CPP 10: Poster: Charged Soft Matter

Time: Monday 17:30–19:30 Location: P2

CPP 10.1 Mon 17:30 P2

Crystallization of β-Lactoglobulin in Solution in the Presence of YCl_3 — •Andrea Sauter, Fajun Zhang, and Frank Schreiber — Institut für Angewandte Physik, Universität Tübingen, Germany.

In order to understand the vitally important tasks of proteins in living organisms, knowledge of their interactions is needed. The determination of the structure of a protein by x-ray diffraction requires high quality single crystals which are not always easy to obtain. During the last years simulations, theories and experiments suggested a two-step process of protein crystal nucleation, differing from classical nucleation theory (CNT). The system we are engaged in consists of an aqueous solution of the globular protein β-Lg with YCl_3. A reentrant phase behavior was observed [1]: The samples show aggregation between two critical YCl_3 concentrations c* and c** while a uniform solution exists for concentrations below c* or above c**. Near c* crystals grow directly from solution, following CNT. Near to c** a critical temperature T_c exists, above which the supernatant of a sample is clear. Below T_c it becomes reversible turbid due the forming of dense liquid drops. At lower initial protein concentrations c_p these are caused by critical concentration fluctuations. The formation of aggregates precedes crystal growth. At higher c_p a metastable liquid-liquid phase separation occurs. Crystallization is observed afterwards in the dense phase or starting from its interface as well as in the dilute phase. This cannot be explained by CNT, instead a two-step mechanism is assumed.

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

CPP 10.2 Mon 17:30 P2

Ion competition in protein solution studied with scattering techniques: SAXS, SLS and DLS — •Elena Jordan[1,2], Fajun Zhang[1], Marcus Hennig[1,2], Ralf Schweins[2], Tilo Seydel[2], Felix Roosen-Runge[1], Sara Leibfarth[1], Frank Schreiber[1], and Giovanna Fragneto[2] — [1]IAP, Universität Tübingen, Germany — [2]ILL Grenoble, France

For advances in protein science a better understanding of the protein interaction is essential. The reentrant phase behavior of proteins, induced by multivalent counterions (Y^{3+}), is a versatile example for protein-protein interactions in electrolyte solutions. At a certain YCl_3 concentration, c*, the proteins phase separate and at a even higher concentration, c**, the proteins redissolve with inversed surface charge [1]. We studied the effect of added NaCl on the reentrant condensation of proteins using SAXS, static and dynamic light scattering. We found that c* and c** are shifted to higher YCl_3 concentrations in the presence of NaCl. The decrease in the low q intensity of SAXS indicates that the attractive interaction around c* is reduced with NaCl. The monovalent ions screen the charges and stabilize the solution. Around c** the SAXS data show that the attractive interaction is enhanced upon adding NaCl. Light scattering data and simulations support the observations. We conclude, that a mixture of YCl_3 and NaCl can be used to fine-tune the overall interaction and phase behavior of proteins.

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

[2] F.Zhang, et al. Proteins Vol. 78, 3450 (2010)

CPP 10.3 Mon 17:30 P2

Active swimming in self-generated ionic gradients — •Michael Hauber, Benedikt Sabass, and Udo Seifert — II Institut für Theoretische Physik, Universität Stuttgart, Germany

A thorough analytic understanding of phoresis in self-generated ionic gradients is still lacking. Therefore, we study here the behavior of a charged spherical particle, which emittes a charged solute with a fixed rate. The equations describing the electrical potential, the chemical potential, and the velocity field are solved through a perturbation theory for small surface charge density. The phoretic velocity of the particle is given as a closed analytical expression, obtained from the balance between electrostatic and hydrodynamic forces. It depends on the value κa, where a is the radius of the particle and κ^{-1} is the Debye screening length. The limiting results of very small values of κa (Debye-Hückel limit) and very large values (Smoluchowski limit) are derived. Further, we investigate the dependence of the particle speed on different ways of solute emission. We also take a look at the possibility of velocity reversion for varying surface charge potential.

CPP 10.4 Mon 17:30 P2

The diffusion of charged nanoparticles at the air/water interface — •Tobias Gehring and Thomas Fischer — The University of Bayreuth

The diffusion of oppositely charged nanoparticles changes differently as we change the ionic strength of the water. The diffusion is not invariant under charge reversal of the particles. We attribute this difference to the finite non vanishing surface potential of the air/water interface. The diffusion slows down with the immersion into the water. Electrodipping might be one reason for our experiment observations, however, this electrodipping force scales with the dipole-densitiy contrast of the nanoparticles and the air/water interface, not with the charge density on the particles.

