

CPP 24: Responsive and Adaptive Systems I

Time: Wednesday 9:30–11:15

Location: H 0110

Invited Talk

CPP 24.1 Wed 9:30 H 0110

Thermoresponsive polymers in aqueous environments: insights by atomistic simulations — ●ESTER CHIESSI — Department of Chemical Science and Technologies, University of Rome Tor Vergata, Via della Ricerca Scientifica I, 00133 Rome, Italy

Atomistic molecular dynamics simulations can reproduce the experimentally observed solution behaviour of thermoresponsive polymers in aqueous environments, accessing hydration features, local conformation and dynamics of the macromolecule, as well as solvent properties. This information contributes to clarify the mechanism of the coil-to-globule, C-G, transition and the influence on this process of polymer stereoregularity and presence of cosolvents/cosolutes, as it will be shown for poly(*N*-isopropylacrylamide), PNIPAM. Then, using PNIPAM as a reference, simulation results on the solution behaviour in water of other amphiphilic polymers will be presented, including a PNIPAM chemical isomer for which the presence of a lower critical solution temperature, LCST, does not imply a C-G transition. The overall picture suggests that the balance between degree of hydrophilicity and conformational aptitudes of the macromolecule determines the occurrence of a thermally-induced coil-to-globule transition and affects the value of the C-G transition temperature in LCST polymer aqueous solutions.

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CPP 24.2 Wed 10:00 H 0110

Soft matter thin films under pressure: a morphological investigation under Grazing Incidence Scattering

— ●APOSTOLOS VAGIAS^{1,2}, THEODORE MANOURAS^{3,4}, ANDREAS BUCHNER¹, PHILIPP GUTFREUND², LIONEL PORCAR², ANDREW NELSON⁵, LEONARDO CHIAPPISI², DAVID P. KOSBAHN⁶, MARCELL WOLF¹, LAURA GUASCO^{7,8}, MARIA VAMVAKAKI^{3,4}, and PETER MÜLLER-BUSCHBAUM^{1,6} — ¹MLZ, TUM, 85748 Garching, Germany — ²Institut Laue Langevin (ILL), 38000 Grenoble, France — ³Institute of Electronic Structure and Laser, Foundation for Research and Technology Hellas, 700 13 Heraklion, Greece — ⁴Department of Materials Science and Technology, University of Crete, 700 13 Heraklion, Greece — ⁵ANSTO, Lucas Heights, NSW 2234, Australia — ⁶TUM School of Natural Sciences, Chair for Functional Materials, 85748 Garching, Germany — ⁷Max-Planck-Institut für Festkörperforschung, D-70569 Stuttgart, Germany — ⁸Max Planck Society Outstation at the MLZ, D-85748 Garching, Germany

Using a custom-designed pressure cell, we tune hydrostatic pressure and combine Grazing Incidence Small Angle Neutron Scattering (GISANS) with specular and off-specular reflectivity under pressure (P) to probe morphologies of soft matter layers immersed in heavy water at $P = 1$ bar and $P = 800$ bar. Our results reveal nanostructural rearrangements upon P-increase for a mixture of strongly segregated (hydrophilic) PDMAEMA and (hydrophobic) POFPPMA homopolymer brushes anchored on Si substrate.

CPP 24.3 Wed 10:15 H 0110

Investigation of the solvent uptake of salt containing PNIPAM thin films — ●JULIJA REITENBACH¹, PEIXI WANG¹, LINUS F. HUBER¹, SIMON A. WEGENER¹, ROBERT CUBITT², DIRK SCHANZENBACH³, ANDRÉ LASCHEWSKY³, CHRISTINE M. PAPADAKIS⁴, and PETER MÜLLER-BUSCHBAUM¹ — ¹TUM School of Natural Sciences, Chair for Functional Materials, Garching, Germany — ²Institut Laue-Langevin, 71 Avenue des Martyrs, CS 20156, 38042 Grenoble Cedex 9, France — ³Universität Potsdam, Institut für Chemie, Karl-Liebknecht-Str. 24-25, 14476 Potsdam-Golm — ⁴TUM School of Natural Sciences, Soft Matter Physics Group, Garching, Germany

Stimuli responsive polymers gained a lot of attention in the past decades due to their unique properties. If polymer thin films exhibit a reversible volume change upon exposure to external stimuli such as temperature, light, pH, or solvents, they become promising candidates for applications such as nanoswitches or sensors. Due to short swelling times and strong volume changes upon solvent incorporation poly(*N*-isopropyl methacrylamide) (PNIPMAM) thin films are of special interest. In this work, the influence of different salts on

the responsiveness of PNIPMAM thin films towards different solvent vapor atmospheres is explored. In situ time-of-flight neutron reflectometry measurements are performed to investigate the macroscopic swelling behavior. To gain further insights on a molecular level and to understand the underlying hydration mechanism, additional in situ Fourier-transform infrared spectroscopy measurements are performed.

