CPP 22: Poster: Charged Soft Matter

Time: Wednesday 11:00–13:00 Location: Poster A

CPP 22.1 Wed 11:00 Poster A

Liquid-liquid phase separation in protein solutions induced by YCl$_3$ — •Marcell Wolf[1], Fajun Zhang[1], Felix Roosen-Runge[1], Roland Roth[2], Maximilian W. A. Skoda[3], Robert M. J. Jacobs[4], and Frank Schreiber[1] — [1]Institut für Angewandte Physik, Universität Tübingen, Germany — [2]Institut für Theoretische Physik, Universität Erlangen-Nürnberg, Germany — [3]ISIS, RAL, Didcot, UK — [4]CRL, University of Oxford, UK

Liquid-liquid phase separation (LLPS) in protein solutions plays an important role for protein crystallization. Phase diagrams of HSA and BSA with Yttrium Chloride (YCl$_3$) in the c$_p$ and c$_s$ plane were determined; a reentrant phase behavior [1] was observed. Here, we show that LLPS can be induced in protein solutions by using YCl$_3$ [2]. Phase boundaries were determined by UV and X-ray absorption. The effective protein-protein interaction upon LLPS was investigated by SAXS. By optical microscopy of the condensed regime the LLPS region was defined by the formation of liquid droplets. In the case of HSA no cluster formation was observed, whereas BSA formed clusters outside and at the LLPS borders. The reduced second virial coefficient B_2/B_2^{HS} for HSA decreased from a slightly negative value in the condensed regime below the critical value of -1.5 in the LLPS region. For BSA, more negative values were observed at the LLPS border than in between. This is consistent with other protein systems studied. LLPS for HSA and BSA by adding YCl$_3$ and the clustering in BSA solutions can be explained by a sufficient low and negative B_2/B_2^{HS}. [1] F. Zhang et al., PRL 101, 2008, 148101; [2] F. Zhang et al. Soft Matter, submitted.

CPP 22.2 Wed 11:00 Poster A

Anomalous Small-Angle X-ray Scattering (ASAXS) Study of Multi-Valent Cations around Proteins in Solution — •Baohu Wu[1], Fajun Zhang[1], Maximilian W.A. Skoda[2], Robert M.J. Jacobs[3], Michael Sztucki[4], and Frank Schreiber[1] — [1]Institut für Angewandte Physik, Universität Tübingen — [2]ISIS, RAL, UK — [3]CRL, University of Oxford, UK — [4]ESRF, France

A detailed understanding of the ion environment is essential for a full description of charged protein systems. ASAXS represents a powerful tool for studying the distribution of targeted ions [1]. We studied protein solutions (β-lactoglobulin, BLG) in the presence of Y3+ using ASAXS. Systematic measurements show clearly energy-dependent ASAXS shifts visible in the scattered intensity. The pure anomalous term which is about 0.02% to 0.2% of the total signal for Y3+ has been successfully separated using the matrix method. The number of ions around the protein, which contribute to the ASAXS signal, is between 1 to 6 per BLG dimer depending on the initial concentration of salt and protein. The number increases from 2.4 to 5 with BLG concentration at a fixed ion concentration, which is due to the cluster formed in re-entrant condensation phase regime [2]. These data are compared with our crystallographic study [3], which indicates 2 to 4 Y3+ binding per BLG dimer. The work will contribute to a comprehensive understanding of the role of the ions in protein crystal growth. [1] M. Sztucki, et al. J. Appl. Cryst. 2010, 43, 1479. [2] F. Zhang, et al. Phys. Rev. Lett. 2008, 101, 148101. [3] F. Zhang, et al. J. Appl. Cryst. 2011, 44, 755.

CPP 22.3 Wed 11:00 Poster A

Substrate effects of the substrate on the formation of polyelectrolyte multilayers — •Maximilian Zerball, Chloé Chevigny, and Regine von Klitzing — Stranski-Laboratorium, Institut für Chemie, TU Berlin

For the past twenty years, the Layer-by-Layer technique (LbL) has made it possible to modify surfaces by covering them with thin films. This technique gives the opportunity for a wide variety of potential applications for polyelectrolyte multilayers (PEM), for example chemical reactors, antireflective coatings or microcontainers.

