BP 46: Biomaterials and Biopolymers II (joint CPP/BP)

Time: Thursday 15:00–18:00 Location: C 264

BP 46.1 Thu 15:00 C 264

Dynamic and static force measurements on (PLL/HA)n multilayer films by atomic force microscopy — •Johannes Hellwig and Regine von Klitzing — Stranksi-Laboratorium, TU Berlin, 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 polyelectrolyte 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, ionic strength and temperature of the surrounding medium changes. Furthermore the viscoelastic film behaviour was measured and calculated by dynamic force measurements.

(1) Volodkin, D. V.; Larionova, N. I.; Sukhorukov, G. B. Biomacromolecules 2004, 5, 1962.

(2) Decher, G. Science 1997, 277, 1232.

(3) Üzüm, C.; Hellwig, J.; Madaboosi, N.; Volodkin, D.; v. Klitzing, R. Beilstein J. Nanotechnol. 2012, 3, 778.

BP 46.2 Thu 15:15 C 264

Mechanical characterization of recombinant spider silk: yarn tensile testing and single fiber deformation via AFM — •Benedikt Neugirg[1], Gregor Lang[2], Thomas Scheibel[2], and Andreas Fery[1] — [1]Physical Chemistry II, University of Bayreuth — [2]Biomaterials, University of Bayreuth

Outstanding mechanical properties combined with biocompatibility render spider silks one of the most promising materials with respect to biomedical applications. Recombinant routes to e.g. dragline silk core proteins of Araneus diadematus provide access to material fabrication at industrially relevant scales. Together with the electrospinning technique, morphologies based on fibrillar structures, from single fiber to nonwovens are readily producible.

In our work, we mechanically characterize recombinant silk yarns and the individual sub-um diameter fibers which the yarns consist of. For this purpose we use macroscopic tensile testing and nanoscopic AFM lateral bending experiments. Furthermore, we investigate the influence of the relative humidity (RH) which is known to have a huge impact on silk mechanics.

We found the recombinant silk to resemble rubber-like properties at higher levels of RH. Enhancing structure crystallinity by post-treatment of the fibers dramatically increases the energy uptake at high RH prior to rupture. In this (physiologically relevant) humidity range, recombinant spider silk can keep up with its natural analog in terms of toughness, the most prominent mechanical characteristic.

BP 46.3 Thu 15:30 C 264

Wang-Landau simulation of protein-like Gō model molecules — •Arne Böker and Wolfgang Paul — Martin-Luther-Universität Halle-Wittenberg

The Wang-Landau method is a recent addition to the Monte Carlo family, able to provide complete thermodynamic information about a system. Contrary to Markovian Monte Carlo, it works in a generalized statistical ensemble, giving the opportunity to access quantities of microcanonical and canonical ensembles in one simulation.

Gō-like protein models have been successful for several decades owing to their simplicity, allowing fast simulation to achieve mostly reasonable results. Thus, they provide a suitable model system for the relatively complicated Wang-Landau algorithm.

We applied this method to a basic Gō model consisting of hard tangent spheres with a square-well attraction to investigate the phase behaviour and especially the influence of the length scale used to define neighbours within the Gō model on these properties.

BP 46.4 Thu 15:45 C 264

The effect of specific interactions on the state diagram of a hard-sphere chain model — •Benno Werlich[1], Timur Shakirov[1], Mark Taylor[2], and Wolfgang Paul[1] — [1]Institut für Physik, Martin-Luther Universität Halle-Wittenberg, Halle(Saale), Germany — [2]Department of Physics, Hiram College, Ohio, USA

Secondary structure formation in proteins is generated by an interplay of unspecific and specific interactions. We employ a coarse-grained, one-bead protein-like model to qualitatively understand the importance of the specific interactions. Based on a hard-sphere chain model with unspecific square well attractions we introduce specific interactions as additional square well potentials. These interactions are selective and correspond to a simple donor acceptor representation in the context of hydrogen bonds. The donor acceptor interaction strength can be changed via variation of the well depth of the square well potential. A comparison between hard-sphere chains with and without specific interactions shows a strong deviation in certain ranges of the density of states (DOS). The DOS is the basic function which encodes the whole thermodynamics and thus the microcanonical and canonical analysis give a more detailed insight. To generate the DOS we applied the Stochastic Approximation Monte Carlo method.

