CPP 44: Charged Soft Matter I

Time: Thursday 9:30–12:30 Location: ZEU 118

CPP 44.1 Thu 9:30 ZEU 118

Absorption of a charged polymer star by an oppositely charged polyelectrolyte brush — •Majid Farzin[1,2], Torsten Kreer[1], and Jens-Uwe Sommer[1,2] — [1]Leibniz institute for polymer research dresden — [2]Technical University of Dresden

By means of molecular dynamics simulations, we investigate the interactions between a polyelectrolyte brush and an oppositely charged polymer star. We explicitly include counterions and vary the strength of Coulomb interactions in two fashions; by varying the Bjerrum length of fully charged polymers and by changing the charge fraction of grafted chains for the Bjerrum length close to that of water. The simulations show that there is a critical Bjerrum length below which the polymer star is located outside the brush. For larger values of the Bjerrum length, the polymer star is absorbed by the brush. In the case of charge fraction variation, the polymer star is absorbed by the brush at all charge fractions. Also, we observe that, in the vicinity of the critical Bjerrum length or for small charge fractions, the shape of the polymer star is pancake-like.

CPP 44.2 Thu 9:45 ZEU 118

Inhomogeneous swelling of Polyelectrolyte Multilayers in water — •Maximilian Zerball[1], Ralf Köhler[2], and Regine von Klitzing[1] — [1]Institut für Chemie - Stranski-Laboratorium, Technische Universität Berlin, Str. 17.Juni 124, 10623 Berlin — [2]Institut für Weiche Materie und funktionelle Materialien, Helmholtz-Zentrum Berlin, Hahn - Meitner-Platz 1, 14109 Berlin

Polyelectrolyte Multilayer (PEM) are organic films built up via subsequent adsorption of oppositely charged polyions. They are interesting materials for nanofabrication and fundamental science due to the possible and precise tunability of there physico-chemical properties, as thickness roughness, or adsorption of molecules and particles. PEM are highly sensitive to external parameter like the relative humidity (RH) of the ambient atmosphere. Increase of RH causes water uptake and swelling, accompanied with changes of the permeability for water. In order to use these films as sensors of for optical devices it is important to understand and to control the swelling mechanism. Neutron Reflectometry (NR) is an excellent tool to investigate the inner structure of PEMs. The usage of PEMs consisting of two different blocks, a deuterated block and a protonated block creates an additional surface inside the PEM which is detectable for NR and allows detecting an inner and an outer part of the sample, but with chemically identical composition. The results show an inhomogeneous swelling across the PEM.

CPP 44.3 Thu 10:00 ZEU 118

Adsorption Behavior of Catanionic Surfactant Mixtures at the Air-Water Interface and in Freestanding Foam Films — •Heiko Fauser, Martin Uhlig, and Regine von Klitzing — Technische Universität Berlin, Stranski-Laboratorium Institut für Chemie, Straße des 17. Juni 124, 10623 Berlin

Although the application of liquid foams is widespread, too little is yet understood about their stability control. One way to tune liquid foam films is the use of oppositely charged surfactant mixtures. Due to electrostatic attraction highly surface active aggregates are formed. Our study addresses the question of whether the adsorption of equimolar or irregular catanionic complexes and thus a variation in surface composition governs foam film properties.

Mixtures of the anionic surfactant SDS with the cationic C12TAB are investigated. We compare the adsorption behavior at liquid/air interfaces and in freestanding foam films at different total concentrations and varying mixing ratio.

Surface tension measurements reveal a high surface activity for these mixtures already at very low concentrations. The same high surface activity is detected over a broad regime varying the mixing ratio. In contrast Thin Film Pressure Balance measurements reveal a variation in the foam film properties. Foam film thickness and stability varies with the mixing ratio. We also discuss a strong impact on adsorption kinetics and foaming of these mixtures.

This shows that for different catanionic surfactant mixtures surface composition and foam film properties changes.

CPP 44.4 Thu 10:15 ZEU 118

Structure of electrolyte solutions in complex solvents — •Markus Bier — Max Planck Institute IS und University of Stuttgart, Germany

Since recently quite some theoretical as well as experimental effort is devoted to investigate structural properties of electrolyte solutions in which the solvent cannot be considered as a structureless medium. The most prominent example are solvents formed by binary liquid mixtures whose components interact differently with the ions. Consequently the presence of ions can influence the phase diagram of the solvent, e.g. the location of the miscibility gap. Conversely, a solvent mixture close to its critical demixing point can perturb the structure of the ions.

This contribution discusses the changes of the structure of electrolyte solutions in binary liquid mixture solvents as one approaches the critical demixing point [1,2]. It is explained how the partial pair distribution functions evolve upon approaching the critical point of the mixture from a monotonic decay on the length scale of the Debye length via an oscillatory decay, reached by Kirkwood crossovers, towards a monotonic decay on the length scale of the bulk correlation length. This scenario is a key to understand recent experimental findings related to the structure of electrolyte solutions in complex solvents.