CPP 10.5 Mon 17:30 P2

Dielectric Spectroscopy of Charged Soft Matter — •Pedro Armando Ojeda May, Marcello Sega, Sofia Kantorovich, Axel Arnold, and Christian Holm — Institute for Computational Physics, Pfaffenwaldring 27, 70569 Stuttgart

We present the results of MD simulations for systems of extended dipoles in presence of charged species. Static and frequency-dependent dielectric permittivities are computed employing charge structure factors, showing how it is possible to isolate the different contributions to the permittivity, namely that of dipoles, of free charges, and the cross contributions.

The results from the simulations are used to shed light on the applicability of theoretical approaches such as those of Caillol [JCP **91** 5544 (1989)] and Schroeder [JCP **126**, 084511 (2007)] for the calculation of dielectric spectra of ionic liquids.

CPP 10.6 Mon 17:30 P2

Charge transport in confined ionic liquids — •Ciprian Iacob[1], Joshua Sangoro[1], Rustem Valiullin[1], Roger Gläser[2], Jörg Kärger[1], and Friedrich Kremer[1] — [1]Institute of Experimental Physics I,University of Leipzig, Leipzig, Germany. — [2]Institute of Chemical Technology ,University of Leipzig, Leipzig, Germany.

Broadband Dielectric Spectroscopy is employed to study charge transport in ionic liquids (ILs) in silica nanoporous membranes [1-3]. The dielectric spectra are interpreted in terms of hopping of charge carriers over spatially randomly varying energy barriers. By applying the Einstein-Smoluchowski relation to the dielectric spectra, diffusion coefficients are obtained. At higher temperatures, the diffusion coefficients of the confined and bulk ionic liquids are identical for all pore sizes while ILs are observed to diffuse faster in comparison to their bulk value at lower temperatures. The results are discussed with respect to the interplay between the dynamic glass transition and charge transport in ILs.

References:

[1] C. Iacob, J.R. Sangoro, A. Serghei, S. Naumov, Y. Korth, J. Kärger, C. Friedrich and F. Kremer. J.Chem.Phys. 129, 234511 (2008).

[2] J.R. Sangoro, C. Iacob, A. Serghei, C. Friedrich and F. Kremer. Phys. Chem. Chem. Phys. 11, 913-916 (2009).

[3] C. Iacob, J.R. Sangoro, P. Papadopoulos, R. Valiullin, S. Naumov, J. Kärger and F. Kremer Phys. Chem. Chem. Phys., 12, 13798-13803 (2010).

CPP 10.7 Mon 17:30 P2

Partial oxidation of Cu(I) based ionic liquids under aerobic conditions monitored by XPS — •Angela Ulbrich[1], Marcel Himmerlich[1], Marion Stricker[2], Jörg Sundermeyer[2], and Stefan Krischok[1] — [1]Institut für Physik and Institut für Mikro- und Nanotechnologien, TU Ilmenau, PF 100565, 98684 Ilmenau, Germany — [2]Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße, 35032 Marburg, Germany

Copper (I) based ionic liquids (ILs) like $[Cu(Im^n)_2][CuX_2]$ (Im^n = 1-alkylimidazole; X = Cl, Br) have great potential for catalytic applications, e.g. the synthesis of dimethyl carbonate from MeOH, CO and O_2 [1]. The $[Cu(Im^6)_2][CuX_2]$ ILs are liquid at room temperature. Detailed knowledge of the electronic structure and their behaviour under environmental conditions is quite important. Due to the low vapour pressure of ILs it is possible to analyse their properties under ultra high vacuum conditions. The electronic structure of these ILs was investigated using X-ray photoelectron spectroscopy (XPS). We have handled these oxygen-sensitive ILs under inert atmosphere and besides the expected elements only traces of oxygen were detected. Generally, strong chemical modifications of $[Cu(Im^6)_2][CuX_2]$ were identified at the near surface region after exposure to air. The oxygen amount increased strongly and two different oxidation states were observed. Also shake-up structures near the Cu 2p core level appeared in the spectra, which are indicative for Cu(II) ions. Even after long exposure to environmental conditions, copper is not completely transformed to Cu(II).

[1] M. Stricker et al., Green Chem. 2010, 12, 1589-1598.

CPP 10.8 Mon 17:30 P2

Equilibrium and non-equilibrium features in the structure of physisorbed poly(styrene sulfonate) layers

— •Stephan Block and Christiane A. Helm — Institut für Physik, Ernst-Moritz-Arndt Universität, Felix-Hausdorff-Str. 6, D-17489 Greifswald, Germany

AFM is used to measure the surface forces and to image sodium poly(styrene sulfonate) (PSS) layers physisorbed from 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. The brush area fraction increases with rising degree of polymerization. The surface forces are a superposition of steric and electrostatic forces, their respective contribution is determined by the brush area fraction.

Unexpectedly, the internal properties of the brush domains (i.e. brush thickness and average chain distance) are independent on the deposition salt concentration. They increase with rising polymer length, while the brush thickness can also be controlled by the surrounding salt concentration (equilibrium feature).

