

## CPP 43: Poster: The Physics of Water Interactions with Biological Matter

Time: Wednesday 18:15–21:00

Location: Poster B2

CPP 43.1 Wed 18:15 Poster B2

**Phase behavior of thermoresponsive polymers in dependence on temperature and pressure** — ●KORA-LEE CLAUDE<sup>1</sup>, SIMON PINZEK<sup>1</sup>, KONSTANTINOS KYRIAKOS<sup>1</sup>, ANNA MIASNIKOVA<sup>2</sup>, ANDRÉ LASCHEWSKY<sup>2</sup>, PETER MÜLLER-BUSCHBAUM<sup>1</sup>, ALFONS SCHULTE<sup>3</sup>, and CHRISTINE M. PAPADAKIS<sup>1</sup> — <sup>1</sup>Technische Universität München, Physik-Department, Garching, Germany — <sup>2</sup>Universität Potsdam, Institut für Chemie, Germany — <sup>3</sup>University of Central Florida, Department of Physics and College of Optics & Photonics, Orlando, U.S.A.

Thermoresponsive polymers constitute an important class of soft matter. Poly(N-isopropyl acrylamide) (PNIPAM) exhibits lower critical solution temperature (LCST) behaviour in aqueous solution: When heated above the cloud point, the chains release water and collapse, leading to phase separation. As an alternative to temperature variation, the phase transition can also be induced applying high pressure, which offers the possibility to map out p-T-phase diagrams.

In the present work, we use temperature- and pressure-resolved turbidimetry to measure the p-T-phase diagram of PNIPAM in a large range and to determine the involved thermodynamic parameters more precisely. Moreover, block copolymers from polystyrene and PNIPAM as well as a novel thermoresponsive polymer are investigated.

CPP 43.2 Wed 18:15 Poster B2

**On the influence of the intermolecular potential on the wetting properties of water on silica surfaces** — ●ELVIRA PAFONG, JULIAN GESKE, and BARBARA DROSSEL — Institut für Festkörperphysik, Technische Universität Darmstadt

Porous amorphous silica is widely used for technological applications such as catalysators, nanotechnology, or biomedicine. Often, an aqueous solution is given into the pores, and it is therefore essential to understand the structure, dynamics and wetting behavior of water in such nanoporous systems. Due to the ability of water to form hydrogen bonds with the surface silanol groups of the silica material, the surfaces are believed to be highly hydrophilic and the water is expected to wet the pores even at moderate filling ratios. However, this is not seen in our molecular dynamics simulations using the standard Brodka-Zerda form of the Lennard Jones potential. We therefore perform an in-depth study of the effect of the choice of the potential and of the thickness of the silica walls on the behavior of water in partially filled pores and on top of silica slabs. We find that the Gulman potential gives more realistic wetting behavior. We also find that the thickness of the silica slab must be chosen carefully in order to well reproduce the electrostatic and van-der-Waals interactions between water and silica surfaces.

CPP 43.3 Wed 18:15 Poster B2

**Molecular dynamics simulations of radon accumulation in water and oil** — ●ELVIRA PAFONG and BARBARA DROSSEL — Institut für Festkörperphysik, Technische Universität Darmstadt, 64289 Darmstadt

Radon is a radioactive gas that can enter the human body from air or from ground water. Radon can accumulate to levels that considerably rise the risk of lung cancer while it is also known as a treatment of various ailments, most notably rheumatoid arthritis. The accumulation of radon differs between tissues, with particularly high concentrations in fatty cells. In order to understand the mechanisms responsible for the different solubility of radon in water and fat, we perform molecular dynamics simulations of radon gas at ambient conditions in contact with a bulk material consisting either of water or oil. We evaluate the diffusion coefficient of radon in both media as well as the equilibrium concentration. The crucial point here is to understand the hydrophobic interaction between water and radon as compared to the dispersive interaction between radon and oil. Therefore, we artificially vary the water charges (i.e., the hydrophobicity) as well as the parameters of the van-der-Waals interaction.

