

CPP 6: Colloids and Complex Fluids II (joint session BP/CPP/DY, organized by CPP)

Time: Monday 9:30–13:00

Location: H51

Invited Talk

CPP 6.1 Mon 9:30 H51

Dynamics of thermosensitive core-shell dumbbells as analyzed by rheo-SANS — ●MATTHIAS BALLAUFF — Helmholtz-Zentrum Berlin

We present a study of the dynamics of dumbbell-shaped colloids. The thermosensitive dumbbell-shaped microgels consist of a solid polystyrene core and a thermosensitive shell of cross-linked poly(N-isopropylacrylamide). These colloidal particles are nearly monodisperse as shown by cryogenic transmission electron microscopy. The aspect ratio L^* defined by the ratio of the center distance L to the diameter D can be varied between 0.24 and 0.3. The effective volume fraction can be varied by temperature and high volume fractions can be achieved easily because of the thermosensitive shell [1]. We observe the formation of a plastic crystal in these suspensions about of volume fraction of 0.5 as predicted by theory. This is shown from rheological evidence and by the Bragg-reflections of the crystals. For higher volume fraction a glassy state is formed. Moreover, oscillatory experiments in the linear viscoelastic regime and flow curves up to volume fractions of nearly 0.7 have been obtained. Recent studies based on a combination of rheoSANS experiments and BD-simulations revealed the formation of a novel, partially oriented phase formed by dumbbells under shear. All data demonstrate that these particles present a novel model system for the study of the rheology of slightly anisotropic particles.

[1] F. Chu, et al., *Macromol. Rapid Comm.* 33 (2012) 1042.

CPP 6.2 Mon 10:00 H51

Phase diagram of polydisperse colloidal dispersions — ●PREECHA KIATKIRAKAJORN¹, JOAQUIM LI¹, BERNARD CABANE², FRANCK ARTZNER³, ROBERT BOTET⁴, and LUCAS GOEHRING¹ — ¹Max Planck Institute for Dynamics and Self-Organization (MPIDS), 37077 Göttingen, Germany — ²LCMD, CNRS UMR 8231, ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 05, France — ³Institut de Physique, CNRS UMR 6626, Univ Rennes, 35042 Rennes, France — ⁴Physique des Solides, CNRS UMR 8502, Univ Paris-Sud, F-91405 Orsay, France

Polydisperse colloidal dispersions have been predicted, for over twenty years, to have a rich and complex phase space of colloidal crystals. However, experiments have consistently suggested that such crystals are kinetically inaccessible, as small amounts of polydispersity poison crystal formation. Here, we show a result of small-angle X-ray scattering experiment of highly polydisperse (yet monomodal) colloidal dispersions in a range of sizes (average size from 8 to 50 nm), with soft, charge-mediated interactions. These dispersions were dialysed and compressed by aqueous solutions of poly(ethylene glycol) to reach 15% to 30% of volume fraction, and crystallize. Their phase diagrams, structure factors and crystal peaks were analysed by the x-ray scattering patterns. We found coexistences of complex crystal structures (two BCC structures and Laves AB₂) for the small particle size, and BCC and FCC crystals for the larger particle size. These results show a fractionation among the particles. We further show how this is possible through numerical simulations, which explain how the fractionation occurs and how the particles distribute among the different coexisting phases.

CPP 6.3 Mon 10:15 H51

Free energies, liquid and crystal phases of the Asakura-Oosawa model: a density functional theory study — ●MOSTAFA MORTAZAVIFAR and MARTIN OETTEL — Institut für Angewandte Physik, Uni Tübingen, Tübingen, Germany

The Asakura-Oosawa(AO) model is a well known model for studying colloid-polymer mixtures in which the depletion interaction between colloidal particles results in a phase diagram similar to molecular liquids. More importantly, it is a generic model system for short range attractive colloidal particles. We have studied the model by means of density functional theory (DFT) by applying a linearization of a two-component fundamental measure hard sphere tensor functional with respect to the second (polymer) component. The linearized functional gives a unified description of gas, liquid, and crystal phases. We have calculated the free energies and phase diagrams for a variety of colloid-polymer size ratios. The results are in good agreement with available simulations. For small size ratios, the model can be mapped exactly to a one-component system with a short-range attractive potential

between the colloids. Standard mean field approximations fail in describing the liquid and crystal phases; here our functional offers novel insights how to construct generically density functional descriptions of interparticle attractions.

CPP 6.4 Mon 10:30 H51

Crystallization of sheared nearly hard-spheres — ●DAVID RICHARD and THOMAS SPECK — Staudingerweg 9, 55128 Mainz

Understanding crystallization pathways and kinetics is a long standing challenge in condensed matter science. Additionally, the effect of impurities and external fields is also a matter of debate. In this study, we look at the effect of a simple linear shear flow on the crystallization of nearly hard-spheres [1]. By varying the density from low to high supersaturation, we find a crossover from shear-suppressed crystallization to an enhanced crystallization kinetics. We attribute this crossover under shear to the vanishing nucleation barrier in the quiescent system, at which nucleation is changing from an activated to a diffusive limited process.