The deposition of PEMs is influenced by various parameters, such as ionic strength, pH value and charge density. But a systematic study of the substrate effect on the PEM is still missing. Especially, for hybrid/composite materials the connection (interphase) between the PEM and a solid material is important. This addresses planar surfaces like metal or semiconductors as substrates, but also solid particles. For this purpose different substrates were studied by directly changing the nature of the substrate (Silicon or Gold), but also by chemical modification of the silicon surface using silanization (change of both substrate charge and interactions with polyelectrolytes). For polyelectrolytes we chose to use the two most widely spread systems, PSS/PAH and PSS/PDADMAC.

The properties of the PEM are monitored after the deposition as a function of the number of layers by a complementary use of ellipsometry (with humidity control) and AFM. The question is, how far and how strong the structure of the PEM is affected by the substrate.

CPP 22.4 Wed 11:00 Poster A

Influence of the surface chemistry on the coexistence of flatly and brush-like physisorbed chains in poly(styrene-sulfonate) layers — •Stephan Block[1], Frank Lawrenz[2], and Christiane A. Helm[2] — [1]ZIK HIKE - Zentrum für Innovationskompetenz Humorale Immunreaktionen bei kardiovaskulären Erkrankungen, Fleischmannstr. 42 - 44, D-17487 Greifswald, Germany — [2]Institut für Physik, Ernst-Moritz-Arndt Universität, Felix-Hausdorff-Str. 6, D-17487 Greifswald, Germany

AFM with a colloidal probe as a tip is used to measure the surface forces and to image sodium poly(styrene sulfonate) (PSS) layers which are physisorbed to different surfaces in the presence of NaCl solutions with an ionic strength ranging between 0 M and 1 M NaCl. Colloidal probe tapping mode imaging shows that domains of PSS brushes coexist with flatly adsorbed PSS. Interestingly, this coexistence is observed on hydrophobic (e.g. HOPG, silanized silica) as well as hydrophilic surfaces (e.g. PEI on silicon, PAH on mica). The surface forces can be described as a superposition of electrostatic and steric forces, the former originating from the flatly adsorbed PSS and the latter from the brushes. This indicates that a heterogeneous layer structure seems to be a general phenomenon for physisorbed PSS layers and has to be regarded in studies concerning the adsorption behavior of polyelectrolytes.

CPP 22.5 Wed 11:00 Poster A

On the internal structure of polyelectrolyte multilayers — •Malte Passvogel[1], Peter Nestler[1], Olaf Soltwedel[2], Ralf Köhler[3], and Christiane A. Helm[1] — [1]Institut für Physik, Uni Greifswald, Felix-Hausdorff-Str. 6, 17487 Greifswald, Germany — [2]FRM II, Lichtenbergstr. 1, 85747 Garching, Germany — [3]Stranski-Lab, TU Berlin, 10623 Berlin; Institut F-I2, HZB Berlin, 14109 Berlin, Germany

Polyelectrolyte multilayers from PSS and PDADMAC formed in 0.1 M NaCl solution are investigated. With in-situ ellipsometry first exponential, then linear growth is observed. In the linear growth regime, with increasing PDADMAC molecular weight the thickness per deposited PDADMAC layer and thus the thickness per PDADMA/PSS layer pair increase for PDADMAC polymer weight below 100 kDa, then they level off. Qualitatively, the same results are obtained with X-ray reflectivity from films formed with a different number of PSS/PDADMA layer pairs. However, quantitative comparison shows that films in the exponential growth regime shrink much more on drying (ca 55 %) than the thicker films in the linear growth regime (35 %). With neutron reflectivity the position and width of an internal interface between protonated and deuterated blocks is determined. While the position of the internal interface does not move after deposition, the width increases due to interdiffusion. It is smallest next to the film/air interface and increases towards the core zone of the film until an equilibrium value is reached.

