CPP 51: Charged Soft Matter II

Time: Thursday 15:00–17:00 Location: ZEU 118

CPP 51.1 Thu 15:00 ZEU 118

Temperature-driven structural and morphological changes in multicompartment responsive films — •Samantha Micciulla and Regine von Klitzing — Tu Berlin

Responsive coatings are promising candidates to create switchable hydrophilic/hydrophobic surfaces, substrates for cell proliferation/detachment or highly selective uptake/release matrices and still preserve macroscopic properties of the substrate. Polymers are very suitable for this purpose, since many systems can be prepared through simple and well established synthetic routes by varying functionalities and constituent materials. In order to design multifunctional systems, more complex coatings are required. Therefore very recently the combination of grafted and physisorbed polymers has been proposed. Despite structure and properties of each single constituent are known, mutual effects could strongly alter them, hence systematic investigations are required. The mentioned aspects were investigated on a multicompartment matrix made of a thermoresponsive P(NIPAM-b-DMAEMA) block copolymer grafted from silica substrate. After quaternization to convert the methacrylate from weak to strong polyelectrolyte, the film is capped with PSS/PDADMAC polyelectrolyte multilayers by dipping. Ellipsometry measurements in water were carried out to monitor the temperature-induced phase transition of the matrix, while Atomic Force Microscopy was used to detect the morphogical changes. Finally, the coating of such polymer films by aluminium oxide revealed some fundamental rules governing the interaction between organic and inorganic materials.

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LCST phase behavior in protein solutions — •Michal Braun[1], Marcell Wolf[1], Felix Roosen-Runge[1], Fajun Zhang[1], Roland Roth[2], and Frank Schreiber[1] — [1]Institut für Angewandte Physik - Universität Tübingen, Auf der Morgenstelle 10, 72076 Tübingen — [2]Institute for Theoretical Physics - Universität Tübingen, Auf der Morgenstelle 14, 72076 Tübingen

The phase behavior of BSA and HSA (bovine and human serum albumin) solutions containing yttrium (Y^{3+}) is investigated. For both proteins, a phase diagram in dependence of protein and salt concentration (c_p and c_s) at room temperature has been established ([1], [2]). In a certain regime, the solutions are turbid which is either due to aggregation or liquid-liquid phase separation (LLPS). The 3-D shape of the LLPS binodal for BSA depending on c_p, c_s and temperature T has been measured. A lower critical solution temperature (LCST) phase behavior has been observed. Dynamic and static light scattering measurements are currently performed in order to monitor the diffusion coefficient as well as the static correlation length while the system approaches the binodal. The molecular mechanisms behind this behavior will be investigated in the future, considering the competing effects of ion bridging and hydration.

[1] F. Zhang et al., Phys. Rev. Lett. 101 (2008) 148101.

[2] F. Zhang et al., Soft Matter 8 (2012) 1313.

CPP 51.3 Thu 15:30 ZEU 118

Influence of Polycation Molecular Weight on Interdiffusion in Polyelectrolyte Mulitlayers — •Peter Nestler[1], Malte Passvogel[1], Olaf Soltwedel[2], Ralf Köhler[3], and Christiane A. Helm[1] — [1]Inst. f. Physik, Uni Greifswald, 17487 Greifswald, Germany — [2]MPI für Festkörperforschung, 70569 Stuttgart, Germany — [3]Inst. of Soft Matter and Functional Materials, HZB, Berlin, Germany

For the past twenty years, the Layer-by-Layer technique (LbL) has made it possible to modify surfaces by covering them with thin films. A wide variety of potential applications for polyelectrolyte multilayers (PEM) are demonstrated, for example chemical reactors, antireflective coatings or microcontainers. For all these applications, it is important to control thickness, structure and internal diffusion of the film under different external conditions.

PEMs are made from poly(diallyldimethylammonium) (PDADMA), poly(styrenesulfonate) (PSS), and deuterated PSS-d. Each film consists of a protonated and a deuterated compartment. The films are annealed in 1 M NaCl and investigated with neutron reflectivity. During annealing the internal interface between both departments broadens due to interdiffusion.

The PSS interdiffusion constant depends non-monotonically on the PDADMA molecular weight, a maximum is observed at 45 kDa, then it decreases by a factor of 3000. The results suggest that PSS and PDADMA move as a complex. Variation of the position of the internal interface as well as the nature of the top layer give insights into the charge distribution within the multilayer films.

