etc. compounds that contain sulphur and are created during fermentation. Here we present our endeavors to use these compounds as driving force for active colloidal particles,[2,3] and study the chemical influences on motility.[4] To complement this culinary experience, we investigate the rheological properties of traditional versus vegan shortbread.



**Figure 1.** View from the Wallace Monument in Stirling of the Ochil Hills, an area where casks of whisky are stored to age.

[1] 'Obituary—Thomas Graham Chemist', *Scientific American* 1869.

[2] M. Wittmann et al., *Chem. Commun* 2022., vol. 58, no. 25, pp. 4052–4055

[3] M. Wittmann, M. Voigtmann, and J. Simmchen, *Small* 2023, vol. 19, no. 15

[4] L. Wang and J. Simmchen, *Condensed Matter* 2019, vol. 4, no. 3, Art. no. 3

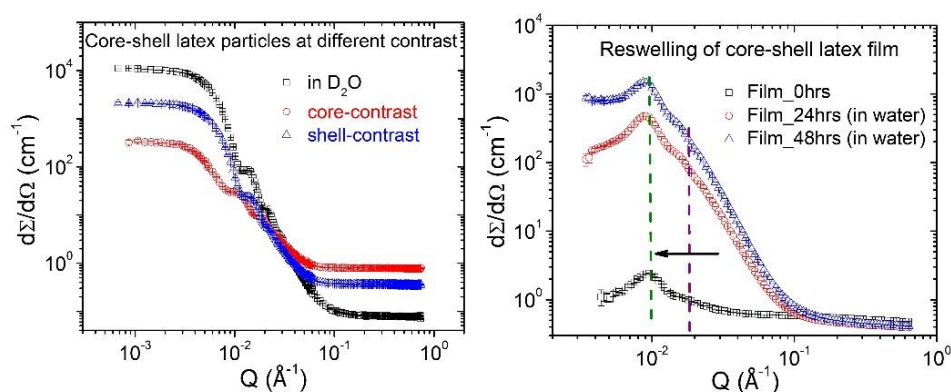
## T48: Interdiffusion of polymer and water in waterborne polymer latex films

*Debasish Saha<sup>1</sup>, Henrich Frielinghaus<sup>1</sup> and Bernd Reck<sup>2</sup>*

<sup>1</sup> Juelich Centre for Neutron Science, Forschungszentrum Juelich, Juelich 52428, Germany

<sup>2</sup> BASF SE, R&D Dispersions & Resins, Ludwigshafen 67056, Germany

Waterborne latex films, obtained from the dispersion of latex particles are of particular interest due to the non-content of volatile organic compounds (VOC), often mandatory under environmental legislation.<sup>1</sup> However, abrupt water penetration inside the films restricting their lifespan and deteriorating the shining of the coating. In order to prepare efficient and solvent-free coatings with the low glass-transition temperature ( $T_g < \text{the drying temperature}$ ) but with higher mechanical strength, we have integrated hydrophilic layers (Acrylic acid/ Poly(acrylamide)) around the hydrophobic cores (mixture of Methyl methacrylate and Butyl acrylate) and also hard shell around the soft core in the latex film. Latex particles with different morphology (hairy layer variants and core-shell particles) have been synthesized using emulsion polymerization.<sup>2</sup> Polymer latex films have been prepared in the next step by evaporating water in a thermo-humidistatic chamber at temperature 25 oC. The structure formation of polymer latex films in the dry state (crystallinity) and in re-swelled state (change in crystallinity and whitening or blushing) have been studied to propose a recipe for the preparation of efficient latex coatings. Small-Angle Neutron Scattering (SANS) study shows the FCC-like structure formation by the latex film, which gets better ordering with the inclusion of the hydrophilic shell. The hydrophilic shell also promotes the formation of the homogeneously water-swollen film and slows down the development of water “pockets”, preventing the deterioration of the latex film over time. On the other hand, the inclusion of hard shell protects the latex films from water whitening and provides additional mechanical strength. The interdiffusion between the latex particles has been analyzed by mixing H/D polymers. The transfer of polymer chains through interparticle boundaries that vanishes the crystalline structure and results in a formation continuous material.



**Figure 1.** Small-angle neutron scattering results of (Left) core-shell dispersion under different contrast (Right) structure and hydration of latex films made of core-shell dispersions.

[1] Konko et al. *Langmuir*, **2019**, 35, 6075.

[2] Abdeldaim et al. *Macromolecules*, **2023**, 56, 3304.

[3] This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 101034266.

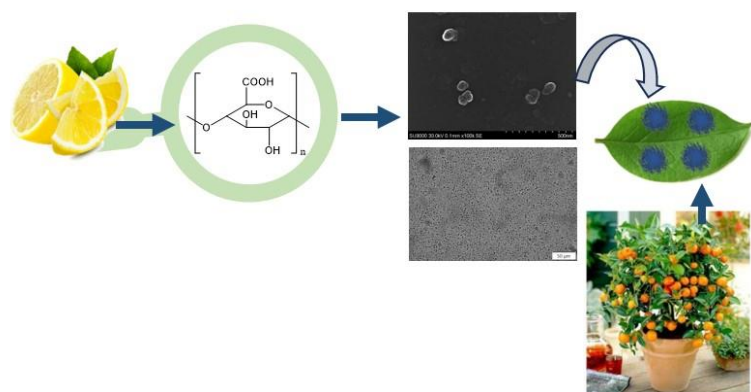
## T50: Bio-based Microgels as Containers for Plant Protection

*Nabanita Hazra<sup>1</sup>, Tuvshinjargal Budragchaa<sup>2</sup>, Ludger Wessjohann<sup>2</sup>, Ulrich Schwaneberg<sup>1</sup> and Andrij Pich<sup>1</sup>*

<sup>1</sup> *DWI - Leibniz-Institut für Interaktive Materialien, Aachen and Germany*

<sup>2</sup> *Leibniz Institute of Plant Biochemistry, Halle and Germany*

Sustainable agricultural production with less use of herbicides, pesticides, and fungicides to decrease drought stress is the main need to preserve our livelihoods. In this case, Biocompatible and biodegradable polysaccharide-based microgel (pectin) as containers play a crucial role in loading the plant protectants and delivery systems and to a sustainable release. [1] Herein, Pectin is readily available from citrus, sugar beet, and inexpensive raw material. We synthesized a wide-size range of Pectin microgels via inverse mini-emulsion polymerization allowing flexible variation of the chemical structure, size, and crosslinking degree of microgels. The chemical modification of polysaccharides [2] will help the integration of reactive groups able to generate covalent/cleavable or supramolecular crosslinks by controlling the swelling degree and programming the degradation profile of microgels. Our synthesis methodology will also allow programming the release kinetics of the bioactives from microgel containers (Fig 1) triggered by the variation of swelling degree a response to the humidity variations, UV-triggered cleavage of phenacyl crosslinks, or enzymatic degradation of polysaccharide chains [3].



**Figure 1.** Bio-based microgels for plant protection.

[1] S.H. Jung, S. Bulut, L.P.B. Busca Guerzoni, D. Günther, S. Braun, L. De Laporte, and A. Pich J, *Colloid Interface Sci*, 2022, 617: p. 409-421.

[2] H. Li, X. Li, P. Jain, H. Peng, K. Rahimi, S. Singh, and A. Pich (2020), *Biomacromolecules*, 2020, 21(12): p. 4933-4944.

[3] The authors acknowledge funding from the Leibniz transfer.

## T51: Physical characterization of surfactants for antibody formulations

Nadine Löw<sup>1</sup>, Coralie Schneider<sup>2</sup> & Matthias Kellermeier<sup>2</sup>

<sup>1</sup>Pharma Solutions, BASF SE, G-ENP/MD – H201, Carl-Bosch-Strasse 38, D-67056 Ludwigshafen, Germany

<sup>2</sup>Material Science, BASF SE, RGA/BM – B007, Carl-Bosch-Strasse 38, D-67056 Ludwigshafen, Germany

Stabilization of liquid therapeutic protein formulations with non-ionic surfactants is imperative to avoid critical loss of the active pharmaceutical ingredient by aggregation or adsorption onto different types of interfaces.

In the present work, we have characterized the interfacial activity of different surfactants – alone and in competition with antibodies, by applying a comprehensive suite of experimental techniques including tensiometry, interfacial rheology and quartz-crystal microbalance with dissipation monitoring (QCM-D).

The obtained data show important differences between the surfactants as well as a clear influence of the type of interface considered on the observed behavior. We have linked these physicochemical results to the performance of the surfactants in stabilization of antibodies.

Our findings and the broad spectrum of tests described in this work are instructive towards a better understanding of protein stabilization in distinct primary packaging systems through surfactants in aqueous formulations.

**Gelation, Hydrogels**  
**& Responsive Colloids**

## T52: From colloidal nanocrystals to (aero-)gels and their applications

*Alexander Eychmüller*

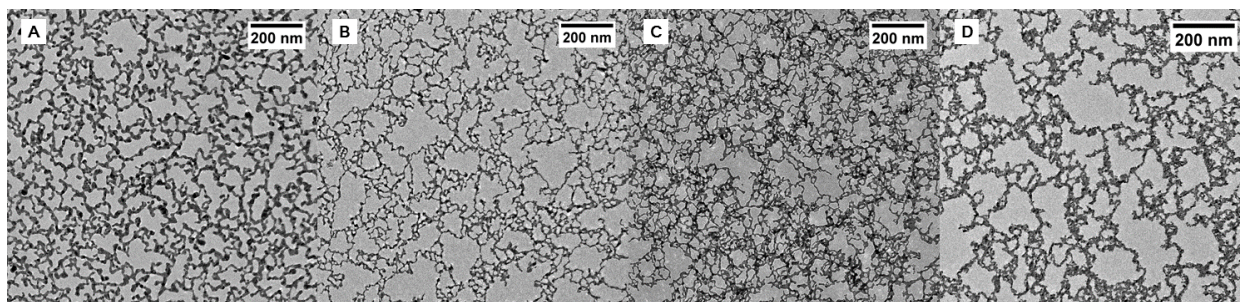
*Physical Chemistry, TU Dresden, Dresden, Germany*

The field of gelation of preformed nanoparticles and subsequent drying for the purpose of aerogel formation can be traced back about 25 years. The focus of my talk is on gels and aerogels prepared from a variety of different colloidal nanoparticles (semiconductor and metal) [1].

Various synthesis routes have been opened up in recent years: Formation of colloidal nanocrystals followed by (photo-)chemically induced or linker-mediated gelation or a “one-step” gelation, which shows similarities to the conventional and well-established sol-gel processes [2].

After some experimental results related to the characterization of the obtained gels and aerogels, I will explain their applications (mainly) in electrocatalysis, namely in the Oxygen Reduction Reaction on Polymer Electrolyte Fuel Cell cathodes, in CO<sub>2</sub> reduction and in water splitting. To achieve the highest performance of these catalysts, both the surface chemistry and the formation mechanisms need to be studied and tuned [3].

To conclude my talk, I will give an overview of the status of investigations on 2D-metal meshes (cf. Figure 1). This will include results that give an insight into the versatility of this approach, a number of interesting physical properties (stretchability and conductivity) and the description of these structures with the aid of Graph Theory [4].



**Figure 1.** 2D Au meshes displaying different fractal dimensions as well as surface coverages.

Financial support of EU and DFG is gratefully acknowledged [5].

[1] Alexander Eychmüller, *J. Phys. Chem. C* **2022**, 126, 1901.

[2] Cui Wang, Juan Herranz, René Hübner, Thomas J. Schmidt, Alexander Eychmüller, *Acc. Chem. Res.* **2023**, 56, 237.

[3] Cui Wang et al., *Adv. Mater.* **2023**, 35, 2211512.

[4] Pavel Khavlyuk et al, *Chem. Mater.* **2023**, 35, 2864.

[5] The author acknowledges funding from the EU (ERC AdG AEROCAT) and the DFG (RTG 2767, CRC 1415, and EY 16/30-1).

## T53: *In situ* investigation of microgels at fluid interfaces

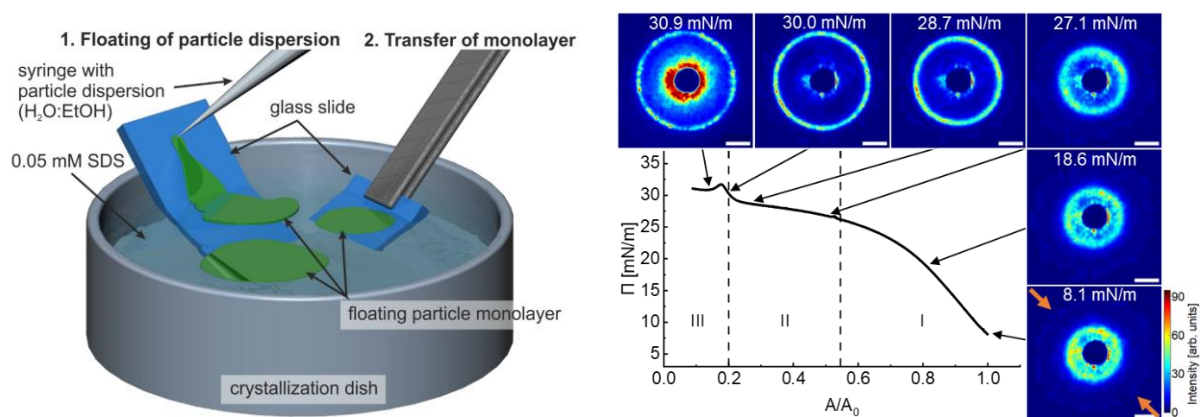
Keumkyung Kuk, Vahan Abgarjan, Julian Tobias Ringling, Christian Washeim, Déborah Feller, and Matthias Karg

Heinrich-Heine-University Düsseldorf, Physical Chemistry I, 40225 Düsseldorf, Germany

Core-shell microgels strongly adsorb to liquid/liquid and liquid/air interfaces [1]. The adsorption to flat fluid interfaces is the basis for the fabrication of  $\text{cm}^2$ -sized colloidal monolayers that can be transferred onto solid supports (Fig. 1, left) [2]. This transfer is often used to study the microstructure *ex situ* by using microscopy. Thereby the phase behavior can be studied in dependence on the packing fraction that is typically adjusted through the movable barriers in a Langmuir trough [3,4]. Interestingly, *in situ* studies are scarce to nonexistent.

In this contribution two methods for the *in situ* investigation of microgel monolayers at air/water interfaces will be discussed: 1) A Langmuir trough combined with small-angle light scattering (LT-SALS) that allows for the large area study during compression with excellent time resolution (Fig. 1, right) [5]. Using LT-SALS in direct comparison to *ex situ* analysis, we find striking differences in the microstructure that are related to drying artefacts during monolayer transfer onto a solid support [5]. 2) A Langmuir trough combined with a custom-build extinction spectrometer that allows to follow the extinction during uniaxial compression. Using plasmonic microgels that feature gold nanoparticle cores, we could study the phase behavior through the distance dependence of plasmon resonance coupling phenomena. During uniaxial compression, we observe a pronounced blue-shift and intensity increase of the plasmon resonance.

The methods presented are non-invasive, can be implemented at relatively low costs and allow for robust, model-free analysis of  $\text{mm}^2$  areas with great resolution and statistics.



**Figure 1.** Left: Basic principle of monolayer preparation at air/water interfaces and subsequent transfer onto solid supports [2]. Right: Compression isotherm measured from CS microgels at the air/water interface in a Langmuir trough (uniaxial compression). Images show diffraction patterns recorded by SALS for selected surface pressures II.

[1] D. Feller, M. Karg, *Soft Matter* **2022**, 18, 6301.

[2] K. Volk et al., *Adv. Mater.* **2015**, 27, 7332.

[3] M. Rey et al., *Soft Matter* **2016**, 12, 3545.

[4] A. Rauh et al., *Soft Matter* **2017**, 13, 158.

[5] K. Kuk et al., *Soft Matter* **2023**, 19, 175.