CPP 22.6 Wed 11:00 Poster A

Influence of two-dimensional lamellar phase of PSS on the condensed phase of oppositely charged TAP monolayers — •Heiko Ahrens, Thomas Ortmann, Andreas Gröning, Frank Lawrenz, and Christiane A. Helm — Institut für Physik, Uni Greifswald, Felix-Hausdorff-Str. 6, 17487 Greifswald, Germany

Polystryene sulfonate (PSS) is adsorbed from dilute solution (0.01 mM with respect to the monomer concentration) onto oppositely charged TAP lipid monolayers. TAP lipids are 1,2-alkyl-trimethylammonium-propane with different alkyl chains (14, 16, 18). PSS adsorption stabilizes the monolayer and changes alkyl chain order (NNN to NN) in the liquid condensed phase as evidenced by grazing incidence X-ray diffraction (GID). Simultaneously, with GID the two-dimensional lamellar phase of PSS is observed. The rod scans of the peaks attributed to the PSS reveal that the two-dimensional lamellar phase imposes a slight vertical distortion on the lipid monolayer. The combined analysis of electron density profiles measured by X-ray reflectivity and the rod scans allow to assign the scattering centers within the lipid monolayers. The results are consistent for the different alkyl chain lengths.

CPP 22.7 Wed 11:00 Poster A

Polyelectrolyte coupling to a charged lipid monolayer: relating lattice and domain structures — •Thomas Ortmann, Heiko Ahrens, Andreas Gröning, Frank Lawrenz, and Christiane A. Helm — Institut für Physik, Uni Greifswald, Felix-Hausdorff-Str. 6, 17487 Greifswald, Germany

Polystyrene sulfonate (PSS) is adsorbed from dilute solution (0.01 mM with respect to the monomer concentration) onto oppositely charged dioctadecyldimethylammonium bromide (DODAB) lipid monolayers. The PSS molecular weight is varied. With grazing incidence X-ray diffraction (GID) the two-dimensional lamellar phase of adsorbed PSS is observed, when DODAB is in the condensed phase. The same ordered PSS phase is also found when the lipids are in the fluid phase and PSS molecular weight exceeds 6.5 kDa. A large spacing between short stretched chains hinders the two-dimensional lamellar phase, presumably the short chains gain rotational entropy.

With Brewster Angle Microscopy (BAM) the nucleation and growth of domains is observed on clean water, but only when low molecular weight PSS ($<$ 8 kDa) is used. For high molecular weight PSS no domains of DODAB with coupled PSS are found, even though GID indicates the nucleation of condensed lipid domains. The domains do not grow, which is attributed to hindered lipid diffusion due to the adsorbed macromolecules.

CPP 22.8 Wed 11:00 Poster A

AFM characterization of structural changes of polycation covered surfaces induced by hydroxyl radicals — •Florian Berg[1], Stephan Block[2], and Christiane A. Helm[1] — [1]Institut für Physik, Uni Greifswald, Felix-Hausdorff-Str. 6, 17487 Greifswald, Germany — [2]ZIK HIKE, Uni Greifswald, Fleischmannstr. 42 - 44, D-17487 Greifswald, Germany

Positively charged, branched polyethylenimine (PEI) adsorbed onto silicon wafers are attacked by free hydroxyl radicals. AFM is used to image the PEI layers in air. After the radical attack the PEI layers show 1.3nm high plateaus (area fraction 5 %). With Colloid Probe technique, the force profiles between adsorbed PEI layers before and after the radical attack are measured in NaCl solution of different ionic strength. The force profiles of freshly deposited flat PEI layers show that an electrostatic repulsion dominates the interaction. After the radical attack we find both surface potential and surface charge are reduced by a factor of about two, while the Debye length remains unchanged.

Negatively charged colloidal gold nanoparticles are adsorbed onto the oppositely charged PEI. After the radical attack we find a reduction in saturation surface coverage consistent with the decreased surface charge. Additionally, the adsorption kinetics is slowed down suggesting that the PEI-layer is no longer a flat, compact layer.

