CPP 31: Responsive and Adaptive Polymers

Time: Wednesday 16:15–18:00 Location: H38

Invited Talk CPP 31.1 Wed 16:15 H38

Moving with minimum effort – Optimal work protocols for systems with memory — •Sarah Loos[1], Samuel Monter[2], Felix Ginot[2], and Clemens Bechinger[2] — [1]DAMTP, University of Cambridge, UK — [2]University of Konstanz

Energy optimization is crucial in engineering and may also govern nonequilibrium processes in chemical and biological systems. Finding optimal solutions for microscale processes–dominated by thermal or nonthermal fluctuations and often displaying memory effects arising from internal degrees of freedom or coupling to viscoelastic environments–posses additional challenges, necessitating general guiding principles. We demonstrate such a general principle for the fundamental problem of dragging a harmonic trap containing a single particle over a finite distance within a given time while minimizing work input. We show that the optimal dragging protocol and the corresponding mean particle trajectory both exhibit time-reversal symmetry, which is a universal and exclusive feature of the optimal solutions. The symmetry principle holds across all media described by a linear generalized Langevin equation, irrespective of the memory kernel or noise properties, including glassy, granular, and active media. For intrinsically driven systems, such as active particles, we show that the optimal protocols remain identical to those for passive systems, but work fluctuations are always increased [2]. [1] S.A.M. Loos, S. Monter, F. Ginot, and C. Bechinger, Phys. Rev. X 14, 021032 (2024). [2] R. Garcia-Millan, J. Schüttler, M.E. Cates, and S.A.M. Loos, ArXiv:2407.18542 (2024).

CPP 31.2 Wed 16:45 H38

Influence of Azobenzene Moieties on the Swelling Behavior of Poly(Dimethylacrylamide) Films in Water Vapor under UV-Irradiation — •David P. Kosbahn[1], Julija Reitenbach[1], Morgan P. Le Dû[1], Lukas V. Spanier[1], René Steinbrecher[2,3], André Laschewsky[2,3], Robert Cubitt[4], and Peter Müller-Buschbaum[1] — [1]TUM School of Natural Sciences, Chair for Functional Materials, 85748 Garching, Germany — [2]Institut für Chemie, Universität Potsdam, 14476 Potsdam-Golm, Germany — [3]Fraunhofer Institut für Angewandte Polymerforschung, 14476 Potsdam-Golm, Germany — [4]Institut Laue-Langevin, 38000 Grenoble, France

This study investigates the swelling behavior of p(AzAm-co-DMAm) films in both isomeric states of the photoswitchable molecule azobenzene (Az). The impact of UV irradiation on swelling in water vapor is examined, with the aim of controlling water uptake, expansion, and nanoscale morphology. This material shows potential for applications in light sensors, photo-actuators, and drug delivery systems. We employ time-resolved FTIR spectroscopy to monitor group vibrations during swelling and irradiation, gaining insights into molecular interactions throughout the isomerization process. Additionally, in situ time-of-flight neutron reflectometry on a thin film provides time- and depth-resolved data on the water distribution along the surface normal. The results shed light on the influence of azobenzene moieties on the polymer's microscopic properties.

CPP 31.3 Wed 17:00 H38

Critical analysis of adhesion work measurements from AFM-based techniques for soft contact — Dmitrii Sychev[1,2], Simon Schubotz[1,2], Quinn A. Besford[1], Andreas Fery[1,3], and •Günter K. Auernhammer[1] — [1]Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany — [2]TU Dresden, Germany — [3]Chair of Physical Chemistry of Polymeric Materials,TU Dresden, Germany

The work of adhesion is a thermodynamic quantity that is frequently measured by atomic force microscopy (AFM). Its determination requires quasi-equilibrium measurements. Here, we address the question of to what extent atomic force microscopy qualifies for quasi-equilibrium measurements. To measure the work of adhesion, we combined soft colloidal probe AFM (SCP AFM) with reflection interference contrast microscopy (RICM). We extract the work of adhesion either from the pull-off force or from the contact radius to measure the adhesion behavior of poly(N-isopropylacrylamide) (PNIPAM) polymer brushes in the swollen and solvent-induced collapsed state. In the swollen state, the adhesion to the PNIPAM brush was fivefold larger and exhibited significant time dependencies when measured with SCP AFM. A strong rate dependence of the pull-off force method was indicative of a non-equilibrium process. In order to reliably determine the equilibrium work of adhesion, the contact radius method was found to be the better because it is not rate dependent. In summary, using optical measurements to determine the contact radius is beneficial when deriving the works of adhesion between colloidal probes and polymer brush surfaces.

