

CPP 8: Hydrogels and Microgels

Time: Monday 15:00–17:45

Location: H40

Invited Talk

CPP 8.1 Mon 15:00 H40

The role of nonlinearities and kinetics at phase transitions in stimuli-responsive polymer solutions and hydrogels — ●MARTINE PHILIPP, WINFRIED PETRY, and PETER MÜLLER-BUSCHBAUM — TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching, Germany

Soft condensed matter often self-assembles in a very rich and complex morphology. Typical examples include block copolymer, surfactant, and colloidal systems. Understanding self-assembly involves understanding of phase transitions, particularly of demixing phase transitions, including their kinetics. Crucial parameters on molecular scales are changes in intermolecular interactions, in conformations, and transport processes. During phase transformations, states of less stability are generally passed through. This potentially provokes mechanical instabilities, manifesting by softening. As the linear elastic moduli are small for intrinsically soft materials and as they might even further decrease by transition-induced softening, one can speculate whether elastic nonlinearities can dominate the elastic instability, and hence self-assembly. Analogies known from solid state physics are acoustic soft modes, which govern structural phase transitions in ferroelastic crystals.

In this talk, the impact of elastic, thermo-mechanical and thermo-optical nonlinearities on the order parameter susceptibilities will be discussed for so-called volume phase transitions within stimuli-responsive polymer solutions and hydrogels. First insights into a molecular-mechanistic understanding are presented.

CPP 8.2 Mon 15:30 H40

Impact of the cononsolvency effect on the temperature response of PNIPAM microgels in water/ethanol-mixtures — ●SEBASTIAN BACKES and REGINE VON KLITZING — Technische Universität Berlin, Stranski-Laboratorium für Physikalische und Theoretische Chemie, Berlin, Germany

Microgels made of N-isopropylacrylamide (NIPAM) are of great interest because of their pronounced temperature response in solution. They possess a volume phase transition temperature (VPTT) below which they are swollen. When the VPPT is exceeded, the gels expel the solvent and shrink. Both pure water and several pure organic solvents like ethanol are good solvents for PNIPAM. In mixtures of water and ethanol however the solubility is significantly decreased, with the microgels showing a minimum volume at a certain mixing ratio of ca. 20% (cononsolvency effect).

After adsorption on a solid substrate the mixing ratio for the minimum value increases from 20% to about 40-50%. Therefore the volume of microgels has been examined both in bulk using dynamic light scattering and on silica wafers using atomic force microscopy for several water/ethanol mixtures and a temperature range from 10 to 50°C.

The volume phase transition temperature has been shown to decrease from 32°C in pure water to values below the measuring range (i.e. <10°C) for intermediate mixing ratios. At higher ethanol content the VPTT reappears in a broadened form rather than a sharp transition.

CPP 8.3 Mon 15:45 H40

Cononsolvency in thermoresponsive micellar solutions: Pathway of aggregate formation — KONSTANTINOS KYRIAKOS¹, ANATOLY V. BEREZKIN¹, MARTINE PHILIPP¹, ALESSIO ZACCONE¹, ISABELLE GRILLO², ANNA MIASNIKOVA³, ANDRÉ LASCHEWSKY^{3,4}, PETER MÜLLER-BUSCHBAUM¹, and ●CHRISTINE M. PAPADAKIS¹ — ¹Technische Universität München, Physik-Department, Garching, Germany — ²Institut Laue-Langevin, Grenoble, France — ³Universität Potsdam, Institut für Chemie, Germany — ⁴Fraunhofer Institut für Angewandte Polymerforschung, Potsdam-Golm, Germany

The switching kinetics of thermoresponsive polymers are of importance for many applications. In mixtures of water and a cosolvent, the cloud point may be reduced, which offers additional possibilities for switching.

We have investigated the switching kinetics of thermoresponsive poly(N-isopropylacrylamide) (PNIPAM) homopolymers and of micelle forming PS-*b*-PNIPAM (PS stands for polystyrene) diblock copolymers in two ways: (i) by addition of the cosolvent methanol to aqueous solutions of the two polymers [1] and (ii) by rapidly heating a PS-*b*-

PNIPAM solution through the cloud point [2]. The aggregate growth was followed by time-resolved small-angle neutron scattering. The process is very different for PNIPAM and for PS-*b*-PNIPAM and depends sensitively on the pathway. We have developed theoretical models to relate the growth rate to the interaction between the collapsed micelles.