CPP 43.4 Wed 18:15 Poster B2

**3D-Depth Profiling of Soft and Hydrated Polymeric Surfaces using Atomic Force Microscopy** — ●MARTIN DEHNERT, MANUEL UHLIG, DIANA VOIGT, and ROBERT MAGERLE — Fakultät für Naturwissenschaften, TU Chemnitz, Germany

Tapping mode atomic force microscopy (AFM) is widely used for imaging surfaces of soft materials such as polymers, biological cells, tissues,

and even liquids. With tapping mode AFM the shape of the surface (the height image) is measured simultaneously with the phase image from which local mechanical properties of the specimen can be inferred. On soft polymeric materials, however, the tip can indent several tens of nanometers into the surface, which can cause artefacts in both height and phase images. [1] The position of the unperturbed surface and the tip indentation can be determined from point-wise measurements of the amplitude and the phase as function of the tip-sample distance. [1] Furthermore, the tip indentation can be used as depth coordinate for reconstructing three-dimensional depth profiles of the tip-sample interaction. [2] Here, we compare 3D-depth profiles of soft and hydrated polymeric surfaces, for example, polystyrene-functionalized graphene oxide, fluid polymers, and hydrated collagen fibrils by means of dynamic and static force distance measurements. We discuss the different contributions to the tip-sample-interaction and show how the unperturbed surface of compliant materials can be measured.

[1] A. Knoll, R. Magerle, G. Krausch, *Macromolecules* **34**, 4159 (2001)

[2] E.-C. Spitzner, C. Riesch, R. Magerle, *ACS Nano* **5**, 315 (2011)

CPP 43.5 Wed 18:15 Poster B2

**Water Transport through 1-nm-Thick Functional Carbon Nanomembranes** — ●YANG YANG<sup>1</sup>, XIANGHUI ZHANG<sup>1</sup>, SERGEY SHISHATSKIY<sup>2</sup>, JAN WIND<sup>2</sup>, VOLKER ABETZ<sup>2</sup>, ANDRÉ BEYER<sup>1</sup>, and ARMIN GÖLZHÄUSER<sup>1</sup> — <sup>1</sup>Fakultät für Physik, Universität Bielefeld, 33615 Bielefeld, Germany — <sup>2</sup>Institute of Polymer Research, Helmholtz-Zentrum Geesthacht, 21502 Geesthacht, Germany

Water transport through two-dimensional materials is fundamentally important for understanding the interactions of water and materials. From an application point of view, membrane thickness plays an essential role in efficient separation since a minimal thickness can minimize the transport resistance and maximize permeate flux. The synthesis of 1-nm-thick functional carbon nanomembranes (CNMs) offers exciting opportunities for enriching our understanding of water interactions as well as for developing a new class of efficient membranes [1]. CNMs are made by electron induced cross-linking of aromatic self-assembled monolayers and can be transferred to almost any surface. Here we present the fabrication of a composite membrane which comprises a CNM top layer and a porous polyacrylonitrile (PAN) support membrane. The membrane thickness, composition and structure were characterized by employing X-ray photoelectron spectroscopy, atomic force microscopy and helium ion microscopy. The water transport through CNMs is investigated in a pressure-driven process and the first permeation results will be presented and discussed.

[1] M. Ai, et al. Carbon Nanomembranes (CNMs) Supported by Polymer: Mechanics and Gas Permeation. *Adv. Mater.* 2014, 26, 3421

CPP 43.6 Wed 18:15 Poster B2

**Specific Effects of Ca<sup>2+</sup> Ions and Molecular Structure of  $\beta$ -Lactoglobulin Interfacial Layers at Air/Water Interfaces** — ●FELIX SCHULZE-ZACHAU and BJÖRN BRAUNSCHWEIG — Institute of Particle Technology (IFG), Friedrich-Alexander University of Erlangen-Nürnberg (FAU), Cauerstrasse 4, 91058 Erlangen, Germany

$\beta$ -lactoglobulin (BLG) adsorbate layers at air-water interfaces were studied on a molecular level with vibrational sum-frequency generation (SFG), tensiometry and ellipsometry and on a macroscopic level by foam property measurements as a function of bulk Ca<sup>2+</sup> concentrations (C). For C < 10 mM, a strong decrease in SFG intensity of O-H stretching bands from interfacial water molecules is observed. This decrease is indicative of charge screening and presumably also of specific ion interactions. Support for the latter comes from a change in polarity of C-H stretching modes from aromatic amino acid residues such as Trp, accompanied by an abrupt increase in layer thickness from 5 to 10 nm. Such a polarity change was previously observed in a pH dependent study where the isoelectric point of BLG was crossed and is likely to be associated with interfacial charge compensation and overcharging due to the presence of Ca<sup>2+</sup>. Macroscopic foam stability, however, is decreased once the interfacial charges become fully screened which is in line with previous studies of thin foam films. Once the negative net charge of BLG is overcharged by Ca<sup>2+</sup> at high C, agglomerates at the interface start to form which increase the layer thickness and interfacial elasticity and decrease the viscosity of the interfacial layer

which leads to much higher foam stabilities and smaller bubble sizes.

