

CPP 4: Complex Fluids and Colloids I (joint session CPP/DY)

Time: Monday 9:30–13:00

Location: C 264

CPP 4.1 Mon 9:30 C 264

Brownian motion of a microbead coated with a temperature-responsive polymer brush layer — ●DAVID VAN DUINEN, DOMINIK PILAT, HANS-JÜRGEN BUTT, and RÜDIGER BERGER — Max Planck Institute for Polymer Research, Mainz, Deutschland

We report on a simple method that allows investigating the mechanical contact between a planar surface and a microbead that is covered with a thin stimuli-responsive polymer brush. The brush consists of linear poly(N-isopropylacrylamide) (PNIPAM), which has a lower critical solution temperature (LCST). Below the LCST, the brush is hydrated and extended. In contrast, above the LCST the polymer collapses; this system can be described using a spring model, which is stiffer in the collapsed state than in the hydrated state. Similarly, we have investigated the effect of cononsolvency on the mechanical contact.

This method allows the following and checking of the characteristics of thin polymer films upon exposure to stimuli. The method is simple, and provides information that is otherwise hard to obtain.

CPP 4.2 Mon 9:45 C 264

Polymer mediated interactions between colloids immersed in a polymer blend — ●ALEXANDER CHERVANYOV — Institut für Theoretische Physik, Westfälische Wilhelms-Universität Münster

We analytically study the polymer mediated (PM) interactions between colloids immersed in a polymer blend. By making use of standard methods of the liquid state theory we have found out a novel mechanism of the PM interactions caused by non-uniformities in the local composition of the polymer blend induced by the colloids. The relative significance of the contributions to the PM interaction potential due to the finite compressibility of the polymer blend and its compositional non-uniformity is found to drastically depend on the polymer-to-colloid size ratio. In the protein limit of relatively small colloids, the mechanism due to the compositional non-uniformity, specific to polymer blends, is shown to play a dominant role in the PM interactions.

CPP 4.3 Mon 10:00 C 264

Spontaneous symmetry breaking of charge-regulated surfaces — ●ARGHYA MAJEE¹, MARKUS BIER¹, and RUDOLF PODGORNİK² — ¹MPI for Intelligent Systems, Stuttgart & University of Stuttgart, Germany — ²J. Stefan Institute, Ljubljana & University of Ljubljana, Slovenia

The interaction between two chemically identical charge-regulated surfaces is studied using the classical density functional theory. In contrast to common expectations and assumptions, under certain realistic conditions we find a spontaneous emergence of disparate charge densities on the two surfaces [1]. The surface charge densities can differ not only in their magnitude, but quite unexpectedly, even in their sign, implying that the electrostatic interaction between the two chemically identical surfaces can be attractive instead of repulsive. Moreover, an initial symmetry with equal charge densities on both surfaces can also be broken spontaneously upon decreasing the separation between the two surfaces. These findings are fundamental for the understanding of the forces between colloidal objects and, in particular, they are bound to strongly influence the present picture of protein interaction.

Reference:

[1] A. Majee, M. Bier, and R. Podgornik, arXiv: 1709.05005 (2017).

CPP 4.4 Mon 10:15 C 264

PFA-PEG particles: A colloidal model system for the investigation of phase diagrams of PEGylated drug carrier systems — ●MARCEL WERNER^{1,2}, JUDITH RULAND², NILS VON SEGGERN¹, MORITZ TAPPE¹, MELANIE WERNET², GABRIELA SCHMIDT², and ECKHARD BARTSCH^{1,2} — ¹Department of Macromolecular Chemistry, University of Freiburg, Freiburg im Breisgau, Germany — ²Department of Physical Chemistry, University of Freiburg, Freiburg im Breisgau, Germany

Pegylated particles like proteins, peptides and lipid- or polymer-based nanoparticles are known as potential drug delivery systems (DDS) or as nano drug carriers (NDC) [1]. Current research deals with e.g. completely new systems [2], shape effects [3] or the influence of the PEG density on the biocompatibility [4]. However, the phase behaviour of the DDS is not really covered. In an attempt to close this gap we syn-

thesised a new model system, consisting of a highly fluorinated core and a sterically stabilizing PEG-shell [5]. With these particles and different light scattering techniques as well as other complementary techniques such as microscopy and rheology, we gained first insights into the phase behaviour of PEGylated particles. Our findings can lead to higher concentrated carrier systems without unwanted inter particle interference and new formulations e.g. gels or cremes.