CPP 24.4 Wed 10:30 H 0110

Vibrational Spectroscopy of Perdeuterated Poly(*N*-isopropylacrylamide) Solutions and Hydration Changes Across the Demixing-Transition — ●ALFONS SCHULTE¹,

NICOLAS HARMS¹, ERIC RENDE¹, DHARANI MULLAPUDI¹, ALEC NIETH¹, CHRISTOPHER BENNETT¹, DIRK SCHANZENBACH², ANDRÉ LASCHEWSKY^{2,3}, and CHRISTINE M. PAPADAKIS⁴ — ¹Physics Department, University of Central Florida, Orlando, USA — ²Universität Potsdam, Institut für Chemie, Potsdam-Golm — ³Fraunhofer-Institut für Angewandte Polymerforschung, Potsdam-Golm — ⁴TUM School of Natural Sciences, TU Munich, Garching

We investigate concentrated aqueous solutions of perdeuterated poly(*N*-isopropylacrylamide) (PNIPAM-d10) employing Raman scattering and infrared absorption spectroscopy. In comparison to PNIPAM the cloud point temperature increases by several degrees in PNIPAM-d10. In the Raman and infrared spectra four C-D bands are discernible due to stretching vibrations of the alkyl groups. These are analogous to the C-H bands in hydrogenated PNIPAM, however they are shifted to lower frequencies by a factor of 1.4 as expected for the isotope effect. With increasing temperature we observe abrupt red-shifts of the peak frequencies of the C-D bands near 36 C at the demixing transition which are attributed to dehydration of the polymer chains at their coil-to-globule transition.

CPP 24.5 Wed 10:45 H 0110

Dynamic Light Scattering for Characterization of PNIPAM Microgels Subjected to Ultrasound — SEBASTIAN STOCK, LEILA SAHEBMOHAMMADI, REGINE VON KLITZING, and ●AMIN RAHIMZADEH — Soft Matter at Interfaces, Technical University of Darmstadt, Darmstadt, Germany

Dynamic Light Scattering (DLS) is a widely employed technique for characterizing particles and molecules in solutions/dispersions, offering insights into their size, size distribution, and conformational changes. This study leverages DLS to explore the ultrasound-induced Volume Phase Transition (VPT) of poly(*N*-isopropylacrylamide) (PNIPAM) microgels. By innovatively integrating ultrasound with a conventional DLS system, we conducted experiments to characterize compact silica particles and microgels under ultrasound influence. Essential parameters, including particle size, frequency, and amplitude of particle vibration, were successfully extracted through analysis of the correlation function of the scattered light intensity. Notably, studies involving non-responsive silica particles demonstrated that ultrasound did not compromise size determination, establishing them as suitable reference systems. Our findings reveal the acousto-responsive nature of PNIPAM microgels, showcasing their ability to undergo VPT over the time of actuation. Microgels exposed to ultrasound exhibit comparable swelling/shrinking behavior to that induced by temperature, albeit with markedly accelerated kinetics. The outcomes of this investigation hold promise for diverse industrial and biomedical applications.

CPP 24.6 Wed 11:00 H 0110

Effect of pressure on the micellar structure of PMMA-*b*-PNIPAM in a water/methanol mixture — ●PABLO A. ÁLVAREZ HERRERA¹, FEIFEI ZHENG¹, PEIRAN ZHANG¹, JULIJA REITENBACH¹, HEINZ AMENITSCH², PETER MÜLLER-BUSCHBAUM¹, CRISTIANE HENSCHEL³, ANDRÉ LASCHEWSKY³, and CHRISTINE M. PAPADAKIS¹ — ¹TU Munich, TUM School of Natural Sciences, Garching, Germany — ²Elettra Sincrotrone, Trieste, Italy — ³Universität Potsdam, Institut für Chemie, Potsdam-Golm, Germany

In pure water, amphiphilic block copolymers consisting of a permanently hydrophobic poly(methyl methacrylate) (PMMA) and a thermoresponsive poly(*N*-isopropyl acrylamide) (PNIPAM) block form core-shell micelles. At atmospheric pressure, the solubility of the micellar shell can be altered by changing the temperature or by adding a water-miscible co-solvent. Here, we study the effect of pressure on

the phase behavior and micellar structure of PMMA₂₁-*b*-PNIPAM₂₈₃ in a 90:10 v/v D₂O/CD₃OD mixture in a pressure range between 10 and 250 MPa. Turbidimetry shows that adding methanol to PMMA-*b*-PNIPAM in D₂O shifts the maximum of the coexistence line to a higher pressure and temperature. Small-angle X-ray scattering reveals the temperature- and pressure-dependence of the core size, shell thick-

ness, shell solvation, micellar correlation, and aggregation behavior of PMMA-*b*-PNIPAM in a water-methanol mixture. We find that adding methanol increases the mobility of the chains forming the micellar core. Also, the degree of solvation and the thickness of the micellar shell feature a maximum at a pressure of around 100 MPa.