

BP 44: Biomaterials and Biopolymers (Joint Session BP/CPP)

Time: Wednesday 15:00–17:15

Location: SCH A251

BP 44.1 Wed 15:00 SCH A251

The microstructural function of the tendon-bone insertion

— •LEONE ROSSETTI¹, LARA A. KUNTZ^{1,2}, ELENA KUNOLD³, JONATHAN SCHOCK¹, KEI W. MÜLLER⁴, HEINRICH GRABMAYR¹, JOSEF STOLBERG-STOLBERG⁵, FRANZ PFEIFFER¹, STEPHAN A. SIEBER³, RAINER BURGMART², and ANDREAS R. BAUSCH¹ — ¹Physik Department, TU München, D-85748 Garching, Germany — ²Klinik für Orthopaedie und Sportorthopaedie, Klinikum rechts der Isar, TU München, D-81675 München, Germany — ³CIPSM, Department of Chemistry, TU München, D-85747 Garching, Germany — ⁴Institute for Computational Mechanics, TU München, D-85748 Garching, Germany — ⁵University Hospital Münster, D-48149 Münster, Germany

The exceptional mechanical properties of the connection of tendon to bone rely on an intricate interplay of its biomolecular composition, microstructure and micromechanics. Here we identify that the Achilles tendon insertion is characterized by a stress reducing mechanism within an interfacial zone of 500 micrometres, with a distinct fiber organisation and biomolecular composition. Proteomic analysis detects enrichment in the interface region that are predominantly involved in cartilage and skeletal development as well as proteoglycan metabolism. Micromechanical testing coupled with multiscale confocal microscopy identifies a heterogenous mechanical response in the interface area, endowing the enthesis with a graded response to strains acting from different angles. The presented mechanisms mark a guideline for further biomimetic strategies to rationally design hard-soft interfaces.

BP 44.2 Wed 15:15 SCH A251

Exposure of leukocytes and hematopoietic stem cells to graphene quantum dots

— •STEFAN FASBENDER¹, SONJA ALLANI¹, CHRISTIAN WIMMENAUER¹, PATRICK CADEDDU², KATHARINA RABA³, JOHANNES FISCHER³, BEKIR BULAT⁴, CLAUS SEIDEL⁴, THOMAS HEINZEL¹, and RAINER HAAS² — ¹Heinrich-Heine-Universität Düsseldorf, Institut für experimentelle Physik der kondensierten Materie — ²Universitätsklinikum Düsseldorf, Klinik für Hämatologie — ³Universitätsklinikum Düsseldorf, Institut für Transplantationsdiagnostik — ⁴Heinrich-Heine-Universität Düsseldorf, Institut für Molekulare Physikalische Chemie

Fluorescent graphene quantum dots (GQDs) are prepared by the method of Wu et. al [1] via hydrothermal treatment of citric acid and dicyandiamide with subsequent dialysis to obtain a pure GQD solution. The obtained aqueous solution is analyzed with fluorescence spectroscopy, UV-vis, XPS and AFM. Human leukocytes and hematopoietic stem cells are exposed to two different concentrations of GQDs for various times and the uptake dynamic is determined using flow cytometry. A higher uptake is observed into cells with phagocytotic properties. The number of incorporated GQDs is estimated by comparing the fluorescence of cells with GQDs and without GQDs. A permeability constant for the various cell types is calculated and the effect of the GQDs on the viability of the cells is assessed with the XTT viability assay.

[1] Wu et al., Nanoscale, 2014, 6, 3868

BP 44.3 Wed 15:30 SCH A251

Guanidinium Salts Can both Cause and Prevent the Hydrophobic Collapse of Biomacromolecules

— •JAN HEYDA^{1,2}, HALIL OKUR³, JOACHIM DZUBIELLA^{2,4}, PAVEL JUNGWIRTH⁵, and PAUL CREMER^{3,6} — ¹Physical Chemistry Department, UCT Prague, Czech Republic — ²Institut für Weiche Materie und Funktionale Materialien, HZB Berlin, Germany — ³Chemistry Department, Penn. State University, Pennsylvania, USA — ⁴Institut für Physik, HU Berlin, Germany — ⁵Institute of Organic Chemistry and Biochemistry, CAS, Prague, Czech Republic — ⁶Biochemistry and Molecular Biology Department, Penn. State University, Pennsylvania, USA