References:

[1] M. Bier, A. Gambassi and S. Dietrich, J. Chem. Phys. **137**, 034504 (2012).

[2] M. Bier and L. Harnau, Z. Phys. Chem. **226**, 807 (2012).

CPP 44.5 Thu 10:30 ZEU 118

Impedance spectroscopy of ions at liquid-liquid interfaces — •Andreas Reindl and Markus Bier — Max Planck Institute IS and University of Stuttgart, Germany

One possibility to examine interfaces between two immiscible liquids is by means of impedance spectroscopy. In order to interpret the measured impedance spectra, frequently equivalent (electric) circuits where each element is intended to represent a certain microscopic process are fitted to the data. In this contribution we highlight two major problems with this procedure and propose a novel approach to avoid them. Both problems of the commonly used one-step fitting of impedance data are related to the phenomenon of actually obtaining circuit elements which lump bulk and interfacial properties together. This leads to the first, more technical problem of a possible overfitting of the bulk elements at the expense of an underfitting of the interfacial elements, which compromises the accuracy of the desired interfacial quantities. The second, more fundamental problem is related to the assignment of microscopic processes to circuit elements, which we show to be approximative in general and which requires ad-hoc interpretations for one-step fitting. In order to overcome both difficulties, we propose to disentangle bulk and interfacial circuit elements by means of a two-step fitting procedure, which we demonstrate for theoretically determined impedance data and which can be expected to be used similarly for real data.

Reference:

A. Reindl and M. Bier, Phys. Rev. E. **88**, 052312 (2013).

CPP 44.6 Thu 10:45 ZEU 118

Effective Interactions in Protein-Salt Solutions Approaching Liquid-Liquid Phase Separation — •Marcell Wolf[1], Felix Roosen-Runge[1], Fajun Zhang[1], Roland Roth[2], and Frank Schreiber[1] — [1]Institut für Angewandte Physik, Auf der Morgenstelle 10, Universität Tübingen, 72076 Tübingen, Germany — [2]Institut für Theoretische Physik, Auf der Morgenstelle 14, Universität Tübingen, 72076 Tübingen, Germany

We present an experimental study combined with a theoretical discussion of the effective interactions in protein solutions approaching a liquid-liquid phase separation (LLPS) induced by addition of multivalent metal ions [1,2]. The reduced second virial coefficient, B_2/B_2^{HS}, is used to describe the interaction and discussed with theoretical predictions for colloidal systems. We have determined the salt and protein partitioning in the two coexisting phases, which provides the isothermal binodal of the LLPS in the $(c_p,\, c_s)$ plane. Two sets of samples, away from and at the LLPS binodal were measured by static light scattering (SLS) and small angle X-ray scattering (SAXS) to determine the second virial coefficient. In all cases, B_2/B_2^{HS} is negative in the condensed regime, and increases upon approaching the upper critical point in the (c_p, c_s) plane. The results are compared with a simple colloidal model with isotropic short-ranged attraction and a thermodynamic criterion based on the reduced second virial coefficient. We discuss the application of this theoretical prediction to interpret experimental observations. [1] M. Wolf et al., J. Mol. Liq., submitted; [2] F.Zhang et al., Soft matter 8, 2012, 1313.

15 min. break

CPP 44.7 Thu 11:15 ZEU 118

Response of the Water Hydration Layer around a Spherical Solute to an Electric Field — •Christian Schaaf and Stephan Gekle — Biofluid Simulation and Modeling, Universität Bayreuth

The behavior of charged particles in aqueous solutions is strongly influenced by the hydration layer. Near these particles the dielectric response function ε is an anisotropic and space-dependent tensor in contrast to the scalar quantity it is in bulk water.

Using molecular dynamics (GROMACS) and linear response theory we calculate the radial component of the local dielectric response tensor in water around a spherical solute. We find an oscillatory behavior for the radial component of the response function which we explain by the nonlocal permittivity calculated from bulk properties. These calculations show that on small length scales the response is mostly determined by the field geometry of a point charge and much less by the actual solute-water interface.

Understanding the dielectric response is essential for the behavior of ion distributions and may improve the accuracy of implicit solvent simulations.

CPP 44.8 Thu 11:30 ZEU 118

Specific Ion Binding to Amphiprotic Surface Groups and the pH Dependence of the Hofmeister Series — •Nadine Schwierz[1] and Roland R. Netz[2] — [1]Physik Department, Technische Universität München, Germany — [2]Physik Department, Freie Universität Berlin, Germany

Ion binding to amphiprotic surface groups is one of the central mechanisms for ion-specificity if ionizable groups are present on the surface of a macromolecule. To gain insight into the microscopic mechanism, we use a combination of atomistic simulations and Poisson-Boltzmann theory and bridge from computational results to macroscopic experimentally accessible properties.

