

## CPP 21: Focus: Smart Hydrogels and Hydrogel Based Devices I - organized by Gerald Gerlach, Walter Richtering and Thomas Hellweg

Time: Tuesday 9:30–13:00

Location: C 130

### Topical Talk

CPP 21.1 Tue 9:30 C 130

**Superresolution microscopy of pNIPAM microgels** — ●FRANK SCHEFFOLD<sup>1</sup>, GAURASUNDAR MARC CONLEY<sup>1</sup>, PHILIPPE AEBISCHER<sup>2</sup>, SOFI NÖJD<sup>2</sup>, MARCO BRAIBANTI<sup>1</sup>, and PETER SCHURTENBERGER<sup>2</sup> — <sup>1</sup>Department of Physics, University of Fribourg, 1700 Fribourg, Switzerland — <sup>2</sup>Physical Chemistry, Department of Chemistry, Lund University, 221 00 Lund, Sweden

Microgels are among the most studied colloidal and polymeric systems of the past two decades. Swelling thermosensitive, poly(*N*-isopropylacrylamide) microgels by lowering the temperature provides a unique mechanism for controlling the porosity and size of colloidal particles on the nanoscale. As a consequence, these smart microgel particles are being considered for applications ranging from viscosity modifiers and sensing to drug delivery and as models for the glass and the jamming transition. Here, we present results from in-situ two-color superresolution microscopy of dye-labelled submicron sized pNIPAM microgels. We first demonstrate direct Stochastic Optical Reconstruction Microscopy (dSTORM) to image single microgels in two and three dimensions, at different stages of the volume phase transition, with a lateral resolution of 30nm. We find that the swelling behaviour observed in real space matches quantitatively with results from traditional light scattering measurements in reciprocal space. Next, we study dye labelled tracer microgels embedded in dense microgel suspensions. As we increase the packing density we map out the different contributions that allow the dense packing of the soft microgels, due to deformation, interpenetration and compression.

CPP 21.2 Tue 10:00 C 130

**Soft photonic crystals from core-shell microgels** — ASTRID RAUH<sup>1</sup> and ●MATTHIAS KARG<sup>2</sup> — <sup>1</sup>Physical Chemistry I, University of Bayreuth, Universitaetsstr. 30, 95447 Bayreuth — <sup>2</sup>Physical Chemistry I, Heinrich-Heine-University Duesseldorf, Universitaetsstr. 1, 40204 Duesseldorf

Photonic crystals are well known for their fascinating angle-dependent opalescence. In contrast to hard sphere building blocks, crystals from soft spheres such as microgels allow for external actuation, e.g. melting and recrystallization induced by pH or temperature changes. In addition, soft spheres can be deformed and thus packing fractions well above the hard sphere limit are accessible. A drawback with respect to the optical diffraction of soft photonic crystals is the typically low refractive index modulation inside the material. This asks for pathways to increase the refractive index contrast in the periodic superstructure.

We prepared cm-sized soft photonic crystals from core-shell microgels with absorbing nanocrystal cores (Au nanoparticles) and systematically studied the crystal structure and diffractive properties. As non-absorbing references, we prepared pitted particles from the same microgel batches by dissolution of the nanocrystal cores. The resulting purely organic microgels allowed for a direct comparison of structural and optical properties. We identify the role of small absorbing nanocrystal cores and show options to alter the photonic behavior of soft photonic crystals in future studies.

[1] A. Rauh et al., *Langmuir* 2017, DOI: 10.1021/acs.langmuir.7b01595

CPP 21.3 Tue 10:15 C 130

**Rational design of Ag@PS-PNIPAM core-shell nanoreactors with tunable activity for catalysis** — ●DANIEL BESOLD<sup>1</sup>, SEBASTIAN RISSE<sup>1</sup>, RAFAEL ROA<sup>1</sup>, YAN LU<sup>1,2</sup>, JOACHIM DZUBIELLA<sup>1,3</sup>, and MATTHIAS BALLAUFF<sup>1,3</sup> — <sup>1</sup>Soft Matter and Functional Materials, Helmholtz-Zentrum Berlin, Germany — <sup>2</sup>Institut für Chemie, Universität Potsdam, Potsdam, Germany — <sup>3</sup>Institut für Physik, Humboldt-Universität zu Berlin, Germany