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Rotational Dynamics of Polyelectrolyte Chain Segments Studied by Spin-Label EPR Spectroscopy — •Uwe Lappan, Brigitte Wiesner, and Ulrich Scheler — Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany

The complex coacervation of oppositely charged polyelectrolytes has been studied by EPR spectroscopy. The spin-label technique employs stable radicals which are covalently attached to diamagnetic macromolecules. Rotational dynamics of such spin labels on time scales between 10 ps and 1 μs can be characterized by basic and fast CW EPR spectroscopy. The dynamics of the spin labels is influenced by the restricted motion of the side group bearing the label and local polymer backbone motions at the point of the covalent attachment of the label. A spin-labeled poly(ethylene-alt-maleic acid) with less than 5 mol-% of spin-labeled repeat units has been prepared. The segmental rotational mobility of the spin-labeled polyanion and the internal rotation of the spin label have been determined simulating the line shapes of the experimental EPR spectra. The complex formation of this weak polyanion with the strong polycation poly(diallyldimethylammonium chloride) has been studied as a function of mixing ratio and pH of the solution. If the spin-labeled polyanion is the excess component, the spectrum of a slow-motion component is superimposed by the spectrum of a fast-motion component. In the opposite case, the spectra are dominated by a slow-motion component.

CPP 51.5 Thu 16:00 ZEU 118

Ion friction causes current blockades in DNA translocation experiments — •Stefan Kesselheim and Christian Holm — Institute for Computational Physics, University of Stuttgart, Germany

We investigate the motion of potassium ions and water molecules parallel to the surface of a double stranded DNA molecule under an applied electric field by means of all-atom simulations. Overall we find, that it is described surprisingly well by a simple charged-cylinder model and the electrokinetic equations. The atomistic model, however, exhibits a significant reduction of the ion mobility close to the surface of the DNA, which we interpret as a microscopic friction effect, that is also mediated by the water.

In nanopore experiments the ion current is the main observable. Its modulation by the presence of macromolecules, such as DNA, can be used to infer information about the molecule. Our simulations indicate that the current reduction observed in most experiments is caused by the ion surface friction effect. Our model predicts the crossover electrolyte concentration between current reduction and current enhancement in agreement with experiments.

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The Hubbard-Onsager dielectric decrement — •Marcello Sega[1], Sofia Kantorovich[1], Christian Holm[2], and Axel Arnold[2] — [1]University of Vienna, Austria — [2]Institute for Computational Physics, Universität Stuttgart, Allmandring 3 70569 Stuttgart Germany

In 1977, Hubbard and Onsager predicted that upon addition of salt to water, the latter should be partly depolarized by an external electric field, resulting in a decrement of the static dielectric permittivity, even though the effect is purely kinetic. This kinetic decrement has never been observed directly, because of the presence of dielectric saturation. Here, we use out-of-equilibrium molecular dynamics simulations to show directly the existence of the kinetic decrement. We show that the kinetic decrement can account to about 10% of the static dielectric permittivity in a NaCl aqueous solution. We compare the simulation results with available theoretical approaches.

CPP 51.7 Thu 16:30 ZEU 118

The Effects of Reactive Oxygen Species on Single Polycation Layers — •Florian Berg[1], Steffen Drache[1], Stephan Block[2], Reiner Hippler[1], and Christiane A. Helm[1] — [1]Inst. f. Physik,

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During times of environmental stress (e.g., UV or heat exposure), levels of reactive oxygen species (ROS) can increase dramatically, causing cell damage. Here, the effects of the molecular changes of a polyelectrolyte functionalized surface are investigated.

Positively charged, branched polyethylenimine (PEI) adsorbed onto silicon wafers is attacked by free hydroxyl radicals. With AFM Colloid Probe technique, the surface forces between the PEI layers are measured. The force profiles show that freshly deposited PEI layers are flat, i.e., electrostatic repulsion dominates the interaction. After radical attack both surface potential and surface charge density are reduced by a factor of about two, while the Debye length remains unchanged. Force volume measurements show a homogeneous distribution of the surface charge on the μm scale. To probe the nm-scale, negatively charged gold nanoparticles (NP) are adsorbed. After radical attack we find a 10 % decrease of saturation coverage consistent with the decreased surface charge density if the electrostatic three-body interaction is considered. Nevertheless, the NP adsorption kinetics is slowed down suggesting that radical attacks induce inhomogeneities on the nm-scale.

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Solvation and ion condensation properties for sulfonated polyelectrolytes in different solvents — •Jens Smiatek[1], Andreas Wohlfarth[2], and Christian Holm[1] — [1]Institut für Computerphysik, Universität Stuttgart, Deutschland — [2]Max Planck-Institut für Festkörperforschung, Stuttgart, Deutschland

In contrast to the broad knowledge about aqueous polyelectrolyte solutions, less is known about the properties in aprotic and apolar solvents. We therefore investigate the behavior of sulfonated polyelectrolytes in sodium form in presence of different solvents via all-atom Molecular Dynamics simulations. The results clearly reveal strong variations of ion condensation constants and polyelectrolyte conformations for different solvents like water, dimethyl sulfoxide (DMSO) and chloroform. The binding free energies of solvent contacts with the polyelectrolyte groups validate the influence of different solvent qualities. With regard to the ion condensation behavior, the numerical findings show that the explicit values for the condensation constants depend on the preferential binding coefficient as derived by the evaluation of Kirkwood-Buff integrals. Surprisingly, the smallest ion condensation constant is observed for DMSO compared to water, whereas in the presence of chloroform, virtually no free ions are present.