## T55: Switching the chaotropic effect by pH: Binding of pH-sensitive Keggin polyoxometalates to cellulose ethers in water

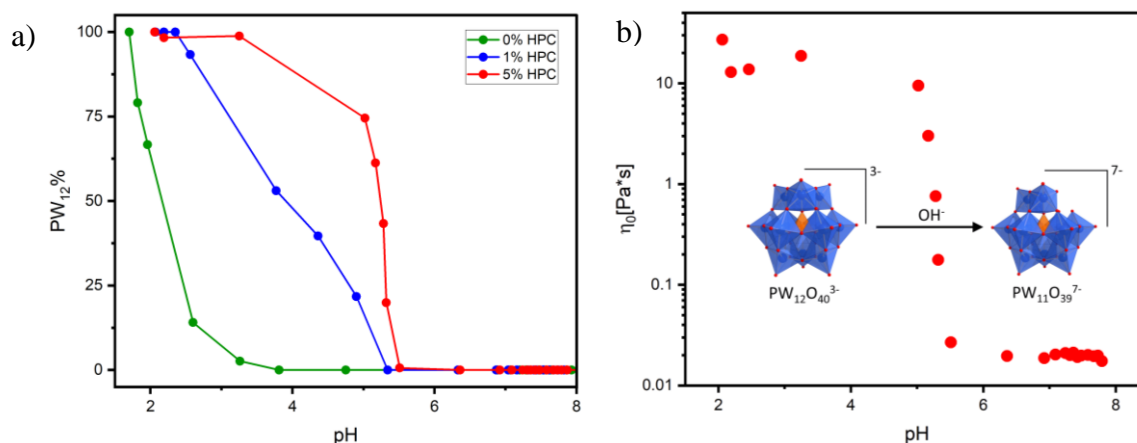
*Vighnesh Balkrishna Lokare<sup>1</sup>, Amina Ledinic<sup>1</sup>, Max Hohenschutz<sup>1</sup>*

<sup>1</sup>Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany

Nanometer-sized ions such as Keggin polyoxometalates (POMs), have recently emerged as powerful gelating agents for non-ionic cellulose ethers (CEs), such as hydroxypropylcellulose (HPC) [1]. Due to their low charge density and weak hydration, these POMs bind to CE by a water-mediated, so-called (super-)chaotropic effect, to release their hydration water [2].

While POMs are widely used in soft matter composites, they are only stable in acidic solution and decompose in water upon addition of base thus limiting the functionality of the composite.

Herein, we show that the stability of the POMs  $\text{SiW}_{12}\text{O}_{40}^{4-}$  and  $\text{PW}_{12}\text{O}_{40}^{3-}$ , but not of  $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$ , is strongly extended by addition of the non-ionic polymer HPC. By performing acid-base titration of the POM with NaOH coupled with Raman and NMR spectroscopy, we identify the solution species of the POMs. For example, for  $\text{PW}_{12}$  the stable range is extended from pH 2 in neat water to pH 3.25 at 5% w/w HPC, see the Fig.1a. This stability increase is related to the chaotropic binding of  $\text{SiW}_{12}^{4-}$  and  $\text{PW}_{12}^{3-}$  (or lack of binding for  $\text{H}_2\text{W}_{12}^{6-}$ ) to the non-ionic polymer, which shields the POM from base-induced hydrolysis. The decomposition species of the POMs, such as  $\text{SiW}_{11}^{8-}$  and  $\text{PW}_{11}^{7-}$ , with high charge densities, do not show interaction with HPC as observed from Small Angle X-ray Scattering and cloud point measurements. Because the chaotropic binding depends on the POM species, switching between the parent POM, e.g.  $\text{PW}_{12}$ , to decomposed POM-species, e.g.  $\text{PW}_{11}$ , can be used as a trigger to tune the viscosity of HPC/POM solutions, see Fig.1b, by orders of magnitude. POM's extended stability in HPC solution, as well as their reversible pH-responsive behavior, is potentially promising towards pH sensitive superchaotropic materials.



**Figure 1.** a) Effect of HPC on the stability domains of  $\text{PW}_{12}\text{O}_{40}^{3-}$ . b) Change in viscosity of 5% HPC with 5 mM  $\text{PW}_{12}\text{O}_{40}^{3-}$  as a function of solution pH values.

[1] M Hohenschutz et al., *Angewandte Chemie International Edition* **2022**, 62 (3).

[2] KI Assaf et al., *Angewandte Chemie International Edition* **2018**, 57 (43).

[3] N Gumerova, A Rompel, *Chemical Society Reviews* **2020**, 49 7568-760.

## T56: The influence of degree of deacetylation and polymerization of chitosans on their photomodulated water vapor permeabilities.

Nils von Seggern<sup>1</sup>, Yannik Thiebes<sup>3</sup>, Stefan Cord-Landwehr<sup>4</sup>, Rainer Niewa<sup>3</sup> and Linus Stegbauer<sup>1,2</sup>

<sup>1</sup> Institute of Interfacial Process Engineering and Plasma Technology, University of Stuttgart, Stuttgart, Germany

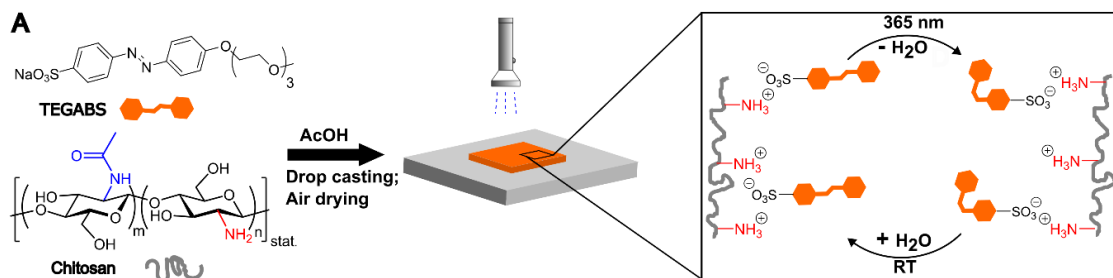
<sup>2</sup> Institute of Nanoscale and Biobased Materials, Technical University Bergakademie Freiberg, Freiberg, Germany

<sup>3</sup> Institute of Inorganic Chemistry, University of Stuttgart, Stuttgart, Germany

<sup>4</sup> Institut für Biologie und Biotechnologie der Pflanzen – IBBP, University of Münster, Münster, Germany

Recently, we have shown, that low molecular weight chitosan with TEGABS shows photomodulation of the mechanical properties and photoactuation.<sup>[1]</sup> Herein, we present a procedure to manufacture several UV-light-responsive chitosan films with different degree of deacetylation (DD) (70-95%) and polymerization (DP, 200-3500) by incorporating the azobenzene derivative Methoxy diethylene glycol azobenzene sulfonate (TEGABS). The films are investigated by Powder X-ray diffraction (PXRD), UV-VIS spectroscopy, Raman spectroscopy, FTIR spectroscopy and nanoindentation. With increasing DD at near constant DP and increasing amount of TEGABS the films show a decrease in efficiency of photoisomerization (E→Z) of TEGABS and in the half-life of thermal relaxation after UV irradiation. This behavior is related to an increasing phase separation: Starting with solid-solutions of TEGABS in the chitosan matrix (low DP and low DD) TEGABS precipitates into nanocrystals with increasing DD and DP, which compromises the responsive properties.

The films not only show an increase of stiffness and hardness while irradiated with UV light, they also show a light-induced removal of residual moisture. The TEGABS/Chitosan films were fabricated into membranes to test water vapor permeabilities with and without UV irradiation. The water vapor permeability decreases during irradiation with UV light. we show the potential of biogenic polysaccharides in the design of humidifying membranes with a light-adjustable permeability by DP and DD.<sup>[2]</sup>



**Figure 1.** Concept of the chitosan-based smart material, along with the categorization of the biopolymers. A indicates the schematic fabrication and function of the material which was established by von Seggern et. al..<sup>[28]</sup>

[1] N. von Seggern, N. Oehlsen, I. Moudrakovski, L. Stegbauer, *Small* **2023**, *n/a*, 2308939.

[2] The authors gratefully acknowledge the Carl Zeiss Stiftung (Perspectives project ChitinFluid, project P2019-02-004) and Fonds der Chemischen Industrie (Fellowship to L.S. and N.O.) for generous financial support, the core facility SRF Advanced Materials Innovation and Characterization (AMICA) at the University of Stuttgart for the support and assistance and Samantha Waechter for the support in conducting experiments and sample preparation.

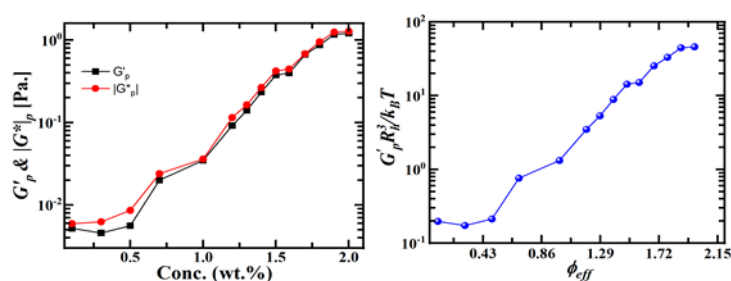
## T57: Glassy and Jamming Dynamics of Conventional and Ultra-Low Crosslinked Thermoresponsive Microgel Dispersions

Chandeshwar Misra<sup>1</sup>, Divya Paloli<sup>2</sup>, Peter Schurtenberger<sup>2</sup>, Walter Richtering<sup>1</sup>, and Jérôme J. Crassous<sup>1</sup>

<sup>1</sup> Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, 52074, Aachen, Germany

<sup>2</sup> Physical Chemistry I, Center for Chemistry and Chemical Engineering, Lund University, 221 00 Lund, Sweden

Soft thermoresponsive microgels offer the advantage over hard colloidal particles to significantly swell and deswell with temperature allowing the fine tuning of their volume fraction, interaction and intrinsic softness [1-2]. Here, dense aqueous dispersions of either 5 mol. % crosslinked or ultra-low crosslinked microgels (ULC) poly(*N*-isopropylacrylamide) (PNIPAM) microgels synthesized via precipitation polymerization have been investigated. A combination of rheology, scattering, and microscopy techniques were employed to demonstrate the influence of the microgel softness on the dispersion structure and dynamics, where softness can also be conveniently further tuned by varying dispersion temperatures [1,3]. In this study, we probe the different regimes from liquid to glass and from glass to jamming varying the microgel number density effective volume fraction,  $\phi_{eff}$ . For both systems, a significant interpenetration of the microgels at high  $\phi_{eff}$  was inferred from scattering experiments. However, whereas regular microgels only slightly deswell approaching the jamming transition, the conformation of ULC microgels is significantly altered at higher  $\phi_{eff}$ . Study of linear viscoelastic and flow behavior reveals a shift of the dynamical arrest and jamming of the dispersions to higher  $\phi_{eff}$ , with decreasing  $T$ , *i.e.*, increasing softness which is more prominent for ULCs that we rationalize within the framework of the mode coupling theory [4-6].



**Figure 1:** (a) Values of the plateau of the storage modulus,  $G'_p$ , and complex modulus,  $|G^*p|$ , vs. concentration of ULC dispersions. (b) Rescaled moduli of the plateau in the elastic modulus,  $G'_p$  vs. effective volume fraction of the ULC microgel dispersions.

[1] H. Senff and W. Richtering, "Temperature sensitive microgel suspensions: Colloidal phase behavior and rheology of soft spheres," *The Journal of Chemical Physics*, **1999**, 111, 1705–1711, 1999.

[2] Romeo et al., "Temperature-controlled transitions between glass, liquid, and gel states in dense p-nipa suspensions," *Advanced Materials*, **2010**, 22, 31, 3441– 3445.

[3] Han et al., "Melting of two-dimensional tunable-diameter colloidal crystals," *Phys. Rev. E*, **2008**, 77, 041406.

[4] Scotti et al. Flow properties reveal the particle-to-polymer transition of ultra-low crosslinked microgels, *Soft Matter*, **2020**, 16, 668-678, 2020.

[5] Mattsson et al., "Soft colloids make strong glasses," *Nature*, **2009**, 462, 83–86.

[6] Crassous et al., Thermosensitive core-shell particles as model system for studying the flow behavior of concentrated colloidal dispersions, *J. Chem. Phys.*, **2006**, 125, 204906.

## T58: Using tetraPEG Hydrogels to Mimic the Properties of Mucus

Robert F. Schmidt<sup>1</sup>, Robert Dalglish<sup>2</sup>, Sylvain Prévost<sup>3</sup> and Michael Gradzielksi<sup>1</sup>

<sup>1</sup> Institut für Chemie, Technische Universität Berlin, 10623, Berlin, Germany

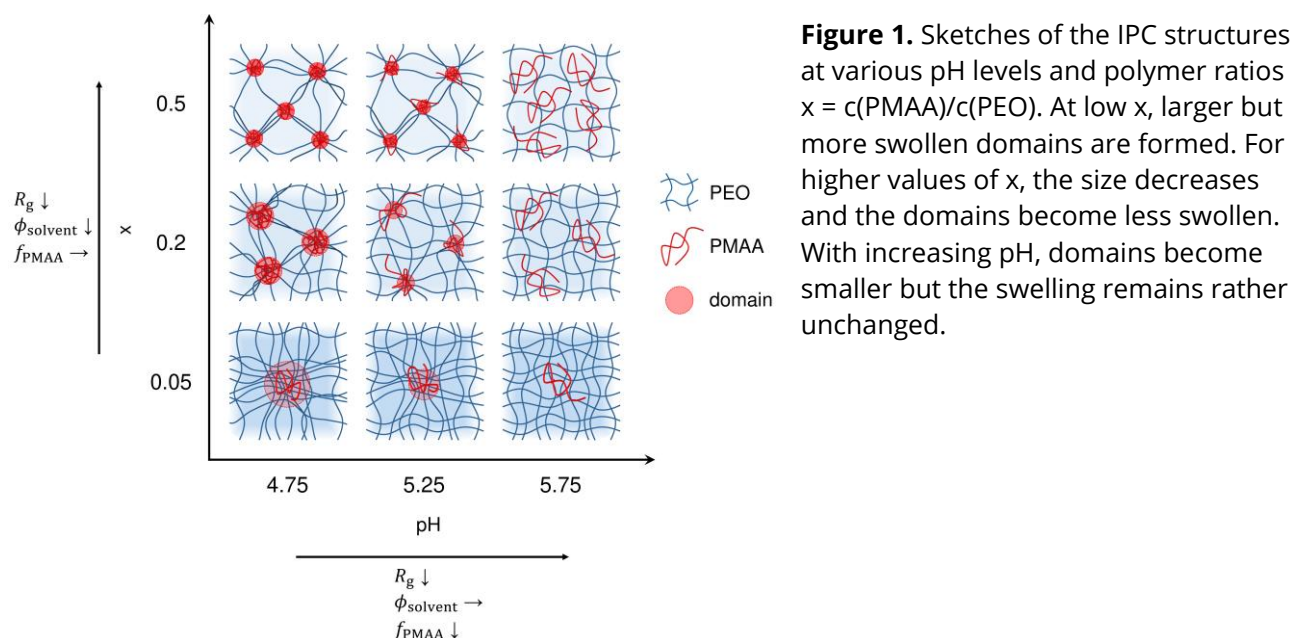
<sup>2</sup> STFC, ISIS, Rutherford Appleton Laboratory, Chilton, Oxfordshire OX11 0QX, United Kingdom

<sup>3</sup> Institut Laue-Langevin, 71 avenue des Martyrs, CS 20156, 38042 GRENOBLE Cedex 9, France

Hydrogen-bonded interpolymer complexes (IPCs) are associations of complementary polymers, held together by hydrogen bonds. Due to their highly tunable rheological properties and biocompatibility, they are interesting for a wide range of pharmaceutical and industrial applications [1]. Our study investigates the structural and rheological properties of IPCs formed between poly(ethylene oxide) (PEO) and poly(methacrylic acid) (PMAA) at different pH levels and polymer ratios.

