

## CPP 56: Hydrogels and Microgels I

Time: Thursday 10:15–13:00

Location: ZEU 260

**Invited Talk**

CPP 56.1 Thu 10:15 ZEU 260

**Functional microgels: simple matter where complexity matters** — ●WALTER RICHTERING — RWTH Aachen University, Aachen, Germany, EU

Microgels are macromolecular networks swollen by the solvent they are dissolved in. They are unique systems that are distinctly different from common colloids, such as, e.g., rigid nanoparticles, flexible macromolecules, micelles or vesicles. When swollen, they are soft and have a fuzzy surface with dangling chains and the presence of cross-links provides structural integrity - in contrast to linear and (hyper-) branched polymers. Obviously, the cross-linker content will allow controlling whether microgels behave more "colloidal" or "macromolecular". Finally, microgels reveal interface activity without being amphiphilic. The combination of being soft and porous while still having a stable structure through the cross-linked network allows for the possibility to introduce chemical functionality at different positions. The architectural diversity and compartmentalization of reactive groups enable thus short-range coexistence of otherwise instable combinations of chemical reactivity. The capability of microgels to adjust both their shape and volume in response to external stimuli provides the opportunity to reversibly tune their physico-chemical properties. From a physics point of view, microgels are particularly intriguing and challenging, since their intra-particle properties are intimately linked to their inter-particle behavior.

CPP 56.2 Thu 10:45 ZEU 260

**Responsive polymer hydrogels: physical gelling through polyion complexation** — MARGARITA A. DYAKONOVA<sup>1</sup>, ANATOLY V. BEREZKIN<sup>1</sup>, NICOLETTA STAVROULI<sup>2</sup>, MARIA T. POPESCU<sup>2</sup>, CONSTANTINOS TSITSILIANIS<sup>2</sup>, and ●CHRISTINE M. PAPADAKIS<sup>1</sup> — <sup>1</sup>Technische Universität München, Physik-Department, Fachgebiet Physik weicher Materie, Garching, Germany — <sup>2</sup>University of Patras, Department of Chemical Engineering, Greece

Responsive polymer-based hydrogels may be formed through association of oppositely charged polyion segments [1]. Network formation is due to charged chains which physically crosslink by ion pair formation arising from intermolecular polyionic complexation of oppositely charged repeating units.

We present results from dynamic mechanical measurements, small-angle neutron scattering and computer simulations on hydrogels formed by triblock copolymers bearing oppositely charged blocks (poly(acrylic acid) and quaternized poly(2-vinylpyridine)) [2]. Due to the weak nature of the involved polyions, these hydrogels respond strongly to pH and to the presence of salt.

1. C. Tsitsilianis, C.M. Papadakis, *Gels*, submitted.

2. Dyakonova M. et al., *Macromolecules* **47**, 7561 (2014) and **48**, 8177 (2015).

CPP 56.3 Thu 11:00 ZEU 260

**Cell-free protein synthesis and enzymatic cascades in polymer microgels** — ●JULIAN THIELE — Leibniz-Institut für Polymerforschung Dresden e.V., Leibniz Research Cluster, Germany

Microfluidic flow cells provide excellent control over the formation of microemulsions, which are widely applied as templates for the fabrication of hydrogel microparticles with defined physicochemical properties and mechanics. The Leibniz Research Cluster group at IPF Dresden utilizes this knowledge to develop biocompatible hydrogel particles as cell-like experimental platform for cell-free biotechnology. Here, spatial organization and confinement of reagents can be easily varied, which directly influence diffusion rates and binding constants, as shown in microgel-based cell-free protein synthesis (Hansen et al. *ChemBioChem* 2016, 17, 228). Currently, we are extending the application of microfluidically prepared microgels as host for cell-free biosyntheses towards the design of polyketide building blocks in enzymatic cascades.