[1] Richard, David, and Thomas Speck. 'The Role of Shear in Crystallization Kinetics: From Suppression to Enhancement.' *Scientific Reports* 5 (2015).

CPP 6.5 Mon 10:45 H51

On the influence of the softness of the potential on the phase diagrams of core-shell micelles - a simulation study — ●HEIKO G. SCHOBERTH, HEIKE EMMERICH, and THOMAS GRUHN — Lehrstuhl Material- und Prozesssimulation, Universität Bayreuth, D-95440 Bayreuth

Quasicrystals are of continuous interest due to their fascinating fundamental properties and their promising applications as advanced photonic materials in a range of optical devices. In the last years colloidal quasicrystals have been found in solutions with spherical polymer core-shell micelles. With these colloids and their intriguing possibility to self-assemble in a broad range of nanoscale and microscale quasicrystalline structures, the demand arises of understanding the complex formation mechanism and the thermodynamic stability of these structures. Especially, it is important to find a direct relation between the stability of the structures and the main parameters of the micelle-micelle interaction. We perform coarse-grained molecular dynamics simulation to investigate the dependence of the phase diagram on the softness of the interaction potential. The core-core interaction is modelled by infinite repulsion, whereas the shell-shell interaction is varied from a stiff to a very soft potential. Varying the core to shell radius and packing fraction we study systematically the change in the phase diagram finding domains with 10-,12-,18-,24-fold quasicrystalline symmetries. With increasing smoothness of the potential the phase diagram changes qualitatively and the geometry of the phase boundaries gets more regular.

CPP 6.6 Mon 11:00 H51

Estimation of crystal nucleation barriers for colloidal crystals from computer simulations — ●PETER KOSS^{1,2}, ANTONIA STATT¹, PETER VIRNAU¹, and KURT BINDER¹ — ¹Institut für Physik, Johannes Gutenberg-Universität Mainz, Staudinger Weg 9, 55128 Mainz, Germany — ²Graduate School of Excellence Materials Science in Mainz, Staudinger Weg 9, 55128 Mainz, Germany

A fluid in equilibrium in a finite volume, with a density exceeding the onset of freezing, may exhibit phase coexistence of a crystal nucleus surrounded by liquid. In classical nucleation theory, the barrier of homogeneous nucleation is given by two contributions, the energy gain of creating a droplet and the energy loss due to surface tension of the newly created interface. Using a computational method suitable for the estimation of the chemical potential of dense fluids we obtain the excess free energy due to the surface of the crystalline nucleus. Our novel analysis method is appropriate for crystal nuclei of all shapes without suffering from ambiguities occurring when one needs a microscopic identification of the crystalline droplet. We report that the nucleation barrier for a soft version of the effective Asakura-Oosawa model[1] is compatible with a spherical shape, and consistent with classical nucleation theory [2].

[1] M. Dijkstra, R. van Roij and R. Evans, *Phys. Rev. E* 59, 5744-

5771 (1999).

[2] A. Statt, P. Virnau, and K. Binder, Phys. Rev. Lett. 114, 026101 (2015).

CPP 6.7 Mon 11:15 H51

Crystal nucleation in metastable hard sphere fluids by confocal microscopy — ACHIM LEDERER¹ and HANS JOACHIM SCHÖPE² — ¹Retsch Technology GmbH, Retsch-Allee 1-5, 42781 Haan, Germany — ²Eberhards Karls Universität Tübingen, Auf der Morgenstelle 10, 72026 Tübingen, Germany

Crystal nucleation in colloidal hard spheres is a longstanding research topic. Light scattering and confocal microscopy as well as simulations had been carried out to characterize the nucleation process and to get a microscopic picture. In these studies results both differ and agree with each other. It is still unclear whether the large disagreement in the nucleation rate densities between the light scattering experiments and simulations are of physical nature or result from differing data analyses. Furthermore, the temporal evolution of the microscopic structure has not yet been characterized sufficiently. Using laser-scanning confocal microscopy we study crystal nucleation in colloidal hard spheres. The used system has been characterized with extreme care to allow for meaningful comparison with other experiments and simulations. Observing a large sample volume we can analyze the nucleation process with high accuracy. This allows us to obtain meaningful data of the nucleation rate density, critical nucleus size and nucleation barrier. Furthermore, we determine the time-dependent interfacial tension through how the cluster size distribution evolves. Analyzing the nucleation process on a microscopic scale, we confirm the scenario of precursor-mediated crystal nucleation. In addition we show in great detail the structure evolution from precursor to crystal.