1.K. Kyriakos et al., *Macromolecules* 2014, **47**, 6867
2.K. Kyriakos et al., *Macromol. Rapid Commun.*, in press.

CPP 8.4 Mon 16:00 H40

Thermal traps trigger sol-gel phase transitions of DNA with single base sequence selectivity — ●CHRISTOF B. MAST, MATTHIAS MORASCH, EMIL AGERSCHOU, JONATHAN LIU, and DIETER BRAUN — Systems Biophysics, Physics Department, Center for Nanoscience, LMU Munich, Germany

Sol-gel phase transitions of DNA normally require long strands, high concentrations and multivalent ions for condensation. We demonstrate that a thermal gradient across a water-filled chamber creates DNA hydrogels from dilute, nanomolar concentrations of short, 36 nts DNA strands without condensation agents. The thermal gradient leads to fluid convection and thermophoresis, which in combination accumulate long biomolecules over short ones. The DNA is composed out of three self-complementary sequences which elongate by hybridization once millimolar concentrations are achieved. At nanomolar concentration, the DNA is an unbound single molecule. Inside the thermal gradient, the molecules accumulate and the self-complementary DNA connect cooperatively to longer and subsequently even better accumulating strands, ultimately leading to the formation of a DNA hydrogel. This localized phase transition is highly sequence selective: self-elongating DNA with a single base pair change per binding site separates from the unchanged DNA upon gelation which leads to the formation of two distinct, sequence pure gels. One single point-mutation at a single binding site can prevent the formation of the hydrogel. The mechanism implements a prebiotic machine that selects and stores oligonucleotides with very similar sequences starting from nanomolar concentration.

15 min. break

CPP 8.5 Mon 16:30 H40

Linear thermoresponsive surface coatings based on acrylamide microgels — OLIVER WREDE, JOHANNES BOOKHOLD, MARIAN CORS, and ●THOMAS HELLEWEG — Bielefeld University, Germany

Polymer coatings are used in a wide range of applications, such as anti fouling, enhancement of wetting abilities or corrosion protection. Combined with stimuli-responsive materials like acrylamide based microgels even more implementations are possible. In these microgels, an external stimulus like temperature, pH or ionic strength leads to a response in the particle size. To implement the particles into systems like sensors or nanoactuators, a well known and precise control of the stimuli response must be obtained. Therefore, we investigated complex microgel architectures obtained by a two-step synthesis protocol. These exhibit a reversible linear size response upon a temperature stimulus. Even if the particles are deposited onto surfaces, this linear dependency of the size on the temperature is still preserved. The properties of the particles and therefore those of the resulting surfaces can be modified by selecting specific conditions during the synthesis (surfactant concentration, cross linker content, etc.). Creating tailor-made surfaces that fulfill the demands of future applications is therefore possible.

CPP 8.6 Mon 16:45 H40

Swelling kinetics of N-*n*-propylacrylamide based microgels upon periodic pressure jumps investigated by time-resolved SANS — ●OLIVER WREDE¹, YVONNE PÜTZ², STEFAN LÜLSDORF³, DIANA ZAUSER³, YVONNE HERTLE¹, RALF SCHWEINS⁴, THOMAS SOTTMANN³, and THOMAS HELLEWEG¹ — ¹Bielefeld University, Germany — ²University of Cologne, Germany — ³University of Stuttgart, Germany — ⁴Institut Laue-Langevin, France

Temperature responsive microgels are particles in the size range between 100 nm and 1 μm, that undergo a reversible microphase separation at a certain temperature. Structure, size and phase transition properties can be controlled by the synthetic conditions. This makes them outstanding candidates for various applications, such as drug

delivery, catalytic particle carriers or nanoactuators. A precise understanding of the underlying processes is necessary to allow to tune the network properties. Therefore, we investigated the swelling and deswelling kinetics of *N-n*-propylacrylamide based microgels upon periodic pressure jumps across the phase transition with different cross-linker contents by time-resolved SANS. Preceding DLS measurements showed, that the phase transition shifts towards higher temperatures with increasing pressure, i.e. a swelling of the particles is induced upon compression. Our findings show, that the time scale of the kinetics changes with cross-linker content by more than one order of magnitude, which confirms the important role of the network morphology. Besides the influence of the cross linker, the kinetics of the swelling is considerably faster than the deswelling process.