Nanoreactors containing metal nanoparticles embedded in stimuli-responsive polymers have recently emerged as promising catalytic systems. The polymer coating not only prevents nanoparticle aggregation but also controls the catalytic activity by changing the local environment for the reactants. For this work we synthesized thermosensitive core-shell nanoreactors, composed of a polystyrene core in a PNIPAM microgel shell, in which silver nanoparticles are immobilized. In this system, we study the catalytic reduction of 4-nitrophenol by borohydride ions. Our kinetic analysis is based on UV-Vis spectroscopic techniques. The spectra are deconvoluted by the Levenberg-Marquardt

algorithm which provides us with the concentration-time dependency of the species involved in the reaction. We tune the catalytic activity of the silver nanoparticles by tuning the temperature of the system. We find two distinct regimes in the catalytic rate at temperatures below and above the volume transition of the PNIPAM shell. By means of a modified Langmuir-Hinshelwood mechanism which accounts for electrostatic effects on the reactant adsorption, we attribute the changes in the rate to changes in the reactant partitioning in the shell.

CPP 21.4 Tue 10:30 C 130

**Smart core-shell microgel/silver nanoparticle hybrids as switchable catalysts** — ●TIMO BRÄNDEL, YVONNE HERTLE, and THOMAS HELLWEG — Physical and Biophysical Chemistry, Bielefeld University, Universitätsstraße 25, 33615 Bielefeld

Hybrid materials combining the interesting properties of nanoparticles with stimuli responsive microgels have obtained considerable attention during the last decade. Our contribution focuses on core-shell microgels based on the monomers, *N*-isopropylacrylamide (NIPAM) *N*-isopropylmethacrylamide (NIPMAM) as core materials and *N*-*n*-propylacrylamide (NNPAM) as shell material. These microgels exhibit a very interesting linear phase transition region between the two volume phase transition temperatures (VPTTs) of the respective homopolymer microgels.

The particle architecture of the core-shell microgels is modified by copolymerization with acrylic acid (AAc) and by a variation of the cross-linker density of the core. These modifications in the core region of the core-shell microgels are important steps to tailor the microgel properties towards an excellent ability to stabilize nanoparticles.

Silver nanoparticles are generated *in situ* inside the core-shell microgel templates and their temperature dependent catalytic activity is studied by following the degradation of *p*-nitrophenole. The results display, that the use of the core-shell microgels is a versatile approach towards catalytic particles with a switchable catalytic activity.

CPP 21.5 Tue 10:45 C 130

**Doping thermosensitive PNIPAM microgels with magnetic nanoparticles** — ●MARCUS U. WITT<sup>1</sup>, STEPHAN HINRICHS<sup>2</sup>, MELISSA HERMES<sup>3</sup>, BIRGIT FISCHER<sup>2</sup>, ANNETTE SCHMIDT<sup>3</sup>, and REGINE V. KLITZING<sup>1</sup> — <sup>1</sup>Technische Universität Darmstadt, Institut für Festkörperphysik, Alarich-Weiss-Straße 10, 64287 Darmstadt — <sup>2</sup>Universität Hamburg, Institut für Physikalische Chemie, Grindelallee 117, 20146 Hamburg — <sup>3</sup>Universität zu Köln, Institut für Physikalische Chemie, Luxemburger Straße 116, 50939 Köln

Poly-*N*-isopropyl acrylamide (PNIPAM) based microgels are of high interest as model systems for thermo-responsive gel structures that exhibit a volume phase transition temperature. First results with the loading of the microgels with magnetic nanoparticles (MNP) showed a small re-sponse of the particle volume to an external magnetic field under geometrical confinement [1]. Theoretical calculations predict a much bigger response. To investigate now the origin of this difference in response the MNP distribution inside the microgel is of interest.

