

## BP 28: Focus: Charge Effects in Soft and Biological Matter II (joint CPP, BP, ST)

Time: Thursday 14:00–17:45

Location: H37

## Invited Talk

BP 28.1 Thu 14:00 H37

**Electrostatic effects on depletion forces** — ●ROBERTO PIAZZA<sup>1</sup>, STEFANO BUZZACCARO<sup>1</sup>, JADER COLOMBO<sup>2</sup>, and ALBERTO PAROLA<sup>2</sup> — <sup>1</sup>Dipartimento CMIC, Politecnico di Milano, Milano (Italy) — <sup>2</sup>Dipartimento di Fisica e Matematica, Università dell'Insubria, Como (Italy)

Short-ranged depletion forces give rise to a phase behavior which is totally foreign to simple molecular systems, allowing to investigate new scenarios of noticeable interest for condensed matter physics. Yet, so far, most experimental and theoretical efforts have concentrated on depletion effects induced by an ideal agent.

Here, conversely, we focus on systems where strong electrostatic coupling is present. After reviewing some recent results we have obtained by sedimentation measurements on a model system of “sticky” hard-spheres, where depletion forces are induced by nonionic surfactants, we shall present novel results pointing out the dramatic effects that the presence of a self-interacting depletant may bring in. In particular, we shall show that electrostatic repulsive forces between the depletant yield a strong increase of depletion effects, scaling with the Debye-Hückel screening length. Conversely, competitive electrostatic forces between the colloidal particles hinder, and may even totally quench depletion-induced phase separation. The observed effects are fairly well accounted for by a theoretical analysis, based on liquid-state theory, of the structural properties of the two-components (colloids + surfactant micelles) fluid.

BP 28.2 Thu 14:30 H37

**Interaction of Proteins with Spherical Polyelectrolyte Brushes** — ●KATJA HENZLER<sup>1,2</sup>, ALEXANDER WITTEMAN<sup>1</sup>, BJÖRN HAUPT<sup>1,2</sup>, OLEG BORISOV<sup>3</sup>, and MATTHIAS BALLAUFF<sup>2</sup> — <sup>1</sup>Universität Bayreuth, Physikalische Chemie I; Universitätsstr. 30, 95440 Bayreuth, Germany — <sup>2</sup>Helmholtz-Zentrum Berlin für Materialien und Energie; Hahn-Meitner-Platz 1; 14109 Berlin, Germany — <sup>3</sup>Institut pluridisciplinaire de Recherche sur l'Environnement et les Matériaux, UMR 5254, CNRS/UPPA, 64053 Pau, France

Spherical polyelectrolyte brushes (SPB) are a novel class of carrier particles for the immobilization of proteins.[1] A high uptake of proteins can be achieved if the ionic strength is low, while both compounds carry an overall negative charge.[1] No adsorption takes place at higher ionic strength. The main driving force for the adsorption is the counterion release force. Counterions from the brush layer are released and the free energy of the system will be decreased. The thermodynamic of the described adsorption process can be investigated by isothermal titration calorimetry (ITC).[2] This method allows us to determine the adsorption isotherm together with the adsorption enthalpy and entropy. We demonstrated that the adsorption of  $\beta$ -lactoglobulin (BLG) onto the SPB is driven by a strong gain of entropy i.e. by the postulated uptake mechanism of the counterion release force. This is the first direct proof for the counterion release force.

**Literature:** [1] Wittemann, A.; Ballauff, M. *Phys. Chem. Chem. Phys.* 2006, 8, 5269. [2] Henzler, K.; Haupt, B.; Lauterbach, K.; Wittemann, A.; Borisov, O.; Ballauff, M. in preparation.