CPP 43.7 Wed 18:15 Poster B2

**Nanoskalige mechanische Eigenschaften hydrierter Kollagenfibrillen** — DIANA VOIGT<sup>1</sup>, MANUEL UHLIG<sup>1</sup>, MARTIN DEHNERT<sup>1</sup>, ANKE BERNSTEIN<sup>2</sup> und ROBERT MAGERLE<sup>1</sup> — <sup>1</sup>Fakultät für Naturwissenschaften, TU Chemnitz, Chemnitz — <sup>2</sup>Orthopädie und Traumatologie, Universitätsklinikum Freiburg, Freiburg

Faserbildende Kollagene sind ein Hauptbestandteil der Bindegewebe von Wirbeltieren. Die häufigste Art ist Kollagen vom Typ I, das 300 nm lange Tropokollagene bildet, die sich zu Fibrillen mit typischerweise 30 bis 300 nm Durchmesser anordnen, wobei die Fibrillen eine periodische Struktur (die D-Bande) mit 67 nm Wiederholeinheit entlang der Fibrillenachse aufweisen. Die Verteilung von Wassermolekülen innerhalb der Kollagenfibrillen bestimmt entscheidend die mechanischen Eigenschaften der Fibrillen. Wir untersuchen die nanoskaligen mechanischen Eigenschaften hydrierter Kollagenfibrillen mittels Rasterkraftmikroskopie und verschiedenen Arten der Kraftspektroskopie, wobei wir den Wassergehalt der Fibrillen über die Luftfeuchte kontrolliert einstellen können. Das nanoskalige Quellverhalten der Fibrillen gibt direkte Hinweise auf unterschiedliche Mengen von freiem und gebundenem Wasser in den Überlapp- und Lückenbereichen der D-Bande. Ferner können wir räumliche Tiefenprofile der mechanischen Eigenschaften der Kollagenfibrillen rekonstruieren.

CPP 43.8 Wed 18:15 Poster B2

**Landau-Ginzburg theory for indirect membrane interactions** — ALEXANDER SCHLAICH<sup>1</sup>, JAN DALDROP<sup>1</sup>, BARTOSZ KOWALIK<sup>1</sup>, MATEJ KANDUC<sup>1,2</sup>, EMANUEL SCHNECK<sup>3</sup>, and ROLAND R. NETZ<sup>1</sup> — <sup>1</sup>Fachbereich Physik, Freie Universität Berlin, 14195 Berlin, Germany — <sup>2</sup>Soft Matter and Functional Materials, Helmholtz-Zentrum Berlin, 14109 Berlin, Germany — <sup>3</sup>Department of Biomaterials, Max Planck Institute of Colloids and Interfaces, 14476 Potsdam, Germany

Hydrophilic interfaces, such as planar lipid membranes, show overwhelming repulsive behavior at nanometer separations in aqueous solution that is not captured within classical continuum theories. It is common consensus that the atomistic degrees of freedom need to be considered explicitly. Marcelja and Radic were the first to propose that water orientation causes a significant contribution to the interaction free energy.

Using field-theoretical modeling, we derive the phenomenological interaction parameters for a Landau-Ginzburg model and show that employing the water dipole orientation we can quantitatively describe the indirect interaction between surfaces, i.e. the contribution of water acting on a single surface.

