

CPP 13: Biomaterials and Biopolymers I (joint session CPP/BP)

Time: Tuesday 9:30–13:00

Location: H34

Invited Talk

CPP 13.1 Tue 9:30 H34

Hierarchical Multi-Step Folding of Polymer Bilayers — GEORGI STOYCHEV^{1,2}, SEBASTIEN TURCAUD³, JOHN DUNLOP³, and •LEONID IONOV¹ — ¹Leibniz Institute of Polymer Research Dresden, Hohestr. 6, 01069, Dresden, Germany — ²Technische Universität Dresden, Physical Chemistry of Polymer Materials, 01062, Dresden, Germany — ³Department of Biomaterials, Max Planck Institute of Colloids and Interfaces, Am Mühlenberg 1, 14424, Potsdam, Germany

We investigated the actuation of patterned bilayers placed on a substrate. We found that films display several kinds of actuation behavior such as wrinkling, bending and folding that result in a variety of shapes. Based on experiments and modeling, we argued that rectangular bilayers start to roll from the corners due to quicker diffusion of water. Rolling from long-side starts later and dominates at high aspect ratio[1].

It was also demonstrated that one can introduce hinges into the folded structure by proper design of the bilayers external shape without having to use site selective deposition of active polymers. Experimental observations lead us to derive four empirical rules backed up by theoretical understanding as well as simulations. We then demonstrated how those rules can be used to direct the folding of edge-activated polymer bilayers through a concrete example - the design of a 3D pyramid[2].

[1] Stoychev et al, "Hierarchical Multi-Step Folding of Polymer Bilayers", *Adv.Func.Mat.*, published online Nov 26, 2012

[2] Stoychev et al, "Shape-Programmed Folding of Stimuli-Responsive Polymer Bilayers", *ACS Nano*, 2012, 6(5), 3925-3934

CPP 13.2 Tue 10:00 H34

Mechanical properties of poly-L-lysine (PLL) / hyaluronic acid (HA) multilayer films measured by AFM — •JOHANNES HELLWIG, CAGRI ÜZÜM, and REGINE VON KLITZING — Stranski-Laboratorium, Institut für Chemie, TU Berlin, Strasse des 17. Juni 124, 10623 Berlin, Germany

In recent years smart biomaterials have become a highly developing field of interest for biomedical applications, e.g. drug delivery. The layer-by-layer (LbL) technique 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 mechanical properties of LbL coated poly(L-lysine)/hyaluronan PLL/HA films were studied by scanning- and colloidal-probe atomic force microscopy as a function of indentation velocity, number of polymer deposition steps and temperature. Film growth was investigated by two independent AFM methods: scratch-and-scan and full-indentation[1]. Film thickness increases linearly with polymer deposition steps. The Young's modulus ranges between 15 and 40 kPa and does not depend on the film thickness. Stress relaxation and creep compliance measurements indicate a viscoelastic film behaviour with multiple relaxation mechanisms.

[1] Üzüml, C.; Hellwig, J.; Madaboosi, N.; Volodkin, D.; v. Klitzing, R. *Beilstein J. Nanotechnol.* 2012, 3, 778*788.

CPP 13.3 Tue 10:15 H34

Single-Virus Force Measurements on sialic acid — •VALENTIN REITER¹, SUMATI BHATIA³, MANUEL GENSLE¹, CHRISTIAN SIEBEN², DANIEL LAUSTER², ANDREAS HERRMANN², RAINER HAAG³, and JÜRGEN P. RABE¹ — ¹Department of Physics, Humboldt-Universität zu Berlin — ²Department of Biology, Humboldt-Universität zu Berlin — ³Department of Chemistry, Freie Universität Berlin

We study the multivalent effects in the binding and dissociation processes of sialic acid with the viral membrane protein hemagglutinin using scanning force microscopy (SFM) based single-virus force measurements (SVFM). Since an infectious disease has to start with the attachment of a virus to the cell membrane, this binding as well as its dissociation has to be carefully analyzed [1]. This is done by creating a mixed self assembled monolayer (MSAM) on gold from synthesized compounds, terminated by lipophilic acid. The compounds are functionalized with sialic acid and disfunctionalized with hydroxide. Inactivated influenza viruses are attached to a silicon nitrate SFM cantilever via a polyethylene glycol spacer. With this setup SVFM is performed

in aqueous solution. The ratio of functionalized to disfunctionalized molecules on the MSAM enables the control of the degree of multivalency of the binding and therefore the realization of mono-, bi-, and trivalent connections. On the other hand SVFM are performed at different loading rates to estimate specific binding parameters, such as the average rupture length and bond life time.

[1] C. Sieben et al., *PNAS*, 2012, 109, 34, 13626-13631.

