

CPP 4: Responsive and Adaptive Systems (joint session CPP/DY)

Time: Monday 9:30–12:15

Location: H8

CPP 4.1 Mon 9:30 H8

H₂O / D₂O swelling and exchange kinetics of a multi-stimuli responsive PNIPAM-based block copolymer thin film — ●LUCAS KREUZER¹, TOBIAS WIDMANN¹, NURI HOHN¹, KUN WANG¹, JEAN-FRANCOIS MOULIN², VIET HILDEBRAND³, ANDRÉ LASCHEWSKY³, CHRISTINE M. PAPADAKIS¹, and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching — ²Helmholtz-Zentrum Geesthacht at Heinz Maier-Leibnitz Zentrum, Lichtenbergstr. 1, 85747 Garching — ³Universität Potsdam, Institut für Chemie, Karl-Liebknecht-Straße 24-25, 14476 Potsdam Golm

Stimuli-responsive polymers can react with a drastic change in properties towards even slight changes in their surrounding environment. Especially in thin film morphology, such films are well-suited for a manifold of applications such as nano-switches, artificial muscles in soft-robotics or sensors. In order to implement stimuli-responsive polymers in the aforementioned application fields, a fundamental understanding of the underlying kinetics is necessary. In our recent work, we followed the H₂O and D₂O swelling and the corresponding exchange kinetics in a multi-stimuli responsive block copolymer thin film with in-situ time of flight (TOF) neutron reflectometry (NR). TOF-NR enables high time resolution with which the mechanisms of water uptake and exchange can be followed. A theoretical model is applied to describe the swelling and exchange kinetics in order to obtain detailed insights about the underlying mechanisms of these dynamic processes.

CPP 4.2 Mon 9:45 H8

Morphology of Thermoresponsive Molecular Brushes with Copolymer Side Arms in Aqueous Solution — ●JIA-JHEN KANG¹, JUNPENG ZHAO², HENRICH FRIELINGHAUS³, LESTER BARNESLEY³, FABIAN KOHLER¹, HENDRIK DIETZ¹, STERGIOS PISPAS², and CHRISTINE M. PAPADAKIS¹ — ¹TU München, Physik-Department, Garching, Germany — ²National Hellenic Research Foundation, Theoretical and Physical Chemistry Institute, Athens, Greece — ³FZ Jülich, JCNS at MLZ, Garching, Germany

Poly (ethylene oxide) (PEO) and poly (propylene oxide) (PPO) are known to be thermoresponsive polymers both exhibiting lower critical solution temperature (LCST) behavior, with the cloud points >100 °C and 8 °C, respectively. In the present work, we aim to investigate the LCST behavior of their densely-grafted analogues, namely molecular brushes, which are polymers composed of a polymeric backbone and side arms attached to virtually every monomer of the backbone. Molecular brushes with PEO-ran-PPO and PEO-block-PPO copolymer side arms were studied in aqueous solution using dynamic light scattering (DLS) and small angle neutron scattering (SANS). They display mixed LCST behavior based on the two components, indicating new properties induced by the densely-grafted architecture.

CPP 4.3 Mon 10:00 H8

Formation and growth of mesoglobules in aqueous poly(N-isopropylacrylamide) solutions at low and high pressures revealed with fast pressure jumps — ●BART-JAN NIEBUUR¹, LEONARDO CHIAPPISI², FLORIAN JUNG¹, XIAOHAN ZHANG¹, ALFONS SCHULTE³, and CHRISTINE M. PAPADAKIS¹ — ¹TU München, Physik Department, Physik weicher Materie, Garching, Germany — ²Institut Laue-Langevin, Large Scale Structures Group, Grenoble, France — ³University of Central Florida, Department of Physics and College of Optics and Photonics, Orlando, U.S.A.

Understanding the kinetics of phase separation is of importance for numerous systems. The thermoresponsive polymer poly(N-isopropylacrylamide) (PNIPAM) presents a model system to investigate the kinetics of phase separation. In aqueous solutions at temperatures above the cloud point, PNIPAM forms stable mesoglobules with their size and hydration state depending strongly on pressure [1]. To elucidate the formation and early stage growth of the mesoglobules, we applied time-resolved small-angle neutron scattering after rapid pressure jumps inducing phase separation at low and high pressures. We find that mesoglobule formation includes the formation of small clusters, growth by diffusion-limited coalescence, and the formation of a dense shell, slowing down further coalescence [2]. The strong dehydration at low pressures results in much slower kinetics than at high pressures, where the chains stay more hydrated. [1] B.-J. Niebuur, C.