CPP 56.4 Thu 11:15 ZEU 260

**Phase behaviour of PNIPMAM in dependence on temperature and pressure** — ●KORA-LEE CLAUDE<sup>1</sup>, BART-JAN NIEBUUR<sup>1</sup>, DIONYSIA ARAVOPOULOU<sup>2</sup>, VIET HILDEBRAND<sup>4</sup>, ANDRÉ LASCHEWSKY<sup>4</sup>, APOSTOLOS KYRITSIS<sup>2</sup>, PETER MÜLLER-BUSCHBAUM<sup>1</sup>, ALFONS SCHULTE<sup>3</sup>, and CHRISTINE M. PAPADAKIS<sup>1</sup> — <sup>1</sup>Technische Universität München, Physik-Department, Physik we-

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Poly(N-isopropylmethacrylamide) (PNIPMAM) is a thermoresponsive polymer which differs from the well-known PNIPAM by having an additional methyl group attached to the vinyl backbone. Thus, it may be expected to be more hydrophobic, however, its cloud point at 42°C is about 10°C higher.

In order to gain more information on the phase behaviour of PNIPMAM in dependence on temperature, pressure and concentration, we investigated the transition by DSC, the structural behaviour by temperature-resolved SANS and mapped out the pressure-dependent phase diagram using turbidimetry.

It seems that the additional methyl group stabilizes the one-phase region, even at higher pressures, which could be explained by steric hindrance.

**15 min break**

CPP 56.5 Thu 11:45 ZEU 260

**Superresolved fluorescence microscopy to gain structural insights into microgels and other soft matter systems** — ●DOMINIK WÖLL, ALEX OPPERMAN, ARJAN GELISSEN, OLEKSIH NEVSKYI, and WALTER RICHTERING — Institute of Physical Chemistry, RWTH Aachen University, Germany

The elucidation of the structure of compartmentalized microgels and microgel structures is challenging since they do not possess strong contrast for electron microscopy, and since classical fluorescence microscopy fails due to the fact that their structures are significantly smaller than the diffraction limit of optical light. However, modern superresolved fluorescence microscopy methods such as dSTORM (direct stochastic optical reconstruction microscopy) reach resolutions down to 10-30 nm and, therefore, are highly suited to fill this gap of structural *in situ* imaging. In this contribution, the success of these methods to visualize microgels and other soft matter systems and their application in determining the spatial distribution of implemented functionalities will be demonstrated.

CPP 56.6 Thu 12:00 ZEU 260

**Modeling of Polyelectrolyte Gels in Equilibrium with Salt Solutions** — TOBIAS RICHTER<sup>1</sup>, PETER KOŠOVAN<sup>2</sup>, JONAS LANDSGESELL<sup>1</sup>, and ●CHRISTIAN HOLM<sup>1</sup> — <sup>1</sup>University of Stuttgart, Germany — <sup>2</sup>Charles University in Prague, Czech Republic

We use hybrid molecular dynamics/Monte Carlo simulations and coarse-grained polymer models to study the swelling of polyelectrolyte gels in salt solutions. Besides existing industrial applications, such gels have been recently proposed as a promising agent for water desalination. We employ the semi-grand canonical ensemble to investigate partitioning of the salt between the bulk solution and the gel, and the salt-induced de-swelling of the gels under free swelling equilibrium and under compression. We compare our simulation data to the analytic model of Katchalsky and Michaeli which captures the deviations in the ion partitioning from the simple Donnan approximation fairly well [1]. We modify the model by replacing the Gaussian elasticity with the Langevin function for finite extensibility and obtain nearly quantitative agreement between theory and simulations both for the swelling ratio and for the partitioning of salt, across the whole range of studied gel parameters and salt concentrations. The modified model provides a very good description of swelling of polyelectrolyte gels in salt solutions for charge densities up to a Manning parameter of one half. We use this improved model to construct a simple desalination cycle and to calculate the corresponding work to desalinate sea water to potable water. [1] P. Kosovan, T. Richter, C. Holm, *Macromolecules* **48**, 7698-7708 (2015).