CPP 13.4 Tue 10:30 H34

Response of major ampullate silk of *Nephila pilipes* to pressure and tensile stress as measured by FTIR spectroscopy — •MARKUS ANTON¹, WILHELM KOSSACK¹, CHRISTOF GUTSCHE¹, ROXANA FIGULI², PERIKLIS PAPADOPOULOS³, and FRIEDRICH KREMER¹ — ¹Universität Leipzig, Institut für Experimental Physik I, Linnéstraße 5, 04103 Leipzig, Germany — ²Karlsruher Institut für Technologie, Institut für Technische Chemie und Polymerchemie, Engesserstraße 18, 76128 Karlsruhe, Germany — ³Max Planck Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

Nanocrystals composed mainly of β -sheet polyalanine are responsible for the high toughness of major ampullate (dragline) spider silk. Fourier-Transform infrared (FTIR) spectroscopy is employed to study their response to (i) uniaxial stress and (ii) hydrostatic pressure. In the former a red shift and in the latter a blue shift of the vibration of polyalanine β -sheets at 965 cm^{-1} is observed. In both cases a linear dependence is evident, which bends off for hydrostatic pressure greater than 1.4 GPa and is fully reversible up to 7 GPa. The seamless connection of negative and positive pressure regimes corroborate quantitatively our structural model of spider silk [P. Papadopoulos et al., *Eur. Phys. J. E* 24 (2007) 193, P. Papadopoulos et al., *Colloid Polym. Sci.* 287 (2009) 231, R. Ene et al., *Soft Matter* 5 (2009) 4568] as composed of *pre-stressed* alanine-rich nanocrystals embedded in a glycine-rich amorphous matrix. It is also confirmed that nanocrystals withstand high pressures without undergoing structural transition or deteriorating their mechanical properties.

CPP 13.5 Tue 10:45 H34

Polarized confocal Raman microscopy and EBSD: A comparative study studying calcite crystalline regions within the tergite cuticle of terrestrial isopods. — •CHRISTIAN REISECKER¹, ERIKA GRIESSHABER², BASTIAN SEIDL³, ANDREAS ZIEGLER³, and SABINE HILD¹ — ¹Institute of Polymer Science, Johannes Kepler Universität Linz, Altenbergstr. 69, 4040 Linz, Austria — ²Department of Earth and Environmental Sciences, LMU, Theresienstr. 41, 80333 München, Germany — ³Facility for Electron Microscopy, University of Ulm, Albert-Einstein-Allee 11, 89069 Ulm, Germany

Recently, isopods gained increasing amount of interest in terms of biomimetics as they combine quite diverse properties within their tergite cuticle such as hardness in the outer parts of the cuticle and softness in the more inner part, where muscles will be attached. This is achieved via a strong hierarchical arrangement of organic-chitin-protein fibers, which are arranged in a twisted plywood structure and inorganic materials. The organic matrix is hardened by carbonates in crystalline (calcite) and non-crystalline modification (amorphous calcium carbonate, ACC). This study focusses on the outer, mainly crystalline parts within the tergite cuticle of isopods. Confocal Raman microscopy is a useful tool to study the chemical and structural composition of isopods, as it provides a spatial resolution below 300 nm. Polarized confocal Raman microscopy and EBSD will be utilized to determine different domains and layers of calcite crystals. It has been demonstrated that depending on the species, the calcite region consists of domains with different orientations concerning its bravais lattice.

CPP 13.6 Tue 11:00 H34

Mineralization of calcium containing compounds at the liquid-liquid interface — •STEFFEN BIEDER¹, FLORIAN WIELAND², PATRICK DEGEN³, MICHAEL PAULUS¹, JULIA NASE¹, ANDRE STEFFEN¹, BRIDGET MURPHY⁴, HEINZ REHAGE³, and METIN TOLAN¹ — ¹Fakultät Physik/DELTA, Technische Universität Dortmund, D-44221 Dortmund, — ²Helmholtz Zentrum Geesthacht, Max-Planck-Straße 1, D-21502 Geesthacht — ³Fakultät Chemie, Technische Uni-

versität, D-44221 Dortmund — ⁴Institut für Experimentelle und Angewandte Physik, CAU, Leibnizstraße 19, D-24098 Kiel

Nature forms structures from inorganic and organic components for different purposes, e.g. protection or stabilization. Accordingly, organisms have developed the concept of biomineralization providing highly controlled growth processes under ambient conditions. For instance the formation of teeth, bones or shells demonstrates the high degree of perfection and control, which can not be reached by human technology until now. We studied the mineralization of calcium containing compounds at the liquid-liquid interface. A solution of water and calciumhydrogencarbonat is covered by toluene. We added different fatty acids in order to investigate their influence on the growing layer at the liquid-liquid interface. We observed the layer formation by grazing incidence diffraction (GID) and x-ray reflectivity (XRR). The extracted data show an formation of calcium soaps at the interface. GID data reveal that the forming crystallites are highly orientated with the 001 axis perpendicular to the sample surface. We acknowledge BMBF(05 K10 FK2) and (05K10PEC) for financial support.