BP 46.5 Thu 16:00 C 264

Characterization of a liposomal drug carrier with continuous contrast variation in SAXS — •Raul Garcia-Diez[1], Christian Gollwitzer[1], Michael Krumrey[1], and Zoltan Varga[2] — [1]Physikalisch-Technische Bundesanstalt (PTB), Abbestr. 2-12, 10587 Berlin, Germany — [2]Biological Nanochemistry Research Group, Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Magyar Tudosok korutja 2, H-1117, Budapest, Hungary

Doxorubicin is an anticancer drug known for its high cardiotoxicity, though a liposomal formulation of it can reduce this side-effect significantly and improve the pharmacokinetics of the drug. In this work, the mean size and average density of pegylated liposomal doxorubicin (Caelyx®) was determined by continuous contrast variation in SAXS with iodixanol, an iso-osmolar suspending medium. The study is focused on the isoscattering point position and the analysis of the Guinier region of the scattering curves recorded at different solvent densities at the four-crystal monochromator beamline of PTB at the synchrotron radiation facility BESSY II. The response of the liposome to increasing solvent osmolality and the structure of the liposome-encapsulated doxorubicin fiber after the osmotic shrinkage of the liposome are evaluated with sucrose contrast variation in SAXS/WAXS.

BP 46.6 Thu 16:15 C 264

Binding of amino acids to bioactive calcite surface — •Robert Stepić[1], Zlatko Brkljača[1], David M. Smith[2,3], and Ana-Sunčana Smith[1] — [1]Institute for Theoretical Physics and Excellence Cluster: Engineering of Advanced Materials, FAU Erlangen-Nürnberg, Nägelsbachstraße 49b, Erlangen, 91052, Germany — [2]Division of Organic Chemistry and Biochemistry, Rudjer Bošković Institute, Bijenička 54, 10000, Zagreb, Croatia — [3]Center for Computational Chemistry, FAU Erlangen-Nürnberg, Nägelsbachstraße 25, Erlangen, 91052, Germany

Biomineralization is a process by which living organisms form minerals. This process is controled mainly by proteins and the resulting end products have distinctively different properties than minerals produced by abiotic mineralization. Better understanding of underlying mechanisms of biomineralization could help us make use of them in wide range of applications. Our goal is to gain further insight into the role of proteins in biomineralization by taking their elementary building blocks, amino acids, and investigating their interactions with a calcite surface in water. To achieve this we use a well established theoretical framework of molecular dynamics implemented in free GROMACS package. Efficient sampling of the phase space is done using the harmonic bias potential along the suitable reaction coordinate. This allows us to construct the potential of mean force and determine the free energies of binding to the surface of various amino acids. Results of this research will give us clues as to what amino acids play a key role in proteins that control the process of biomineralization.

15 min. break

BP 46.7 Thu 16:45 C 264

Investigation of the lateral arrangement of phospholipid monolayers with respect to the adsorption of hyaluronan* — •Florian Wieland[1], Thomas Zander[1], Sören Gayer[1], Andra Dedinaite[2], Per Claesson[2], Vasyl Haramus[1], and Regine Willumeit-Römer[1] — [1]Helmholtz Zentrum Geesthacht, Max Planck Str. 1, 21502 Geesthacht — [2]KTH Royal Institute of Technology, School of Chemical Sciences and Engineering, Department of Chemistry, Surface and Corrosion Science, Drottning Kristinas väg 51, SE-10044 Stockholm, Sweden

The unmatched tribological performance of articulated joints is due to both the properties of the cartilage itself and the assumed self-organization of the molecules in the synovial fluid and at the surface of cartilage. Phospholipids form lamellar structures on cartilage surfaces and are able to reduce friction and wear. We performed x-ray reflectivity and grazing incidence diffraction measurements on Langmuir layers of Dipalmitoylphosphatidylcholine and investigated how the adsorption of hyaluronan (HA) changes the arrangement of the lipids. In the course of the experiment we changed parameters like the molecular weight (MW) and the salt concentration in the subphase, in order to determine the key parameters.

Our data indicate that the adsorption strongly depends on the MW of HA and further on the presence of divalent ions in the subphase.

BP 46.8 Thu 17:00 C 264

Interaction of Hyaluron and Phospholipids at high hydrostatic pressure — •Thomas Zander[1], Florian Wieland[1], Min Wang[2], Akanksha Raj[2], Per Claesson[2,3], Andra Dedinaite[2,3], Vasyl Haramus[1], Regine Willumeit-Römer[1], and Andreas Schreyer[1] — [1]Helmholtz Zentrum Geesthacht, Institute for Materials Research, DE-21502 Geesthacht — [2]KTH Royal Institute of Technology, School of Chemical Sciences and Engineering, SE-10044 Stockholm — [3]SP Technical Research Institute of Sweden, SP Chemistry, SE-11486 Stockholm

Articular joints are bio-lubrication systems with the lowest friction coefficients found in nature. The friction coefficient is provided by the synovial fluid, which is an intricate composition of different macromolecules (e.g. phospholipids and hyaluronan) and which keep the exceptional good lubrication properties even under high loads and shear rates. It is thought that the different constituents form complex structures in order to enable this low friction coefficients.