In our modeling approach, we first extract single-ion surface interaction potentials at atomistically resolved surfaces composed of uncharged carboxyl-groups and of charged carboxylate-groups. The surface affinity of single ions depends strongly on whether the carboxyl group is dissociated or not and is even reversed for cations.

Phase diagrams, based on long-ranged forces between two heterogeneous surfaces containing carboxyl and carboxylate groups interacting across electrolyte solutions, feature direct, reversed and altered Hofmeister series in dependence of the salt concentration and pH. The results provide a microscopic explanation for the pH dependence of the Hofmeister series due to specific and diverse ion binding to carboxyl and carboxylate surface groups.

CPP 44.9 Thu 11:45 ZEU 118

Elastic/viscoelastic properties of polyelectrolyte multilayer films (PLL/HA) as measured by AFM nano-indentation — •Johannes Hellwig and Regine von Klitzing — Stranski-Laboratorium, Department of Chemistry, TU Berlin, Strasse des 17. Juni 124, D-10623 Berlin

In recent years smart biomaterials have become a highly developing field of interest for biomedical applications, e.g. drug delivery(1). The layer-by-layer (LbL) technique (2) gives the opportunity to build up self assembled polyelectolyte multilayer films (PEM) with defined architecture, physical and chemical properties. PEM made of poly(L-lysine) (PLL) and hyaluronic acid (HA) were produced by using the LbL technique. Potential applications of these PEMs require controlling of the adhesion behaviour by tuning their elastic/viscoelastic properties. In this study elastic(3) and viscoelastic properties of LbL coated poly(L-lysine)/hyaluronic acid PLL/HA films were studied by colloidal probe atomic force microscopy. It was shown that the indentation modulus of PLL/HA films measured in different pH and ionic strength of the surrounding medium changes. Increasing the temperature shows a slight decrease in modulus at higher temperatures. Furthermore the viscoelastic film behaviour was measured and calculated by stress relaxation and creep compliance measurements.

CPP 44.10 Thu 12:00 ZEU 118

Observation of Polarization in the Leaning Plane of a Bent-Core Molecular Compound — •Nattaporn Chattham[1,2], Maria Gabriela Tamba[1], Eduard Westphal[4], Hideo Takezoe[1,3], Ralf Stannarius[1], Carsten Tschierske[4], and Alexey Eremin[1] — [1]Otto-von-Guericke-Universität Magdeburg, IEP/ANP, D-39106 Magdeburg, Germany — [2]Department of Physics, Faculty of Science, Kasetsart University, Bangkok 10900 Thailand — [3]Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo 152-8552, Japan — [4]Institute of Chemistry, Martin-Luther-University Halle-Wittenberg, D-06120 Halle,Germany

Bent-core molecules have been of interest to liquid crystal scientists for over decades. Designing molecules and identifying their phase structures provide much knowledge to understand the complexity of molecular organization of these phase structures. In the conventional polar SmCP (B2) phase of bent-core mesogens, the tilting of molecules with respect to the layer normal occurs by the rotation about the bend direction, so that the spontaneous polarization is perpendicular to the tilt plane. In contrast, molecules lean within their bend plane in the SmC leaning phase, where the polarization is in the leaning plane and deviates from the layer plane. Here we report a clear evidence of this structure, i.e., the polarization lying in the leaning plane from direct observations of thick freely suspended films at inclined incidence under an in-plane electric field. The induced polarization was also confirmed by second-harmonic generation (SHG) activity. This work was supported by Alexander von Humboldt Foundation.

CPP 44.11 Thu 12:15 ZEU 118

Modelling of neutron spectroscopy of hydrogen bonded organic crystals using first principles density functional theory — •Sanghamitra Mukhopadhyay — ISIS Facility, Rutherford Appleton Loboratory - STFC, Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0QX

Hydrogen bonded organic crystals are important both for fundamental chemical interests as well as for technological applications. Neutron spectroscopy is used to understand these hydrogen bonded materials experimentally. The static lattice dynamics are not often suitable to analyse these spectroscopic results, specially, where complex picosecond order dynamics are involved. In this work we will present our work on modelling of neutron spectroscopic results using first principles lattice and molecular dynamics.

We employed state-of-the-art calculations based on plane wave pseudo potential density functional theory to predict the structure of croconic acid, an organic molecular crystal, showed room temperature ferroelectricity, and compared with in-house neutron diffraction and inelastic neutron scattering (INS) spectrum to understand the nature of hydrogen bonds in this material. The quasielastic spectrum were calculated by analysing the trajectory of the molecular dynamical simulations and also compared with experiments.

We will discuss the neutron spectrum in terms of motions of hydrogen ions. The calculated Born effective charge tensors are used to understand the nature of dynamic charges and the origin of ferroelectricity.