15 min. break

CPP 13.7 Tue 11:30 H34

Probing the electronic structure of Proline in aqueous solution by soft RIXS — ●FRANK MEYER¹, ANDREAS BENKERT^{1,2,8}, SANKARANARAYANAN NAGARAJAN³, REGAN WILKS⁴, MARCUS BÄR⁴, WANLI YANG⁵, MICHAEL ZHARNIKOV³, CLEMENS HESKE^{2,6,7}, LOTHAR WEINHARDT^{2,6,7}, and FRIEDRICH REINERT^{1,8} — ¹Exp. Phys. VII, Universität Würzburg — ²Inst. for Photon Science, KIT — ³Angew. Phys. Chemie, Universität Heidelberg — ⁴Solar Energy Research, HZB — ⁵ALS, Lawrence Berkeley National Laboratory — ⁶Dept. of Chemistry, University of Nevada, Las Vegas — ⁷ANKA Synchrotron Radiation Facility, KIT — ⁸Gemeinschaftslabor für Nanoanalytik, KIT

Amino acids are organic molecules that are highly relevant for many biological macro-molecules. Defining their function, the electronic structure of these molecules and, in particular, the interaction with biologically relevant solvents is of fundamental interest. In contrast to the majority of amino acids in which the functional groups (carboxyl, amino, side chain) are connected via one carbon atom, in proline the amino group and the side chain are connected in a heterocyclic compound, forming a pyrrolidine ring. We present resonant inelastic soft x-ray scattering (RIXS) maps of proline in aqueous solution at different pH values. Upon protonation and deprotonation, strong changes in the maps are observed. The results will be compared with RIXS data of solid state and gas phase proline, as well as other amino acids (i.e., glycine, cysteine). We find a distinctly different electronic structure than that observed for glycine and cysteine, as well as a significantly influence of the water environment.

CPP 13.8 Tue 11:45 H34

Structure formation in homologous peptides: Ac-Ala₆-Lys(H⁺) versus Ac-βAla₆-Lys(H⁺) — ●FRANZISKA SCHUBERT, CARSTEN BALDAUF, MARIANA ROSSI, VOLKER BLUM, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der MPG, Berlin

β-peptides are non-natural peptides composed of β-amino acid residues that feature one additional methylene group in the backbone compared to natural α-amino acids. Due to their larger flexibility, β-peptides are valuable for the design of new peptides with specific chemical or pharmacological properties. We here investigate the differences in structure formation between α- and β-peptides from first principles employing density-functional theory (DFT) with the PBE functional corrected for van der Waals interactions[1]. We focus this presentation on a comparison of Ac-βAla₆-Lys(H⁺) and Ac-Ala₆-Lys(H⁺) under *in vacuo* “clean-room” conditions and compare to experimental ion mobility spectrometry[2]. Our conformational search is based on replica exchange molecular dynamics. After generating a large pool of force field-based structures, we relax thousands of conformers with DFT. For the β-peptide, the finite-*T* vibrational free energy part is essential to recover a conformational hierarchy consistent with experiment. While Ac-Ala₆-Lys(H⁺) is found to be α-helical at 300K, Ac-βAla₆-Lys(H⁺) is seen to vary between 3₁₀, α, and π analog helices. Our simulations show that conformational entropy plays a critical role, and an *ab initio* quantitative assessment is a big challenge that we (and the field) must meet next. [1] A. Tkatchenko, M. Scheffler, PRL **102**, 073005 (2009); [2] S. Warnke, K. Pagel, G. von Helden, Fritz-Haber-Institut.

CPP 13.9 Tue 12:00 H34

Structure and Dynamics of Myelin Basic Protein as a Model System for Intrinsically Disordered Proteins — ●ANDREAS STADLER¹, LAURA STINGACIU², AUREL RADULESCU³, OLAF HOLDERER³, CLEMENT BLANCHET⁴, RALF BIEHL¹, and DIETER RICHTER¹ — ¹Forschungszentrum Jülich, JCNS-1/ICS-1, 52425 Jülich, Germany — ²Forschungszentrum Jülich, JCNS, Outstation at the Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA — ³Forschungszentrum Jülich, JCNS, Outstation at FRM II, 85747 Garching, Germany — ⁴EMBL, Hamburg Unit, EMBL c/o DESY, Notkestrasse 85, Hamburg 22607, Germany

Myelin basic protein (MBP) is a major component of the myelin sheath in the central nervous system. In aqueous solution MBP is primarily unstructured. From a biophysical point of view, the disordered protein can serve as a model system to study the physical properties of disordered or unfolded proteins.

