

CPP 10: Colloids and Complex Fluids III (joint session BP/CPP/DY, organized by CPP)

Time: Monday 15:00–18:00

Location: H42

CPP 10.1 Mon 15:00 H42

Directed assembly of soft colloids through rapid solvent exchange — ●ARASH NIKOUBASHMAN¹, VICTORIA E. LEE², CHRIS S. SOSA², ROBERT K. PRUD'HOMME², RODNEY D. PRIESTLEY², and ATHANASSIOS Z. PANAGIOTOPOULOS² — ¹Institute of Physics, Johannes Gutenberg University of Mainz, Germany — ²Department of Chemical and Biological Engineering, Princeton University, USA

We studied the directed assembly of soft nanoparticles through rapid micromixing of polymers in solution with a non-solvent. Both experiments and computer simulations were performed to elucidate the underlying physics and to investigate the role of various process parameters. In particular, we discovered that no external stabilizing agents or charged end-groups are required to keep the colloids separated from each other, when water is used as the non-solvent. The size of the nanoparticles can be reliably tuned through the mixing rate and the ratio between polymer solution and non-solvent. Furthermore, we were able to fabricate a wide variety of patchy colloids, such as Janus particles, when polymer blends were used in the feed stream. Our results demonstrate that this mechanism is highly promising for the mass fabrication of uniformly-sized colloidal particles, using a wide variety of polymeric feed materials.

CPP 10.2 Mon 15:15 H42

Directed Assembly of Janus Particles through Flow — ●ARASH NIKOUBASHMAN — Institute of Physics, Johannes Gutenberg University of Mainz, Germany

We investigate the self-assembly of colloidal Janus particles under shear and Poiseuille flow, by employing hybrid molecular dynamics simulations that explicitly take into account hydrodynamic interactions. Under quiescent conditions, the amphiphilic colloids form spherical aggregates with a large size polydispersity. The solvophobic hemispheres are directed towards the core, whereas the solvophilic caps are exposed to the solvent. When sufficiently strong shear is applied, the micelles disaggregate with a consequent decay of the average cluster size. However, we find an intermediate regime where the balance between rearrangement and dissociation favors the growth of the aggregates, where the majority of clusters consist of 13 particles in an icosahedral arrangement. This bias is due to the high geometric symmetry of the icosahedron, which maximizes the internal bonding energy of the aggregate. Our findings demonstrate how self-assembly can be directed towards specific structures via external fields, and open up new applications for Janus particles, ranging from biotechnology to sensor systems.

CPP 10.3 Mon 15:30 H42

Self-organized velocity pulses of dense colloidal suspensions in microchannel flow — ●PHILIPP KANEHL and HOLGER STARK — Institut für Theoretische Physik, Technische Universität Berlin, 10623 Berlin, Germany

Colloids in dense suspension exhibit shear-induced migration and size segregation under pressure driven flow [1]. If the density is increased further, the steady flow becomes unstable and regular oscillations in flow velocity emerge [2]. To develop a theoretical understanding of these oscillations, we simulate colloidal particles with frictional contact under pressure-driven flow in two dimensions using the mesoscale simulation technique of multi-particle collision dynamics.

We present a detailed parameter study on how friction generates transient jamming in the colloidal flow. The jammed regions are un-jammed by rarefaction pulses travelling upstream similar to the experimental observations. Moreover, we address the role of fluid permeation and channel confinement.

Finally, a linear stability analysis of a newly developed continuum model predicts scaling laws for stability condition, wavenumber, and pulse speed, which agree well with our numerical data.

[1] P. Kanehl and H. Stark, *J. Chem. Phys.* 142, 214901 (2015).

[2] L. Isa, R. Besseling, A. N. Morozov, and W. C. Poon, *Phys. Rev. Lett.* 102, 058302 (2009).

CPP 10.4 Mon 15:45 H42

An empirical correction for multiple scattering in integral laser Doppler velocimetry experiments — ●DENIS BOTIN¹, LUDMILA MAROTTA MAPA^{1,2}, CHRISTOPHER WITTENBERG¹, HOLGER

SCHWEINFURT¹, and THOMAS PALBERG¹ — ¹Institute of Physics, JGU, D-55099, Mainz, Germany — ²Federal University of Itajuba, Brazil

Super-heterodyne laser Doppler velocimetry (SHLDV) provides an integral measurement of the velocity distribution in electro-kinetic experiments[1]. This allows simultaneous evaluation of the electro-phoretic and electro-osmotic mobilities of the particles and along the cell wall, respectively [2]. Here, we introduce an extension of the method to the regime of concentrated samples, where multiple scattering affects the signal [3]. Multiple scattering distorts the signal shape, creating an additional hump in the background and prohibiting any meaningful fit. We use an empirical correction scheme for the spectra, in which we fit the multiple scattering contribution and subtract it from the raw data. This leaves the velocity dependent singly scattered contribution unaffected. First applications to measurements of the concentration dependence of the electro-phoretic mobility of charged colloidal spheres are reported.

[1]T. Palberg et al. *J. Phys. Chem.* 96, 8180 - 8183 (1992)

[2]T.Palberg et al. *J. Phys.: Condens. Matter* 24, 464109 (2012).