BP 28.3 Thu 14:45 H37

**On the Question of Universality of Charge Induced Reentrant Condensation of Proteins** — ●FAJUN ZHANG<sup>1</sup>, BENJAMIN HECK<sup>1</sup>, MARCELL WOLF<sup>1</sup>, LUCA IANESSELLI<sup>1</sup>, MICHAEL ZILLER<sup>1</sup>, MAXIMILIAN W. A. SKODA<sup>2</sup>, ROBERT M. J. JACOBS<sup>3</sup>, OLIVER KOHLBACHER<sup>4</sup>, SOPHIE WEGGLER<sup>5</sup>, ANDREAS HILDBRANDT<sup>5</sup>, and FRANK SCHREIBER<sup>1</sup> — <sup>1</sup>Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany — <sup>2</sup>ISIS, Rutherford Appleton Laboratory, UK — <sup>3</sup>Department of Chemistry, CRL, University of Oxford, UK — <sup>4</sup>Zentrum für Bioinformatik Tübingen, Tübingen, Germany — <sup>5</sup>Zentrum für Bioinformatik Saar, Saarbrücken, Germany

The effective interactions and phase behavior of protein solutions under strong electrostatic coupling conditions are a challenge to our understanding due to the complex charge pattern and irregular geometry of protein surfaces, which distinguishes them from related systems such as DNA or conventional colloids. In this work, we discuss the question of the universality of the reentrant condensation (RC) of proteins in solution induced by multivalent counterions, i.e. redissolution upon adding further salts after phase separation, as recently discovered [1].

The discussion is based on a systematic investigation of five different proteins with different charge patterns with five typical multivalent counterions. Zeta potential measurements confirm the effective charge inversion of proteins in the reentrant regime via binding of multivalent counterions. [1] F. Zhang, et al., *Phys. Rev. Lett.* 2008, 101, 148101.

BP 28.4 Thu 15:00 H37

**Effective charge of globular proteins and dendrimers** — UTE BÖHME and ●ULRICH SCHELER — Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, 01069 Dresden

The density of charges on macromolecules is usually so high, that the thermal energy of the respective counterions is insufficient to escape the electric field generated from the charges on the macromolecule. Therefore a fraction of counterions condenses on the macromolecule, lowering the effective charge of the. The combination of diffusion and electrophoresis NMR provides an unambiguous possibility for the experimental determination of the effective charge, which is in good agreement with molecular simulations [1, 2]. This approach has been applied to linear polyelectrolytes as well as proteins and other globular molecules [3]. PAMAM dendrimers exhibit only two types of chargeable groups, therefore counterion condensation can easily be quantified, where the degree of protonation of the amino groups is inferred from proton NMR spectra. At low generations the fraction of condensed counterions increases with increasing molecular weight to level at about 70%. [1] U. Böhme, U. Scheler, *Colloids and Surfaces A*, 222, (2003), 35 [2] K. Grass, U. Böhme, U. Scheler, H. Cottet, C. Holm, *Physical Review Letters* 100, (2008) 096104 [3] Ute Böhme, Ulrich Scheler *Chemical Physics Letters* 435, (2007), 342

BP 28.5 Thu 15:15 H37

**Charge effects in protein diffusion** — ●MARCUS HENNIG<sup>1,2</sup>, FELIX ROOSEN-RUNGE<sup>2</sup>, FAJUN ZHANG<sup>2</sup>, TILO SEYDEL<sup>1</sup>, and FRANK SCHREIBER<sup>2</sup> — <sup>1</sup>Institut Laue-Langevin, Grenoble, France — <sup>2</sup>Institut für Angewandte Physik, Universität Tübingen, Germany