By combining potentiometric titration, rheology, and small-angle neutron scattering (SANS), we have gained detailed insights into the behavior and pH-responsiveness of these hydrogen-bonded networks. The rheological experiments showed that the IPCs exhibit strong viscoelastic behavior at low pH, with a predominantly elastic response that is up to 1000 times higher than a pure PEO solution. As the pH is increased above 5.5, the complexes transition from elastic to more viscous behavior. The SANS experiments reveal that at low pH, compact domains are formed around the PMAA molecules. As pH increases, these domains become smaller and less dense, reflecting the progressive dissociation of PMAA and a loss of polymer interaction.

This work provides valuable new insights for the design of pH-responsive hydrogels, with potential applications in drug delivery, bioadhesion, and tissue engineering. By fine-tuning the pH and polymer ratio, it is possible to create materials with tailored structural and mechanical properties.



[1] V. V. Khutoryanskiy, *Int. J. Pharm.* **2007**, 1-2, 15–26.

## T59: Effect of Shear on Phase Separating Gelatin Methacryloyl (GelMA)-Dextran by Rheo-Small Angle Light Scattering, Rheo-UV Curing and Confocal Microscopy

*Evdokia Stefanopoulou*<sup>1,2</sup>, *Rodrigo Salazar Ortiz*<sup>3</sup>, *Ghazi Ben Messaoud*<sup>4</sup>, *Sanja Aveic*<sup>3</sup>, *Horst Fischer*<sup>2</sup> and *Walter Richtering*<sup>1,2</sup>

<sup>1</sup> Institute of Physical Chemistry, RWTH Aachen, Germany

<sup>2</sup> DWI-Leibniz Institute for Interactive Materials, Aachen, Germany

<sup>3</sup> Dental Materials and Biomaterials Research (ZWBF), Uniklinik, RWTH Aachen, Germany

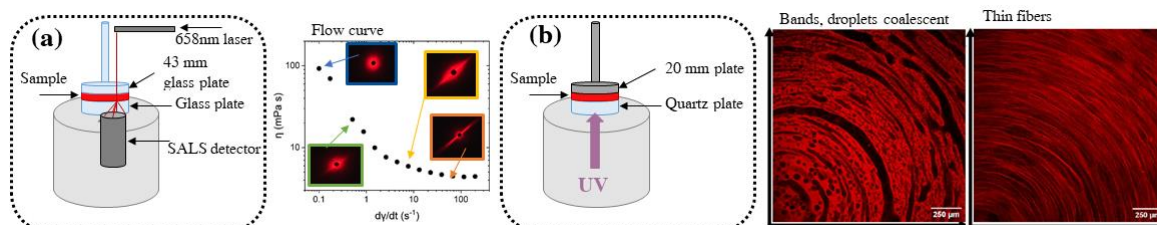
<sup>4</sup> INRAE, Institute Agro, UMR STLO, Rennes, France

Hydrogels are soft, self-standing and highly porous materials that are excellent candidates for applications ranging from tissue engineering and wound dressing to sensors and actuators [1]. There are different methods with which porosity can be introduced in hydrogels, like freeze-drying or micro-emulsions, but the aqueous-two-phase-system (ATPS) approach stands out due to its fully aqueous environment and because there is no requirement for special equipment.

In this work, GelMA, a polyampholytic protein, and dextran, a neutral polysaccharide, are phase separating in water. A hydrogel can be obtained by UV-crosslinking of the GelMA phase and then the dextran phase is washed away to produce the pores. Segregation, based on the electroneutrality principle and the entropy of the system, can evolve either by nucleation-and-growth or by spinodal decomposition, therefore inducing different microstructures and porosities.

By varying the polymer concentrations and physicochemical conditions, it is possible to target both phase separation mechanisms and to study the evolution of them under shear using two approaches. In the first approach, we apply shear during phase separation, at 37°C, and observe the changing small-angle light scattering (SALS) 2D pattern in the inverse space, from which we estimate the characteristic length scales of the resulting microstructures. In the second two-step approach, we couple rheology with UV curing to quench the sheared microstructure. The resulting hydrogels are afterwards observed by confocal microscopy.

Both approaches complement each other and show high alignment and anisotropy of the microstructures along the shear direction, due to the low interfacial tension, hence high sensitivity to shearing, of the ATPS [2]. Bands, thin fibers, coalescent dextran droplets and GelMA microparticles are observed [3]. The various resulting microstructures in presence or absence of shear can be of interest for casting or 3D printing, respectively, artificial extracellular matrices with different porosity requirements based on different cell types.



**Figure 1.** (a) Rheo-SALS: Anisotropic/ aligned microstructures along shear direction. (b) Rheo-UV and Confocal Microscopy: Bands, thin fibers or GelMA microparticles formation while shearing and before UV.

[1] F. Ullah et al., *Materials Science and Engineering C* **2015**, 57, 414-433.

[2] M. Vis et al., *Physical Review Letters* **2015**, 115, 078303.

[3] G. B. Messaoud et al., *Soft Matter* **2024**, 20, 773-787.

[4] The authors acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG).

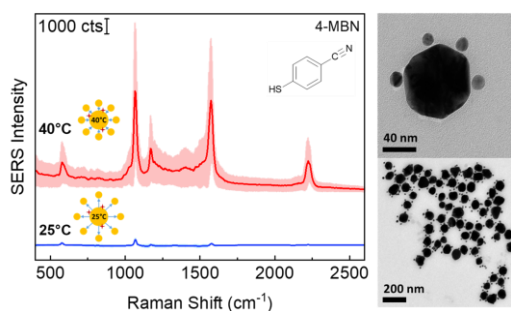
## T60: Turning on hot spots: Supracolloidal SERS probes made brilliant by an external activation mechanism [1]

*Sophie Jancke*<sup>1</sup>, *Liu, C.*<sup>2</sup>, *Wang, R.*<sup>1</sup>, *Sarkar, S.*<sup>1</sup>, *Besford, Q. A.*<sup>1</sup>, *König, T. A. F.*<sup>1</sup>, *Popp, J.*<sup>2</sup>, *Cialla-May, D.*<sup>2</sup>, and *Rossner, C.*<sup>1</sup>

<sup>1</sup>*Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, D-01069 Dresden, Germany*

<sup>2</sup>*Leibniz-Institute of Photonic Technology, Albert-Einstein-Str. 9, 07745, Jena, Germany*

In clusters of plasmonic nanoparticles, coupled localized surface plasmon resonance (LSPR) modes give electromagnetic hotspots with drastic field enhancement that can be used for surface-enhanced Raman spectroscopy (SERS). [2] Planet-satellite-type clusters show well-defined inter-particle separation [3] with high density of such hotspots [4] in narrow inter-particle gaps. However, concomitantly arises the challenge of hotspot accessibility. Previous works [5,6] used dense spacers that either acted as analyte themselves or required implementation of the analyte during assembly, which impedes in-situ analyte detection. Macromolecular spacers [7] on the other hand lead to non-dense layers and thereby facilitate analyte access [8] but associated increased inter-particle distances result in only moderate SERS enhancement. The current challenge therefore is to provide small inter-particle gaps and at the same time sufficient accessibility for the analyte. To address these seemingly irreconcilable demands, we introduced stimuli-responsive macromolecular linkers [7] to enable external activation: In swollen, dilute state, analyte uptake is facilitated while a critical phase transition can be triggered on-demand to give small inter-particle distances and high field-enhancement in the hotspots. We used Reversible Addition-Fragmentation chain Transfer (RAFT) [8] polymerization to obtain thermoresponsive poly-N-isopropylacrylamide (PNIPAM) with 4-arm star-topology [3] as responsive macromolecular spacer. Cluster assembly was optimized, and the role of surface charges explored based on DLVO theory. The cluster switching behaviour was demonstrated using UV-vis extinction spectroscopy and dynamic light scattering (DLS). SERS measurements correlated with FDTD optical simulations show on-demand hotspot activation. [1,9]



**Figure 1.** Left: SERS signal of 4-MBN at 25°C and 40°C, demonstrating a drastic increase in signal intensity by hotspot activation through conformational change of the polymer spacer. Right: TEM images of the planet-satellite clusters. [1]

[1] S. Jancke, *et al.*, *Nanoscale* **2023**, *15*, 18687.

[2] C. Rossner, T. A. F. König, A. Fery, *Adv. Optical Mater.* **2021**, *9*, 2001869.

[3] C. Rossner, Q. Tang, O. Glatter, M. Müller, P. Vana, *Langmuir* **2017**, *33*, 2017.

[4] P. Dey, *et al.*, *Journal of Materials Chemistry B* **2014**, *2*, 2827.

[5] M. Gellner, *et al.*, *Small* **2011**, *7*, 3445.

[6] N. Gandra, A. Abbas, L. Tian, S. Singamaneni, *Nano Lett.* **2012**, *12*, 2645.

[7] C. Rossner, A. Fery, *MRS Communications* **2020**, *10*, 112.

[8] J. Chiefari, *et al.*, *Macromolecules* **1998**, *31*, 5559.

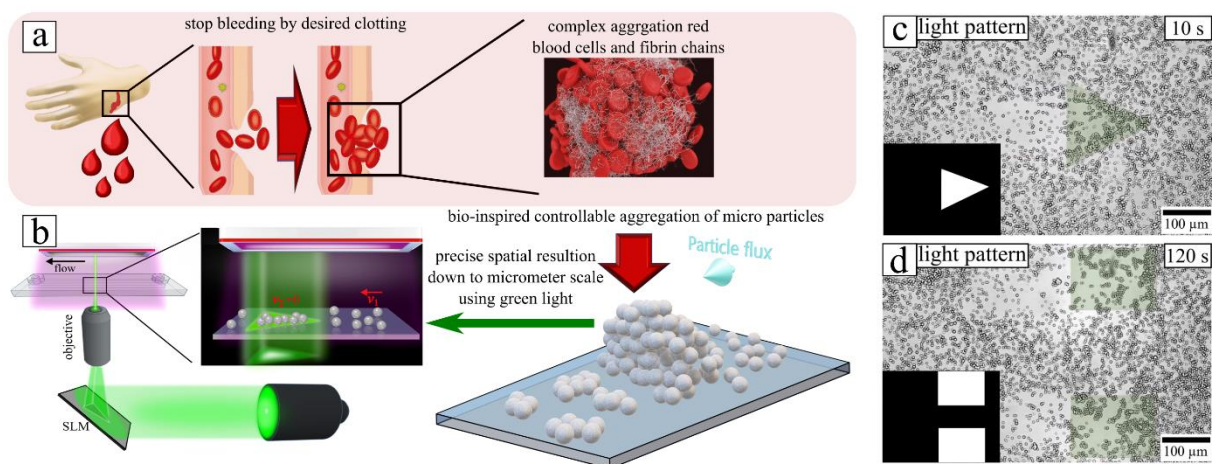
[9] The authors thank DFG for funding (466182523).

## T61: Versatile and Remotely Controllable Light-Induced Coagulation of Particles Under Flow in a 2D Channel

*Marek Bekir*

*Institut für Physik und Astronomie, Karl-Liebknecht-Str.24-25, 14476 Potsdam-Golm*

On-demand switch on/off blood clotting is of paramount importance for the survival of mammals, for example as a quick response to seal damage wounds via gelation of red blood cells. This complex process initiated from red blood cell aggregation/clogging at the target location (open wound) yields quick sealing of the damaged flash. Inspired by nature we developed an on-demand switchable particle clogging mechanism for inorganic microparticles with high spatial resolution down to micrometer size using light as an external non-invasive stimulation. The state and strength of particle clogging can be precisely controlled, where aggregated microparticle can even withstand pressure-driven fluid flow. Further we demonstrate light induced wall formation of aggregated particles able to stop the momentum of big particles under shear, too. The principle relies on a photosensitive surfactant, which induces under light illumination a long-ranged lateral attractive phoretic-osmotic activity of silica microparticles forcing them to aggregate. The strength of aggregation and therefore motion reduction or even stop of the particles against the fluid flow depends on the ratio between the aggregation strength and the velocity of the particles. The aggregation strength can be precisely controlled by the applied light intensity and adjusted particle concentration. Increasing both parameters results into strong gelation of the particles at illuminated area.[1]



**Figure 1.** (a) Cartoon of bio-inspired aggregation of blood cells, (b) where porous silica microparticles ( $D = 3 \mu\text{m}$ ) with light induced “attractive phoretic activity” aggregate at the illumination spot and stop their motion along a flow. (c,d) Snapshots of porous microparticles following a flow (left to right), where local illumination (c) with triangle or (d) double rectangular illumination leads to local stopping of the particle. Green area illustrates the illumination spot from applied light pattern controlled over a spatial light modulator (SLM).

[1] D. Vasquez-Muñoz, F. Rohne, A. Sharma, N. Lomadze, S. Santer, M. Bekir *Small* **2024**, 2401144.

[2] The author M.B. acknowledges financial support from the German Research Foundation (DFG) through the grant number 469240574.



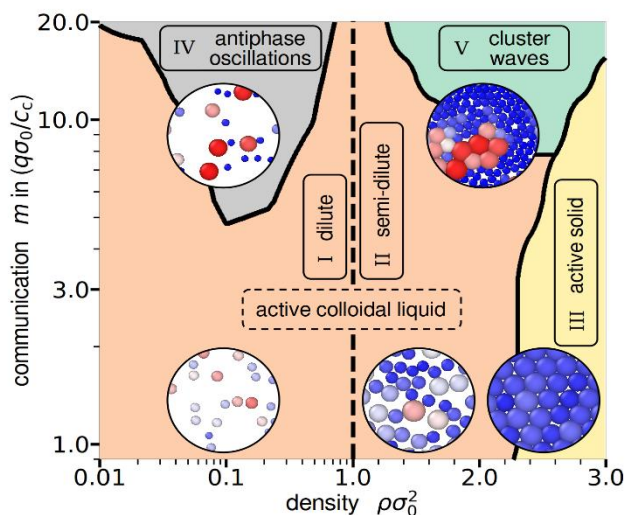
## T62: Collective oscillations and elasto-chemical cluster waves in communicating colloids

*Nils Göth*<sup>1</sup> and *Joachim Dzubiella*<sup>1,2</sup>

<sup>1</sup> Applied Theoretical Physics – Computational Physics, Physikalisches Institut, Albert-Ludwigs-Universität Freiburg, Freiburg, Germany

<sup>2</sup> Cluster of Excellence livMatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies, Albert-Ludwigs-Universität Freiburg, Freiburg, Germany

Chemical communication, response, and feedback are key requirements for the function of adaptive materials with life-like properties. However, how communication on the single cell-level impacts the collective structural, dynamical and mechanical behavior of active soft matter is not well understood. Here, we extend an existing model of responsive colloids [1] by including chemical communication between the colloids. We report how communication controls the spatiotemporal structure and phase behavior of hydrogel-based colloidal liquids using simulations with explicit resolution of the chemical signaling waves as well as the elastic response to communication and crowding. We find a rich topology of nonequilibrium active phases in dependence of density and signaling magnitude, in particular, synchronization transitions from uncorrelated non-oscillatory liquids to antiphase oscillatory states, or to in-phase oscillations with accompanying elasto-chemical cluster waves (see Fig. 1). Our work employs minimal physical principles required for communication-mediated dynamics, thus uncovering universal aspects in signaling soft systems [2,3].



**Figure 1.** Dynamical state diagram in the communication-density space. The collective dynamic behavior is governed by the (chemical) communication strength  $m$ , and by the mechanical/elastic interactions which are tuned by the (number) density  $\rho$ .

[1] Upayan Baul, Joachim Dzubiella, *J. Phys.: Condens. Matter* **2021**, 33 (17), 174002.

[2] Nils Göth, Joachim Dzubiella, *submitted* **2024**.

[3] The authors acknowledge the support by the state of Baden-Württemberg through bwHPC and the DFG through Grant No. INST 39/963-1 FUGG (bwForCluster NEMO) under Germany's Excellence Strategy-EXC-2193/1-390951807 ("LivMatS").