[3]H.C. Van de Hulst., *Multiple Light Scattering: Tables, Formulas, and Applications*, Academic Press, New York., (1980).

CPP 10.5 Mon 16:00 H42

Multiscale modelling of complex (macro-)molecular fluid mixtures — ●CHRISTOPH JUNGHANS¹, TIAGO E. DE OLIVEIRA^{2,3}, PAULO A. NETZ^{2,3}, DEBASHISH MUKHERJI², and KURT KREMER² — ¹CCS Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA — ²Max-Planck Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz Germany — ³Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil

Many biophysical processes in water are determined by the interactions of cosolvents within the hydration shells of dissolved molecules. Computational approaches are mostly limited to the "mid sized" all-atom simulation protocols. While all-atom simulations are suitable in some cases, problems arise when concentration fluctuations are large, thus requiring efficient simulation methods. Therefore, we develop two distinct, yet related, multiscale methods. In one case, we develop a semi-grand canonical MD that heals the particle depletion [1] that uses the AdResS scheme [2], coupled with a metropolis particle exchange criterion. In AdResS, an all-atom region is coupled to a coarse-grained (CG) reservoir, where the particle exchange is performed. In the second protocol, we develop a "parameter free" CG model, which uses cumulative coordination within an iterative procedure [3]. Both methods preserve pair-wise structure of complex fluids and their solvation thermodynamics. We apply these methods to study several cases of (macro)molecular solvation in aqueous mixtures [1,3].

[1] D. Mukherji and K. Kremer, *Macromolecules* (2013). [2] S. Fritsch, et al. *PRL* (2012). [3] T. E. de Oliveira, et al. (2016).

CPP 10.6 Mon 16:15 H42

Kinetics of liquid-liquid phase transition in protein solutions exhibiting LCST phase behavior studied by USAXS — ●FAJUN ZHANG¹, STEFANO DA VELA¹, MICHAL BRAUN¹, MICHAEL SZTUCKI², and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen — ²ESRF, Grenoble, France

We present the results of the early stage kinetics of liquid-liquid phase separation (LLPS) in protein-salt solutions studied by ultra-small angle x-ray scattering (USAXS). The model system of bovine serum albumin (BSA) with YCl₃ [1,2] shows LLPS and a lower critical solution temperature (LCST) phase behavior and can be rationalized using an ion-activated patchy-colloid model [3]. We focus on the phase transition of the dense liquid phases after a T-jump aiming at the arrested or slowed down kinetics. The USAXS curves of sample solutions after a T-jump exhibit a peak that grows in intensity and shifts to lower q values with time. The characteristic length (ξ) obtained from this scattering peak increases with time approximately as $t^{0.3}$. The interface between the dilute and dense phase is quickly established as a Porod region (q^{-4}) is visible within a few seconds. Thus the kinetics of the intermediate stage of phase transition was followed by USAXS. It is interesting to see that $\xi(t)$ is nearly independent on the jump temperatures (below 40 °C). At a higher temperature jump (45 °C), a slowed down kinetics was observed indicating that the gelation line

was approached. [1] F. Zhang, et al. Phys. Rev. Lett. 101, 148101 (2008) Proteins 78, 3450 (2010). [2] F. Zhang, et al. Soft Matter 8, 1313 (2012). [3] F. Roosen-Runge, et al. Sci. Rep. 4, 7016 (2014).

15 min. break

CPP 10.7 Mon 16:45 H42

Hydration and hysteresis of triblock copolymers — ●BERNHARD SCHUMMER, STEFAN GERTH, and RANDOLF HANKE — Universität Würzburg, Lehrstuhl für Röntgenmikroskopie

Ternary polyether are block ABA copolymers consisting of polyethyleneoxide (PEO) (A) and polypropylenoxide (PPO) (B). They change their hydrophilic or hydrophobic balance dramatically with their temperature and their concentration in water. This change causes a micellisation. In this case P123 will be used as a copolymer and SAXS will be the method of examination. For micelles an appropriate model is the core-shell model where the shell mostly consists of PEO and the core mainly of PPO. In this model the SLD's for core and for shell heavily depend on each other. A new parameter $\kappa = \frac{\rho_c - \rho}{\rho_s - \rho}$ is presented to describe the change of the conformation and hydration of the micelle while including the radii of shell and core. Here ρ_c is the SLD of the core ρ_s the SLD of the shell and ρ the SLD of the solvent. The new parameter indicates that the SLD of the core decreases and thus dehydrates with increasing temperature. For instance the SLD's of the poloxamer L51 show a similar dependency as P123. The heating and cooling curves of the sample for different small concentrations will be presented and show a hysteresis in the form phase diagram. This can be observed in a diagram where κ is plotted against the temperature. At higher concentrations poloxamers form a liquid crystal. It has already been shown that there is a hysteresis in the cell parameter at high concentrations. This effect can now be attributed to a single component of the system, the form change of the micelle.

