

## CPP 8: Colloids and Complex Liquids II (joint session CPP, BP, DY)

Time: Monday 15:00–18:45

Location: C 130

CPP 8.1 Mon 15:00 C 130

**TIRM at liquid/liquid interfaces** — ●KILIAN DIETRICH — University of Stuttgart, Germany

Total Internal Reflection Microscopy (TIRM) is a well-established method for the direct measurement of interaction potentials between a spherical colloidal particle and a solid wall. It is based on the tracking of the particle's vertical motion from which interaction forces with the interface can be inferred with a resolution down to 10fN. In contrast to previous measurements, which were performed at solid/liquid interfaces, here we demonstrate that TIRM can be applied also to liquid/liquid interfaces. These are of special interest not only due to their frequent appearance but they also exhibit an exceptional smoothness. In our study, we present a novel inverted TIRM apparatus which is capable to measure the motion of a colloidal probe particle in water close to an oil-water interface. First measurements indicate the counterplay of electrostatic interactions and van-der-Waals forces for interfaces treated with different ionic and non-ionic surfactants. In each case surface charge densities of particle and interface could be determined. The detailed knowledge of interactions can provide valuable information for the stability of emulsions and dispersions.

CPP 8.2 Mon 15:15 C 130

**Short Ranged Repulsive Energy in Oscillatory Structural Forces** — ●SEBASTIAN SCHÖN and REGINE VON KLITZING — Technische Universität Berlin Strasse des 17. Juni 124 D-10623 Berlin

Oscillatory structural forces are a genuine feature observed for simple and complex fluids in the vicinity of smooth wall. The origin of these forces is related to the characteristic quality of molecules or nanoparticles to form well-ordered layers in the vicinity of a confining wall. These forces can be described by the following function as proposed by Israelachvili:  $f(x) = -A \cdot e^{-x/\xi} \cdot \cos(2\pi(x-\Delta x)/\lambda)$ , with  $f$  the force as a function of  $x$ , the separation. The Amplitude  $A$  describes the strength of the particle interaction, the decay length  $\xi$  is a measure of how fast the order decays and the wavelength  $\lambda$  is directly related to the inter-particle distance. Structural oscillation forces are long ranged compared to the common DLVO forces and can be used in a variety of applications e.g. oil removal or separation of bidisperse particle suspensions. For both it is important to know the strength of the oscillatory forces at very small separations. An additional repulsive term is introduced to describe deviations observed between experimental data and the common fit function, this allows accurate fitting of experimental data down to very small separations and removes systematic deviations in  $A$ ,  $\lambda$  and  $\xi$  depending on the starting point of the fit. The short ranged repulsive energy described by the new term is investigated at different particle concentrations, measurement speed and under the addition of NaOH, HCl and NaCl at different concentrations.

CPP 8.3 Mon 15:30 C 130

**Complex nanoparticle arrangements via wrinkle-assisted self-assembly** — ●CHRISTOPH HANSKE, MORITZ TEBBE, CHRISTIAN KUTTNER, MUNISH CHANANA, TOBIAS KÖNIG, and ANDREAS FERY — Physical Chemistry II, University of Bayreuth, 95447, Germany

Template-assisted assembly enables the arrangement of colloidal particles into well-defined structures that often demonstrate special optical, biological, or catalytic functionality due to the hierarchical internal organization. A major bottleneck so far is the limited scalability of lithographic template fabrication. As an alternative strategy, we utilize wrinkled elastomer substrates exhibiting periodicities on the micron or submicron scale. The topographic features of such templates allow the arrangement of hydrophilic nanoparticles into regular, close-packed chains, which can further be transferred site-selectively onto flat substrates by wetting controlled printing. This versatile method is applicable for polymeric, inorganic and metallic particles with spherical as well as anisotropic shapes. We discuss the influence of interfacial properties originating from the employed particle and substrate coatings and demonstrate the formation of complex structures on chemically patterned substrates.[1] Further, the realization of macroscopic, gold nanoparticle assemblies is shown.[2, 3] Due to small interparticle distances of few nanometers, strong plasmonic coupling is achieved, which grants access to surfaces with tailored optical properties.

[1] C. Hanske et al., *Langmuir*, 2012, 28, 16745-16750. [2] C. Hanske et al., *Nano Letters*, 2014, DOI:10.1021/nl502776s. [3] M. Tebbe et

al., submitted.