Proteins in solution form highly monodisperse colloidal suspensions. Hence, protein solutions are of fundamental interest in a context of soft matter science. A distinguishing feature to simple colloidal systems is the inhomogeneous surface charge distribution of proteins, which is assumed to have a fundamental biological relevance in controlling for instance aggregation phenomena and docking processes. In their native environment proteins are embedded in a crowded solution of various macromolecules and salt ions. These salt ions are crucial for the understanding of the effective interactions of proteins and the dynamics. We study the self-diffusion of the model globular protein Bovine Serum Albumin in aqueous solutions with different salt concentrations by quasi-elastic neutron scattering performed at selected temperatures and in high protein concentrations. Furthermore, by using spin-echo spectroscopy we investigate the collective diffusion behavior. We found that trivalent salts, particularly yttrium chloride, have a pronounced effect on the self and collective diffusion on a nanosecond time scale. Whereas monovalent and divalent salts, such as sodium chloride and calcium chloride, exhibit little or no effect, we observe that the diffusion decreases nearly 50% for a 19mM yttrium chloride concentration.

## 15 min. break

## Invited Talk

BP 28.6 Thu 15:45 H37

**In-silico simulation of reentrant protein condensation with highly valent counterions** — SOPHIE WEGGLER<sup>1</sup>, MICHAEL ZILLER<sup>2</sup>, FAJUN ZHANG<sup>2</sup>, FRANK SCHREIBER<sup>2</sup>, OLIVER KOHLBACHER<sup>3</sup>, and ●ANDREAS HILDBRANDT<sup>1</sup> — <sup>1</sup>Center for Bioinformatics, Bld. E 2.1, Saarland University, 66123 Saarbrücken, Germany — <sup>2</sup>Institut für Angewandte Physik, Universität Tübingen, Auf der Morgenstelle 10, 72076 Tübingen, Germany — <sup>3</sup>Zentrum für Bioinformatik Tübingen, Sand 14, 72076 Tübingen, Germany

Recently, it has been shown experimentally that negatively charged globular proteins in solution undergo a condensation upon adding trivalent counterions between two critical concentrations  $C^*$  and  $C^{**}$ ,  $C^* < C^{**}$ . This reentrant condensation had previously been observed for DNA and suitable colloidal systems, where the phenomenon is well-understood theoretically, but not for proteins: while the former systems can be well approximated by simple geometries and constant

surface charge distributions, proteins feature complex charge patterns on their surface and can occur in diverse geometrical arrangements.

Consequently, the mechanism behind reentrant protein condensation differs from that behind reentrant DNA condensation and can be explained by short-ranged electrostatic interactions between multivalent cations and acidic residues of the protein.

In my talk, I will present a theoretical model for reentrant protein condensation and will introduce a Monte Carlo technique for its numerical simulation.

BP 28.7 Thu 16:15 H37

**Oligolamellar Lipid Layers Under Load: A Model For Artificial Implants** — ●MARTIN KREUZER<sup>1</sup>, REINER DAHINT<sup>1</sup>, and ROLAND STEITZ<sup>2</sup> — <sup>1</sup>Universität Heidelberg, Physikalisch Chemisches Institut, 69120 Berlin, Germany — <sup>2</sup>Helmholtz-Zentrum Berlin GmbH, 14109 Berlin, Germany

The mechanisms and physicochemical parameters to reduce friction in a natural joint are not yet clear and subject of controversial discussions. We represented the biological interface by a suitable model system and employed Neutron Reflectivity for studying the relevant structural features on the molecular scale. The model interface consisted of a lipid covered silicon disc measured against a model synovial fluid at elevated hydrostatic pressure. Measurements in a pressure cell against D2O showed, that the as-prepared lipid coating remained stable on the substrate up to a hydrostatic pressure of 900bar when the lipid molecules were in their gel-like  $P\beta^*$  phase. However, the lipid main phase transition from the gel to fluid-like  $L\alpha$  phase at 450 bar and 38°C lead to a loss of most of the lipid bilayers and only one double layer remained on the substrate. Measurements against the model synovial fluid (3mg/ml hyaluronic acid in D2O) showed that the lipid multilayer coatings remained stable on the substrate at 450 bar and 38°C, where formerly the phase transition into the fluid-like  $L\alpha$  phase occurred. Beside that, a pronounced swelling of the oligo-lamellar films was observed. Therefore, we conclude that the synovial fluid not only plays an important role in the reduction of friction in the human joint, but also significantly stabilizes the lipid multilayer coating.