CPP 31.4 Wed 17:15 H38

Chain conformation of thermo- and photo-responsive polymers — •Peiran Zhang[1], René Steinbrecher[2], Cy M. Jeffries[3], André Laschewsky[2], Peter Müller-Buschbaum[1], and Christine M. Papadakis[1] — [1]TUM School of Natural Sciences, Technical University of Munich, Garching, Germany — [2]Institute of Chemistry, University of Potsdam, Potsdam-Golm, Germany — [3]European Molecular Biology Laboratory, DESY, Hamburg, Germany

Endowing thermoresponsive polymers with additional photoresponsivity is of interest for applications such as drug delivery and soft robotics, owing to the non-invasive nature of these stimuli and the high temporal and local resolution of the photostimulus. The lower critical solution temperature (LCST) behavior in aqueous solution, characterized by a coil-to-globule transition at the cloud point (CP), can be finely tuned by incorporating photoswitches. Among these, azobenzene (AB) is the most widely used due to its pronounced trans-cis isomerization without side reactions. However, due to the weak change of dipole moment, its influence on the CP is only small. To enhance this photo effect, we used various amino acids as flexible linkers between the thermoresponsive backbone and the AB moiety. Dynamic light scattering reveals that a higher AB content leads to a larger shift of the CP, while small-angle X-ray scattering indicates that the amino acid linker reduces the influence of the inherent rigidity of the AB side groups, making the entire polymer chain more flexible. This approach allows adjusting the CP in wide ranges of temperature, thereby enhancing the range of applications.

CPP 31.5 Wed 17:30 H38

Acoustic levitation for dynamic studies of poly(N-isopropylacrylamide) microgels at the air-water interface — •Atieh Razavi[1], Regine von Klitzing[1], Romain Bordes[2], and Amin Rahimzadeh[1] — [1]Soft Matter at Interfaces, Institute for condensed Matter Physics, Technical University of Darmstadt, Hochschulstraße 8, 64289 Darmstadt, Germany — [2]Applied Surface Chemistry, Chalmers University of Technology, Gothenburg, Sweden

Acoustic levitation provides a unique platform for studying the surface dynamics of an air-water interface covered with poly(N-isopropylacrylamide) (PNIPAM) microgels. By utilizing standing acoustic waves, droplets are trapped at nodal positions, creating a contact-free environment to examine the effects of microgel stiffness, droplet evaporation, and amplitude modulation on droplet deformation. The research focuses on quantifying the aspect ratio (AR) of levitated droplets as a function of frequency of amplitude modulation, microgel concentration, and cross-linker content over time. In addition, we modulate the amplitude of the acoustic pressure at different frequencies (0.005 Hz0 to 05 Hz) to get insight into the interfacial rheology. With this new method, we can qualitatively characterize the interfacial behavior of microgels at the air-water interface such as the elastic modulus of the interface and adsorption kinetics[1].

CPP 31.6 Wed 17:45 H38

Structure and dynamics in injectable hydrogels from thermoresponsive triblock terpolymers — •Feifei Zheng[1], Pablo A. Álvarez Herrera[1], Wenqi Xu[1], Joachim Kohlbrecher[2], Sohila Abdelhafiz[3], Anna P. Constantinou[4], Theoni Georgiou[4], Aristide Dogariu[3], and Christine M. Papadakis[1] — [1]Technical University of Munich, TUM School of Natural Sciences, Garching, Germany — [2]Paul Scherrer Institut, Villigen, Switzerland — [3]CREOL, University of Central Florida, Orlando, USA — [4]Imperial College London, Department of Materials, London, UK

Block copolymers with blocks featuring lower critical solution temperature behaviour have attracted great interest for 3D bioprinting because they form a runny solution at room temperature, but a hydrogel at body temperature. The structure of the solution and the hydrogel as well as dynamic information and their changes upon gelation are essential for understanding. Here we address an ABC triblock terpolymer consisting of a hydrophilic A block, a hydrophobic B, and a thermoresponsive C block. The results from small-angle neutron scattering on 15 wt% polymer solutions indicate that ABC form spherical core-shell micelles, that transform into cylinders in the gel state and form a more compact structure upon heating. By the combination of dynamic light scattering (DLS) and spatiotemporal coherence-gated DLS measurements, the dynamic information of gelation process was retrieved, which reveals the thermoresponsive C block contracts and the micelles aggregate to from the gel upon heating.