[1] T. M. Allen et al., *Science*, 2004, 303, 1818. [2] E. Ruiz-Hernandez et al., *Polym. Chem.*, 2014, 5, 1674. [3] Y. Li et al., *Nanoscale*, 2015, 40, 16631. [4] J. L. Perry et al., *Nano Lett.*, 2012, 12, 5304. [5] D. Burger et al., *Colloids Surf. A: Physico. Eng. Aspects*, 2014, 442, 123.

CPP 4.5 Mon 10:30 C 264

Interactions in Protein Solutions in the Vicinity of the Gas-Liquid Binodal — ●JAN HANSEN¹, FLORIAN PLATTEN¹, JAN-NIK NEDERGAARD PEDERSEN², JAN SKOV PEDERSEN², and STEFAN U. EGELHAAF¹ — ¹Condensed Matter Physics Laboratory, Heinrich Heine University, Düsseldorf, Germany — ²Department of Chemistry & iNANO, Aarhus University, Denmark

Intermolecular interactions in protein solution depend on a delicate balance of electrostatic, van der Waals and hydrophobic interactions, hydration and other specific contributions. Under certain conditions, short-ranged attractions dominate. Then, proteins can be described as adhesive hard spheres, i.e. their equilibrium phase diagram contains a solubility line below which the metastable gas-liquid binodal is submerged. Here, we examine in how far effective interaction models from colloid science can help to rationalize the phase behavior and interactions of protein solutions in the vicinity of the gas-liquid binodal. For different solution compositions, binodals have been determined by cloud-point measurements, yielding estimates of the critical temperature T_c . The effective structure factor of protein solutions has been determined for various protein concentrations and temperatures by small-angle X-ray scattering. The data is well described by a one-parameter fit based on Baxter's model, from which the second virial coefficient B_2 is inferred. If plotted as a function of temperature normalized by T_c , the values of B_2 follow a universal behaviour for various solution conditions, as suggested by the extended law of corresponding states.

CPP 4.6 Mon 10:45 C 264

Behavior under shear of solutions of bovine serum albumin and trivalent cations — ●STEFANO DA VELA¹, MIRIAM SIEBENBÜRGER², ALESSIO ZACCONI³, FAJUN ZHANG¹, MATTHIAS BALLAUFF^{2,4}, and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, University of Tübingen, Tübingen, Germany — ²Helmholtz Zentrum für Materialien und Energie, Berlin, Germany — ³Dept. of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge, UK — ⁴Department of Physics, Humboldt-University, Berlin, Germany

Trivalent cations such as Y(III) and La(III) have been shown to induce a rich phase behavior in aqueous solutions of acidic proteins. Thanks to the specific association of the cations with the negatively charged groups on the protein surface, these systems feature directional, patchy interactions. Here we show how shear stress can trigger aggregation in solutions of the acidic protein bovine serum albumin (BSA) in the presence of La(III). The trivalent cation renders the system unstable at high shear rates and the solutions become turbid. Simultaneously a low wavevector upturn develops in small-angle neutron scattering profiles. We discuss the findings in relations to the available theoretical models. As directionality and anisotropy of the interaction are common in proteins, a better understanding of the role of patchiness for shear-induced aggregation is important for many biotechnological operations such as filtration, stirring, filling of containers, and pumping.