## T63: Impact of Microgel Softness on Cellular Uptake: Insights from AFM Measurements

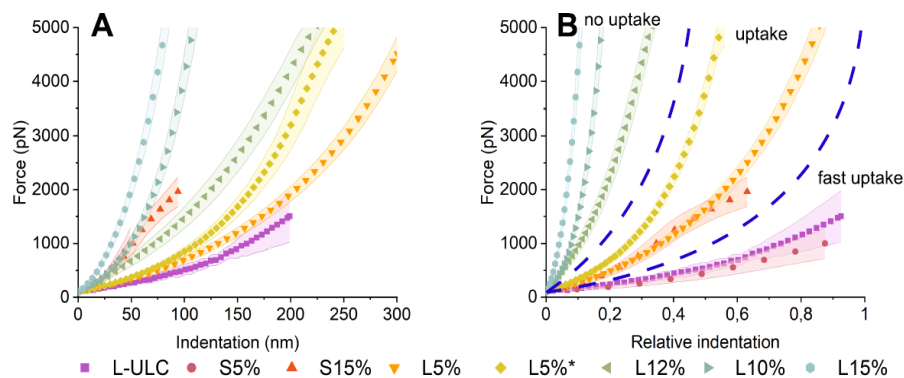
Andrey Babenyshev<sup>1</sup>, Victoria Switacz<sup>2</sup>, Marc Spehr<sup>2</sup> and Walter Richtering<sup>1</sup>

<sup>1</sup> Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany

<sup>2</sup> Institute for Biology II, RWTH Aachen University, Aachen, Germany

PNIPAM microgels hold great promise for a wide range of biomedical applications. Recent works showed that the concentration of cross-linker content and the size of the microgels significantly affect their cellular uptake[1]. In this study, we investigated how the mechanical properties of microgels influence the cellular uptake mechanism using atomic force microscopy (AFM) and confocal fluorescence microscopy.

AFM is an effective technique for the examination of mechanical properties associated with the internal structure of microgels[2]. We measured microgels adsorbed at the glass-liquid interface. The structure of the microgels determines their adsorption behaviour. The difference between force-distance curves of the central parts of the microgels allow distinguishing between microgels with a low and a high amount of cross-linker (Fig. 1A). At the same time, the simultaneous consideration of the force-distance curves with the deformation of the microgels at the interface allows us to divide the microgels into three groups (Fig. 1B). For example, small microgels with 5% cross-linker content and extremely soft large ULC microgels correspond to the softest group, which we have named 'fast uptake', as these microgels also exhibit the fastest cellular uptake rates.



**Figure 1.** Averaged force-distance curves corrected by the contact-point for the vertical approach of an AFM tip towards microgel's center. As X-axis were used indentation that describes how deep inside microgels sharp tip immersed (A) and relative indentation that is ratio of indentation to the height of the adsorbed

microgel (B). L-ULC is large ultra-low cross-linked microgels, S means small, L – large and percentage shows the cross-linker content.

Our results show that AFM-defined softness could predict the possibility of cellular uptake. In the case of particularly soft polymer networks, size ceases to play a fundamental role, allowing the uptake of both small and large microgels. As the stiffness increases, the combination of size and softness begins to play a role. In future studies, this knowledge will allow the specific design of microgels for various biomedical applications[3].

[1] V. Switacz et. al., *Biomacromolecules*, 21 11 (2020), p. 4532-4544.

[2] F. Schulte, et al., *Chemical Society Reviews* 51.8 (2022), p. 2939-2956.

[3] The authors acknowledge funding from the German Research Foundation Deutsche Forschungsgemeinschaft (DFG) for funding of the collaborative research centre SFB 985.

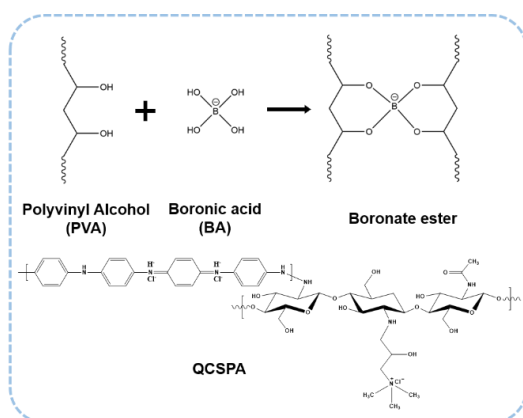
## T64: Characterization of electronically controlled drug release hydrogels for diabetes treatment

*Yining Sun<sup>1</sup>, Clement Blanchet<sup>2</sup> and Michael Gradzielski<sup>1</sup>*

<sup>1</sup> *Stranski-Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 124, D-10623 Berlin, Germany*

<sup>2</sup> *European Molecular Biology Laboratory, Hamburg Outstation, Notkestrasse 85, 22603 Hamburg, Germany*

Real-time monitoring and precise control of drug release are crucial in diabetes treatment to prevent underdosing or overdosing. Recent research has increasingly concentrated on the development of conductive drug release hydrogels. These hydrogels uniquely merge superior electrical conductivity with biocompatibility, enabling the modulation of drug release in response to the physiological state of the human body to allow real-time adjustments in drug delivery. [1] Herein, we present the fabrication of a conductive hydrogel prepared by mixing quaternized chitosan grafted with polyaniline (QCSPA), polyvinyl alcohol (PVA), and boronic acid (BA) shown in Figure 1. This hydrogel was dynamically crosslinked by i) boronate ester between PVA and BA, ii) ionic interaction within QCSPA and BA. The modified polymer QCSPA endows the good conductivity to the QCSPA/PVA/BA hydrogel. We studied the crosslinking properties of this hydrogel by rheology, with using the Springpot model to capture the power-law behavior and get viscoelastic information. The small angle scattering (SAXS and SANS) is also used to analyze the network structure as a function of composition. We found that the addition of QCSPA enhances the hydrogel rigidity but also introduces systematic inhomogeneities inside of the network. Furthermore, we explored the free diffusion and electro-triggered insulin release behavior through SAXS analysis, elucidating the relationship between hydrogel structure and insulin release kinetics. The obtained results underline the importance of the mesh size in the release procedure, which can be tailored by varying the different hydrogel components. The resultant hydrogel exhibits electronic responsivity, facilitating triggered insulin release, thereby getting closer to the ultimate goal of localized and on-demand therapeutic delivery.



**Figure 1.** Molecular Structures of the QCSPA/PVA/BA hydrogel.

[1] T. Zhu, Y. Ni, G. M. Biesold, Y. Cheng, M. Ge, H. Li, J. Huang, Z. Lin, Y. Lai, *Chem. Soc. Rev.* **2023** 52, 473-509.

[2] The authors acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)-SFB 1449, China Scholarship Council (CSC). We gratefully acknowledge the European Molecular Biology Laboratory (EMBL Hamburg) for providing beam time.

**Theory, Modelling and Simulation  
of Colloids & Interfaces,  
Predictive Modelling & Artificial Intelligence,  
Deep Learning Approaches**

## T65: Interaction of ultra-soft microgels at the interface under shear

Jose Ruiz-Franco, Tom Höfken<sup>2</sup>, Andrea Scotti<sup>3</sup>, and Emanuela Zaccarelli<sup>4</sup>

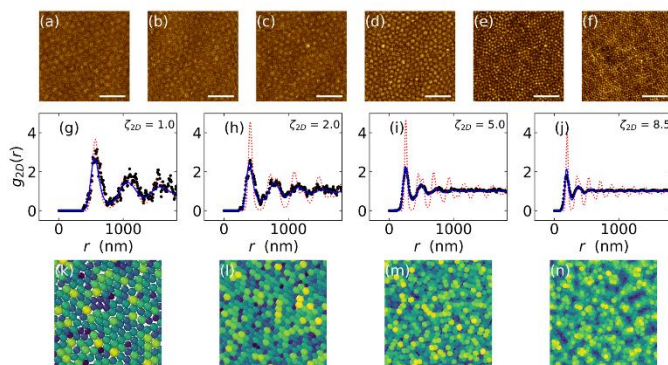
<sup>1</sup> Department of Condensed Matter Physics, University of Barcelona, 08028 Barcelona

<sup>2</sup> Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, 52074 Aachen, Germany

<sup>3</sup> Department of Biomedical Science, Faculty of Health and Society, Malmö University, SE-205 06, Malmö, Sweden

<sup>4</sup> Department of Physics, Sapienza University of Rome, Piazzale Aldo Moro 2, 00185 Rome, Italy

For colloidal particles, softness can be an important degree of freedom that governs both static properties like phase behavior and dynamic properties, such as the behavior under flow. Here, we studied soft ultra-low crosslinked (ULC) microgels at the interface, whose deformability greatly influences their behavior, especially at higher concentrations. ULC microgels exhibit a strong colloid-polymer duality, which is further enhanced by their adsorption to an interface [1]. We combine the experimental techniques AFM and interfacial rheology, with molecular dynamics simulations to comprehend their pair interaction in 2D. Employing a modified Hertzian pair potential enables us to successfully describe both static properties, represented by the radial distribution function, and their behavior under shear. Interestingly, with increasing area fraction, the storage modulus,  $G'$ , of the system does not steadily increase, but instead undergoes multiple increases and decreases. This observation is consistent in the experiment and simulation and has also been previously noted for microgels with 5% crosslinking [2]. The decreasing value of  $G'$  is interpreted as the work required to compress the individual microgels [3].



**Figure 1:** AFM Images of ULC microgels at the interface with increasing area fraction from (a) to (f); radial distribution function for experiment and simulation (g) to (j) and corresponding simulation snapshots (k) to (n).

[1] Scotti, Andrea, et al. "Exploring the colloid-to-polymer transition for ultra-low crosslinked microgels from three to two dimensions." *Nature communications* 10.1 (2019): 1418.

[2] Schmidt, Maximilian M., et al. "Interfacial fluid rheology of soft particles." *Physical Review Letters* 131.25 (2023): 258202.

[3] We acknowledge financial support from the Deutsche Forschungsgesellschaft (DFG) within the SFB 985 "Functional microgels and microgel systems".

## T66: Using a pre-trained AI model to break new ground in colloidal particle analysis

Gabriel A. A. Monteiro<sup>1</sup>, Bruno A. A. Monteiro<sup>2</sup>, Jefersson A. dos Santos<sup>2,3</sup> and Alexander Wittemann<sup>1</sup>

<sup>1</sup>Colloid Chemistry, Department of Chemistry, University of Konstanz, Konstanz, D-78457, Germany

<sup>2</sup>Pattern Recognition and Earth Observation Laboratory, Department of Computer Science, Federal University of Minas Gerais, Belo Horizonte, 31270-901, Brazil

<sup>3</sup>Department of Computer Science, University of Sheffield, S1 4DP, Sheffield, United Kingdom

Complex structures are made up of smaller, more basic elements. To understand them, we need to look at their parts and how they are arranged. In colloidal science, complex colloidal particles and supracolloidal assemblies are important. Micrograph analysis is useful for these systems. However, its potential is often not used in its entirety. This paper presents an automated route to the analysis of complex colloidal particles from micrographs. This is demonstrated using 'colloidal molecules', which are structured into individual segments [1, 2]. The approach identifies the subdivisions within the particles, thus eliminating the need for training dedicated artificial intelligence (AI) models. This is achieved through semantic segmentation of particle subdivisions using the pre-trained neural network Segment Anything Model [3]. The subdivisions found within the image are then sorted and organized into sets representing the individual particles. This novel technique in the field allows for the morphological characterization of not only the subdivisions within a particle, but also of their global morphology. The approach of combining different datasets enhances the insights obtained from microscopic images of complex nanoparticles. Comparisons with previously published results using model colloids validate the efficacy of this novel method [4]. This demonstrates the SAM's ability to circumvent systemic errors and human biases (Fig. 1) when characterizing complex colloidal structures [5].



**Figure 1.** Scanning electron micrograph of colloidal trimers (A). Two image segmentation processes are performed: (B) identification of the trimers as a whole (B), and then their segments (C). The two datasets can be combined through mathematical processing, thereby providing additional information. The scale bars are 250 nm.

[1] R. Stuckert, C. S. Plüsch, A. Wittemann, *Langmuir* **2018**, 34, 13339.

[2] R. Stuckert, A. Lüders, A. Wittemann, P. Nielaba, *Soft Matter* **2021**, 17, 6499.

[3] G. A. A. Monteiro, B. A. A. Monteiro, J. A. dos Santos, A. Wittemann, submitted.

[4] G. A. A. Monteiro, A. Wittemann, *Colloid Polym. Sci.* **2023**, 301, 801.

[5] This research was co-funded by the DFG, CAPES, CNPq (312102/2017-8, 424700/2018-2, and 311395/2018-0), FAPEMIG, and Serrapilheira Institute (grant #R-2011-37776). Technical support from the Nanostructure Laboratory (nano.lab) and the Particle Analysis Centre (PAC) at the University of Konstanz is gratefully acknowledged.

## T67: Predicting Temperature-Dependent CMCs of Single Surfactants with Graph Machine Learning

*Christoforos Brozos<sup>1,2</sup>, Jan G. Rittig<sup>2</sup>, Sandip Bhattacharya<sup>1</sup>, Elie Akanny<sup>1</sup>, Christina Kohlmann<sup>1</sup>, and Alexander Mitsos<sup>2,3,4</sup>*

<sup>1</sup> BASF Personal Care and Nutrition GmbH, Henkelstrasse 67, 40589 Duesseldorf, Germany

<sup>2</sup> RWTH Aachen University, Process Systems Engineering (AVT.SVT), Aachen 52074, Germany

<sup>3</sup> Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research IEK-10 -- Energy Systems Engineering, Jülich, Germany

<sup>4</sup> JARA Center for Simulation and Data Science (CSD), Aachen, Germany,

The critical micelle concentration (CMC) constitutes a vital property for many surfactant applications [1,2]. Hence, accurately predicting the CMC with computer-aided methods can reduce experimental efforts and enhance product development in a sustainable way. Numerous quantitative structure-property relationship (QSPR) and graph neural network (GNN) models have been successfully developed to predict the CMC of single surfactant molecules [3,4,5,6]. However, all previous models are applied to CMC values measured only at a constant temperature. As the temperature strongly impacts the CMC in a nonlinear, complex way, which varies from surfactant class to surfactant class, it is a great interest to accurately predict the CMC of single component surfactants at various temperatures [7]. Although empirical equations to model the temperature dependency of the CMC have been derived in the past [8], they are only applicable to a limited amount of surfactant systems.

We present a GNN model for the prediction of temperature-dependent CMCs of surfactants of all surfactant classes [9]. To train the GNN, we assembled a data set containing CMC measurements from public literature sources. The GNN model developed here builds on our previous work where GNNs were used to predict the CMC at a constant temperature for a wide spectrum of surfactants [6]. To assess the predictive performance, we evaluate the model for predicting the temperature-dependent CMC of surfactant in two cases: (i) when CMC data for the same surfactant at different temperatures was present during training, (ii) when no CMC data for the same surfactant was used in training, i.e., generalizing to previously unseen surfactant at various temperatures. We find that the GNN model can predict the CMC of surfactants with high accuracy in both test scenarios, e.g.,  $R^2 \geq 0.95$ . We find scenario (ii), e.g., generalizing on new surfactant structures, to be more challenging for the model and hence slightly higher errors are observed. However, the model exhibits high temperature sensitivity and successfully captures the temperature dependency of CMC for previously unseen surfactants. Therefore, the GNN model can enhance research speed by fast and accurate initial screening of potential candidates in future work.

[1] T. Majeed et al., Foamstability: The interplay between salt-, surfactant- and critical micelle concentration, *Journal of Petroleum Science and Engineering* 187 (2020) 106871.

[2] D. R. Perinelli et al., Correlation among chemical structure, surface properties and cytotoxicity of n-acyl alanine and serine surfactants, *European Journal of Pharmaceutics and Biopharmaceutics* 109 (2016) 93–102.

[3] A. R. Katritzky et al., Qspr study of critical micelle concentrations of nonionic surfactants, *Ind. Eng. Chem. Res.* 47 (23) (2008) 9687–9695.