CPP 43.9 Wed 18:15 Poster B2

**The local structure in concentrated yttrium(III) chloride aqueous solutions under high hydrostatic pressure** — MIRKO ELBERS<sup>1</sup>, KARIN JULIUS<sup>1</sup>, MICHAEL PAULUS<sup>1</sup>, CHRISTIAN STERNEMANN<sup>1</sup>, FLORIAN WIRKERT<sup>1</sup>, JULIA NASE<sup>1</sup>, PAUL SALMEN<sup>1</sup>, GÖRAN SURMEIER<sup>1</sup>, RALPH WAGNER<sup>2</sup>, and METIN TOLAN<sup>1</sup> — <sup>1</sup>Fakultät Physik/DELTA, TU Dortmund, Germany — <sup>2</sup>Fachbereich C - Physik, Bergische Universität Wuppertal, Germany

We present an extended X-ray absorption fine structure (EXAFS) study on the hydration properties of yttrium(III) chloride (YCl<sub>3</sub>) under high hydrostatic pressures. In order to take a closer look at ion-ion interactions, aqueous salt solutions with different concentrations were

investigated. In nature, the interaction between macromolecules or nanoparticles is mediated by the surrounding aqueous phase. Thus, changes in the water structure, e.g. by the application of pressure or the addition of ions, have a direct impact on the particle-particle interaction potential. For example, in a pressure dependent small angle X-ray scattering study of dense aqueous lysozyme solutions, we found a minimum of the attractive interaction strength at a hydrostatic pressure of 2 kbar. This effect was assigned to a collapse of the second hydration shell of the surrounding water, which might be affected by the addition of ions. Hence, we studied the pressure dependence of the local structure of salt solutions by EXAFS measurements between 1 bar and 5 kbar at concentrations of up to 3M. Furthermore, we performed additional molecular dynamics (MD) simulations of the investigated sample system to interpret the experimental data.

CPP 43.10 Wed 18:15 Poster B2

**Lower critical solution temperature behaviour in protein solutions caused by cation-induced hydration effects** — OLGA MATSARSKAIA<sup>1</sup>, MICHAL BRAUN<sup>1</sup>, FELIX ROOSEN-RUNGE<sup>2</sup>, MARCELL WOLF<sup>1</sup>, ROLAND ROTH<sup>3</sup>, FAJUN ZHANG<sup>1</sup>, and FRANK SCHREIBER<sup>1</sup> — <sup>1</sup>Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen — <sup>2</sup>Institut Laue-Langevin, Grenoble, France — <sup>3</sup>Institut für Theoretische Physik, Universität Tübingen

Upper and lower critical solution temperatures (UCST / LCST) are well known in systems such as mixtures of organic liquids. Here, we demonstrate for the first time an LCST in an aqueous protein (bovine serum albumin, BSA) solution which is induced by trivalent metal cations such as Y<sup>3+</sup>. The LCST manifests itself as a liquid-liquid phase separation (LLPS) above a certain temperature. Supported by calorimetric data, in their contribution we rationalise the mechanism behind this new case of LCST as follows. It is known from crystal structures that the Y<sup>3+</sup> cations bind to negatively charged carboxyl groups of acidic residues on the protein surface and can bridge protein molecules [1]. Both Y<sup>3+</sup> and carboxyl groups are strongly hydrated. For protein-cation binding to occur, both binding partners need to shed their hydration shells. Hydration water molecules are thus released into bulk water, increasing the entropy of the system. With increasing temperature, this entropy-driven binding process becomes more efficient, inducing a short-range attraction into the system which ultimately leads to LLPS.

[1] Zhang et al. (2011). J. Appl. Cryst., 44, 755.

CPP 43.11 Wed 18:15 Poster B2

**Tracer diffusion in heterogeneous environments: Towards analytical fit functions** — FELIX ROOSEN-RUNGE, DOMINIQUE BICOUT, and JEAN-LOUIS BARRAT — Institut Laue-Langevin, Grenoble, France

Tracer diffusion in heterogeneous environments is a relevant and frequently studied phenomenon in experiment, simulation and theory. A paradigmatic example is water diffusion through hydration shells around biomacromolecules or membranes. Analytical fit functions for complex systems such as these are rare, although they would be an interesting means to connect conceptual ideas to experimental results. We report on an approach to recover effects of geometry and position-dependent diffusivity by approximate solutions well-suited for data fitting. We derive an analytical function for an isotropic motion switching between different diffusive states, and extend the approach towards anisotropic systems such as layer structures. Finally, we discuss the challenges, limitations and potentials of the outlined method for data analysis integrating experimental and theoretical knowledge.