A combination of experimental methods with theory and simulations were performed to probe the mechanisms by which guanidinium (Gnd^+) salts influence the stability of the collapsed vs. uncollapsed state of an elastin-like polypeptide (ELP). The Gnd^+ action was found highly dependent upon its counteranion, resulting in three distinct physical regimes. (1) Well-hydrated Gnd_2SO_4 salt was depleted from the ELP/water interface and was found to stabilize the collapsed state of the macromolecule. (2) Salts (e.g. GndSCN), which interacted

very strongly with the polymer, stabilized the collapsed state at low salt concentrations, when both ions were found to be enriched in the collapsed state of the polymer. The collapsed state is stabilized due to crosslinking of the polymer chains. At higher salt concentrations, the same strong salt-polymer interaction results in stabilization of the uncollapsed state. (3) GndCl interacted in an intermediate fashion favored the uncollapsed state at all salt concentrations.

BP 44.4 Wed 15:45 SCH A251

Altering Synthetic Semiflexible DNA Nanotube Networks by Tunable Cross-linking

— •MARTIN GLASER^{1,2}, PAUL MOLLENKOPF^{1,2}, CHRISTIN MÖSER², CARSTEN SCHULDT^{1,2}, JÖRG SCHNAUSS^{1,2}, JOSEF KÄS¹, and DAVID SMITH² — ¹Faculty of Physics and Earth Sciences, Institute of Experimental Physics I, Leipzig University, Germany — ²Fraunhofer Institute for Cell Therapy and Immunology IZI, DNA Nanodevices Group, Germany

The mechanical properties of complex soft matter have been subject to various experimental and theoretical studies. The underlying constituents often cannot be modeled in the classical physical frame of flexible polymers or rigid rods. Polymers in the semiflexible regime, where the finite bending stiffness leads to a non-trivial mechanical contribution, are a highly interesting subclass and can be found in the cytoskeleton of living cells. A natural occurring model system for such polymers is the protein actin. However, experimental studies of actin networks to validate existing theories, are limited since the persistence length cannot be altered. Here, we establish a tunable system of cross-linked, synthetically DNA nanotubes to overcome this limitation. We present first results of the impact tunable cross-linking has on the well-characterized entangled DNA nanotube networks. These studies enable investigations of the impact of a crucial parameter of semiflexible polymers, namely the persistence length, on emerging network properties. Also, the study will allow a deeper insight into the underlying mechanics of biomaterials, such as hydrogels, which are extensively used for in vitro as well as in vivo applications.

BP 44.5 Wed 16:00 SCH A251

Ion and Molecule Transport in Surface Modified Nanopores - a NMR Study

— •SARAH SCHNEIDER and MICHAEL VOGEL — TU Darmstadt Solid State Physics, Darmstadt, Germany

We analyze ion and molecule transport in surface modified nanopores. It is part of a project that aims to develop a new generation of nanosensors by combining biological and synthetic nanopores. While being highly selective and sensitive, biological ion channels lack the robustness for technological applications. Contrarily silica pores are well-proven in industrial and clinical environments, but possess inferior capabilities, e.g. no selectivity. A hybrid system would combine the favorable properties of both fields.

To optimize such pores, it is of strong interest to understand the influence of this confinement on the ion and molecule transport inside. Such confined dynamics depend on the pore geometry and the guest-host interactions determined by the properties of the inner surfaces.

We vary these parameters systematically, in particular by peptide functionalization of the silica surfaces and study their effects on the dynamics by NMR. This includes various techniques aiming at local dynamics. SFG NMR is applied to measure self-diffusion coefficients of aqueous salt solutions in bulk and nanopore confinement. The experimental setups include ^1H and ^2H NMR to selectively investigate water dynamics as well as ^7Li and ^{23}Na NMR to analyze the diffusion of various ionic species. We find a slowdown of dynamics in confinement. The extent of the effect and the relation between short- and long-range dynamics substantially depends on the confinement properties.