CPP 8.4 Mon 15:45 C 130

**Linking intermolecular interactions, microstructure, and macroscopic rheology in protein suspensions** — ●ALESSIO ZACCONE<sup>1</sup>, MIRIAM SIEBENBÜRGER<sup>2</sup>, HENNING WINTER<sup>3</sup>, FRANK SCHREIBER<sup>4</sup>, and MATTHIAS BALLAUFF<sup>2</sup> — <sup>1</sup>Physics-Department, Technische Universität München — <sup>2</sup>Helmholtz-Zentrum Berlin für Materialien und Energie — <sup>3</sup>University of Massachusetts Amherst — <sup>4</sup>Applied Physics, University of Tübingen

We propose a microscopic framework based on nonequilibrium statistical mechanics to connect the microscopic level of colloidal biopolymer self-assembly with the macroscopic rheology of protein gelation. The method is based on the master kinetic equations for the time evolution of the self-assembled cluster size distribution, from which the relaxation time spectrum during the gelation process can be extracted. The relaxation spectrum is a simple stretched-exponential, with a stretching exponent related to the mass fractal dimension of the self-assembling clusters. In the case of thermoreversible gelation, for weak interparticle attractions, the attraction energy is finite and plays the role of the control parameter driving a nonequilibrium phase transition into a nonequilibrium steady-state (the gel). Our theory is in good agreement with experimental data of different systems published by other authors, for which no theory was available. Further, it allows us to interpret new experimental data on the gelation of BSA which provides a benchmark system to connect the level of coarse-grained protein interactions with the macroscopic oscillatory rheology of the protein suspension.

CPP 8.5 Mon 16:00 C 130

**Molecular versus macroscopic perspective on the phase separation mechanisms of thermo-responsive solutions** — ●MARTINE PHILIPP<sup>1</sup>, RALITSA ALEKSANDROVA<sup>2</sup>, ULRICH MÜLLER<sup>2</sup>, JAN K. KRÜGER<sup>2</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1</sup> — <sup>1</sup>TU München, Physik-Department, LS Funktionelle Materialien, Garching, Germany — <sup>2</sup>Université du Luxembourg, LPM, Luxembourg, Luxembourg

The phase separation of thermo-responsive solutions is known to strongly affect the volume expansion behaviour and the elastic properties, being directly coupled to the macroscopic order parameter [1-3]. On the molecular scale, massive changes in H-bond and hydrophobic interactions, and in structure govern the demixing process. However, the relationship between the molecular and macroscopic order parameters is poorly understood for such complex segregating solutions. We contribute to the clarification of this problem by first following the diffusion behaviour of the hydration water across the phase transition of model aqueous poly(N-isopropylacrylamide) solutions using quasi-elastic neutron scattering [2]. By probing the molecular bond polarisabilities, we adopt an alternative, highly revealing perspective on the changes in molecular interactions and in structure happening within dilute to concentrated phase-separating solutions [1, 3]. [1] M. Philipp, et al., *Soft Matter* 10, 7297-7305 (2014), [2] M. Philipp, et al., *J. Phys. Chem. B* 118, 4253-4260 (2014), [3] R. Aleksandrova, et al., *Langmuir* 30, 11792-11801 (2014)

CPP 8.6 Mon 16:15 C 130

**Conosolvency in P(S-*b*-NIPAM) diblock copolymers - a time-resolved SANS study of the aggregation process** — KONSTANTINOS KYRIAKOS<sup>1</sup>, MARTINE PHILIPP<sup>1</sup>, JOSEPH ADELBERGER<sup>1</sup>, SEBASTIAN JAKSCH<sup>1</sup>, ANATOLY V. BEREZKIN<sup>1</sup>, DERSY M. LUGO<sup>2</sup>, WALTER RICHTER<sup>2</sup>, ISABELLE GRILLO<sup>3</sup>, ANNA MIASNIKOVA<sup>4</sup>, ANDRÉ LASCHEWSKY<sup>4</sup>, PETER MÜLLER-BUSCHBAUM<sup>1</sup>, and ●CHRISTINE M. PAPADAKIS<sup>1</sup> — <sup>1</sup>TU München, Physik-Department, Garching — <sup>2</sup>RWTH Aachen University, Institut für Physikalische Chemie — <sup>3</sup>Institut Laue-Langevin, Grenoble, France — <sup>4</sup>Universität Potsdam, Institut für Chemie, Potsdam-Golm

In mixtures of water and methanol, the thermoresponsive poly(N-isopropylacrylamide) (PNIPAM) exhibits the conosolvency effect, i.e. an enhanced tendency for phase separation at certain solvent compositions. We investigate the effect of adding methanol to (i) micellar solutions of polystyrene-*b*-poly(N-isopropylacrylamide) (PS-*b*-PNIPAM) diblock copolymers and (ii) PNIPAM homopolymers in D<sub>2</sub>O using

a stopped-flow instrument. The structural changes on mesoscopic length scales were followed by time-resolved small-angle neutron scattering (TR-SANS) with a time resolution of 0.1 s. In both systems, the pathway of the aggregation depends on the content of deuterated methanol; however, it is fundamentally different for homopolymer and diblock copolymer solutions. We propose a logarithmic coalescence model based on an energy barrier which is proportional to the aggregate radius.