These properties suggest that flatly and brush-like physisorbed chains can be understood as two different PSS phases, whereby the ratio of both phases is controlled by the salt concentration in the deposition solution. Furthermore, the amount of brush-like physisorbed PSS chains is related to the increase in PSS surface coverage, which is also observed after addition of salt to the deposition solution with other techniques and which is extensively described in literature.

CPP 10.9 Mon 17:30 P2

Structural changes of polycation covered surfaces induced by oxygen radicals

— Markus Butto, Peter Nestler, •Florian Berg, Stephan Block, and Christiane A. Helm — Inst. für Physik, Uni Greifswald, Felix-Hausdorff-Str. 6, D-17487 Greifswald

Positively charged, branched polyethylenimin (PEI) is adsorbed onto silicon wafers and attacked by hydroxyl radicals. Changes of the PEI layer are monitored on the mesoscopic length scale by Au nanoparticle (AuNP) adsorption, using AFM imaging and UV-vis absorption. Bulk diffusion controls the AuNP adsorption. A lower saturation coverage of the AuNP demonstrates a decreased positive surface charge of the PEI layer after the radical attack. Also, we find a reduced diffusion constant of AuNPs. This is attributed to conformational changes of the PEI layer.

To measure the surface forces of a PEI layer before and after a radical attack the AFM colloidal probe (CP) technique is used. The force curves of PEI layers adsorbed from pure water show that the repulsive electrostatic force dominates the interaction (DLVO theory) and PEI adsorbs flatly. After attacking the PEI layer with hydroxyl radicals, the first force curves show a steric force suggesting PEI branches dangling into solution, additionally a short ranged attraction is found. Furthermore, the surfaces appear laterally inhomogeneous.

CPP 10.10 Mon 17:30 P2

Odd-even and even-odd effect in polyelectrolyte multilayers observed with multiple angle ellipsometry

— •Peter Nestler, Stephan Block, and Christiane A. Helm — Inst. für Physik, Uni Greifswald, Felix-Hausdorff-Str. 6, D-17487 Greifswald

Within a liquid cell the growth of polyelectrolyte multilayers (PEMs) by sequential adsorption of oppositely charged polyelectrolytes is observed using ellipsometry. The polyanion is poly(styrenesulfonate) (PSS), the polycation poly(allylamine hydrochloride) (PAH), and the substrate a Si wafer. The salt content is varied between 1 and 4 mol/L NaCl, the preparation temperature between 20 and 55°C. On rise of the temperature, the thickness of a polycation/polyanion bilayer increases. After each adsorption step the PEM thickness and index of refraction is determined at several angles of incidence. A film which is always immersed in aqueous solution is at least 40% thicker than a film which is dried in air. The increase in PEM thickness after an adsorption step shows an alternating pattern (even-odd effect) due to an unequal PSS- and PAH-contribution to the thickness of one double layer. At temperatures up to 45°C, the outermost PSS layer is thicker. Then a cross-over from even-odd to odd-even effect occurs, and a top PAH layer is thicker than a top PSS layer. A similar even-odd effect is observed in the refractive index of the PEM and allows an estimation of the refractive index of the outermost monolayer. At high temperature, the thicker outermost polyelectrolyte layer always has a higher water content, irrespective of its chemical nature.

CPP 10.11 Mon 17:30 P2

The 2-dimensional Lamellar Phase of PSS Adsorbed onto an Oppositely Charged Lipid Monolayer

— •Thomas Ortmann, Heiko Ahrens, Jens-Uwe Günther, Frank Lawrenz, and Christiane A. Helm — Inst. für Physik, Uni Greifswald, Felix-Hausdorff-Str. 6, D-17487 Greifswald

Monolayers of cationic lipids with adsorbed polystyrene sulfonate (PSS) are studied by isotherms, grazing incidence X-ray diffraction and X-ray reflectivity. Dioctadecyldimethylammonium bromide (DODA) is used as lipid, the PSS molecular weight is varied. For a PSS concentration of 0.01 mM (with respect to the monomer concentration) in pure water Bragg peaks of flatly adsorbed, aligned PSS chains are observed for PSS both beneath the lipids in the solid (chain separation 2-2.7 nm) and in the fluid phase (chain separation 3-6 nm), the latter only if the PSS contour length Lc exceeds 10 nm. The peak position is independent of the chain length. However the isotherms depend strongly on PSS chain length: the surface pressure of the liquid/condensed phase transition is largest for the shortest PSS used (Lc = 5.5 nm) and decreases the longer the polymer gets until a limiting value is reached (contour length Lc exceeds 25 nm). The latent heat of the phase transition shows nonmonotic behaviour with an extremum at Lc = 8 nm, and levels off at Lc = 25 nm. We suggest an explanation based on the rotational entropy of very short chains, and the confinement of very long chains. First experiments with salt in the subphase show the two-dimensional lamellar phase for low molecular weight PSS and suggest a dependence of the electron density profile on the PSS contour length.