15 min break

BP 44.6 Wed 16:30 SCH A251

Model-independent measurements of ATP diffusion in PEG-DA hydrogels with various mesh sizes

— •GÜNTER MAJER¹ and ALEXANDER SOUTHAN² — ¹MPI für Intelligente Systeme, Heisenbergstr. 3, 70569 Stuttgart, Germany — ²Institut für Grenzflächen-verfahrenstechnik und Plasmatechnologie IGVP, Universität Stuttgart, Nobelstraße 12, 70569 Stuttgart, Germany

Hydrogels are semi-solid polymer networks formed by cross-linked hy-

drophilic polymer chains, with mesh sizes that can be tailored by varying the concentration and/or the molecular mass of the polymers. Well-defined hydrogels are ideal materials for various applications including drug delivery, transport of nutrients, or devices to separate small molecules chromatographically. In this context, a fundamental understanding of the diffusion processes of solutes in hydrogels with different mesh sizes is important. A powerful tool to determine the diffusion coefficients of solutes directly, i.e. without the need of a fluorescent label and independent of any diffusion-model assumptions, is pulsed field gradient nuclear magnetic resonance (PFG-NMR). In this work, polyethylene glycol diacrylate (PEG-DA)-based hydrogels with mesh sizes ranging from 1.35 to 3.70 nm were prepared using polymers with molecular masses between 700 and 8000 g/mol and concentrations of up to 30%. The diffusion coefficients of adenosine triphosphate (ATP) in these hydrogels were studied by PFG-NMR. The correlation between the mesh sizes and the diffusion coefficients is analyzed and discussed.

BP 44.7 Wed 16:45 SCH A251

Stress-induced long-range ordering in spider silk — •JOHANNES WAGNER and FRAUKE GRÄTER — Heidelberg Institute for Theoretical Studies, Heidelberg, Germany

A range of composite or semi-crystalline materials consist of particles or crystallites embedded randomly in a much softer phase. Emergence of long-range order of these particles within the softer matrix could result in lowering the mechanical energy of the system upon stretching, in consistence with the well-known coalescence of defects in materials. Using small-angle neutron scattering (SANS) and finite element (FE) models we show the presence of such stress-induced ordering in spider silk fibers. Both methods show striking quantitative agreement of the position, shift and intensity increase of the long period upon stretching. We demonstrate that this mesoscopic ordering does not originate from strain-induced crystallization at the atomistic scale, and instead arises

from a non-affine deformation that enhances density fluctuations of the two phases along the direction of stress. Our results suggest long-range ordering as a wide-spread phenomenon that can be exploited for tuning the mechanical properties of many hybrid materials with stiff and soft phases.

BP 44.8 Wed 17:00 SCH A251

Tuning coiled coils mechanically and thermodynamically by histidine-metal coordination — •ISABELL TUNN, KERSTIN G. BLANK, and MATTHEW J. HARRINGTON — Max Planck Institute of Colloids and Interfaces, Science Park Potsdam Golm, 14424 Potsdam

Coiled coils serve as structural motifs in proteins with mechanical function, such as myosin or α -keratin. In the field of bioinspired materials, naturally occurring and synthetic coiled coils with high binding specificity have become versatile material building blocks, which are used as crosslinkers for hydrogels with applications in cell culture and tissue engineering. Very little is currently understood about the mechanical properties of coiled coils. Yet, this information is critical for controlling and tuning bulk properties of coiled coil-based materials. In order to generate mechanically tunable coiled-coil based materials, metal coordination sites were engineered into a well-characterized heterodimeric coiled coil. Protein-metal coordination bonds are strong, non-covalent interactions mediated by amino acid ligands. Here, two histidine residues were introduced at the coiled coil termini with the goal of stabilizing helical turns. Histidine-metal coordination increased the stability of the coiled coil mechanically and thermodynamically, as demonstrated by AFM single molecule force spectroscopy and CD spectroscopy. We conclude that increasing the stability of single helical turns via metal binding directly affects the overall stability of the coiled coil, providing the potential for generating mechanically tunable biomimetic polymers. Furthermore, these results also provide crucial information about the failure mechanism of coiled coils under load.