BP 28.8 Thu 16:30 H37

**Ion specificity and the Jones-Ray effect at liquid-liquid interfaces** — ●MARKUS BIER — Max-Planck-Institut f. Metallforschung, Heisenbergstr. 3, 70569 Stuttgart, Germany

The solvation shells around ions in solution are one of the key features which determine, e.g., the kinetics of electrochemical reactions and the charge transport across ion channels in biological membranes. Ion specificity of certain properties is, to a large extent, brought about by a variation of the structure or the stability of the solvation shell when considering different types of ions. In the present contribution the interfacial tension between two immiscible liquids as a function of the ionic strength is studied theoretically. For large ionic strengths the well-known linear behaviour is found, which is related to a finite size of the solvation shells. For small ionic strengths a decrease with the negative square root occurs due to an unequal partitioning of ions near the interface, which is induced by a difference of the solvation free energy contrasts between the two liquids. The crossover ionic strength between both regimes turns out to be strongly ion specific. A minimum of the interfacial tension can occur close to the crossover ionic strength, similar to the Jones-Ray effect of the electrolyte-air surface. The theoretical results are compared with experimental data and the relation to the limiting case of an electrolyte-air surface is discussed. It is argued that the dependence of the liquid-liquid interfacial tension on the ionic strength could serve as a sensitive probe to study solvation shells of various ions in various liquids.

BP 28.9 Thu 16:45 H37

**Three-layer piezoelectrets from fluoroethylenpropylene (FEP) copolymer films: Arrangement, preparation and characterization** — ●PENG FANG<sup>1</sup>, FEIPENG WANG<sup>1</sup>, WERNER WIRGES<sup>1</sup>, HEITOR CURY BASSO<sup>2</sup>, and REIMUND GERHARD<sup>1</sup> — <sup>1</sup>Applied Condensed-Matter Physics, Department of Physics and Astronomy, Faculty of Science, University of Potsdam, Potsdam-Golm, Germany — <sup>2</sup>Department of Electrical Engineering, São Carlos School of Engineering, University of São Paulo, São Carlos - SP, Brazil

Piezoelectrets are very useful transducer materials for electromechanical and electroacoustical sensors and actuators. A new process for the preparation of three-layer FEP-sandwich piezoelectrets is introduced. The samples are prepared from commercial FEP films by means of simple procedures such as laser cutting, laser bonding, electrode evap-

oration and high-field poling. The resulting dielectric-resonance spectrum demonstrates the piezoelectricity of the FEP sandwich. A DC poling voltage of around -4 kV is sufficient to achieve piezoelectric d33 coefficient as high as 40 to 50 pC/N. After a continuous dynamic measurement of d33 over 5000 cycles (around 1 day), samples still retain 90% of their initial piezoelectricity. Higher measuring frequencies lead to a decrease of d33. At 100 Hz, d33 is 70% of the value at 2 Hz. Samples charged at elevated temperatures show much better thermal stability of d33. No obvious decay of d33 is found on samples charged at 130 degree C after one-hour storage at 120 degree C. Samples retain more than half of their initial piezoelectricity after a thermal treatment at 140 degree C and are still piezoelectric at 160 degree C.

BP 28.10 Thu 17:00 H37

**The conformation of poly(styrene sulfonate) layers physisorbed from salt solutions of different concentration studied on two different length scales: superposition of electrostatic and steric forces** — ●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 and NaCl concentration in the adsorption solution. Colloidal probe technique reveals that the surface forces are a superposition of steric and electrostatic forces, their respective contribution is determined by the brush area fraction. Interestingly, the internal properties of the brush domains (i.e. brush thickness and average chain distance) are independent on the adsorption salt concentration and depend only on the degree of polymerization and (for the brush thickness) on the surrounding salt concentration. Using these complementary techniques we derive the scaling laws for the average chain distance and the brush thickness and area fraction. Thereby it is possible to form PSS brushes with the desired properties (brush thickness between 20 and 400 nm, brush area fraction between zero and full surface coverage) and hence to control the range and magnitude of the surface forces by choosing the appropriate preparation conditions.