CPP 4.7 Mon 11:00 C 264

Unification of Lower and Upper Critical Solution Temperature Transitions in Aqueous Protein Solutions — ●NAFISA BEGAM, STEFANO DA VELA, FAJUN ZHANG, and FRANK SCHREIBER — Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen

Phase separation in aqueous protein solution is of primary interest in the field of many biological and chemical processes. In particular,

phase separated protein solutions exhibiting lower/upper critical solution temperature (LCST/UCST) behavior have been of significant importance in the food and pharmaceutical industries. Based on theoretical calculations [1] and experimental observations, it is predicted that proteins can be designed with tunable LCST and UCST. Here, our goal is to experimentally design such aqueous protein system showing tunable LCST and UCST transitions. The UCST phase of β -Lactoglobulin - Yttrium Chloride (YCl_3) based aqueous systems at a salt concentration higher than a critical concentration, c^* , has been already reported by our group [2]. However, we obtain evidence of LCST phase behavior of this system at a lower salt concentration but higher than c^* . The solution becomes turbid at high temperature and clear at low temperature. Similar indication of the presence of both LCST and UCST phase behavior we get from the SAXS measurements on Bovine serum Albumin (BSA) - YCl_3 system. The findings of this study suggest a controllable dual phase of aqueous protein solution by tuning the ionic strength. [1] Jianguo Li et. al, *J. Chem. Phys.*, **128**, 235104, (2008) [2] F. Zhang et. al, *J. App. Crystal.*, **44**,755-762, (2011)

Invited Talk

CPP 4.8 Mon 11:15 C 264

Reconfigurable colloidal structures — ●DANIELA J. KRAFT — Soft Matter Physics, Huygens-Kamerlingh Onnes Laboratory, Leiden Institute of Physics, Leiden, The Netherlands

Reconfigurability is an essential feature of functional micro- and nanomachines. One way to realize reconfigurability is to introduce microscopic hinges, that is, elements that allow rotation while conserving the relative order of their arrangement. We have developed two experimental realizations of these pivotal elements on the colloidal length scale: I will first show how the deposition of oil droplets in colloidal aggregates lubricates the contact area and thereby enables and drives the reconfiguration into uniform, compact structures. Secondly, I will introduce colloidal particles with surface-mobile DNA linkers that enable the formation of strong and specific hinging bonds. I will describe how this bond mobility affects the self-assembly pathway and demonstrate the assembly of a variety of reconfigurable structures, such as floppy lattices, colloidal polymers and flexible colloidal molecules. These novel colloidal building blocks give access to a new class of materials with great potential in shape-shifting systems, actuators and colloidal robots.

CPP 4.9 Mon 11:45 C 264

Preparation of amphiphilic asymmetric patchy particles and their effect on emulsion properties — ●MARCO REHOSEK, AKILAVASAN JEGANATHAN, and FRANK MARLOW — Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr/Germany

Asymmetric patchy particles (APPs) have two different functionalities on the opposing sides of such a micro- or nanoparticle. These functionalities can be of a magnetic, chemical, or optical nature. Here we study different chemical polarities. Amphiphilic APPs having hydrophobic and hydrophilic regions show interesting performance as emulsifying agent. This effect enhances the so-called Pickering stabilization resulting in a "breathable skin" at a liquid|liquid interface.

In this work, the preparation of amphiphilic APPs and their effect on emulsions is studied. Titania&organosilane APPs were prepared via a wax-masking-symmetry breaking step. The unmasked part was modified by vapor deposition. The effect of the APPs on emulsion stability and aging effects of APP-stabilized emulsions was studied qualitatively by liquid-phase-distribution measurements. For a deeper understanding, rheological properties of the emulsions were investigated. Viscometry gave information on stress-dependent viscosity effects, while oscillation measurements reveal the viscoelastic properties. Long-time measurements resulted in information on aging processes in the emulsion i.e. creaming, coalescence and Ostwald ripening.

CPP 4.10 Mon 12:00 C 264

On effective sphere models for self-diffusion of nonspherical particles — ●FELIX ROOSEN-RUNGE, JIN SUK MYUNG, PETER SCHURTENBERGER, and ANNA STRADNER — Division of Physical Chemistry, Lund University, Sweden

Modeling diffusion of nonspherical particles presents an unsolved and considerable challenge, despite its importance for the understanding of crowding effects in biology and nanotechnology. A common approach is the mapping of nonspherical objects on effective spheres to subsequently approximate phenomena for nonspherical particles with the established predictions for spheres. Using hydrodynamic simulations, we show that this so-called effective sphere model fundamentally fails

to represent the short-time self-diffusion of nonspherical particles even at low volume fractions and small to moderate nonsphericities. Based on analytical theory of hydrodynamic interactions, we discuss possible improvements for the modeling as well as the implications of our findings for studies employing effective spheres.