CPP 22.9 Wed 11:00 Poster A

The effect of a wedge on the ionic distribution of an electrolyte solution — •Dmitriy Rozhkov[1], Sofia Kantorovich[1,2], and Marcello Sega[2] — [1]Ural Federal University, Lenin av 51, 620083, Ekaterinburg, Russia — [2]Institute for Computational Physics, Pfaffenwaldring 27, 70569 Stuttgart, Germany

Nanoscopic confinement of ionic solutions is often met in both biological systems and technical applications. As long as the behaviour of ionic solutions in confinement is not fully understood, computer simulations are often employed to investigate the subject. However, electrostatic effects, which occur due to the presence of interfaces, should be properly allowed for. Here, we present molecular dynamics simulations of monovalent salt confined in a rectangular, charged box which releases counterions into the solution. Different height to width ratios and various salt concentrations are studied.

CPP 22.10 Wed 11:00 Poster A

Effective interactions in electrolyte solutions — •Markus Bier and S. Dietrich — Max-Planck-Institut IS, Stuttgart, Germany

The effective interactions between walls or colloidal particles are known to be significantly influenced by the properties of a liquid medium in contact. Well-known examples are dispersion forces, which are determined by the permittivity, electrostatic forces, which become short-ranged due to the screening of the Coulomb potential by ions, and solvation forces, which arise due to solvent adsorption or desorption. Commonly these contributions to the effective interactions are assumed to be independent, i.e. the effective interactions are expected to be a simple superposition. However, recently experimental observations for a binary liquid mixture containing salt were reported [1] which cannot be understood by assuming solvation forces being uncoupled from the screened electrostatic forces. Here a possible mechanism [2] is discussed in terms of which all experimental evidence can be explained consistently.

[1] U. Nellen, J. Dietrich, L. Helden, S. Chodankar, K. Nygard, J. van der Veen and C. Bechinger, Soft Matter **7**, 5360 (2011).

[2] M. Bier, A. Gambassi, M. Oettel and S. Dietrich, EPL **95**, 60001 (2011).

CPP 22.11 Wed 11:00 Poster A

Influence of charge density on bilayer bending rigidity in lipid vesicles: a combined dynamic light scattering and neutron spin-echo study — •Beate-Annette Brüning[1], Ralf Stehle[1,2], Peter Falus[3], and Bela Farago[3] — [1]Helmholtz Zentrum Berlin, Hahn-Meitner Platz 1, 14109 Berlin, Germany — [2]Universität Bayreuth, Postfach 10 12 51, 95440 Bayreuth, Germany — [3]Institut Laue-Langevin, B.P. 156, 6 rue Jules Horowitz, 38042 Grenoble, France

We report a combined dynamic light scattering and neutron spin-echo study on vesicles composed of the uncharged helper lipid DMPC and the cationic lipid DOTAP. Mechanical properties of a model membrane and the corresponding fluctuation dynamics can be tuned by changing composition. We compare the bilayer undulation dynamics in lipid vesicles composed of DMPC/DOTAP to vesicles composed of DMPC and the also uncharged reference lipid DOPC. We find, that on the local scale, lipid headgroup composition and charge change the vesicle fluctuations less than acyl chain packing inhomogenities between the composite lipids. We discuss this result on the basis of domain formation in the lipid mixtures containing charged (DMPC/DOTAP) and uncharged reference lipid (DMPC/DOPC). First, we investigate lipid vesicle size and mass diffusion using dynamic light scattering, then we study collective bilayer undulations and bulk diffusion on two distinct time scales around 25ns and 150ns, using neutron spin-echo spectroscopy. Finally, we estimate bilayer bending rigidities κ_B for the charged and uncharged lipid vesicles.

CPP 22.12 Wed 11:00 Poster A

Interfacial engineering of polymer multilayers with polarized biomolecules: a new approach in growing supramolecular layer structures — •Neelima Paul[1,2], Amitesh Paul[3], Stephan Mattauch[4], Peter Müller-Buschbaum[2], and Martha Ch. Lux-Steiner[1] — [1]Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, 14109 Berlin, Germany — [2]TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching, Germany — [3]TU München, Physik-Department, LS Neutronenstreuung, James-Franck-Str. 1, 85748 Garching, Germany — [4]JCNS Forschungszentrum Jülich GmbH Outstation at FRM II Lichtenbergstrae 1, 85747 Garching, Germany

The development of polymer-based structures is hindered due to the difficulties in realizing well-defined modulated structures with very small interlayer roughness out of charged polymers. We compare two types of heterostructures, one of them was prepared with embedded layers of polarized biomolecules. Using specular and off-specular neutron scattering, we observe,in the heterostruture containing the biomolecule, formation of ordered modulated structures with a drastic decrease in the roughness parameter. For the multilayer without the biomolecule we have indications of formation of island-like structures. Our study thus demonstrates that polarized biomolecules can interrupt the propagation of island-like structures at such interfaces which can be effectively used in achieving well defined supramolecular layer structures out of charged polymers.