1. Kyriakos et al., *Macromolecules* **47**, 6867 (2014)

CPP 8.7 Mon 16:30 C 130

**Cation-activated attractive patches to control protein interactions** — ●FELIX ROOSEN-RUNGE<sup>1</sup>, FAJUN ZHANG<sup>2</sup>, FRANK SCHREIBER<sup>2</sup>, and ROLAND ROTH<sup>3</sup> — <sup>1</sup>Institut Laue-Langevin, Grenoble, France — <sup>2</sup>Institut für Angewandte Physik, Universität Tübingen — <sup>3</sup>Institut für Theoretische Physik, Universität Tübingen

We present evidence for an explicit ion-activated mechanism to cause a patchy attraction between proteins [1]. Experimentally, ion bridges of multivalent cations between protein molecules have been observed in protein crystals [2]. Modeling this mechanism via particles with ion-activated attractive patches, a broad variety of experimental results for protein solutions with multivalent cation is explained and understood very naturally, including charge reversal, reentrant condensation, metastable liquid-liquid phase separation, cluster formation and different pathways of crystallization [1,3]. The good agreement between theory and experiments indicates that protein-cation solutions represent a natural model system for patchy particles. The mechanism of ion-activated patches can be embedded seamlessly into theory and simulations of charged soft matter, and promises rational design of phase behavior and crystallization pathways in protein solutions based on the statistical physics of patchy particles.

[1] F. Roosen-Runge, F. Zhang et al. *Sci. Rep.* **4** (2014) 7016

[2] F. Zhang, A. Sauter et al. *J. Appl. Cryst.* **44** (2011) 755

[3] F. Zhang, R. Roth et al. *Soft Matter* **8** (2012) 1313

CPP 8.8 Mon 16:45 C 130

**Buckling of paramagnetic chains in soft gel** — ●SHILIN HUANG and GÜNTER K. AUERNHAMMER — Max Planck Institute for Polymer Research, Mainz, Germany

We study the magneto-elastic coupling behavior of paramagnetic chains in a soft polymer gel. To this end, the laser scanning confocal microscope is used to observe the morphology of the paramagnetic chains as well as the deformation field in the polymer gel. The paramagnetic chains in a soft polymer gel show rich morphologies under an oblique magnetic field. Depending on the chain length, the chains rotate, bend and buckle. In a perpendicular magnetic field, longer chains form wavy structure with higher number of buckles. A higher magnetic field strength and a lower modulus of gel matrix lead to higher amplitude of the buckling. The deformation field around a deformed magnetic chain confirms that the polymer network is strongly coupled with the paramagnetic chain. A theoretical model is developed to describe the buckling of the chain.

15 min. break

CPP 8.9 Mon 17:15 C 130

**Environmentally compatible microemulsion at solid surfaces: Wetting behavior and extraction properties** — ●SALOMÉ VARGAS RUIZ<sup>1</sup>, CHRISTOPH SCHULREICH<sup>2</sup>, RAMASIA SREICH<sup>2</sup>, MARTIN JUNG<sup>3</sup>, REGINE VON KLIZING<sup>1</sup>, THOMAS HELLEWEG<sup>2</sup>, and STEFAN WELLET<sup>1</sup> — <sup>1</sup>Stranski Laboratory, TU Berlin, Str. d. 17 Juni 124, 10623 Berlin, Germany — <sup>2</sup>Physical Chemistry III, University Bielefeld, Universitätsstraße 25, 33615 Bielefeld, Germany. — <sup>3</sup>Armed Forces Scientific Institute for NBC Protection, Humboldtstraße 1, 29633 Munster, Germany.