CPP 10.8 Mon 17:00 H42

Phase behaviour and interactions in a three components γ -globulin based depletion interaction system — ●STEFANO DA VELA¹, FAJUN ZHANG¹, SARAH EL-ASFAR¹, CHRISTIAN EXNER¹, MICHAEL SZTUCKI², and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen — ²ESRF, Grenoble, France

Aqueous solutions of bovine γ -globulin with polyethylene glycol (PEG) added as non-interacting polymer, provide a tunable protein system for the study of depletion-driven phase behaviour: range and strength of the interaction are adjusted by appropriate choice of PEG molecular weight and concentration. An extensive study of the phase behaviour of the system for different effective attraction strengths reveals a set of conditions for which a Liquid-Liquid Phase Separation (LLPS) phase boundary emerges above the freezing temperature of the solvent. Addition of bovine serum albumin (BSA), results into an effective three components system. BSA, while not inducing depletion interaction on its own, appears to enhance it in presence of PEG, shifting the LLPS boundary to higher temperatures while being preferentially excluded from the resulting protein-dense liquid phase. In order to investigate the effect of BSA on the phase boundaries and on the interaction, phase diagrams as a function of temperature, protein and PEG concentration are presented together with small angle X-ray scattering data. Optical microscopy, turbidimetry and size exclusion chromatography are employed as supplementary techniques. The findings are relevant to the understanding of protein mixtures and their separation.

CPP 10.9 Mon 17:15 H42

Clusters of proteins – are they transient or static? — ●MICHAL BRAUN¹, MARCO GRIMALDO^{1,2}, FELIX ROOSEN-RUNGE², CHRISTIAN BECK¹, FAJUN ZHANG¹, FRANK SCHREIBER¹, and TILO SEYDEL² —

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Signatures of protein clusters have been observed for globular proteins such as lysozyme [1], crystallins and bovine serum albumin [2,3]. The nature of these clusters, whether static or transient, however, is still a debated question and depends sensitively on environmental conditions. A better understanding would be key to use protein clusters as precursors for protein crystallization or in drug delivery.

We report cluster formation in solutions of β -lactoglobulin (BLG), as systematically investigated using static and dynamic scattering techniques. From small-angle scattering (SAXS/SANS), we obtain a cluster signature from the missing shift of the correlation peak with concentration and related data fitting. Neutron quasi-elastic backscattering (QENS) evidences the formation of oligomers via the short-time self-diffusion coefficient at nanosecond time scales. Finally, neutron spin-echo spectroscopy (NSE) allows to compare structural information from the structure factor with the dynamical features of collective diffusion on time scales of several tens of nanoseconds, which ultimately allows to determine the nature of the observed protein clusters.

[1] Stradner et al. Nature 432 (2004) 492

[2] Soraruf et al. Soft Matter 10 (2014) 894

[3] Grimaldo et al. J. Phys. Chem. Lett. 6 (2015) 2577

CPP 10.10 Mon 17:30 H42

Self-assembled micelles as drug carriers: Influence of molar mass and chain architecture — ●BART-JAN NIEBUUR¹, XIAOHAN ZHANG¹, NATALYA VISHNEVETSKAYA¹, PETR CHYTL², SERGEY K. FILIPPOV², and CHRISTINE M. PAPADAKIS¹ — ¹Technische Universität München, Physik-Department, Garching, Germany — ²Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic

A promising way to achieve site-specific delivery of anticancer agents is to use the enhanced permeation and retention (EPR) effect of self-assembled polymeric micelles. At this, a low critical micelle concentration (CMC) and particle sizes in the range of 1-100 nm are of importance.

In the present work, we focus on the importance of (i) the overall molar mass and (ii) the chain architecture. We investigate both N-(2-hydroxypropyl) methacrylamide (HPMA) [1] homopolymers with randomly distributed cholesterol side groups and diblock copolymers having a pure HPMA block and an HPMA block with cholesterol. Using fluorescence correlation spectroscopy and small-angle neutron scattering (SANS), the CMC as well as the size and structure of the micelles are determined in phosphate buffer. We find that the CMC decreases with increasing molar mass, but does not depend on chain architecture. The micellar radius is with 4-5 nm in the desired range.

[1] Filippov, S.K. et al., *Biomacromolecules* **13**, 2594 (2012) and **14**, 4061 (2013)

CPP 10.11 Mon 17:45 H42

Modeling Viscoelastic Properties of Complex Fluids — ●JULIUS SCHULZ, ALEXANDER SCHLAICH, ROLAND NETZ, and JULIAN KAPPLER — Fachbereich Physik, Freie Universität Berlin, 14195 Berlin

The viscoelastic response of a complex liquid like water differs significantly from more simple models such as a Lennard-Jones fluid or methane. Using all-atom molecular dynamics simulations, we calculate the frequency-dependent viscosity for two liquids: TIP4P/2005 water and a glycerol/water solution. The corresponding elastic spectrum exhibits two peaks and cannot be described by simple viscoelastic models. We discuss the origins of these features and present a novel extension of the Maxwell model for viscoelastic fluids which is capable of reproducing the relevant features of the frequency-dependent viscosity. Extracted shear relaxation times for the glycerol-water mixtures compare well with experiments.