M. Papadakis et al., *ACS Macro Lett.* 2017, 6, 1180. [2] B.-J. Niebuur, C. M. Papadakis et al., *ACS Macro Lett.* 2018, 7, 1155

CPP 4.4 Mon 10:15 H8

The structural and dynamic behavior of the thermoresponsive polymer Poly(N-isopropylmethacrylamide) — ●CHIA-HSIN KO¹, KORA-LEE CLAUDE¹, DIRK SCHANZENBACH², BART-JAN NIEBUUR¹, HENRICH FRIELINGHAUS³, LESTER BARNESLEY³, VITALY PIPICH³, ALFONS SCHULTE⁴, PETER MÜLLER-BUSCHBAUM¹, ANDRÉ LASCHEWSKY^{2,5}, and CHRISTINE M. PAPADAKIS¹ — ¹TU München, Physik-Department, Garching, Germany — ²Universität Potsdam, Institut für Chemie, Germany — ³FZ Jülich, JCNS at MLZ, Garching, Germany — ⁴University of Central Florida, Department of Physics, Orlando, U.S.A — ⁵Fraunhofer-Institut für Angewandte Polymerforschung, Potsdam-Golm, Germany

Poly(N-isopropylmethacrylamide) (PNIPMAM) is a thermoresponsive polymer, exhibiting lower critical solution temperature (LCST) behavior in aqueous solution. Compared to the well-investigated poly(N-isopropylacrylamide) (PNIPAM), which has similar chemical structure, PNIPMAM has a higher transition temperature (43 °C instead of 32 °C). This may be due to the presence of the additional methyl groups on the vinyl backbone, which cause steric hindrance and weaken the intramolecular interactions. We investigate the temperature- and concentration-dependent phase behavior of PNIPMAM in D₂O using turbidimetry, dynamic light scattering (DLS), small-angle neutron scattering (SANS) and Raman spectroscopy. The main difference from PNIPAM are inhomogeneities in the one-phase state due to physical crosslinks caused by the methyl groups.

CPP 4.5 Mon 10:30 H8

All-in-One 'Schizophrenic' Self-assembly of Orthogonally Tuned Thermo-responsive Diblock Copolymers — NATALYA S. VISHNEVETSKAYA¹, VIET HILDEBRAND², PETER MÜLLER-BUSCHBAUM¹, ANDRÉ LASCHEWSKY^{2,3}, and ●CHRISTINE M. PAPADAKIS¹ — ¹TU München, Physik-Department, Garching, Germany — ²Universität Potsdam, Institut für Chemie, Germany — ³Fraunhofer-Institut für Angewandte Polymerforschung, Potsdam-Golm, Germany

Smart, fully orthogonal switching was realized in a diblock copolymer system with variable trigger-induced aqueous self-assembly [1]. The polymers are composed of non-ionic and zwitterionic blocks featuring lower and upper critical solution temperatures (LCST, UCST). Due to the salt-sensitivity of the zwitterionic block, the UCST can be varied by addition of salt. Superimposed orthogonal switching by electrolytes results in 'schizophrenic' micellization, in which the roles of the core and the shell block are interchanged. The following switching scenarios are observed by turbidimetry and SANS: i) via a molecularly dissolved state at low NaBr concentrations, or (ii) via an insoluble state at high NaBr concentrations. The versatile and tunable self-assembly of such diblock copolymers offers manifold opportunities, e.g. for smart emulsifiers.

1. N. S. Vishnevetskaya et al., *Macromolecules* 51, 2604 (2018)

CPP 4.6 Mon 10:45 H8

PNIPAM microgel-stabilized aqueous foams and foam films — ●MATTHIAS KÜHNHAMMER and REGINE VON KLITZING — Technical University of Darmstadt, Soft Matter at Interfaces, Darmstadt, Germany

Cross-linked, short-chained poly-N-isopropylacrylamide (NIPAM) polymers have been in the focus of numerous studies in the past years and are still being discussed very actively in the context of multiple possible applications, because of their ability to respond to external stimuli like temperature. A prominent example are thermo-responsive emulsions stabilized by microgel particles adsorbed at the water-oil interface. In these systems the emulsion stability can be controlled by changing the temperature.

In this contribution the interfacial activity of PNIPAM microgels is exploited to stabilize aqueous foams. These foams are very stable at temperatures below the volume phase transition temperature (VPTT) of NIPAM and can be destabilized by increasing the temperature above the VPTT. In addition, the relation between the properties of individual microgels (e.g. size, elasticity, particle concentration) and the

properties of foams prepared with them is studied. The properties of foam films are studied with a thin film pressure balance and are related to features of macroscopic foams investigated in drainage experiments and with neutron scattering.

CPP 4.7 Mon 11:00 H8

Reversible surface structuring of photosensitive polymer films: In-situ atomic force microscopy and diffraction efficiency measurements — ●JOACHIM JELKEN, BURKHARD STILLER, CARSTEN HENKEL, and SVETLANA SANTER — Institute of Physics and Astronomy, University of Potsdam, Potsdam, Germany