Therefore gels of different internal polymer structure are synthesized: heterogeneously cross linked microgels (batch) and homo-geneously cross linked microgels (feeding) [2]. The MNP distribution is different in the two cases and is of interest for further investigations of the magnetic response for magnetic microgels particles.

#### References

[1] S. Backes, M. U. Witt, R. v. Klitzing, *J. Phys. Chem. B* 2015, 119, 12129-12137 [2] R. Acciaro, *Langmuir*, 2011, 27, 7917-7925

### 15 min. break

CPP 21.6 Tue 11:15 C 130

**Film-coupled plasmonic arrays based on core-shell microgel particles** — ●YANNIC BRASSE<sup>1</sup>, MAREEN B. MÜLLER<sup>2</sup>, MATTHIAS KARG<sup>3</sup>, CHRISTIAN KUTTNER<sup>1,4</sup>, TOBIAS A. F. KÖNIG<sup>1,4</sup>, and ANDREAS FERY<sup>1,4</sup> — <sup>1</sup>Leibniz-Institut für Polymerforschung Dresden e.V., Institute of Physical Chemistry and Polymer Physics, Hohe Str. 6, 01069 Dresden, Germany — <sup>2</sup>Physical Chemistry II, University of Bayreuth, Universitätsstr. 30, 95447 Bayreuth, Germany — <sup>3</sup>Department of Physical Chemistry 1, Heinrich-Heine-Universität

Düsseldorf, 40225 Düsseldorf, Germany — <sup>4</sup>Cluster of Excellence Center for Advancing Electronics Dresden (cfaed), Technische Universität Dresden, 01062 Dresden, Germany

We study the optical properties of a metal-film-coupled gold nanoparticle system, separated by a Poly(N-isopropylacrylamide) (PNIPAM) layer, as cost-efficient and scalable platform for screening of plasmonic properties. As shown in earlier work, a monolayer of gold-core/PNIPAM-shell particles featuring a gradient in core-sizes, results in lateral variation of plasmonic resonances.[1] Coverage with a 35 nm gold layer induces plasmonic coupling between cores and the film. We study the tunability of the array by swelling of PNIPAM for various particle sizes, which reveals a reversible plasmonic shift of up to 40 nm. With this lithography-free method we produce a platform for systematic screening of fundamental optical effects and for application in surface plasmon resonance (SPR) sensing.[2]

[1] M.B. Müller et al., ACS Nano, 2014, 8, 9410 [2] Funding from ERC Starting Grant METAMECH-306686 is acknowledged

CPP 21.7 Tue 11:30 C 130

**Water swelling and exchange kinetics of multi-stimuli responsive polymer thin films** — ●LUCAS KREUZER<sup>1</sup>, TOBIAS WIDMANN<sup>1</sup>, NURI HOHN<sup>1</sup>, KUN WANG<sup>1</sup>, JEAN-FRANCOIS MOULIN<sup>2</sup>, VIET HILDEBRAND<sup>3</sup>, ANDRÉ LASCHEWSKY<sup>3</sup>, CHRISTINE M. PAPADAKIS<sup>1</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1</sup> — <sup>1</sup>TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching — <sup>2</sup>HZG at MLZ, 85747 Garching — <sup>3</sup>Universität Potsdam, Inst. für Chemie, 14476 Potsdam Golm

Responsive polymers can react with a strong change in volume towards even small changes of an external stimulus. This behavior makes them attractive for a manifold selection of applications such as nano-sensors, artificial pumps and muscles or optical switches. In order to implement responsive polymers in the aforementioned application fields, a fundamental understanding of the underlying water kinetics of these polymers is necessary. We follow the water and deuterated water swelling and the corresponding exchange processes in a multi-stimuli responsive block copolymer thin film via in-situ time of flight neutron reflectometry (TOF-NR). The kinetic processes are followed with a high time resolution. The observed swelling and exchange kinetics are modelled to obtain detailed insights about the underlying mechanisms of water uptake and exchange.