X-ray reflectivity measurements at different hydrostatic pressures (60bar - 2kbar) on silicon supported phospholipid- and phospholipid hyaluronen composite layers have been performed in order to gain information about their structural arrangement. Parameters like, temperature, molecular weight of the hyaluronan and ions in the solvent solution have been varied, to identify possible key parameters for good lubrication. Our results clearly reveal differences in the behaviour of the phospholipid hyaluronen composites due to different solvent conditions.

BP 46.9 Thu 17:15 C 264

Establishing Short-Range Gradients of Cytokines to Mimic Paracrine Cell Interactions in vitro — •Michael Ansorge and Tilo Pompe — Universität Leipzig, Institute of Biochemistry

Cells in various tissues receive myriads of exogenous signals, which in sum determine their fate. Many signaling molecules act in a gradient fashion to guide cell migration, differentiation and proliferation. We set up a microparticle-based system for generating biomimetic short-ranged gradients to analyze dynamic cell behavior with high resolution in vitro. The modification of agarose microbeads with glycosaminoglycans (GAG) with different degree of sulfation provides a toolbox to tune the binding and release of various cytokines.

Using chemically sulfated hyaluronic acid (HA) as GAG we were able to load the microbeads with different cytokines (SDF-1, TGF-beta, IL10) in dependence on their affinity to sulfated and non-sulfated HA. By following the local concentration decrease of fluorescently labeled cytokine inside the microbeads over days with confocal microscopy we could determine released amounts and diffusion-based transport properties. We were able to calculate local cytokine gradients surrounding the microbeads, which are estimated to be in the range of some tens of micrometers at physiological concentrations of pg/ml. We currently verify these local gradients using fluorescence correlation spectroscopy.

Studies on the dynamic cell behavior within the cytokines gradients address biomedical questions on cell fate of hematopoietic stem cells and fibroblasts in 3D collagen-based matrices.

BP 46.10 Thu 17:30 C 264

Characterising the water vapour sorption behaviour of wood — •Alexander Murr and Roman Lackner — Institut for Structural Engineering and Material Science, University of Innsbruck

Wood is a cellular material with a hierarchical structure based on polymers (cellulose, hemicelluose and lignin). As variations of humidity causes a change of its physical properties, a detailed knowledge of the interaction between water and wood is of importance. A common method for such investigations are water vapour sorption (wvs) experiments where relative humidity is varied and the related change of sample mass is measured. As this change of mass deviates from classical diffusion, various macroscopic models appeared in literature, ranging from relaxation limited to transport limited approaches. To identify which of these descriptions could be used for further investigations, a precise identification of the macroscopic behaviour is necessary.

In the given presentation the sorption kinetics of Norway spruce wood (Picea abies) will be discussed. Based on a series of wvs experiments on grained wood the influence of grain size and temperature on the sorption behaviour will be shown. A comparison of similar sample masses with different grain sizes illustrates diffusion along the cell wall not being the limiting factor in the observed sorption experiments. Additionally, an outlook on further theoretical and experimental investigations shall be given.

BP 46.11 Thu 17:45 C 264

Kinetics of mutarotation in fucose-saccharides as monitored by dielectric and infrared spectroscopy — •Wilhelm Kossack[1], Wycliffe Kiprop Kipnusu[1], Mateusz Dulski[2], Karolina Adrjanowicz[2], Olga Madejczyk[2], Emanuel Urandu Mapesa[1], Martin Tress[1], Kamil Kaminski[2], and Friedrich Kremer[1] — [1]University of Leipzig, Linnestr. 5, Leipzig, Germany — [2]University of Silesia, Katowice, Poland

Fourier Transform Infrared Spectroscopy and Broadband Dielectric Spectroscopy are combined to trace kinetics of mutarotation in L-fucose. After quenching molten samples to temperatures between $T = 313$ K and 328 K, the concentrations of two anomeric species change according to a simple exponential time dependence, as seen by the increasing absorbance of specific IR-vibrations. In contrast, the dielectric spectra reveal a slowing down of the structural (α-) relaxation according to a stretched exponential time dependence (stretching exponent of 1.5 ± 0.2). The rates of change in the IR absorption for α- and β-fucopyranose are (at $T = 313$ K) nearly one decade faster than that of the intermolecular interactions as measured by the shift of the α-relaxation. This reflects the fact that the α-relaxation monitors the equilibration at a mesoscopic length scale, resulting from fluctuations in the anomeric composition.