15 min. break

Invited Talk

CPP 6.8 Mon 11:45 H51

Percolation in colloidal model systems — TANJA SCHILLING¹, HUGUES MEYER¹, MOHIT DIXIT¹, MARK MILLER², and PAUL VAN DER SCHOOT³ — ¹Physics and Materials Science Research Unit, University of Luxembourg, Luxembourg — ²Department of Chemistry, Durham University, United Kingdom — ³Theory of Polymers and Soft Matter, Technische Universiteit Eindhoven, 5600 MB Eindhoven, The Netherlands

Connectivity percolation is the transition in which isolated clusters of solid particles in a fluid become connected in some sense to form a system-spanning network. This network has a significant effect on the transport properties of the material on a macroscopic scale. If, for example, an electrically insulating polymer is mixed with conductive fibres such as carbon nanotubes, the conductivity of the composite increases by ten or more orders of magnitude near the percolation transition of the filler material.

We discuss percolation in suspensions of fibres and of platelets. Our study covers the entire range of aspect ratios from spheres to extremely slender rods and infinitely thin disks. The percolation threshold for rod-like particles of aspect ratios below 1000 deviates significantly from the inverse aspect ratio scaling prediction, thought to be valid in the limit of infinitely slender rods and often used as a rule of thumb for fibres in composite materials. We also show the effects of polydispersity on the percolation transition. The main result is that the percolation threshold shows universal behaviour, i.e. it depends only on certain cumulants of the size distribution.

CPP 6.9 Mon 12:15 H51

Towards flexible and dynamic self-assembly from colloids with magnetic anisotropy — GABI STEINBACH^{1,5}, DENNIS NISSEN², MANFRED ALBRECHT², EKATERINA V. NOVAK³, PEDRO SÁNCHEZ⁴, SOFIA KANTOROVICH^{3,4}, SIBYLLE GEMMING^{1,5}, and ARTUR ERBE⁵ — ¹Technische Universität Chemnitz, 09107 Chemnitz,

Germany. — ²University of Augsburg, 86159 Augsburg, Germany. — ³Ural Federal University, 620000, Ekaterinburg, Russia. — ⁴University of Vienna, 1090 Vienna, Austria. — ⁵Helmholtz-Zentrum Dresden-Rossendorf, 01328 Dresden, Germany.

Magnetic colloidal particles are a suitable model system for the study of self-assembly and dynamic processes on the microscale. Here, we illustrate the potential of directed, but flexible bonds for tailored structure formation. As an example, we present a system of colloidal microspheres that have an off-centered net magnetic moment pointing perpendicular to the particle surface. They are an experimental realization of the theoretical model of spheres with radially shifted point dipole (sd-particles). Experimentally we observed the formation of branched structures as result of two coexisting self-assembly patterns, which is untypical for homogeneous systems. We show that the bistability can be explained by an extended model of sd-particles. This framework takes the broad magnetization distribution in the experimental particles into account. We will further show that the interacting particles exhibit interesting non-equilibrium dynamics when exposed to time-dependent fields, leading to reversible structural reconfigurations.

CPP 6.10 Mon 12:30 H51

Enhanced magneto-optical response in dispersions of anisometric pigment particles — KATHRIN MAY, ALEXEY EREMIN, and RALF STANNARIUS — Institute of Experimental Physics, Otto von Guericke University Magdeburg, Universitätsplatz 2, 39016 Magdeburg, Germany

Colloidal suspensions of anisometric particles show a variety of unique properties depending on particle concentration and external electric fields, such as the formation of ordered phases, phase separation, electro-optical effects, and non-linear rheology. Electro- and magneto-optical properties of colloids are of particular interest because of the possible applications in electrophoretic ink displays and other technologies. We demonstrate a binary colloidal system with an unusually strong magneto-optical response which is comparable with that of thermotropic liquid crystals. This system is based on a binary mixture of elongated non-magnetic pigment particles and a small volume fraction < 0.1 v/% of spherical magnetic nanoparticles. The birefringence is caused by a partial alignment of the pigment particles, controlled by anisometric agglomerates of the magnetic particles that form in a magnetic field. This effect is discussed in the frame of the Onsager-Lekkerkerker theory of steric alignment transfer in binary mixtures of colloidal particles.

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CPP 6.11 Mon 12:45 H51

The initial magnetic susceptibility of cube-like magnetic colloids in dilute suspensions — JOE DONALDSON¹ and SOFIA KANTOROVICH^{1,2} — ¹Faculty of Physics, University of Vienna, Boltzmanngasse 5, 1090 Vienna, Austria — ²Ural Federal University, Lenin av. 51, 620083, Ekaterinburg, Russia

Magnetic nano/micro-particles are currently applied in many diverse research and industrial disciplines. These particles exhibit a number of interesting properties that can be utilised, leading to a number of established and developing applications. Most notably: magnetic drug targeting; magnetic hyperthermia cancer treatment; and ferrofluids. In each of these applications, a crucial piece of information is required; namely, some sort of insight into the magnetic behaviour of these particles. Ideally, one would like some indication of this a priori. As such, we present here theoretical and simulation studies on permanently magnetised particles that are actually cube-like in shape [1]. We have investigated the differences in magnetic behaviour arising from this additional directional interaction, focussing on the initial magnetic susceptibility of low-density suspensions.

[1] J. G. Donaldson and S. S. Kantorovich, Nanoscale, 2015, 7, 3217