Microemulsions based on sugar surfactants and food grade oil are potential decontamination media for the remediation of sorptive surfaces exposed to highly toxic compounds (e.g. nerve agents, pesticides). The main advantage of microemulsions relies on their capability to degrade the solubilized toxic compound by means of active ingredients hosted in the water phase. Although microemulsions have good performance on the detoxification process, the overall efficiency of the decontamination process is also determined by their ability to wet the treated surfaces and to extract the contaminants. In this study, we examined firstly the wettability and penetration properties of microemulsion formulated with sugar surfactant SL55 and methyl oleate oil, and sec-

ondly we evaluated their ability to extract lipophilic contaminants via spectroscopic and chromatographic techniques. Here, the formulated microemulsions can wet and penetrate hydrophobic and hydrophilic sorptive surfaces and their extraction properties are greatly influenced by their structure and oil content.

CPP 8.10 Mon 17:30 C 130

**Supramolecular structure of pure and mixed monohydroxy alcohols** — ●THOMAS BÜNING<sup>1</sup>, CHRISTIAN STERNEMANN<sup>1</sup>, SEBASTIAN PETER BIERWIRTH<sup>1</sup>, CATALIN GAINARU<sup>1</sup>, JENNIFER BOLLE<sup>1</sup>, MICHAEL PAULUS<sup>1</sup>, CHRISTOPH J. SAHLE<sup>2</sup>, ROLAND BÖHMER<sup>1</sup>, and METIN TOLAN<sup>1</sup> — <sup>1</sup>Fakultät Physik / DELTA, Technische Universität Dortmund, D-44221 Dortmund, Germany — <sup>2</sup>European Synchrotron Radiation Facility (ESRF), F-38000 Grenoble, France

Hydrogen bonds are essential for the structure and dynamics of alcohols, aqueous solutions, and water. Due to their low tendency of crystallization and large variability in molecular configuration, monohydroxy alcohols (MAs) are often studied as model systems for hydrogen-bonded fluids in general [1]. MAs are supposed to form supramolecular structures such as chains and rings via hydrogen bonding in the liquid phase. Based on their small dielectric absorption, ringlike arrangements were suggested for neat MAs with a sterically hindered polar hydroxyl group [1], e.g., for 4-methyl-3-heptanol and 2-hexyl-1-decanol. Mixtures of these MAs show a significantly enhanced dielectric absorption which hints at a change of supramolecular topology [2]. We present combined X-ray diffraction and X-ray Raman measurements of MA mixtures. Here, the first X-ray diffraction peak and the shape of the oxygen K-edge, respectively, are sensitive to the local arrangement of MAs. The results are interpreted with respect to a transformation from ringlike to chainlike structures upon mixing. [1] R. Böhmer et al. *Phys. Reports* **545** 125-195 (2014) and references therein; [2] S. P. Bierwirth, et al. *Phys. Rev. E* **90**, 052807 (2014).

CPP 8.11 Mon 17:45 C 130

**The role of the cation and polarization on lithium ion coordination in ionic liquids** — ●VOLKER LESCH<sup>1</sup>, ZHE LI<sup>2</sup>, DMITRY BEDROV<sup>2</sup>, and ANDREAS HEUER<sup>1</sup> — <sup>1</sup>Westfälische Wilhelms-Universität Münster — <sup>2</sup>University of Utah

MD-simulations are a powerful tool to investigate microscopic processes in complex systems as ionic liquids. The interactions between the cation and the anion are only weak but in the case of adding lithium to an ionic liquid the anions strongly interact with this small lithium ion. The role of the cation on this interaction was never investigated.

Here, we compare the cations 1-ethyl-3-methylimidazolium with N-methyl-N-propylpyrrolidinium and as counterion bis-(trifluoromethanesulfonyl)-imide was used. Both cations differ in size and viscosity but on the microscopic scale only a comparison for pure ionic liquids is published. We performed MD-simulations for the two ionic liquids doped with lithium salts at different temperatures and different oxygen polarizations. The change of the TFSI oxygen polarization was necessary due to new DFT calculations that predicts the Li<sup>+</sup> - Ntf<sub>2</sub> binding energy more accurate. We observed a dramatic influence of the polarization on structural properties while the dynamics are only slightly affected. The comparison of the cations shows only small differences for the lithium ion coordination.