Neutron and X-ray scattering experiments were performed on the protein in solution. Small angle scattering and neutron spin-echo spectroscopy allowed us to gain quantitative information on the structural and the dynamical properties of MBP. The results of these experiments will be presented and compared to different models of polymer theory.

CPP 13.10 Tue 12:15 H34

Structure and disintegration of nanoparticles from clinically relevant polymers — ●MARGARITA DYAKONOVA¹, ANNA BOGOMOLOVA², SERGEY FILIPPOV², AUREL RADULESCU³, and CHRISTINE M. PAPADAKIS¹ — ¹TU München, Physik-Department, Physik weicher Materie, Garching — ²Institute of Macromolecular Chemistry, Prague, Czech Republic — ³JCNS at FRM II, Garching

We investigate clinically relevant polymers based on N-(2-hydroxypropyl methacrylamide) (HPMA) which carry both a cancer drug, namely doxorubicin, and a hydrophobic targeting group, namely cholesterol derivatives. We focus on the dependence of the structure of the nanoparticles formed by these conjugates on the polymer architecture, the cholesterol content of cholesterol and the pH value [1]. Fluorescence correlation spectroscopy showed that the onset of nanoparticle formation depends on the cholesterol content. A step-like increase of the hydrodynamic radius with conjugate concentration indicates that the existing nanoparticles associate rather than to grow continuously. SANS revealed that even small amounts of cholesterol derivatives results in the formation of nanoparticles. At neutral pH values, these are ellipsoids, whereas under acidic conditions, cholesterol is released and forms large crystals. Time-resolved SANS during a stopped-flow experiment showed that, in dependence of the hydrophobicity of the cholesterol derivatives, a change in pH leads to changes of the conformation of the HPMA chains.

[1] S. Filippov, M. Dyakonova, C.M. Papadakis et al., *Biomacromolecules* **13**, 2594 (2012)

CPP 13.11 Tue 12:30 H34

Reduction - oxidation photocycle dynamics of flavins in starch films — ●ALFONS PENZKOFER — Fakultät für Physik, Universität Regensburg, Universitätsstrasse 31, D-93053 Regensburg, Germany

The blue-light photo-reduction and dark re-oxidation of the flavins riboflavin and lumiflavin in starch (α-amylase) films was studied by absorption and luminescence spectroscopy. Blue-light sample excitation caused an absorption, fluorescence, and phosphorescence decrease which recovered in the dark. The photo-reduction and dark re-oxidation cycle could be repeated. The efficiency of photo-reduction decreased with exposed excitation energy, and the speed of re-oxidation in the dark slowed down with time after excitation. The absorption did not fully recover. The fluorescence efficiency after long time of storage in the dark increased beyond the initial oxidized flavin fluorescence efficiency. Flavin photo-excitation is thought to cause a starch-flavin restructuring (static fluorescence quenching center formation) enabling enhanced photo-induced starch to flavin electron transfer with subsequent flavin reduction and starch oxidation (oxystarch formation). In the dark after light switch-off, thermal reversion of flavin reduction and starch oxidation occurred and fluorescence quenching decreased.

CPP 13.12 Tue 12:45 H34

Study of phase transitions on DPPC bilayers deposited by PVD on top of low viscosity chitosan scaffolds of different thicknesses — ●MARIA J. RETAMAL, CARMEN GONZALEZ, MAURICIO SARABIA, MARCELO CISTERNAS, and ULRICH G. VOLKMANN — Surface Lab, Fac. de Física, P. Universidad Catolica de Chile, Chile

The porous nature of chitosan and its non-solubility in water could be an efficient matrix able to absorb water molecules and their delivery to a system. Chitosan of low viscosity (CH) and 1,2 *dipalmitoyl-sn-3-phosphoglycerocholine (DPPC) over silicon wafer (SiO₂/Si(100)) as substrate were used to conform an artificial membrane, silicon wafer/CH-DPPC. The deposition was made by Physical Vapor Deposition (PVD) and thickness was controlled in situ with Very High Resolution Ellipsometry (VHRE), achieving chitosan films with precise thicknesses between 10Å and 200Å, and a 60Å thin DPPC bilayer on top. We focus on the precise thickness control of the thin films, and

the related formation of interstitial channels, that favor the prolonged humidification in the system and the discovery of the most suitable thickness of the chitosan scaffold for best artificial membrane formation and stability. The characterization of the artificial membrane was realized using VHRE, IE (Imaging Ellipsometry) and Atomic Force Microscopy (AFM), with the finality to determine the possible phase transition temperatures.

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