CPP 41: Charged Soft Matter, Polyelectrolytes and Ionic Liquids I

Time: Friday 9:30–11:15 Location: H38

Invited Talk CPP 41.1 Fri 9:30 H38

Simulations of reaction equilibria in macromolecular systems — •Peter Košovan — Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Prague, Czechia

Most molecular simulations are performed assuming a fixed chemical composition, focusing on structural and conformational changes and intermolecular interactions, while neglecting the possible chemical changes which may occur simultaneously. In this lecture, we present an overview of our modeling work, addressing how reversible chemical reactions affect the properties of macromolecular solutions and gels. In particular, we discuss the effect of acid-base equilibria on the net charge of peptides, synthetic polyelectrolytes, polyelectrolyte hydrogels, and proteins. By comparing with experiments, we show that our models can quantitatively predict how this net charge depends on pH of the solution. Next, we show that a change in the pH can trigger attraction between macromolecules, resulting in the formation of condensates, precipitation or gelation. Finally, we show how changes in the pH can be used to control the uptake of charged proteins into coacervates, and how the pH affects the properties of protein solutions during purification processes used by the pharmaceutical industry: dialysis and ultra- or dia-filtration.

CPP 41.2 Fri 10:00 H38

Surface Charged Polymeric Micelles - A Tunable Model System Studied by SANS — Lingsam Tea[1], Luis Willner[1], Christin Waldorf[1], Olga Matsarskaia[2], Ralf Schweins[2], Stephan Förster[1], Lutz Willner[1], and •Jörg Stellbrink[1] — [1]JCNS-1, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany — [2]Institut Laue-Langevin, 38042 CEDEX 9 Grenoble, France

We investigate surface charged micelles in aqueous solution formed by carboxy terminated n-octacosyl-poly(ethylene oxide) block copolymers, C-PEO5-COOH with 5 the PEO molar mass in kg/mol, by small angle neutron scattering (SANS), zeta-potential measurements and rheology. The -COOH end group was introduced by selective oxidation of the CH_3OH end group of a C-PEO5-OH precursor using Bobbitt's salt. Micellar solutions of different concentrations in the dilute and semidilute range were investigated at pH 2, 6 and 12 to vary ionic strength and the number of effective surface charges Z. Z was further varied by using mixtures of C-PEO5-COOH and C-PEO5-OH at different mixing ratios. SANS measurements reveal that the intramicellar form factor is identical at the different pH-values which implies that the individual micellar structure is unaffected by the number of surface charges. On the contrary, the intermicellar structure factor and the phase behavior show a strong dependence on Z. In particular, we observe a distinct shift of the liquid - fcc crystal phase boundary. A quantitative analysis in terms of a screened Hard Sphere Yukawa potential reveals a very good agreement between experiment and theory.

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Orientation analysis in polyelectrolyte multilayer and brush coatings by dichroic ATR-FTIR spectroscopy — •Martin Müller, Mirjam Hofmaier, Patricia Flemming, Olga Guskova, Alexander Münch, and Petra Uhlmann — Leibniz-Institut für Polymerforschung Dresden e.V.

Dichroic ATR-FTIR spectroscopic data on two types of thin oriented polyelectrolyte (PEL) coatings relevant for life science are presented. Trapezoidal silicon multiple internal reflection elements, sealed in-situ cell in ATR mirror attachment with polarizer and commercial FTIR spectrometer were used. (i) At first dichroic ATR-FTIR data on thin PEL multilayer (PEM) coatings composed of a-helical poly(L-lysine) and various polyanions (PLL/PA) at unidirectionally texturized silicon substrates are presented. Based on experimental dichroic ratios RATR, the known angles theta between transition dipole moment (TDM) of Amide I and Amide II vibration and a-helix axis (38°, 73°) and on calculated electrical field components Ex,y,z high in-plane y-axial orientation of PEM was identified. (ii) Secondly, thin cationic PEL brushes with three different grafting densities at silicon substrates were characterized by dichroic ATR-FTIR. Using concept of (i) and angle theta between TDM of n(C=O) vibration of PDMAEMA and molecular main axis (69°), which was determined by atomistic simulations, high out-of-plane z-axial orientation was identified. Swelling in water increased the orientation if compared to dry state. Both PEL coating types may be used as bioactive platforms towards proteins and microorganisms.