CPP 22.13 Wed 11:00 Poster A

Charge-Controlled Metastable Liquid-Liquid Phase Separation in Protein Solutions as a Universal Pathway Towards Crystallization — •Felix Roosen-Runge[1], Fajun Zhang[1], Roland Roth[2], Marcell Wolf[1], Maximilian W.A. Skoda[3], Robert M.J. Jacobs[4], and Frank Schreiber[1] — [1]Institut für Angewandte Physik, Universität Tübingen — [2]Institut für Theoretische Physik, Universität Erlangen-Nürnberg — [3]ISIS, RAL, Chilton, Didcot, UK — [4]CRL, University of Oxford, UK

We demonstrate that a metastable liquid-liquid phase separation (LLPS) can be induced by multivalent metal ions in solutions of globular proteins at room temperature [1]. Importantly, the approach is applicable to proteins, which otherwise show no LLPS in the full accessible temperature range. The ion and protein partitioning in the coexisting phases is determined in solutions of human serum albumin (HSA) and YCl_3. We interpret the finding on the basis of a phase diagram with three control parameters: temperature, metal-ion and protein concentration. The underlying mechanism of specific ion binding is discussed along the lines of charge inversion and reentrant condensation [2,3]. Interestingly, we find protein crystallization close to the metastable LLPS, consistent with theoretical predictions and simulations suggesting a two-step crystallization process. Thus, multivalent ions can be used to control the phase behavior of protein solutions, including metastable LLPS and protein crystallization.

[1] F. Zhang, et al., Soft Matter, submitted; [2] F. Zhang, et al., PRL (2008) 101:148101; [3] F. Zhang et al., Proteins (2010) 78(16):3450-7

CPP 22.14 Wed 11:00 Poster A

Ionic force field optimization and modified ion-pair mixing rules — •Maria Fyta[1] and Roland Netz[2] — [1]Physik Department, Technische Universität München, 85748 Garching, Germany — [2]Fachbereich Physik, Freie Universität Berlin, 14195 Berlin, Germany

We propose an optimization scheme to obtain good ionic force fields for classical simulations of salt solutions, also of biological relevance. Our work is based on Molecular Dynamics simulations with explicit water for different halide and alkali ions forming salt solutions at finite ion concentration. The force field derivation technique we propose is based on a simultaneous optimization of single-ion and ion-pair properties and the determination of the cation-anion interaction parameters (traditionally given by the mixing rules). From the finite-concentration simulations, thermodynamic properties of the salt solutions are derived, using the Kirkwood-Buff theory of solutions, and compared to relevant experimental data. For the rather size-symmetric salt solutions involving bromide and chloride ions, this scheme using the standard mixing rules works fine. For the iodide and fluoride solutions, corresponding to the largest and smallest anion we have considered, a rescaling of the mixing rules was necessary. In this respect, we have introduced scaling factors for the cation-anion Lennard-Jones interaction that quantify deviations from the standard mixing rules. We discuss the efficiency and complications of the proposed ionic force field optimization scheme.

CPP 22.15 Wed 11:00 Poster A

Chain conformation of polyelectrolytes at surfaces as deduced from the surface forces — •Stephan Block[1] and Christiane A. Helm[2] — [1]ZIK HIKE - Zentrum für Innovationskompetenz Humorale Immunreaktionen bei kardiovaskulären Erkrankungen, Fleischmannstr. 42 - 44, D-17487 Greifswald, Germany — [2]Institut für Physik, Ernst-Moritz-Arndt Universität, Felix-Hausdorff-Str. 6, D-17487 Greifswald, Germany

The measurement of force profiles can be used to determine the chain conformation adopted by polymers and polyelectrolytes after deposition to a surface. Usually, for each conformation a characteristic length scale exists which sets the interaction length of the force profile. E.g., the electrostatic interaction usually dominates the surface forces of flatly physisorbed polyelectrolytes in aqueous solution; the characteristic length scale is the Debye length which is controlled by the ionic strength. We show how the scaling of the characteristic length can be used to obtain information about the chain conformation when the ionic strength is varied. Additionally, we apply existing theories to measured force profiles and evaluate their feasibility.