- [4] D. Seddon et al., Machine learning hybrid approach for the prediction of surface tension profiles of hydrocarbon surfactants in aqueous solution, *Journal of Colloid and Interface Science* 625 (2022) 328–339.
- [5] S. Qin et al., Predicting critical micelle concentrations for surfactants using graph convolutional neural networks., *The Journal of Physical Chemistry. B* 125 (2021) 10610–10620.
- [6] C. Brozos et al., Graph neural networks for surfactant multi-property prediction, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* (2024) 134133.
- [7] M. Rosen, J. Kunjappu, *Surfactants and Interfacial Phenomena: Rosen/Surfactants 4E*, John Wiley & Sons, Ltd, 2012.
- [8] H.-U. Kim et al., A model on the temperature dependence of critical micelle concentration, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 235 (1) (2004) 121–128.
- [9] C. Brozos et al., Predicting the temperature dependence of surfactant cmcs using graph neural networks, preprint arXiv (2024).



## T68: Predictive Design in Color: Optimizing the Absorber Position in Colloidal Photonic Crystals and more

*Guidrun Bleyer<sup>1</sup>, Nico Nees<sup>2</sup>, Andrian Uihlein<sup>2</sup>, Satoshi Watanabe<sup>3</sup>, Lukas Pflug<sup>2</sup>, Michael Stingl<sup>2</sup>, and Nicolas Vogel<sup>1</sup>*

<sup>1</sup>*Institute of Particle Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany*

<sup>2</sup>*Department of Mathematics and Center for Scientific Computing, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany*

<sup>3</sup>*Department of Chemical Engineering, Kyoto University, Kyoto 615-8510, Japan*

Structural colour in nature can be seen in countless animals and plants, resulting in remarkable optical effects. While natural structures display irregularities and defects, their visual appearance often outperforms more regular, man-made products. One important way they mitigate the influence of defects is the use of melanin pigments as broadband absorbers, suppressing incoherent scattering and thus increasing color saturation. Typically, this absorber is either employed as a building block of the structure or layered below.

Consequentially, there have been many investigations for the inclusion of various absorber types and amounts for bright and saturated synthetic structural color. However, there have been less efforts on the quantification and comparison between the different arrangements.

Here, we use colloidal crystals as a model system to systematically investigate the influence of the amount and position of the absorber within the material. For this purpose, we synthesise monodisperse polystyrene colloidal particles and modify their absorbing properties by adding a shell of controlled thickness of polydopamine, a synthetic melanin.

To provide control over the absorber position within the formed colloidal crystal, we resort to an interface-mediated approach allowing us to assemble hexagonally packed 2D crystals with controlled absorber content. Using a Layer-by-Layer method, we subsequently stack individual monolayers of particles with adjustable absorber contents.

Accessing this wide design space, we can optimize our desired colour properties: chroma and lightness. Using a combination of bioinspired and property-guided, predictive design from mathematical optimization, we explore possible absorber arrangement designs.

The resulting structure “blueprints” are then produced experimentally, characterized micro- and macroscopically to correlate structural and optical properties. With this, we can not only quantify the effect of absorber content, but also compare different placements of the absorber, from a theoretical and a practical point of view.

Finally, we show how the very same predictive design strategy can be transferred to plasmonic color design.

[1] Bittner et al., *Adv. Mat. Int.* **2024**, 11 (12), 1-13.

## T69: Geometric Frustration Directs the Self-Assembly of Nanoparticles with Crystallized Ligand Bundles

Federico Tomazic<sup>1</sup>, Aswathy Muttathukattil<sup>1</sup>, Afshin Nabiyan<sup>2,3,4</sup>, Felix Schacher<sup>2,3,4</sup>, and Michael Engel<sup>1</sup>

<sup>1</sup> Institute for Multiscale Simulation, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany

<sup>2</sup> Jena Center for Soft Matter, <sup>3</sup> Institute of Organic Chemistry and Macromolecular Chemistry,

<sup>4</sup> Center for Energy and Environmental Chemistry, Friedrich Schiller University Jena, 07734 Jena, Germany

Polymer-grafted nanoparticles are versatile building blocks capable of self-assembling into diverse mesostructures, with applications in electronic and optical materials, medicine, and biological imaging. Traditional coarse-grained molecular simulations have modeled these nanoparticles as spheres with flexible polymer ligands uniformly distributed on their surfaces, predicting structures such as fibers, platelets, and three-dimensional agglomerates [1]. However, this approach does not capture the behavior of systems where ligands crystallize and form rigid bundles. An example is poly(2-isopropyl-2-oxazoline) (PiPrOx) ligands, which crystallize directionally and, when grafted onto SiO<sub>2</sub> nanoparticles, can create intricate hybrid nanostructures [2].

We propose an alternative coarse-grained model: the silica nanoparticle is represented as a sphere and the stretched crystalline polymer bundle as a rigid rod. This rod-sphere model represents not only nanoparticles with crystallized ligands but also other complex building blocks like rigid surfactants, block-copolymers with lyophobic segments, and end-tethered nanorods. By varying the ratio of sphere size to rod radius, the model stabilizes self-limited clusters and other mesostructures of reduced dimensionality due to geometric frustration. To classify these structures, we introduce new dimensionality and order parameters that provide a robust framework for identifying the resulting clusters. Surfactant self-assembly into various micelle shapes can be explained by the aspect ratio between the hydrophilic head and the hydrophobic tail. Similarly, the geometric hindrance caused by the sphere head in our model leads to self-limiting assembly into finite mesostructures, driven by geometric frustration [3].

[1] P. Akcora et al., *Nature Materials* **2009**, 8, 354.

[2] A. Nabiyan, A. Muttathukattil, F. Tomazic, D. Pretzel, U.S. Schubert, M. Engel, F.H. Schacher, *ACS Nano* **2023**, 17, 21216.

[3] M. Lenz, T.A. Witten, *Nature Physics* **2017**, 13, 1100.

## T70: Quasi-two-dimensional Dispersions with Competing Interactions

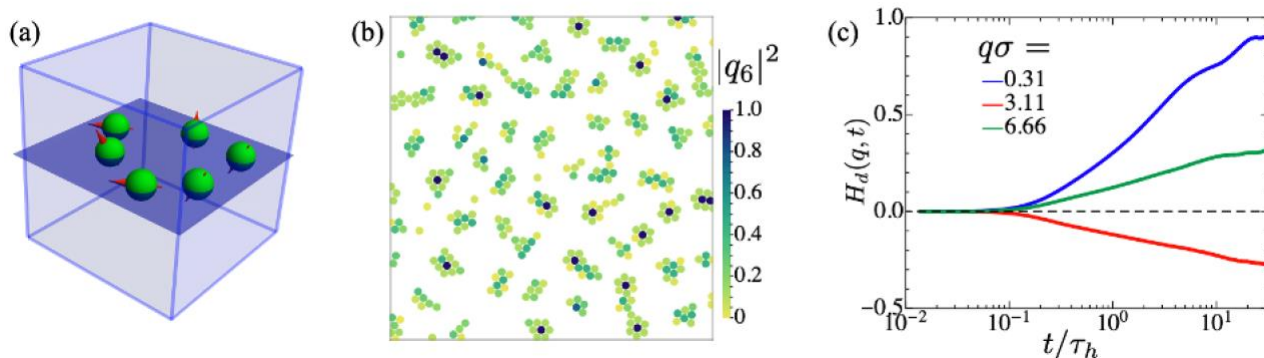
*Gerhard Nägele*

*Forschungszentrum Jülich, Institute of Biological Information Processing (IBI-4), Jülich, Germany*

Dispersions of globular proteins or colloids with competing short-range attractive (SA) and long-range repulsive (LR) interactions show a rich phase behavior with various cluster phases. While three-dimensional SALR dispersions have been intensely studied also regarding their cluster dynamics [1], little is known about quasi-two-dimensional (Q2D) dispersions. The particles in a Q2D dispersion form essentially a planar monolayer inside the bulk fluid.

Using mesoscale simulations, we determine the phase diagram, and the cluster shape and size distributions of a generic Q2D model dispersion of SALR particles [2]. The particles are described as Brownian spheres interacting by short-range generalized Lennard-Jones and long-range repulsive screened Coulomb forces. The Q2D phases resemble those in three dimensions but are different in their microstructure invoking different levels of hexagonal ordering. With decreasing temperature, the cluster morphology crosses over from disk-like shapes in the equilibrium cluster phase to double-stranded anisotropic hexagonal cluster segments in a cluster-percolated gel phase. We have identified indicators for the transition from the high-temperature dispersed fluid phase to the lower-temperature equilibrium cluster phase. Akin to three-dimensional SALR systems, this transition is signaled by a low-wavenumber peak of the static structure factor, with an associated thermal correlation length of about twice the particle diameter. The transition peak height and mean coordination number, however, are distinctly smaller than in three dimensions.

Furthermore, we have uncovered the dynamics of Q2D - SALR systems including self-diffusion with its non-Gaussian statistics [2]. The interplay of Q2D motion and hydrodynamic interaction gives rise to anomalously enhanced collective diffusion related to out-of-plane fluid backflow. This enhancement masks a low - wavenumber peak in the hydrodynamic function visible in three dimensions. The buildup of hydrodynamic interaction by vorticity diffusion and sound is revealed from the time-resolved hydrodynamic function.



**Figure 1.** (a) Q2D layer of particles. (b) Simulation snapshot of cluster-fluid phase with degree of hexagonal ordering. (c) Time-resolved hydrodynamic function,  $H_d(q,t)$ , at different wavenumbers  $q$  as indicated.

[1] S. Das, J. Riest, R. Winkler, G. Gompper, J.K.G. Dhont, G. Nägele, *Soft Matter*, **2018**, 14, 92.

[2] Z. Tan, V. Calandrini, J.K.G. Dhont, G. Nägele, *submitted*, **2024**.

## **T71: The Potential of Chemometrics for Predictive Modeling in Colloid and Interface Science**

*Rafael Teixeira Freire, Ivan Garcia Romero, Christiane Nagel, Frank Runge, and Grit Baier*

*BASF SE, Carl-Bosch-Strasse 38, 67056 Ludwigshafen am Rhein, Germany*

Chemometrics and artificial intelligence (AI) models have become increasingly popular in predictive modeling, offering new possibilities for understanding and adapting the behavior of materials in colloid and interface science. Here, we present the potential of chemometrics and AI models for predicting polymer solubility which is a crucial property in various fields of colloid and interface science.

We will provide an example of the application of chemometrics to predict solubility based on infrared (IR) data. By exploiting the vast amounts of experimental data generated, these models are trained to recognize patterns and correlations between physicochemical properties and application performances, enabling accurate predictions for a range of materials systems such as defoamers, dispersing agents, natural materials, polymers in aqueous applications etc. We will show that chemometrics can predict solubility with high accuracy for many solvents tested. This approach not only offers the possibility of replacing time-consuming solubility tests with AI models but also provides a means to compare laboratory results with AI predictions for possible human error identification. Furthermore, the integration of multiple data sources in the future, such as NMR and full IR spectra, can enhance the accuracy of predictions by fusing orthogonal information from these techniques. The application of chemometrics and AI models in predictive modeling presents a promising approach for efficient material profiling in colloid and interface science. By providing insights into the behavior of materials, these models facilitate the rational design of formulations, optimization of processes, and the creation of sustainable colloidal systems with very high physicochemical stability. Moreover, the incorporation of chemometrics and AI approaches further enhances the predictive capabilities, enabling the exploration of previously unexplored areas and the discovery of novel materials with tailored properties.

In summary, our work enables predictive modeling in colloid and interface science, emphasizing its relevance and its focus on particle-based functional materials and predictive modeling. The presentation will give insights in methodology, showcase successful case studies, and discuss the implications for the development of advanced colloidal systems and sustainable formulations.

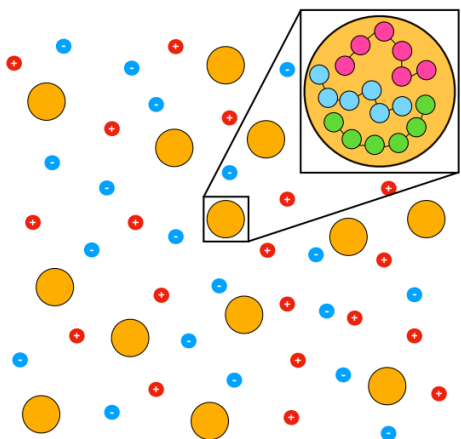
## T72: Does the intraparticle glass transition temperature control the colloidal stability? A theoretical study

Carmine Anzivino<sup>1</sup> and Alessio Zaccone<sup>1,2</sup>

<sup>1</sup> Department of Physics, University of Milan, Milano, Italy

<sup>2</sup> Institute for Theoretical Physics, Georg-August Universität Göttingen, Göttingen, Germany

In many colloidal suspensions, the dispersed colloidal particles are amorphous solids resulting from vitrification. Understanding how the latter process, i.e. the intra-particle glass transition, affects the stability of a colloidal suspension is a crucial open problem. By means of a molecular-level approach based on the glass transition theory of Ref. [1], we established a proportionality relation between the intra-particle glass transition temperature,  $T_g$ , and the Hamaker constant,  $A_H$  [2]. The latter quantifies the strength of the van der Waals attraction among the colloids dispersed in a hosting solvent, and hence is a key parameter to control the stability of colloidal systems. Within DLVO theory, we show that the novel relationship, connecting  $T_g$  to  $A_H$ , implies the critical coagulation ionic strength (CCIS) to be a monotonically decreasing function of  $T_g$ . We connect our predictions to recent experimental findings [3].



**Figure 1.** Sketch of the colloidal suspension considered. Dispersed colloids (depicted in yellow) have a spherical shape and, as showed in the zoom, consist of many tightly packed molecules or e.g. polymer chains (each chain is depicted with a different colour in the sketch) having the same length and chemical structure. All colloids are amorphous solids resulting from a glass transition, with the glass transition temperature  $T_g$  being a material property. Small red and blue particles indicate positive and negative electrolytes, respectively, eventually present in the solution.

[1] Alessio Zaccone and Eugene M. Terentjev, *Physical Review Letters* **2013**, 110 (17), 178002.

[2] Carmine Anzivino and Alessio Zaccone, *The Journal of Physical Chemistry Letters* **2024**, 14 (39), 8846-8852.

[3] The authors acknowledge funding from the US Army Research Office, Grant Number W911NF-22-2-0256 and from the EU through Horizon Europe ERC Grant number: 101043968 "Multimech".

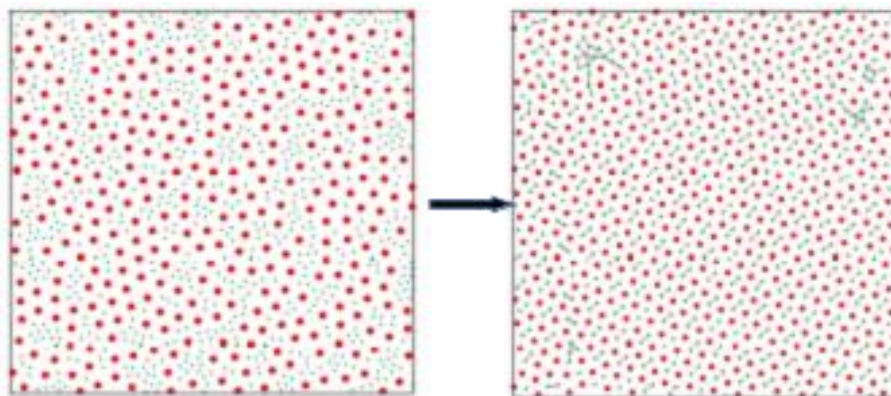
## T73: Binary crystals formation from molecular simulations of hard disc fluid mixtures

*Praveen Kumar Bommineni*<sup>1,2</sup> and *Michael Engel*<sup>2</sup>

<sup>1</sup> *Department of Chemical Engineering, National Institute of Technology Warangal, India*

<sup>2</sup> *Institute for Multiscale Simulations, Friedrich Alexander University Erlangen, Germany*

In this contribution, we present ordered structures formation in 2D from binary fluid mixtures. For this purpose, the interaction between particles is modeled as hard particle interactions. Hard particle interactions are one of the simplest interactions that are used to understand phase behavior, nucleation, crystallization and self-assembly of colloidal particles [1,2]. Hard discs (hard spheres in 3D) packing has been studied for many years now. However, binary hard disc packing arrangements are not realized from simulations except for only one binary structure [2]. Formation of binary structures sensitively depends on packing fraction, size ratio of two different size discs and composition. Depending on the combination of these parameters, a variety of crystals with square, hexagonal, tetragonal symmetries forms. Our simulations show that in some cases adding more small particles to make the system off-stoichiometric compositions helps crystallization of a variety of crystals. We present detailed state diagrams showing the condition at which these binary structures forms directly from fluid.