CPP 4.11 Mon 12:15 C 264

Ultrasoft colloids under pressure driven flow — ●DEEPIKA DEEPIKA and ARASH NIKOUBASHMAN — Institute of Physics, Johannes Gutenberg University, Staudingerweg 7, 55128 Mainz, Germany

Star-shaped polymers show a continuous change of properties from flexible linear chains to soft colloids, as the number of arms is increased. To investigate the effect of macromolecular architecture on the flow behavior, we employed computer simulations of single star polymers as well as of mixtures of star and linear polymers under dilute conditions. Hydrodynamic interactions were incorporated through the multi-particle collision dynamics (MPCD) technique, while a bead-spring model was used to describe the polymers. At rest, the polymers were distributed homogeneously in the slit channel, irrespective of the number of arms. Once flow was applied, however, we found that the stars migrated more and more towards the channel center as the number of arms increased and the polymers became more rigid. These findings are in contrast to previous findings for deformable vesicles, where the softer particles moved to the channel center. We surmise that the observed behavior for polymers is due to effective arm stretching and hydrodynamic repulsion with the channel walls. In the star-chain mixtures, we found a flow-induced separation between stars and chains, with the stars being in the center and the chains closer to the walls. The results from our study give valuable insights for designing microfluidic devices for separating particles based on their rigidity.

CPP 4.12 Mon 12:30 C 264

Control of physico-chemical properties of Pickering emulsions for catalysis — ●DMITRIJ STEHL¹, TOBIAS POGRZEBA², LENA HOHL³, YURI LVOV⁴, MATTHIAS KRAUME³, REINHARD SCHOMÄCKER², and REGINE VON KLITZING¹ — ¹Festkörperphysik, TU Darmstadt, Darmstadt, Deutschland — ²Institut für Chemie, TU Berlin, Berlin, Deutschland — ³Prozess- und Verfahrenstechnik, TU Berlin, Berlin, Deutschland — ⁴Institute for Micromanufacturing, Louisiana Tech University, Louisiana, USA

Pickering-emulsions (PEs) are particle-stabilized emulsions. Different solid nanoparticles stabilize emulsion droplets against coalescence. Halloysite nanotubes (HNT) can be used as emulsifier. These particles are multiwall, inorganic tubes with negative charges at the outer surface and positive charges at the inner surface. The length of the HNTs in this study is 800 +/- 200 nm and the outer diameter is 50 nm. HNTs adsorb laterally at the water/oil interface and the energy of detachment is several 10.000 kT. Due to the anisotropy of the HNT, the behavior of the nanotubes at the interface is different from spherical particles and the stability of the respective PE is higher which is studied in detail. The effect of different parameters on the structure of the PEs is studied, like HNT surface modification and energy input by the PE-fabrication, effect of HNT concentration, salt (NaCl) concentration and pH. In this study, the hydroformylation of long chain olefins (1-Dodecene) in PEs was used as a model system. The water phase contains the homogeneous Rh-catalyst and the oil phase (1-Dodecene) is simultaneous the reactant.

CPP 4.13 Mon 12:45 C 264

Crystal-fluid surface tension in the two dimensional binary hard disk mixture, a DFT study — ●SHANG-CHUN LIN and MARTIN OETTEL — Institut für Angewandte Physik, Universität Tübingen, Tübingen, Germany

Using fundamental measure theory, we investigate phase diagrams and crystal-fluid surface tensions in additive and nonadditive two-dimensional hard disk mixtures of small and large spheres with size ratio q . In the nonadditive case, the small disks act as ideal "polymeric" depletants (Asakura-Oosawa model) and the surface tension (for small q) shows a minimum with increasing small sphere concentration. We compared to the additive case, with an interface between fluid and crystals with substitutional disorder, and find a similar behavior (for small q). For larger q , the surface tension is almost constant upon adding the small spheres. In these investigations, the fluid-solid transitions were first-order due to the assumption of a periodic unit cell in the DFT calculations. We examine the possibility of relaxing this assumption and finding a hexatic phase in fundamental measure theory.