CPP 21.8 Tue 11:45 C 130

**Swelling Behavior of Thin Hydrogel Films in Humidity and when Water-immersed** — ●FABIAN MURALTER and ANNA COCLITE — Institute of Solid State Physics, TU Graz, Austria

Hydrogels are water-containing networks of hydrophilic polymers, whose distinct properties allow for a number of different applications (e.g. in drug delivery, contact lenses). Their characteristic swelling behavior makes hydrogels particularly interesting for sensor & actuator setups. However, as water diffusivity is the time-limiting step in (de-)swelling, film thickness is crucial for fast response times. In this study, hydrogels are synthesized by initiated Chemical Vapor Deposition (iCVD), with film thicknesses ranging from tens to several hundreds of nanometers. iCVD is a solvent-free technique that allows for precise thickness control and enables a plethora of chemical compositions to be studied. Depending on monomer and crosslinker choice, these hydrogels show different response characteristics depending on the environment (humidity/water immersion). Addition of temperature-sensitive groups such as NIPAAm facilitates also temperature-dependent swelling. The swelling behavior is studied by spectroscopic ellipsometry, which records the evolution of (polymer) optical parameters during swelling as a function of temperature and humidity. This allows for the detection of thickness changes in the Å-range (e.g. thermal expansion) up to full swelling of the hydrogels, with thickness increases of up to 100%. For example, DEAAm-based copolymers show swelling response-times in humidity in the seconds-range, making them highly promising for sensing applications.

CPP 21.9 Tue 12:00 C 130

**Transport and solvation of penetrant molecules in a thermoresponsive hydrogel** — ●MATEJ KANDUC<sup>1</sup>, WON KYU KIM<sup>1</sup>, RAFAEL ROA<sup>1</sup>, and JOACHIM DZUBIELLA<sup>1,2</sup> — <sup>1</sup>Soft Matter and Functional Materials, Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany — <sup>2</sup>Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 15, D-12489 Berlin, Germany

Thermoresponsive hydrogels have become increasingly interesting materials for pharmaceutical and biomedical applications, primarily due to their high water content and rubbery nature, which is similar to natural tissue, as well as their biocompatibility. External stimuli, such as changes in temperature, trigger the transition from a swollen into a collapsed state of the polymer, which dramatically alters the thermodynamic and transport properties of penetrant molecules. We employ molecular dynamics simulations of a Poly(N-isopropylacrylamide) (PNIPAM) hydrogel with explicit water in its collapsed as well as in the swollen state. The simulations enable us to gain insights into the diffusion and solvation mechanisms of various penetrant molecules in the hydrogel. We find that formations of water pockets, the presence of crosslinkers in the hydrogel, and the polarity of the molecules play a detrimental role for the diffusion mechanisms and solvation free energies. Finally, we discuss how can the observed phenomena be exploited in hydrogel-based applications of responsive nanoreactors for nanocatalysis.

CPP 21.10 Tue 12:15 C 130

**Water uptake and diffusion in thin PNIPAM microgel films** — ●TOBIAS WIDMANN<sup>1</sup>, LUCAS KREUZER<sup>1</sup>, NURI HOHN<sup>1</sup>, LORENZ BIESSMANN<sup>1</sup>, KUN WANG<sup>1</sup>, JEAN-FRANÇOIS MOULIN<sup>2</sup>, YVONNE HERTLE<sup>3</sup>, THOMAS HELLWEG<sup>3</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1</sup> — <sup>1</sup>TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching — <sup>2</sup>HZG at MLZ, 85747 Garching — <sup>3</sup>Universität Bielefeld, Fakultät für Chemie, Physikalische und Biophysikalische Chemie III, 33615 Bielefeld

Microgels out of thermoresponsive polymers show a strong change in volume by a variation of the temperature across the lower critical solution temperature (LCST), which in a thin film geometry translates into a change of the film thickness. This offers new functionality and is of high interest e.g. for biomedical applications. In order to gain detailed insights in the kinetics during the volume change, the diffusion of water molecules through the interconnected polymer network during the uptake and release of water is analyzed. Thin PNIPAM microgel films crosslinked with N,N'-methylenebisacrylamide are investigated with time-of-flight neutron reflectometry (TOF-NR). H<sub>2</sub>O and D<sub>2</sub>O are used to apply different humidity conditions at a constant temperature below the LCST of PNIPAM. The H<sub>2</sub>O and D<sub>2</sub>O swelling as well as the H<sub>2</sub>O - D<sub>2</sub>O and D<sub>2</sub>O - H<sub>2</sub>O exchange processes are studied. Results from the TOF-NR analysis are modelled with a model which accounts for the temporal evolution of the humidity.