CPP 56.7 Thu 12:15 ZEU 260

**Structure and Dynamics of highly concentrated PNIPAm microgels.** — ●LARA FRENZEL<sup>1,2</sup>, FELIX LEHMKÜHLER<sup>1,2</sup>, MICHAEL HÖLTIG<sup>1</sup>, and GERHARD GRÜBEL<sup>1,2</sup> — <sup>1</sup>DESY, Hamburg, Germany

— <sup>2</sup>The Hamburg Centre for Ultrafast Imaging, CUI, Hamburg, Germany

Poly (N-isopropylacrylamide) (PNIPAm) is a stimuli responsive cross-linked microgel with a coil-to-globule transition at a lower critical solution temperature (LCST) in water around 32°C, which results in a rapid collapse of the particle radius by increasing the temperature. With this volume phase transition PNIPAm is both applicable in technical as well as medical fields. Furthermore, it became a frequently examined system in research such as a model to study the specific phase behavior of soft colloids. Via x-ray photon correlation spectroscopy (XPCS) we investigate the change in structure and dynamics of PNIPAm microgels at high concentrations around the LCST. Thereby highly brilliant x-rays from the coherence beamline P10 at PETRA III have been used in the XPCS study. Since the swollen microgel shows a low refractive index difference compared to water we studied both pure PNIPAm as well as silica-PNIPAm core-shell systems.

CPP 56.8 Thu 12:30 ZEU 260

**A mesoscale hydrodynamic simulation study of polymer dynamics in responsive microgels** — ●ALI GHAVAMI, HIDEKI KOBAYASHI, and ROLAND G. WINKLER — Institute for Advanced Simulation, Forschungszentrum Juelich GmbH, 52425 Juelich, Germany

We analyze the internal polymer dynamics in microgel systems under different swelling conditions. A microgel particle consists of tetra-functionally crosslinked linear polymers in solution, which undergoes conformational changes in response to the external stimuli. Here, a broad range of microgel sizes, extending from hydrophobically collapsed to charged swollen particles, are considered and hydrodynamic interactions are accounted through multiparticle collision dynamics method. The polymer dynamics is analyzed in terms of the monomer mean square displacement and the intermediate scattering functions. For microgels in good solvent, the scattering function decays in a stretched-exponential manner, with a decay rate exhibiting a crossover

from a collective diffusive-like dynamics at low wavenumbers to a hydrodynamic-dominated dynamics at larger wavenumbers. There is little difference between the intermediate scattering functions of microgels under good solvent conditions and strongly swollen gels, but strongly collapsed gels exhibit a faster decay at short times as the hydrodynamic interactions become screened. In addition, we present results for the dynamics of the crosslinks, which exhibit an unexpected, semiflexible polymer-like dynamics.

CPP 56.9 Thu 12:45 ZEU 260

**Polymer dynamics within soft confinement** — ●BJÖRN KUTTICH and BERND STÜHN — Institut für Festkörperphysik, Technische Universität Darmstadt, D-64289, Germany

Microemulsions in the droplet phase are a well suited system to provide a three dimensional soft confining geometry on the length scale of several nano metres. Due to the softness of the confinement molecules which are introduced into the microemulsion droplets will change structural and dynamical properties of the confinement. In case of water in oil microemulsions stabilised by the an-ionic surfactant AOT we studied these changes for the case of the water soluble polymer poly(ethylene oxide) (PEO) enclosed in droplets of different sizes.[1]

Furthermore, structure and dynamics of the confined polymer PEO, are investigated by small angle neutron scattering (SANS) and neutron spin echo spectroscopy (NSE). The SANS results show a significant increase of the polymer's radius of gyration, which is related to an attractive interaction between PEO and the AOT head groups. Furthermore the internal correlations of the polymer change to that of a collapsed polymer chain.

For the NSE data the effective diffusion coefficient was investigated. On length scales larger than the droplet size pure droplet diffusion is observed. The polymer is confined to the extent of the droplet. On smaller length scales, thus at larger  $q$  values dynamics show a significantly increased effective diffusion coefficient due to the polymer dynamics.

[1] B. Kuttich et al., J. Chem. Phys. **145**, 164904 (2016)