CPP 41.4 Fri 10:30 H38

Vertical Polyelectrolyte and Site Diffusion of PSS in PSS/PDADMA Multilayers — Annekatrin Sill, •Per-Ole Hilken, and Christiane A. Helm — Institute of Physics, University of Greifswald, Germany

The spontaneous formation of polyelectrolyte multilayers or polyelectrolyte complexes depends on the (inter)diffusion of polyelectrolytes. We investigate the transport of extrinsic sites - charged polyelectrolyte repeat units balanced by counterions - and their relationship to polymer diffusion. We determine the vertical diffusion coefficient D_{PSS} of polystyrene sulfonate (PSS) repeat units in polyelectrolyte multilayer films from poly (diallyldimethylammonium) (PDADMA) and PSS using a quartz crystal microbalance with dissipation (QCM-D) and analyze the observed film growth. Varying the NaCl concentration c_{NaCl} results in $D_{PSS} = 3.2 \cdot 10^{-20}\ \mathrm{m}^2/\mathrm{s} \cdot e^{\alpha \cdot c_{NaCl}}$. As known from the free volume model, the prefactor is constant for each system. For site diffusion, the exponent is also constant ($\alpha \approx 4.9\ \mathrm{M}^{-1}$). For polymer diffusion, however, α increases linearly with M_{PSS}, the molecular weight of PSS. The results for site diffusion quantitatively agree with those of Fares and Schlenoff (JACS (2017) 139; 14656). Polymer diffusion occurs when $M_{PSS} < 65\,\mathrm{kDa}$ (for $M_{PDADMA} = 117\,\mathrm{kDa}$). For these low PSS molecular weights, the diffusion coefficient is $D_{PSS} = B \cdot M_{PSS}^{-\gamma}$. The dependence of B on c_{NaCl} is a power law, while γ increases linearly with c_{NaCl}.

CPP 41.5 Fri 10:45 H38

Understanding the Mechanisms of pH-Sensitive Collapse of Hydrophobic Polymers — •Varun Mandalaparthy and Nico F. A. van der Vegt — Technical University, Darmstadt

The hydrophobic effect is a important contributor to the stability of proteins and may be influenced by many factors including the pH of the solution. To simplify the study of pH effects on proteins, we parameterize biologically motivated titratable monomers which we insert into the sequence of a hydrophobic polymer and study via constant pH molecular dynamics (MD) simulations. We calculate the potential of mean force of the polymer at different pH values and observe that the collapsed state of the polymer is destabilized when the titratable monomer is more charged (high pH for an acid and low pH for a base). Further, the extent of the destabilization is influenced by the position of the titratable monomer along the polymer sequence. The $\mathrm{p}K_\mathrm{a}$ value of the titratable monomer is also observed to be sensitive to polymer conformation, in agreement with studies of proteins. We further study a zwitterionic polymer with an acidic and a basic monomer in the same sequence which presents a pH-dependent hairpin formation. Our model provides a simplified yet powerful framework to study pH effects on the hydrophobic effect, providing insights into mechanisms governing the behavior of intrinsically disordered proteins (IDPs) and pH-sensitive drug delivery, among other applications.

CPP 41.6 Fri 11:00 H38

Machine learning potentials for redox chemistry in solution — •Redouan El Haouari[1,2], Emir Kocer[1,2], and Jörg Behler[1,2] — [1]Theoretische Chemie II, Ruhr-Universität Bochum, Germany — [2]Research Center Chemical Sciences and Sustainability, Research Alliance Ruhr, Germany

Machine-Learning Potentials (MLPs), which can offer the accuracy of quantum mechanics at a fraction of the costs, have been applied with great success in atomistic simulations of many systems. Still, most MLPs rely on environment-dependent atomic energies, and are thus unable to distinguish different oxidation states of simple ions in solution. Here, we show for the example of ferrous (Fe2+) and ferric (Fe3+) chloride in aqueous solution that this limitation can be overcome with 4th-Generation High-Dimensional Neural Network Potentials (4G-HDNNPs), in which the local atomic energies are complemented with global charges from a charge equilibration scheme. We find that the iron oxidation states match the total number of chloride ions in the system irrespective of their positions. Furthermore, the model captures charge transfers between ferrous and ferric ions, enabling the general simulation of redox chemistry in solution involving different oxidation states.