CPP 8.12 Mon 18:00 C 130

**A systematic study of the influence of trivalent metal ions on phase behaviour in protein solutions** — ●OLGA MATSARSKAIA<sup>1</sup>, MICHAL BRAUN<sup>1</sup>, ANDREA SAUTER<sup>1</sup>, MARCELL WOLF<sup>1</sup>, ROLAND ROTH<sup>2</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 für Theoretische Physik, Universität Tübingen

Thermodynamic phenomena such as reentrant condensation (RC) and liquid-liquid phase separation (LLPS) are involved in various protein-related processes, e.g. protein condensation diseases and protein crystallisation. We could show that these transitions are inducible in protein solutions using various trivalent cations [1], [2]. In this work, the influence of cation size on such phase behaviour in bovine serum albumin (BSA) was studied systematically in the presence of salts with increasing cation sizes (YbCl<sub>3</sub>, YCl<sub>3</sub>, GdCl<sub>3</sub>, CeCl<sub>3</sub> and LaCl<sub>3</sub>). The results reveal that charge inversion, the prerequisite of RC and LLPS in these systems, is found independent of cation size. Interestingly, however, salt concentration ranges in which macroscopic LLPS is observed decrease with increasing cations: while Yb<sup>3+</sup> leads to the largest LLPS area, Ce<sup>3+</sup> features the smallest one. La<sup>3+</sup>, the largest cation studied, induces RC, but does not lead to LLPS at all. The findings thus

indicate that the size of cations present in the environment of a protein influences the strength of protein-cation interactions and therefore plays an important role in phase transitions of the protein.

[1] Zhang et al (2008). *Phys. Rev. Lett.*, 101(14), 148101; [2] Zhang et al (2012). *Soft Matter*, 8, 1313-1316.

CPP 8.13 Mon 18:15 C 130

**New relaxation process for water in electric fields** — ●ZORAN MILIČEVIĆ<sup>1</sup>, DAVID M. SMITH<sup>2,3</sup>, and ANA-SUNČANA SMITH<sup>1,3</sup> — <sup>1</sup>Institut für Theoretische Physik and Cluster of Excellence: Engineering of Advanced Materials, FAU Erlangen-Nürnberg, Erlangen, Germany — <sup>2</sup>Computer Chemie Centrum, FAU Erlangen-Nürnberg, Erlangen, Germany — <sup>3</sup>Ruder Bošković Institute, Zagreb, Croatia

Despite a heavily increasing number of electrochemical applications, theoretical and experimental studies of solvent shear properties in the presence of electric fields are almost non-existent. Here we study the shear viscosity of water by performing extensive MD simulations using the GROMACS software package as a function of the electric field strength which breaks the otherwise isotropic nature of the solvent. The shear viscosity is related to the autocorrelation function (ACF) of the off-diagonal elements of the pressure tensor by the Green-Kubo relation. The value of the shear viscosity is determined from the plateau value of the time integral of the ACF or, alternatively, by exploiting the Kohlrausch fit curve of the ACF using a uniform 2-step (fast plus slow) relaxation function. Apart from the fact that the two approaches show an excellent agreement, we find that the field decreases the component of the shear viscosity perpendicular to itself and increases the components which are parallel. Importantly, the field induces an additional slow relaxation process (decoupled from the fast relaxation) only in the parallel direction, increasing by about tenfold the total relaxation

time with respect to the perpendicular direction. Furthermore, the overall water shear viscosity increases slightly with the field strength.

CPP 8.14 Mon 18:30 C 130

**Excess entropy scaling for the segmental and global dynamics of polyethylene melts** — ●EVANGELOS VOYIATZIS, MICHAEL BÖHM, and FLORIAN MÜLLER-PLATHE — Eduard-Zintl-Institut für Anorganische und Physikalische Chemie and Center of Smart Interfaces, Technische Universität Darmstadt, Alarich-Weiss-Strasse 4, D-64287 Darmstadt, Germany

The range of validity of the Rosenfeld and Dzugutov excess entropy scaling laws is analyzed for linear polyethylene chains. We consider two segmental dynamical quantities, the bond and the torsional relaxation times, and two global ones, the chain diffusion coefficient and the viscosity. The excess entropy is approximated by either a series expansion of the entropy in terms of the pair correlation function or by an equation of state for polymers. For all temperatures and chain lengths considered, the two excess entropy estimates are linearly correlated. The scaled segmental relaxation times fall into a non-linear master curve. For a fixed chain length, the reduced diffusion coefficient and viscosity scale linearly with the excess entropy. An empirical reduction to a chain length independent master curve is accessible for both quantities. The Dzugutov scheme predicts an increased value of the scaled diffusion coefficient with increasing chain length which contrasts physical expectations. The origin of this trend can be traced back to the density dependence of the scaling factors. In connection with diffusion coefficients and viscosities, the Rosenfeld scaling appears to be of higher quality than the Dzugutov. An empirical excess entropy scaling is also proposed which leads to a chain length-independent correlation.