CPP 21.11 Tue 12:30 C 130

**Multiscale modeling of multiresponsive smart soft matter** — CHATHURANGA DE SILVA<sup>1</sup>, PORAKRIT LEOPHAIRATANA<sup>1</sup>, TAKAHIRO OHKUMA<sup>2</sup>, JEFFREY KOBERSTEIN<sup>1</sup>, KURT KREMER<sup>3</sup>, and ●DEBASHISH MUKHERJI<sup>3</sup> — <sup>1</sup>Department of Chemical Engineering, Columbia University, New York USA — <sup>2</sup>Central Research Division, Bridgestone Corporation, Kodaira, Tokyo 187-8531 Japan — <sup>3</sup>Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz Germany

Design of multiresponsive smart, soft materials is at the onset of many developments in polymer physics, chemical physics, biophysics and biochemistry research. A system is known as smart responsive when a slight change in external stimuli can drastically alter its structure, function, and stability. Because the properties of these systems are dictated by large conformational/compositional fluctuations, it is very difficult to address these problems within both experimental and theoretical setups. On such system is the acetal based copolymers, consisting of repeat units of hydrophobic (methylene) and hydrophilic (ethylene oxide) monomers [1]. In this context, polymer properties are inherently multiscale in nature, where delicate local interaction details play a key role in describing their global conformational behavior. In this presentation, we will discuss the recently developed segment-based multiscale model of these polymers [2]. Furthermore, we will show how our approach can be used to interpreting and guiding experiment towards new directions. [1] Samanta, Bogdanowicz, Lu, and Koberstein, Macromolecules 49, 1858 (2016). [2] De Silva, Leophairatana, Ohkuma, Koberstein, Kremer, and Mukherji, JCP 147, 064904 (2017).

CPP 21.12 Tue 12:45 C 130

**Crosslinking Effect on Solute Adsorption in Swollen Thermoresponsive Hydrogels** — ●SEBASTIAN MILSTER<sup>1,2</sup>, RICHARD CHUDOBA<sup>1</sup>, MATEJ KANDUC<sup>1</sup>, and JOACHIM DZUBIELLA<sup>1,2</sup> — <sup>1</sup>Helmholtz-Zentrum Berlin — <sup>2</sup>Humboldt-Universität zu Berlin

Polymeric networks of poly(N-isopropylacrylamide) (PNIPAM) and

N,N'-methylenebisacrylamide crosslinkers (BIS/MBA) are used for tailoring thermoresponsive hydrogels, which exhibit a sudden, yet reversible collapse when exceeding a critical temperature (LCST) of approximately 305K. Along with the volume change, selective solute permeability and adsorption in the gel also undergo a transition. This yields great potential for many applications in which controlled release or uptake of solutes is required. In this work we investigate the impact of crosslinking on solute adsorption in the swollen hydrogel by means of classical molecular dynamics (MD) at 290K. We perform all-atom, explicit water simulations of representative hydrogel subunits in

the crosslinker vicinity. The studied system consists of one BIS-linker with four atactic PNIPAM 12-mers in a tetrahedral setup. The interaction between the polymer and cosolutes such as ions, alkanes and aromatics is examined by analysing the radial distribution function. We observe that the solute-specific binding known from single chains<sup>1</sup> is magnified, which should be considered in future hydrogel modeling.

[1] Matej Kanduč et al. "Selective solute adsorption and partitioning around single PNIPAM chains" PCCP 19.8 (2017).