CPP 8.7 Mon 17:00 H40

Superresolved fluorescence and electron microscopy to visualize the core-shell structure of microgels — •DOMINIK WÖLL¹, ARJAN GELISSEN¹, ALEX OPPERMAN¹, TOBIAS CAUMANN², PASCAL HEBBEKER¹, RAHUL TIWARI³, JOACHIM MAYER², WALTER RICHTERING¹, and ANDREAS WALTHER³ — ¹Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, 52056 Aachen, Germany. — ²GFE Central Facility for Electron Microscopy, RWTH Aachen University, Mies-van-der-Rohe-Straße 59, 52074 Aachen, Germany. — ³DWI - Leibniz-Institute for Interactive Materials, Forckenbeckstr. 50, 52074 Aachen, Germany

Microgels are an interesting class of soft matter materials with properties depending on their internal structure. Electron and superresolved fluorescence microscopy will be presented as methods to open up the possibility to visualize the core-shell structure of single microgels. In both cases, appropriate labelling conditions had to be chosen to gain sufficient contrast. As the approaches used so far cannot distinguish between different axial (*z*-)position, the obtained images consist of 2D projections of the 3D positions of labels. From these projections, we developed a method to calculate the 3D radial distribution function using appropriate core-shell models established in microgel research.

CPP 8.8 Mon 17:15 H40

CP-AFM Study on elastically switchable core-shell microgel particles with constant adhesion properties — •MAXIMILIAN SEUSS¹, WILLI SCHMOLKE², SEBASTIAN SEIFFERT², and ANDREAS FERY¹ — ¹Leibniz Institute of Polymer Research Dresden, Dresden, Germany — ²Institute of Chemistry and Biochemistry, FU Berlin,

Berlin, Germany

We present a novel class of thermo-responsive core-shell microgel particles. They allow to change their mechanical properties while their adhesive properties remain unaffected. The switching is introduced by a thermo-responsive hydrogel core exhibiting a volume phase transition, e.g. poly(*N*-isopropylacrylamide). Exceeding its lower critical solution temperature, the microgel deswells, densifies, and therefore becomes stiffer. Usually, this process is accompanied by a change in surface chemistry since the microgel switches from hydrophilic to hydrophobic.[1] These effects can be decoupled from each other by encapsulating the microgel in a thermally non-responsive polyacrylamide shell in a droplet-based microfluidics approach.[2] Using colloidal probe AFM, we validated the constant adhesion properties of such core-shell particles between 28 and 40 °C. Further, we have proven that the elastic changes of the core material are preserved attenuatedly in the corresponding core-shell microgel particles.

[1] S. Schmidt, Adv. Funct. Mater. 2010, 20, 3235

[2] S. Seiffert, J. Am. Chem. Soc. 2010, 132, 168

CPP 8.9 Mon 17:30 H40

Microgel ultrafiltration — •RAFAEL ROA¹, JONAS RIEST², and GERHARD NAEGELE² — ¹Helmholtz-Zentrum Berlin, Institute for Soft Matter and Functional Materials, Berlin, Germany — ²Forschungszentrum Juelich, Institute of Complex Systems (ICS-3), Juelich, Germany

Membrane ultrafiltration (UF) is a pressure driven process allowing for the separation and enrichment of protein solutions and dispersions of nanosized microgel particles. The permeate flux and the near-membrane concentration-polarization (CP) layer in this process is determined by advective-diffusive dispersion transport and the interplay of applied and osmotic transmembrane pressure contributions. The UF performance is thus strongly dependent on the membrane properties, the hydrodynamic structure of the Brownian particles, their direct and hydrodynamic interactions, and the boundary conditions. We present a macroscopic description of cross-flow UF of microgels. We analyze the CP layer properties and the permeate flux at different operating conditions. Our results show that the proper specification of the concentration-dependent transport coefficients is important for reliable filtration process predictions. We also show that the solvent permeability of microgels is an essential ingredient to the UF modeling. The particle permeability lowers the particle concentration at the membrane surface, thus increasing the permeate flux.