Here we report on light induced reversible structuring of azobenzene containing polymer films under dynamic changing of local distribution of electrical field vector in interference pattern used for the polymer irradiation. This is achieved utilizing a homemade setup which consists of three parts: a two beam interference setup for topography structuring, an atomic force microscope (AFM) for in-situ recording (during irradiation) of surface morphology [1,2], and a diffraction efficiency (DE) setup which enables to obtain information about the birefringence grating at the same time. Introducing a phase delay between the two interfering beams results in a shift of the whole interference pattern along the sample plane. Depending on the shifting speed the topography grating follows the redistribution of electrical field vector. In this way one can reversible structure and flatten surface topography in controlled manner. Using the measured kinetics of topography and birefringence gratings we aim to further understand the process of surface relief grating formation in azobenzene containing polymer films [3]. [1]S. N. Yadavalli, M. Saphiannikova and S. Santer, *Appl. Phys. Lett.*, 2014, 105, 051601 [2]S. N. Yadavalli and S. Santer, *J. of Appl. Phys.*, 2013, 113, 224304-12 [3]V. Toshchevnikov, J. Illytskyi and M. Saphiannikova, *J. Phys. Chem. Lett.* 2017, 8, 1094

15 min. break

CPP 4.8 Mon 11:30 H8

Modelling of light-induced deformations in side-chain azopolymers — ●BHARTI YADAV, JAN DOMURATH, and MARINA SAPHIANNIKOVA — Leibniz-Institut für Polymerforschung Dresden e. V., Hohe Str. 6, 01069 Dresden

Photopolymers deform in the presence of light, even below the glass transition temperature, because the stress produced by the light is greater than the yield stress [1]. The deformations in the photopolymers are directional i.e. they depend on the polarization of light [2]. For linearly polarized light the deformation is in the direction of the polarization and for circularly polarized light in the plane perpendicular to the propagation vector. These directional deformations are caused by the light-induced orientation potential, which acts on each chromophore attached to the main chain. From the orientation potential one can calculate the light-induced stress in the sample. We model these photopolymers as visco-plastic materials by implementing the light-induced stress using ANSYS, a finite element modelling software. We calculate the strain and elongation as a function of time for both linearly and circularly polarized light.

[1] Toshchevnikov, V. et al. *J. Phys. Chem. Lett.* 8 (2017) p.1094-1098

[2] Kang, H. S. et al. *Adv. Funct. Mater.* 24 (2014) p.7273-7283

CPP 4.9 Mon 11:45 H8

Columnar clusters of three-arm azobenzene stars - MD simulations of a light-induced phase transition — ●MARKUS KOCH¹, MARINA SAPHIANNIKOVA¹, SVETLANA SANTER², and OLGA GUSKOVA¹ — ¹Institute Theory of Polymers, IPF Dresden, Germany — ²Institute of Physics and Astronomy, University of Potsdam, Germany

In this study we investigate star-shaped molecules consisting of a central benzenetricarboxamide (BTA) core and three symmetrically attached azobenzene groups. In aqueous solution these molecules exhibit a distinctive photoresponsive self-assembly behavior. In the absence of light or exposed to blue visible light they form long fibrous structures. When irradiated with UV light the columns disassemble but can be restored after resuming exposure to the initial conditions [1]. This phase transition is a result of the trans-cis photoisomerization of the centrally anchored azobenzene arms. We demonstrate, using DFT and MD simulations, that the solvophilicity of azo stars increases with the number of azo groups present in the cis state [2]. Further on using MD simulations, the stability of the columnar clusters in water is tested, while again varying the amount of trans and cis arms per molecule. Our results indicate that clusters with a large fraction of cis-arms display higher disorder or may even break apart. Lastly, also the kinetics of cluster self-assembly from random initial distributions is studied.

We gratefully acknowledge support from the German Research Foundation (DFG), projects GU 1510/3-1 and SA 1657/13-1.

[1] Lee, S. et al. *Langmuir* 29 (19), 5869 (2013)

[2] Koch, M. et al. *J. Phys. Chem. B* 121, 8854 (2017)

CPP 4.10 Mon 12:00 H8

Dissipative systems with nonlocal delayed feedback — ●JOSUA GRAWITTER, REINIER VAN BUEL, CHRISTIAN SCHAAF, and HOLGER STARK — Institut für Theoretische Physik, Technische Universität Berlin, Berlin, Germany

We present a linear model, which mimics the response of a spatially extended dissipative medium to a distant perturbation and investigate its dynamics under delayed feedback control [Grawitter *et al.*, *New J. Phys.* **20**, 113010 (2018)]. In our model the time it takes a perturbation to travel to the location of measurement is described by an inherent delay time. We investigate the resulting double-delay differential equation using linear stability analysis and numerical integration.

For nonzero delay, linear stability analysis reveals that sufficiently strong feedback destabilizes the system's trivial fixed point. When feedback is bounded by a smooth sigmoid function, the stability-instability transition follows a supercritical Hopf bifurcation and a stable limit cycle occurs. Its frequency and amplitude respond to parameter changes like the dominant eigenvalue of the linearized problem. In particular, they show similar discontinuities along specific lines. These results are largely independent of the chosen sigmoid function and match previous findings on the feedback-induced instability of vortex diffusion in a rotationally driven Newtonian fluid. Because our model captures the essential features of nonlocal delayed feedback in dissipative systems, we consider it a valuable reference case for studies of more complex and spatially extended systems such as photoresponsive fluid interfaces.