**Figure 1.** Ordering of binary fluid mixture (left) into ordered structure(right). Small and large particles are represents by green and red colors.

[1] Praveen K Bommineni, Marco Klement, Michael Engel, *Phys. Rev. Lett.* **2020**, 124 (21), 218003.

[2] M Isobe , *Molecular Simulation* **2016**, 42(16), 1316-1329.

## T74: Inside Nature portfolio: editorial process and innovations

Christian Kuttner

*Nature Communications, Nature Portfolio, Springer Nature, Heidelberger Platz 3, 14197 Berlin, Germany.*

Publishing your research in an esteemed journal in the Nature portfolio (Nature, Nature Materials, Nature Communications, etc.) involves more than just solid research. My talk aims to demystify the editorial journey within Nature-branded journals, revealing the hidden steps that a submitted manuscript goes through on the way to becoming an accepted article.

I will explain the criteria our experienced in-house editors use to evaluate submissions and the process by which we shortlist which manuscripts will be sent into peer review. We will discuss how to effectively convey your research to both editors and reviewers, ensuring your message is clear and impactful. I will then guide you through the entire peer-review process, shedding light on the rigorous selection of referees by our editors and the decision-making process based on the reviewers' feedback. We will also discuss new developments towards a more transparent peer-review, including the integration of early career researchers in peer reviewing, handling of multi-disciplinary research, and open data. Along the way I will tell anecdotes from the life of an editor and, if time permits, some best practices that will help you to craft compelling cover letters, persuasive response letters, and successful appeals - empowering you to enhance your chances of publication success in Nature-branded journals.

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Dr. Kuttner is a Senior Editor at Nature Communications [1] and since 2021 responsible for the physical chemistry content with a focus on nanomaterials. [2] Before becoming a full-time editor, he conducted research as a Marie Skłodowska-Curie fellow at the CIC biomaGUNE in Donostia-San Sebastian, Spain, and as a postdoctoral researcher at the Leibniz Institute of Polymer Research (IPF) in Dresden, Germany. [3]

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[1] [nature.com/ncomms](https://nature.com/ncomms)

[2] [christiankuttner.de/edited](https://christiankuttner.de/edited)

[3] [christiankuttner.de/cv](https://christiankuttner.de/cv)

## Wetting Phenomena



## T75: From Supraparticles to Liquid Marbles

*Umair Sultan<sup>1</sup>, Syuji Fujii<sup>2</sup> and Nicolas Vogel<sup>1</sup>*

<sup>1</sup> *Institute of Particle Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany*

<sup>2</sup> *Department of Applied Chemistry, Osaka Institute of Technology, Osaka, Japan*

Liquid marbles are liquid droplets encased by solid non-wetting particles. They exhibit powder-like attributes and thus enable different applications, such as sensors, pressure-sensitive adhesives, miniature reactors, and material carriers. The ability to form liquid marbles, and the resulting stability and properties are directly influenced by the physico-chemical characteristics of the solid particles.

Here, we systematically explore how particle surface roughness impacts the formation and stability of liquid marbles, employing well-defined supraparticles as a model system with a high level of control. Supraparticles are spherical aggregates comprised of uniform colloidal primary particles. By changing the size of the silica primary particles within the range of 240 nm to 970 nm, we adjust the characteristic dimensions of the surface topography of these supraparticles. Additionally, exploiting the segregation phenomena inherent in supraparticles formed by binary particles with varying size ratios, we fabricate polystyrene core and silica shell supraparticles to further adjust the spacing between primary particles forming the surface topography. To render the supraparticles hydrophobic, vital for the formation of liquid marbles, we chemically modify their silica surface using perfluoro-octyl silane.

Through the direct visualization of the water/air interface of the liquid marble by interface freezing, we probe the influence of surface roughness on the adsorption and the resultant contact angle of supraparticles adsorbed to the liquid marble surface. We then investigate how the roughness and the associated contact angle affects the mechanical stability of such liquid marbles. Finally, we show that such supraparticles allow stabilization of liquid marbles from low surface tension organic liquids and, establish a direct relation between their roughness and the surface tension of the stabilized liquid. Our systematic study provides detailed structure-property relations, connecting surface properties of particles with the ability to prepare stable liquid marbles.

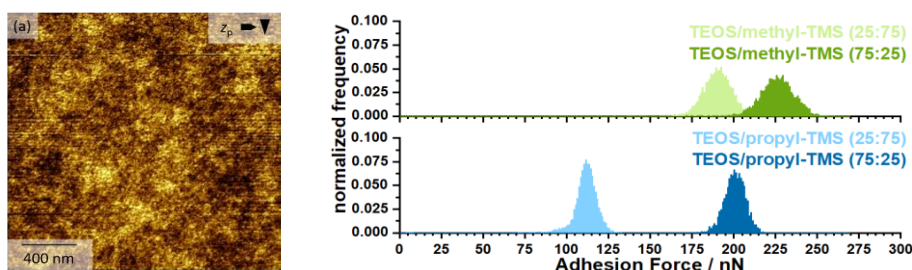
## T76: Surface and wetting properties of TEOS/alkyl-TMS coatings for application on solar panels

*Franziska Sabath, Tarik Karakaya, Sa'id Albarqawi, Azadeh Sharifi-Aghili, Hans-Jürgen Butt, Emre Yavuz, and Doris Vollmer*

*Department of Physics at Interfaces, Max Planck Institute for Polymer Research, 55128 Mainz, Germany*

The number of solar panels has risen sharply in recent years, as they are an efficient and cost-effective way of generating renewable energy. However, the efficiency of solar panels is significantly reduced by the deposition of dirt particles, i.e., dust or pollen. It is therefore essential to clean the solar panels in order to maintain their efficiency. A wide range of cleaning methods are known in the literature, e.g. manual cleaning or robotic cleaning, but they are time-consuming or resource-intensive, expensive or complicated to install. One possibility to improve the cleaning of solar cells is to coat them. However, this involves a number of requirements for the coating: Transparency, light resistance, mechanical stability and water repellency. Furthermore, the coating should not contain any perfluorinated or polyfluorinated substances for health and environmental reasons.

To reduce soiling of solar panels, we fabricated coatings showing low drop friction force and particle adhesion force [1]. Therefore, we have prepared acid-catalyzed coatings from mixtures of tetraethyl orthosilicate (TEOS) and various alkyl trimethoxysilanes (alkyl-TMS). Here we investigate the effects of the alkyl-TMS chain length and the ratio between TEOS and alkyl-TMS on the wetting and surface properties. As demonstrated by atomic force microscopy (AFM), the roughness of all investigated coatings remained in the range of several angstroms, Fig. 1a. This result is supported by the measurement of friction forces using scanning droplet friction force microscopy (sDoFFI). The coatings hardly suffer from pronounced pinning points. In contrast, the alkyl-TMS chain length and the TEOS/alkyl-TMS ratio impact the adhesion force measured with colloidal probe AFM. Thereby, higher amounts of TEOS show in general lower adhesion forces compared to samples with the same alkyl-TMS and lower amounts of TEOS Fig. 1b. Additional contact angle measurements show that both the alkyl-TMS chain length and the TEOS/alkyl-TMS ratio effects the advancing and receding contact angles. Notably, all of our coatings have advancing contact angles between 80 and 110°, which is, among other things, a result of the low surface roughness and the increased hydrophobicity by incorporating alky-groups. In summary, we have shown that a low TEOS concentration reduces drop friction, while a high TEOS concentration reduces particle adhesion.



**Figure 1:** (a) AFM height image of a TEOS/methyl-TMS (25:75) coating. The scan directions are indicated by the arrows in the upper left corner. (b) Normalized frequency distribution of the adhesion

force measured with colloidal probe AFM on four different TEOS/alkyl-TMS coatings.

[1] F. Geyer et al., *Sci. Adv.* **2020**, 6(3).

## T77: Non-Wettable Ultra-Slippery Aerophilic Surfaces

*Alexander B. Tesler,<sup>1</sup> Stefan Kolle,<sup>2,3</sup> Lucia H. Prado,<sup>4</sup> Ingo Thievessen,<sup>1</sup> David Böhringer,<sup>1</sup> Shane Stafslie,<sup>5</sup> Matilda Backholm,<sup>6</sup> Bhuvaneshwari Karunakaran,<sup>6</sup> Heikki A. Nurmi,<sup>6</sup> Mika Latikka,<sup>6</sup> Anca Mazare,<sup>4</sup> Ulrich Lohbauer,<sup>7</sup> Sannakaisa Virtanen,<sup>4</sup> Ben Fabry,<sup>1</sup> Robin H.A. Ras,<sup>6,8</sup> Joanna Aizenberg,<sup>2,3</sup> Wolfgang H. Goldmann<sup>1</sup>*

<sup>1</sup> *Biophysics Institute, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91052 Erlangen, Germany.*

<sup>2</sup> *Wyss Institute for Biologically Inspired Engineering, Harvard University, Cambridge, MA 02138, USA.*

<sup>3</sup> *John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA.*

<sup>4</sup> *Institute for Surface Science and Corrosion, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany.*

<sup>5</sup> *Department of Coatings and Polymeric Materials, North Dakota State University, Fargo, ND 58102, USA.*

<sup>6</sup> *Department of Applied Physics, School of Science, Aalto University, P.O. Box 15100, Espoo FI-02150, Finland.*

<sup>7</sup> *Department of Operative Dentistry and Periodontology, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91054 Erlangen, Germany.*

<sup>8</sup> *Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Espoo FI-02150, Finland.*

Wetting describes the ability of liquids to maintain contact with a solid surface, a phenomenon that is ubiquitous in nature. However, in engineering and medical applications, contact of solid surfaces with aqueous media leads to undesirable phenomena such as corrosion, chemo- and biofouling, which have extremely negative economic, health, and environmental impacts. Therefore, control of wetting on solid surfaces is key to mitigating its detrimental effects. The latter can be achieved by minimizing the contact of the solid substrate with aqueous media, so-called superhydrophobic surfaces (SHS).[1] Although SHS have been studied for decades to overcome wetting challenges, they are still rarely used in engineering applications. When immersed underwater, a special type of SHS can trap air on its surface, a so-called plastron, also known as aerophilic surfaces.[2] To date, plastrons have been reported to be impractical for underwater engineering applications due to their short lifetime. Here, I will describe aerophilic surfaces with an extended lifetime of plastron conserved for months underwater. The extended methodology was developed to unambiguously describe the wetting regime on such aerophilic surfaces since conventional goniometric measurements are simply impractical. Our aerophilic surfaces drastically decay corrosion, reduce the adhesion of blood, and when immersed in aqueous media, prevent the adhesion of bacteria, and marine organisms such as barnacles, and mussels. Applying thermodynamic stability theories, I describe a generic strategy to achieve the long-term stability of plastrons on aerophilic surfaces for demanding and hitherto unattainable applications.[3]

[1] A. Lafuma, D. Quéré, *Nat. Mater.* **2003**, 2, 457.

[2] A. B. Tesler, S. Kolle, L. H. Prado, I. Thievessen, D. Böhringer, M. Backholm, B. Karunakaran, H. A. Nurmi, M. Latikka, L. Fischer, S. Stafslie, Z. M. Cenev, J. V. I. Timonen, M. Bruns, A. Mazare, U. Lohbauer, S. Virtanen, B. Fabry, P. Schmuki, R. H. A. Ras, J. Aizenberg, W. H. Goldmann, *Nat. Mater.* **2023**.

[3] The authors acknowledge funding from the German Research Foundation (DFG), Grant Numbers: 540989797 and 442826449.

## T78: Sliding water drops: Influence of spontaneous charging on the deposition of dissolved molecules

Xiaoteng Zhou,<sup>1</sup> Yuwen Ji,<sup>1</sup> Zhongyuan Ni,<sup>1</sup> Kalina Peneva,<sup>2</sup> Pravash Bista,<sup>1</sup> Shan Jiang,<sup>3</sup> Kaloian Koynov,<sup>1</sup>  
Hans-Jürgen Butt<sup>1</sup>

<sup>1</sup>Max Planck Institute for Polymer Research, Ackermannweg 10, 55128, Mainz, Germany

<sup>2</sup>Friedrich Schiller University, Jena, Germany

<sup>3</sup>Department of Materials Science and Engineering, Iowa State University, IA 50011, Ames, USA

In the last decade, it has been realized that when water drops slide on hydrophobic surfaces, they spontaneously leave negative charges on the drop path. The drops get positively charged with potentials up to kV. This process, called slide electrification, influences drop motion. Here, we demonstrate a second effect of slide electrification: the preferential deposition of dissolved molecules with a positive charge as compared to negatively charged ones.

Using composite confocal microscopy, we visualize the track of water drops with dissolved charged fluorophores. As fluorophores we applied two perylene derivatives, one with a positive, PDI<sup>+</sup>, one with a negative charge, PDI<sup>-</sup>, at neutral pH. Even at a concentration of 0.5  $\mu\text{M}$ , PDI<sup>+</sup> was deposited during the short contact time of  $\approx 20$  ms, whereas PDI<sup>-</sup> only deposited at 10  $\mu\text{M}$ .

Experiments with grounded drops or thin polystyrene films on conducting substrates indicate that the electric field emanating from the negative surface charges behind the drop causes the preferential co-deposition of the dissolved cationic molecules.

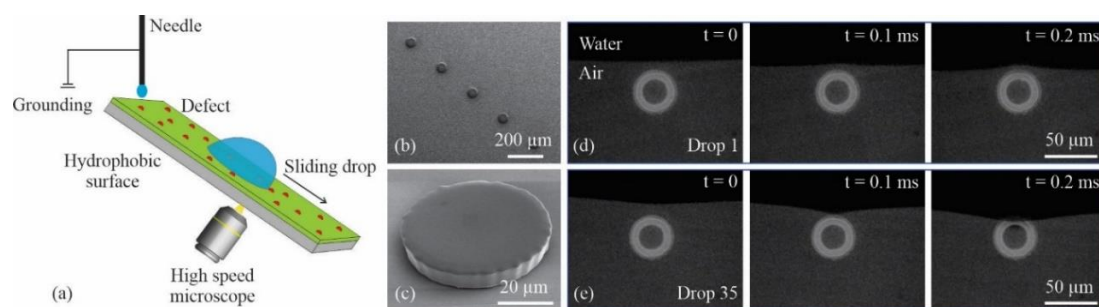
## T79: Spontaneous charging affects the dynamics of contact line moving over defect

Yaolei Xiang<sup>1</sup>, Diego Cortes<sup>1</sup>, Hans-Jürgen Butt<sup>1</sup>, and Kaloian Koynov<sup>1</sup>

<sup>1</sup> Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany.

The dynamics of three-phase contact lines are crucial in various natural phenomena and numerous industrial applications, including painting, coating, and lubricating [1]. The behavior of contact lines is significantly influenced by surface defects. These defects can be topographical structures, such as protrusions or holes, or they can be regions with different surface chemistry. The influence of defects on contact line dynamics is pervasive, as defects ranging from the nanometer to the millimeter scale could cause dynamic changes in the contact line. The common understanding is that the impact of topographical heterogeneities on contact line dynamics is constant, which means that every time the contact line approaches and traverses a defect, its deformation should be the same.

In this contribution, by using ultra-fast high-resolution reflection microscopy (Fig. 1a), we show that the impact of topological defects (Figs. 1b, 1c) on the contact line is not constant, but related to the history of fluid motion on the surface. As water drops slide over a hydrophobic surface with protrusions, an attraction between these topological defects and the contact line appears and intensifies with the drop number (Figs. 1d, 1e). The behavior is evident in two ways: first, the range of attraction between the contact line and the defect increases; second, the maximum resistance of the defect to the contact line changes, with the resistance on the advancing contact line decreasing and that on the receding contact line increasing. The observed interaction between defects and the contact line is proved to be related to the spontaneous electrification of the drop on the surface. Drops and the surface spontaneously acquire opposite charges as the drops slide over the surface. The attraction between charges on the drops and the topological defects is the reason for the change in contact line dynamics. This study may contribute to a better understanding of contact line dynamics and the development of applications related to droplet manipulation, microfluidic chips, and frictional nanogenerators [2].