CPP 22.16 Wed 11:00 Poster A

Quasilinear electro-optic effect in ferroelectric polymer-dispersed nematic liquid crystals due to remanent polarization — •Lars Hollänedr, Werner Wirges, and Reimund Gerhard — Universität Potsdam, Institut für Physik und Astronomie, Potsdam

Polymer-dispersed liquid crystal (PDLC) films were prepared using ferroelectric poly(vinylidenefluoride-trifluoroethylene) (P(VDF-TrFE)) and nematic 4-cyano-4-n-hexylbiphenyl (6CB). Inside the composite material the liquid crystal 6CB was separated in discrete micrometer-sized droplets with nearly spherical shape. The transparency change due to an applied external electric field was measured for non-poled and poled samples.

Usually the change in transmittance of nematic PDLC-films depends only on the absolute value of the electric field and not on the polarity. But after the poling of the PDLC device the remanent polarization of the P(VDF-TrFE) creates an internal electric field, which acts as an offset. It is assumed that due to the internal field the preferred orientation of the nematic liquid crystal inside the droplets is changed from a radial to an axial one. This pre-alignment in field direction causes a quasilinear transmittance behavior as well as a general increase of transparency.

CPP 22.17 Wed 11:00 Poster A

Mixtures of Chitosan and Oppositely Charged Alkyl Ethoxy Carboxylates: Complex Hierarchical Structures — •Leonardo Chiappisi[1], Sylvain Prévost[1,2], and Michael Gradzielski[1] — [1]Stranski-Laboratorium für Physikalische Chemie und Theoretische Chemie, Institut für Chemie, Technische Universität Berlin, Berlin, Germany — [2]Helmholtz-Zentrum Berlin, Berlin, Germany

Mixtures of polyelectrolytes and surfactants are widely used in a large number of fields, such as detergency, pharmaceutical formulations, food industry, etc. Their aggregation is driven by several forces, ranging from electrostatic to hydrophobic interaction and mostly by the entropic gain due to the release of counterions from both polymer and surfactant micelles.

Here, we present a comprehensive structural study on mixtures of the biopolycation chitosan and the highly biocompatible alkyl ethoxy carboxylates. In order to elucidate the structure of these complexes, static and dynamic light scattering (SLS and DLS) have been used to explain the large scale structure, whereas small angle neutron scattering (SANS) has been employed to determine the internal structure of the complexes.

The results show that the shape of the micelle is retained within the complex, that they are locally linearly ordered and that the large scale structure is determined by the folding of the polymerchain. In addition, the formation at higher surfactant content of larger and hierarchically ordered structures made up of many polyelectrolyte chains is proven.

CPP 22.18 Wed 11:00 Poster A

Dielectric spectrum of salt solutions from molecular dynamics simulations — •Marcello Sega[1], Sofia Kantorovich[1,2], Axel Arnold[1], and Christian Holm[1] — [1]Institute for Computational Physics, Pfaffenwaldring 27, 70569 Stuttgart, Germany — [2]Ural Federal University, Lenin av 51, 620083, Ekaterinburg, Russia

We present the results of MD simulations for water salt solutions with various salt concentrations. Following the experimental approach, we use several fit-functions in order to determine static dielectric permittivities. We show, that the permittivity obtained via Einstein-Helfand fit is extremely sensitive to the statistics and, as a result is very difficult to use reliably. However, the static value of the dielectric permittivity can be evaluated by fitting the complete frequency-dependent spectrum, using, for example, the Cole-Cole relation. We compare our results to the experimental data from [Buchner et al, J. Phys. Chem. A, Vol. 103, 1999, P. 1], which show an initial linear decrease of the static dielectric permittivity as a function of salt concentration, and a saturation at high concentrations.