BP 28.11 Thu 17:15 H37

**Changes of the Molecular Structure in Supported Polyelectrolyte Multilayers under Mechanical Stress** — ●JOHANNES FRÜH<sup>1</sup>, MAREIKE KIEL<sup>1,2</sup>, RALF KÖHLER<sup>1,3</sup>, and RUMEN KRASSTEV<sup>1,4</sup> — <sup>1</sup>Max Plank Institut für Kolloid- und Grenzflächenforschung, 14424 Potsdam, Germany — <sup>2</sup>Uni Potsdam, 14476 Potsdam, Germany — <sup>3</sup>Helmholtz-Zentrum Berlin, 14109 Berlin, Germany — <sup>4</sup>NMI an der Universität Tübingen, 72770 Reutlingen, Germany

Polyelectrolyte multilayers (PEM) are extensively applied in contemporary technique. They are composed of oppositely charged polymers. The build-up process is based on the electrostatic interactions between the interface and the polymer molecules. Application of lateral stress on PEM changes the molecular conformation and the orientation of the polymers, and the electrostatic interactions between them. This leads to changes in the interfacial properties of the PEM coatings. The pyrene fluorescence is a tool to study the molecular coiling and polarity in PEM. We used this to follow the changes in the molecular structure of PEM prepared from pyrene labelled poly-styrene sulphonate and poly-(diallyldimethylammonium) chloride deposited on sheets of PDMS. We found that PEM undergo a plastic deformation under mechanical stretching. The polymer molecules organised in PEM experience a transition from coiled to decoiled state. The deformation strongly depends on the salt concentration of the solution from which the PEM are prepared, respectively on the molecular coiling and electrostatic interactions.

BP 28.12 Thu 17:30 H37

**About the interfacial behaviour of PEM films of different charge density** — ●RALF KÖHLER<sup>1,2</sup>, INGO DÖNCH<sup>1</sup>, PATRICK OTT<sup>3</sup>, ANDRÉ LASCHEWSKY<sup>3</sup>, ANDREAS FERY<sup>4</sup>, and RUMEN KRASSTEV<sup>1,5</sup> — <sup>1</sup>MPI of Colloids and Interfaces, 14424 Potsdam — <sup>2</sup>Helmholtz Centre Berlin for Materials and Energy, 14109 Berlin — <sup>3</sup>University of Potsdam, 14476 Potsdam — <sup>4</sup>University of Bayreuth, 95440 Bayreuth — <sup>5</sup>NMI at the University of Tübingen, 72770 Reutlingen, Germany

Polyelectrolyte Multilayers (PEM) consist in complexed layers of organic polyions of opposite charge build-up on solid substrate by layer-

by-layer deposition. Although PEM materials are studied since more than a decade, the interplay of internal interactions and structure is still far from being understood.

We investigate the internal structure of PEM by means of swelling experiments, i.e. an internal mechanical stress is induced into PEM by uptake of solvent molecules from adjacent solvent vapour (H<sub>2</sub>O) of varying saturation. Here neutron reflectometry proves to be a powerful tool due to its ability to test for the thickness of the sample and for

its specific material content at the same time.

Three different PEM systems made from PSS/PDDA (1) are investigated; each containing a derivative of the polycation PDDA of 75, 89, or 100% charge density, also the number of adsorbed layers is varied.

It shows that the swelling characteristics changes continuously with the initial film thickness indicating internal transitions of structure and swelling. (1) poly-styrene sulphonate/ poly-diallyldimethyl ammonium