**Figure 1.** (a) Experimental setup. (b), (c) SEM images of the sample – PFOTS coated glass slide with SU8 pillars. (d), (e) Advance contact line dynamics as the drop approaches a defect. In drop 35, the contact line is attracted to the defect. However, in drop 1, the contact line does not display this attraction.

[1] H-J Butt, et al., *Current Opinion in Colloid & Interface Science* **2022**, 59, 101574.

[2] The authors acknowledge funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grant agreement 883631) (F.D., D.D., H.-J.B.).

## T80: Sliding electrification and surface potential of hydrophobic surfaces

*Mariana D. Sosa, Benjamin Leibauer and Hans-Jürgen Butt*

*Department of Physics at Interfaces. Max Planck Institute for Polymer Research. Ackermannweg 10, Mainz, 55128 Germany.*

When droplets slide on hydrophobic surfaces, charges deposit behind the drop through a process known as sliding electrification. If a water drop and a hydrophobic surface get into contact, an electrical double layer (EDL) forms. When the droplet starts to slide, charges are left behind the receding contact line of the drop. Consequently, both the liquid and the surface acquire charge. The charge in the droplet depends on pH and ionic strength. *Bista et al.* present a model, which describes the relationship between surface potential and the charge measured in the sliding drop [1]. In this work, this model was put on the test at different pH conditions by comparing the model-predicted surface potential with the experimental zeta potential obtained by streaming potential measurements. Results show that the model predicts a surface potential in the order of the experimental zeta potential for low pH, while a discrepancy appears as pH increases. Several factors, which may explain this observation, will be discussed. Therefore, the aim of this work is to discuss the possibility of using sliding electrification phenomenon as a technical tool for measuring surface potential.

[1] Bista et al., *J. Phys. Chem. Lett.* **2023**, 14 (49), 11110.

## T81: Dynamic wetting of concentrated granular suspensions

*Reza Azizmalayeri<sup>1</sup>, Peyman Rostami<sup>1</sup>, Thomas Witzmann<sup>1</sup>, Christopher O. Klein<sup>2</sup>, and Günter K. Auernhammer<sup>1</sup>*

<sup>1</sup> *Leibniz Institute of Polymer Research Dresden (IPF), Institute of Physical Chemistry and Polymer Physics, 01069 Dresden, Germany*

<sup>2</sup> *Karlsruhe Institute of Technology, Institute of Chemical Technology and Polymer Chemistry (ITCP), 76131 Karlsruhe, Germany*

Concentrated granular suspensions are employed in a variety of applications including 3D printing, painting, etc., where the contact line dynamics and the internal structure of the suspension interact. Shear rate increases sharply towards moving contact lines. This localized shear rate profoundly affects suspension non-Newtonian rheological behaviour. Frictional contacts gain more prominence in dense suspensions as force-carrying particles approach each other. When particle concentrations are not too high, recent publications affirm the applicability of hydrodynamic solutions to granular suspensions. At higher particle concentrations, the impact of particles on the overall flow field and the microstructure of the densely packed granular suspension close to the contact line remains unexplored. In this study, suspensions of silica particles in two distinct dispersion media, each having a refractive-index match to the particles are used. Index-matching is based on a complex alcohol solution or a salt solution. We observe a significant variation in the rheological response of the suspension, including shear thinning, shear thickening, and a yield stress behaviour. A configuration consisting of a pinned droplet on a moving substrate is utilized. Using astigmatism particle tracking velocimetry (APT<sub>V</sub>), we precisely track the 3D motion of tracer particles within the suspension. Near the advancing contact line, we observe distinct behaviours based on interparticle interactions and the resulting suspension rheology. A concentrated suspension of weakly interacting particles violates hydrodynamic solution assumptions, especially when particle friction becomes a significant factor. The shape of the droplet close to the receding contact line exhibits a dynamic surface curvature that undergoes a transient phase before reaching a stationary state.

## T82: Rationalizing the Berg limit of 65° in surface phenomena

Matej Kanduč<sup>1</sup>, Emanuel Schneck,<sup>2</sup> and Roland R. Netz<sup>3</sup>

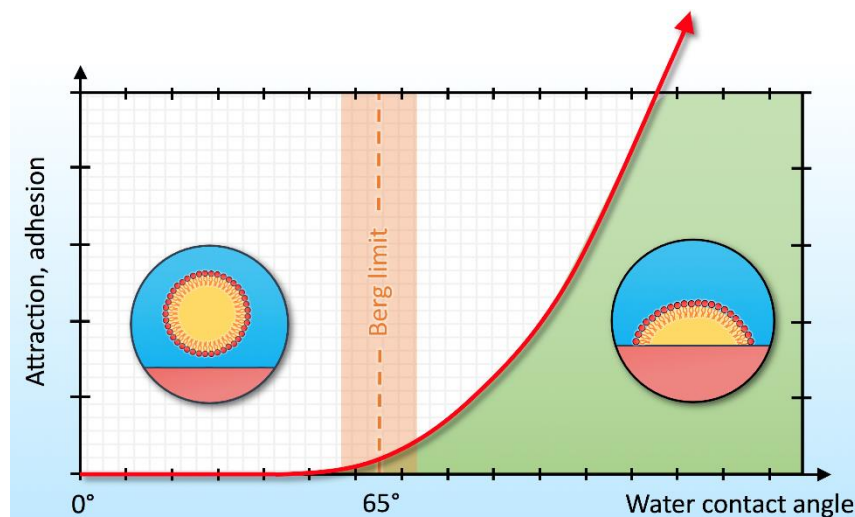
<sup>1</sup> Department of Theoretical Physics, Jožef Stefan Institute, Ljubljana 1000, Slovenia

<sup>2</sup> Department of Physics, Technische Universität Darmstadt, Darmstadt 64289, Germany

<sup>3</sup> Fachbereich Physik, Freie Universität Berlin, Berlin 14195, Germany

I will discuss the intriguing universality of the fundamental water contact angle of 65°, known as the "Berg limit" [1], which represents the threshold for phenomena such as long-range hydrophobic attraction, macromolecular and colloidal adhesion, and biofouling in aqueous environments (see Fig. 1). By conceptualizing these interactions as three-phase problems, involving a surface, water, and a representative oil-like material indicative of nonpolar entities, we have recently offered a new understanding of this threshold [2,3]. Our analysis, supported by molecular simulations [3], indicates that attraction and adhesion are associated with surfaces displaying underwater oleophilic properties, a condition termed "under-oil hydrophobicity." This condition typically arises when the contact angle exceeds 65°.

The insights gained from this approach not only clarify the mechanistic underpinnings of the Berg limit across various scenarios but also suggest broader implications for technological applications and material design. I will also discuss the complexities introduced by real-world variations such as surface roughness, heteroatoms in the hydrophobic components, and the electrostatic properties of surfaces, which contribute to the observed range of behaviors and the practical applicability of the Berg limit in diverse colloidal and biological contexts.



**Figure 1.** Adhesion, adsorption, attraction, and biofouling significantly increase once the contact angle of the surface surpasses the threshold of around 65°, known as the Berg limit.

[1] E. Vogler, *Adv. Colloid Interface Sci.* **(1998)** 74, 69

[2] M. Kanduč, E. Schneck, R.R. Netz, *Phys. Chem. Chem. Phys.* **(2024)** 26, 713

[3] M. Šako, F. Staniscia, E. Schneck, R.R. Netz, M. Kanduč, *PNAS Nexus* **(2023)** pgad190

[4] Financial support from the Slovenian Research and Innovation Agency ARIS (contracts P1-0055 and J1-4382) is acknowledged.



## T83: Stood-up drops as a novel, easiest and fastest way to measure receding contact angles

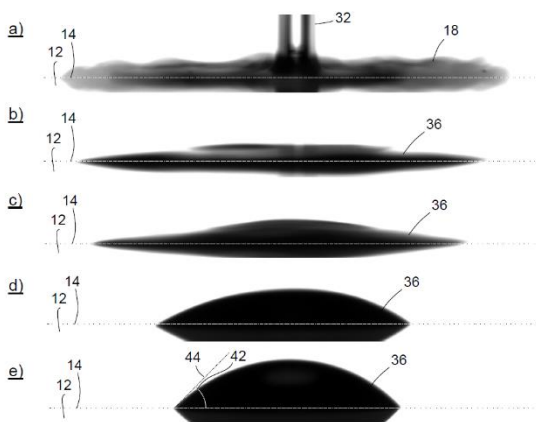
*Thomas Willers<sup>1</sup>, Katrin Oetjen<sup>1</sup>, Diego Ignacio Diaz Diaz<sup>2</sup>, Doris Vollmer<sup>2</sup>, Hans-Jürgen Butt<sup>2</sup>*

<sup>1</sup> KRÜSS GmbH, Borsteler Chaussee 85, 22453 Hamburg

<sup>2</sup> Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz

It is well-established that the receding contact angle (CA) plays a vital role in various applications where repelling liquids, preventing fouling, promoting self-cleaning, and drop friction are essential requirements and that it can also provide very relevant information for coating and bonding processes. However, measurements of the receding CA are typically time-consuming, challenging, and necessitate extensive protocols [1]. In this study, we introduce a novel drop deposition method that enables the rapid measurement of the recently receded CA within a few seconds and is entirely user-independent.

The method builds upon the existing "liquid-needle method" used to measure advancing CAs [2,3], wherein a thin liquid jet is meticulously controlled to deposit a droplet on the surface without imparting excess kinetic energy from the dosing process. In contrast to the liquid-needle method for advancing CA, our novel method for receding CA involves the liquid first spreading radially during dosing, forming a pancake-shaped film, and subsequently retracting to form a spherical cap-droplet shape, as illustrated in Figure 1. Consequently, we refer to such droplets as "stood-up drops" (SUD) [4].



**Figure 1.** Temporal evolutions (from top to bottom) of "Stood-up drop" drop deposition process.

We elucidate the crucial dosing parameters necessary to ensure that the contact angle of SUD accurately represents the recently receded contact angle and compares favorably to classically determined dynamic receding contact angles. Furthermore, we provide several real industrial application examples wherein this straightforward method of receding CA measurement could address production problems hitherto unresolvable with classical (advancing) contact angle measurements.

[1] Huhtamäki et al., Nat Protoc 13, 1521–1538 (2018)

[2] Ming Jin et al., Colloid and Polymer Science 294(4), 657-665, (2016).

[3] A. Ahmed et al., J. of Coll. and Interf. Sci., Volume 608, Part 1, 2022, Pages 1086-1093 (2021)

[4] T. Willers, K. Oetjen; European Patent, EP4109072

**Particle Based Functional Materials:**  
**Towards Device Integration**

## T84: More than just color: Inverse opals as sensors

*Giulia Magnabosco,<sup>1</sup> Annette Andrieu Brunsen,<sup>2</sup> Nicolas Vogel<sup>1</sup>*

<sup>1</sup>*Institute of Particle Technology, Friedrich-Alexander-University Erlangen-Nürnberg, Cauerstraße 4, 91058 Erlangen*

<sup>2</sup>*Ernst-Berl Institut für Technische und Makromolekulare Chemie, Technische Universität Darmstadt, Alarich-Weiss-Str. 8, 64287 Darmstadt*

Nanostructured materials are widespread in nature and are an invaluable source of inspiration for scientists. Among them, periodic porous materials are often responsible for structural coloration, as observed in butterfly wings and beetle shells. An approach to mimic such structures is to exploit colloidal templating to generate ordered, interconnected porous materials, named inverse opals (IOs). Here, we demonstrate that IO have applications much beyond pigments and can be used to create simplistic sensing devices that exploit both coloration and the interconnected periodicity.

IOs display structural color due to the periodic variation of refractive index (RI) resulting from the porous structure. The coloration can be selectively suppressed by infiltrating the pores with a liquid with a RI close to the one of the matrix, and this principle can be used to fabricate sensors. So far, mostly sensors based on surface functionalization sensible to changes in the physical properties of the infiltrating liquid were developed. In contrast, we developed sensors exploiting selective surface functionalization, which are able to change the wettability of the surface itself upon the adsorption of an analyte, e.g. volatile organic compounds or water pollutants [1].

IOs are also ideal to improve the performance of established electrochemical sensors thanks to their high surface area. However, overcoming the insulating nature of typical IO matrix materials is a key challenge for their application as electrode materials. I will show how we combine colloidal assembly, atomic layer deposition and surface functionalization to design conductive IOs as glucose sensing platforms. An insulating IO scaffold is coated with uniform layers of conducting aluminium zinc oxide and platinum, and subsequently functionalized with glucose oxidase embedded in a polypyrrole layer. The final device can sense glucose down to 1 nM and is not affected by the presence of common interferents, providing a promising platform for miniaturized sensors [2, 3].

[1] Magnabosco et al., *submitted*

[2] Papiano et al., *Materials Horizons*, **2023**, 10, 4380–4388

[3] The authors acknowledge funding from DFG grant number AN 1301/5-2, VO1824-5/2, 431791331 – SFB 1452, and from the “Bavarian Equal Opportunities Sponsorship – Realisierung von Frauen in Forschung und Lehre (FFL) – Promotion Equal Opportunities for Women in Research and Teaching.”.

## T85: Macro- and Mesoscopic Gradients in Self-Assembled Colloidal Systems

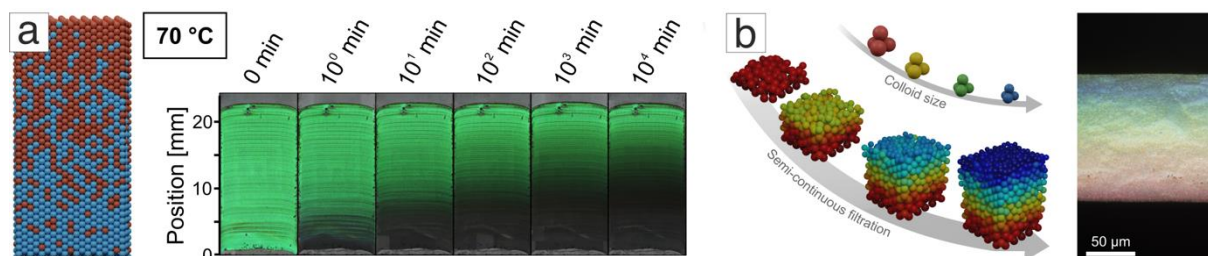
Markus Retsch

*Physical Chemistry I, University of Bayreuth, Bayreuth, Germany*

Structures prepared via self-assembly of monodisperse, spherical colloids have been of great interest in a multitude of research areas for a long time. [1] An emerging new aspect in this field is the fabrication of colloidal assemblies with a gradient of a specific physical property along one axis. We focus on the fabrication of two classes of gradients comprising densely packed colloids via novel synthesis and assembly methods.

In the first example (Figure 1a), we use an infusion-withdrawal coating to prepare binary colloidal crystals with a composition gradient along the coating axis. [2] The gradual transition from primarily high to low thermal stability allowed us to showcase this material as a temperature sensor with an extremely simple readout. Using machine learning, we extended the capabilities of such film-forming sensors to achieve a higher accuracy for the measurement of time and temperature.[3] Furthermore, the gradual composition variation in such a gradient can be combined with microspectroscopy opening the possibility for data-driven materials analysis.

In the second example (Figure 1b), we will outline a general approach to fabricating mesoscopic gradient structures along the z-axis of a colloidal film. Accessing such structures requires a novel concept for the synthesis of colloidal dispersions that we will elaborate on. The resulting gradient mesostructures exhibit unique scattering properties, which highlight the relevance of this materials class for future functional devices.[4]



**Figure 1.** a) Infusion-withdrawal coating is used to fabricate lateral colloidal crystal gradients.[2] b) Using a novel emulsion polymerization technique, continuous gradients of size-varying colloidal glasses can be fabricated along the z-axis. [4]

[1] N. Vogel, et al., *Chemical Reviews*, **2015**, 115, 6265-6311

[2] M. Schöttle, et al., *Advanced Materials*, **2021**, 33, 2101948

[3] M. Schöttle, et al., *Advanced Science* **2023**, 10, 2205512.

[4] M. Schöttle, et al., *Advanced Materials* **2022**, 35, e2208745.

## T86: Advancing Nanophotonic Devices with Particle-Based Colloidal Metasurfaces

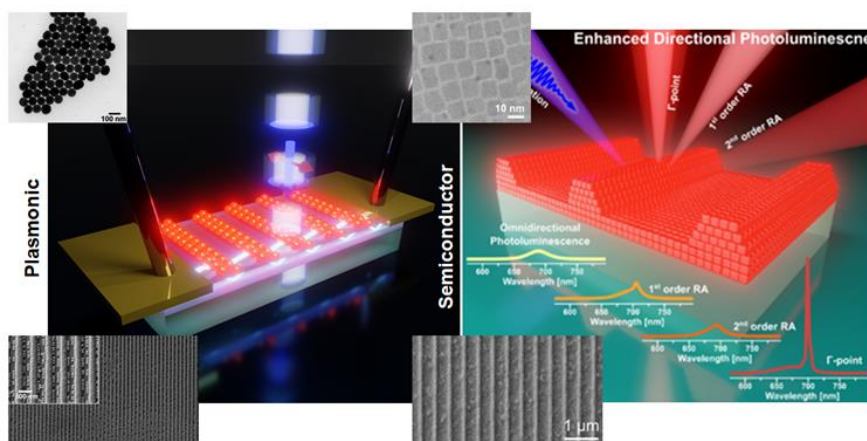
*Swagato Sarkar*<sup>1</sup>, *Tobias A. F. König*<sup>1,2,3</sup>

<sup>1</sup> *Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany*

<sup>2</sup> *Center for Advancing Electronics Dresden (cfaed), Technische Universität Dresden, Helmholtzstraße 18, 01069 Dresden, Germany*

<sup>3</sup> *Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, Bergstraße 66, 01069 Dresden, Germany*

Colloidal metasurfaces, utilizing finely tuned particle-based systems, significantly advance nanophotonic device integration by facilitating precise optical manipulation at the nanoscale. This approach dramatically enhances the functional capacities of devices in energy harvesting, sensing, and signal processing through the strategic use of ultra-thin films and carefully engineered lattice structures. By employing a diverse array of plasmonic and semiconductor colloidal nanoparticles and implementing template-assisted self-assembly combined with electromagnetic simulations, we achieve a highly efficient fabrication route for realizing these metasurfaces. The structured arrangement of plasmonic nanoparticles/semiconductor quantum dots offers substantial improvements in quality factors and transforms these structures into highly functional integrated forms through hybridization, often exceeding those of their individual components by several orders of magnitude. Our research demonstrates the adaptability of colloidal metasurfaces, showcasing their potential in generating hybrid plasmon-photon coupled modes for enhanced photodetection [1], efficient photocatalysis [2], and Fano-coupled fluorescence emission that enables directional amplification [3]. Thus, our methodology opens new pathways for developing nanophotonic devices with tailored optical properties while pushing the boundaries of possibilities within the realm of particle-based functional colloidal metasurfaces.



**Figure 1.** Plasmonic and semiconductor metasurfaces for nanophotonic applications

[1] S. Sarkar, V. Gupta, T. Tsuda, J. Gour, A. Singh, O. Aftenieva, A. M. Steiner, M. Hoffmann, S. Kumar, A. Fery, J. Joseph, and T. A. F. König, *Adv. Funct. Mater.*, **2021**, 31, 2011099.

[2] V. Gupta, S. Sarkar, O. Aftenieva, T. Tsuda, L. Kumar, D. Schultz, J. Schultz, A. Kiriy, A. Fery, N. Vogel, and T. A. F. König, *Adv. Funct. Mater.*, **2021**, 31, 2105054.

[3] O. Aftenieva, J. Brunner, M. Adnan, S. Sarkar, A. Fery, Y. Vaynzof, and T. A. F. König, *ACS Nano* **2023**, 17, 2399– 2410.

## T87: Molecularly Cross-Linked Metal Nanoparticle Assemblies for Monitoring Physiological Signals and Selective Detection of Volatile Organic Compounds

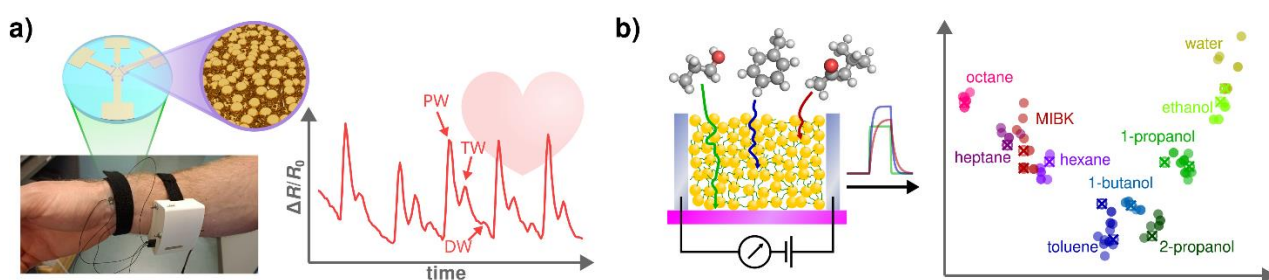
Hendrik Schlicke

Leibniz Institute of Polymer Research Dresden, Hohe Straße 6, 01069 Dresden, Germany.

Hybrid composites from molecularly stabilized or cross-linked nanoparticles represent a new class of highly configurable and functional materials. Their unique electronic, optical, (electro)mechanical and chemical properties, as well as facile ink-based deposition options offer a strong application potential for future generations of sensors and flexible electronics. This drives significant research efforts targeting new device architectures and device integration schemes.

Here we report the investigation of the anisotropic strain sensitivity observed for the tunneling-based charge transport in dithiol cross-linked gold nanoparticle (GNP) composites and demonstrate the integration of these materials into wearable sensors, capable of resolving pulse waves and gestures (Figure 1a).[1] Further, we demonstrate that the high strain sensitivity and elasticity[2] of GNP composites can be exploited for the fabrication of pressure sensors with record sensitivities, when being integrated as freestanding membranes.[3]

Aside from being sensitive to strain, metal nanoparticle composites respond with strong resistance changes to sorption of volatile organic compounds (VOCs).[4] We report current research activities aiming at investigating the dynamics of nanocomposites' molecular uptake, and at making use of them by fabricating sensors using transient sensing signals for identification of analytes and analyte mixtures (Figure 1b).[5] Our research in this field targets the fabrication of inexpensive and portable sensors, suitable for medical diagnosis via breath analysis, detection of VOCs emitted by food for quality control, and environmental sensing.



**Figure 1.** a) Pulse wave recorded by a gold nanoparticle composite based wearable sensor.[1] b) Schematic showing dynamic responses of a nanoparticle composite based VOC sensor and their use for machine-learning based analyte recognition.[5]

[1] B. Ketelsen, H. Schlicke, V. R. Schulze, S. C. Bittinger, S. Wu, S. Hsu, T. Vossmeier, *Adv. Funct. Mater.* **2023**, *33*, 2210065.

[2] H. Schlicke, S. Kunze, M. Finsel, E. W. Leib, C. J. Schröter, M. Blankenburg, H. Noei, T. Vossmeier, *J. Phys. Chem. C* **2019**, *123*, 19165.

[3] H. Schlicke, S. Kunze, M. Rebber, N. Schulz, S. Riekeberg, H. K. Trieu, T. Vossmeier, *Adv. Funct. Mater.* **2020**, *30*, 2003381.

[4] H. Schlicke, S. C. Bittinger, T. Vossmeier, *ACS Appl. Electron. Mater.* **2020**, *2*, 3741.

[5] H. Schlicke, S. C. Bittinger, H. Noei, T. Vossmeier, *ACS Appl. Nano Mater.* **2021**, *4*, 10399.

[6] The authors acknowledge funding from the DFG, RTG2767, Grant Number 451785257.

## T88: Efficient Sulfur Host Based on Functional Colloidal particles for Lithium-Sulfur Batteries

Dongjiu Xie,<sup>1</sup> Zdravko Kochovski,<sup>1</sup> Yan Lu<sup>1,2,3</sup>

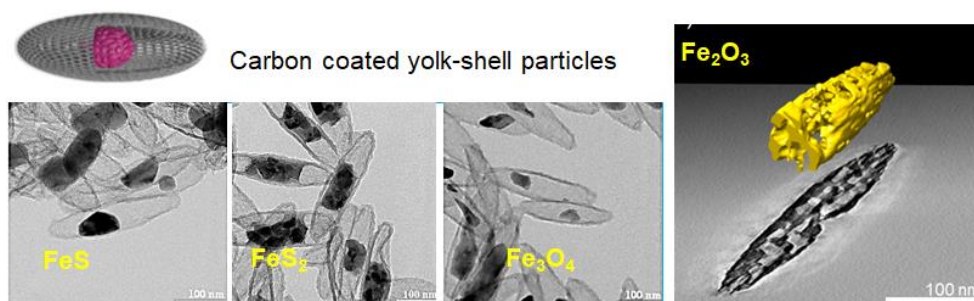
<sup>1</sup> Helmholtz-Zentrum Berlin für Materialien und Energie, 14109 Berlin, Germany

<sup>2</sup> Institute for Technical and Environmental Chemistry, Friedrich-Schiller-Universität Jena, 07743 Jena, Germany

<sup>3</sup> Helmholtz Institute for Polymers in Energy Applications Jena (HIPOLE Jena), 07743 Jena, Germany

Colloidal route is one of the favored ways toward cost-effective large-scale production of various nanostructures [1]. In our study, different types of nanoparticles have been designed and synthesized via colloidal approach, which can be applied as electrode materials for various supercapacitor [2] and battery systems [3]. Metal-based sulfur host materials have been developed either using polymeric colloidal particles as soft template [3,4] or inorganic particles as hard template [5,6] (as shown in Figure 1).

For example, carbon-coated mesoporous  $\text{Fe}_3\text{O}_4$  nanospindles ( $\text{C@M-Fe}_3\text{O}_4$ ) with interconnected pore structures have been synthesized using  $\text{FeOOH}$  particles as hard template, which can work effectively as sulfur-host material for Li-S batteries [7]. These porous  $\text{C@M-Fe}_3\text{O}_4$  particles exhibit an efficient confinement ability to lithium polysulfides, thanks to the synergistic properties of physical confinement in the mesoporous structure and the chemisorption of  $\text{Fe}_3\text{O}_4$  particle. This approach can be extended to complex hybrid carbon nanostructures with potential use in electrochemical energy storage and conversion.



**Figure 1.** TEM images of iron-based nanospindles with different morphologies, which have been used as sulfur host materials of Li-S batteries.

[1] W. Li, G. Zheng, Y. Yang, Z.W. Seh, N. Liu, Y. Cui, *PNAS* **2013**, 110, 7148.

[2] T. Quan, Y. Xu, M. Tovar, N. Goubard-Bretesché, Z. Li, Z. Kochovski, H. Kirmse, K. Skrodzky, S. Mei, H. Yu, D. Abou-Ras, M. Wagemaker, Y. Lu, *Batteries & Supercaps* **2020**, 3, 1-11.

[3] S. Mei, C. J. Jafta, I. Lauermaun, Q. Ran, M. Kärgell, M. Ballauff, Y. Lu, *Adv. Funct. Mater.* **2017**, 1701176.

[4] D. Xie, Y. Xu, Y. Wang, X. Pan, E. Härk, Z. Kochovski, A. Eljarrat, J. Müller, C. T. Koch, J. Yuan, Y. Lu, *ACS Nano* **2022**, 16, 10554-10565.

[5] M. K. Elibol, L. Jiang, D. Xie, S. Cao, X. Pan, E. Härk, Y. Lu, *Global Challenges* **2023**, 7, 2300005.

[6] D. Xie, S. Mei, Y. Xu, T. Quan, E. Hark, Z. Kochovski, Y. Lu, *ChemSusChem* **2021**, 14, 1404-1413

[7] D. Xie, Y. Xu, E. Härk, Z. Kochovski, X. Pan, X. Zhang, J. Schmidt, Y. Lu, *Mater. Today Energy* **2023**, 36, 101344.

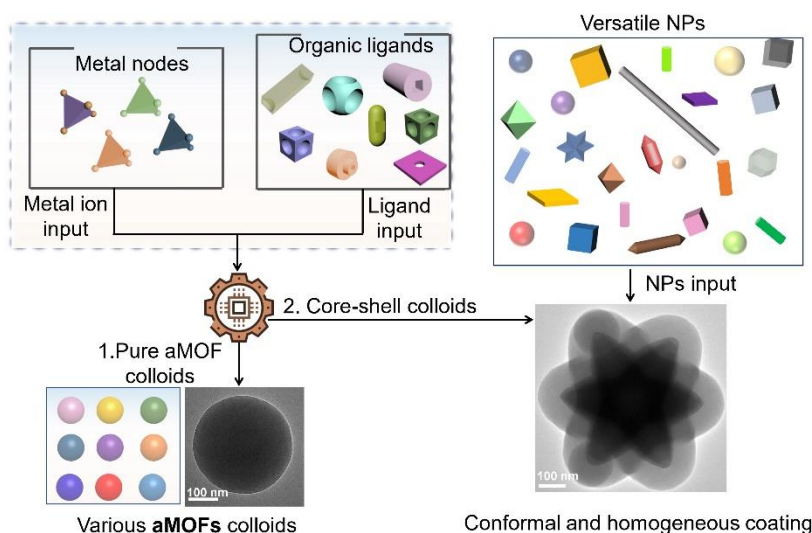
## T89: Stöber Method to Amorphous Metal-Organic Frameworks and its application in Li-S battery

Wei Zhang<sup>1</sup>, Nicola Pinna<sup>2</sup> and Yan Lu<sup>1</sup>

<sup>1</sup> Institute of Electrochemical Energy Storage, Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

<sup>2</sup> Department of Chemistry, IRIS Adlershof & The Center for the Science of Materials Berlin, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany

The Stöber method is a widely-used sol-gel route for synthesizing amorphous SiO<sub>2</sub> colloids and conformal coatings.<sup>[1]</sup> Nonetheless, the material systems compatible with this method are still limited. Herein, by mimicking the Stöber method, we have extended the approach to metal organic frameworks (MOFs), a category of organic-inorganic hybrid materials.<sup>[2]</sup> We introduce a general synthesis route to amorphous MOFs by making use of a vapor diffusion method,<sup>[3]</sup> which allows to precisely control the growth kinetics. Twenty-four different amorphous MOF colloids were successfully synthesized by selecting 11 metal ions and 17 organic ligands.<sup>[2]</sup> Moreover, by introducing pre-formed core-nanoparticles (NPs), a conformal and homogeneous amorphous MOFs coating with controllable thickness can be grown on core-NPs to form core-shell colloids. The versatility of this amorphous coating technology was demonstrated by synthesizing over 100 new core-shell composites from 19 amorphous MOF shells and over 30 different core-NPs. For applications, the stability of the sulfur cathode was significantly enhanced through this uniform amorphous MOF coating technology. The conformal shell not only alleviates the shuttle effect of polysulfides but also accelerates the kinetics of polysulfide conversion, thereby leading to better performance in Li-S batteries.



**Figure 1.** Schematic illustration of the synthesis of amorphous Metal Organic Frameworks (aMOFs) colloids with adjustable metal nodes and organic ligands, and conformal core@shell structures consisting of different nanoparticle cores and aMOFs shells.

[1] Stöber W, Fink A, Bohn E. C., *J. Colloid Interface Sci.* **1968**, 26, 62-69.

[2] Zhang, W. et al, *Nat. Commun.*, in press.

[3] Zhang, W., Bojdys, M. J., Pinna, N., *Angew. Chem. Int. Ed.* **2023** 62, e202301021.

[4] The authors acknowledge the Alexander von Humboldt Foundation, Bonn, Germany, for a postdoctoral fellowship and research grant.