CPP 28: Colloids and Complex Liquids I

Time: Wednesday 15:00–18:45 Location: C 130

Invited Talk CPP 28.1 Wed 15:00 C 130

The glass transition is continuous but gelation is discontinuous in sticky spheres — •Paddy Royall[1], Stephen Williams[2], and Hajime Tanaka[3] — [1]University of Bristol, UK — [2]Australian National University, Canberra, Australia — [3]The University of Tokyo, Japan

We identify dynamic and structural signatures which distinguish gels and glasses in a colloidal model system of hard and sticky spheres. Since gels are identified with arrested spinodal decomposition, this presents a thermodynamic basis upon which to identify gelation, and distinguish it from vitrification. We base our findings on confocal microscopy experiments of and confirm these with molecular dynamics simulations.

In the gel transition, upon crossing the spinodal line at a packing fraction 0.35, we find a sharp change in the structural relaxation time, and enter an ageing regime. Simultaneously, our novel structural analysis shows a large and sudden change in local structure. This is confirmed in simulation where the pressure turns negative upon gelation. Thus gelation is 'first-order-like'. By contrast, the approach to the glass is continuous, and not associated with any phase transition.

In 'sticky spheres', since gelation occurs at the spinodal line, it appears 'first-order-like', while on the timescales we access, the glass transition is continuous. Arrested states lying in the metastable gas-liquid regime are gels and those outside glasses. Significantly, the gel extends to packing fractions of at least 0.59.

CPP 28.2 Wed 15:30 C 130

Zigzag transition and nonequilibrium explosions in a one-dimensional colloidal crystal — •Arthur Straube[1], Lutz Schimansky-Geier[1], Roel Dullens[2], and Ard Louis[3] — [1]Department of Physics, Humboldt University of Berlin, Germany — [2]Physical and Theoretical Chemistry Laboratory, Department of Chemistry, University of Oxford, UK — [3]Rudolf Peierls Centre for Theoretical Physics, University of Oxford, UK

We study the equilibrium zigzag transition and nonequilibrium pattern formation that emerges when magnetically repelling colloids, trapped individually in a line by optical tweezers, are abruptly released, forming colloidal explosions [EPL **94**, 48008 (2011); J. Chem. Phys., submitted]. We show experimentally and explain theoretically why for certain nonharmonic traps the equilibrium zigzag transition is impossible. Colloidal explosions demonstrate a nonequilibrium zigzag pattern that persists even when magnetic interactions are much weaker than those that break the linear symmetry in equilibrium. Theory and computer simulations, including hydrodynamic interactions, quantitatively describe these phenomena both in and out of equilibrium.

CPP 28.3 Wed 15:45 C 130

Wrinkle-assisted linear assembly of plasmonic-core/soft-shell particles: A lithography-free approach towards anisotropic nanostructures — •Mareen Mueller[1], Matthias Karg[2], Andrea Fortini[3], Thomas Hellweg[4], and Andreas Fery[1] — [1]Physical Chemistry II, University of Bayreuth, Germany — [2]Physical Chemistry I, University of Bayreuth, Germany — [3]Theoretical Physics II, University of Bayreuth, Germany — [4]Physical Chemistry III, Universty of Bielefeld, Germany

This contribution addresses wrinkle assisted assembly of silver-poly-(N-isopropylacrylamide) core-shell particles. Anisotropic alignment is found on two length scales, macroscopically guided through the wrinkle structure and locally due to deformation of the polymer shell leading to smaller inter-core separations as compared to assembly on flat substrates without confinement. The structures were analyzed by means of scanning electron microscopy. Radial distribution functions are shown, clearly highlighting the impact of confinement on nearest neighbor distances and symmetry. The observed ordering is directly compared to Monte-Carlo simulations for hard-core/soft-shell particles, showing that the observed symmetries are a consequence of the soft interaction potential and differ qualitatively from a hard-sphere situation. As a first evidence for the impact of the alignment on optical properties, we show UV-vis absorbance measurements revealing optical anisotropy of the generated structures due to plasmon coupling. Furthermore, the high degree of order of the assembled structures on macroscopic areas is demonstrated by laser diffraction effects.

CPP 28.4 Wed 16:00 C 130

Guided self-assembly of microgels: From particle arrays to anisotropic nanostructures — •Marco-Philipp Schürings[1], Patrick Wünnemann[1], Stephanie Hiltl[1], Andrij Pich[2], and Alexander Böker[1] — [1]Lehrstuhl für Makromolekulare Materialien und Oberflächen RWTH Aachen, D-52056 Aachen, Germany — [2]Lehrstuhl für Funktionale und Interaktive Polymere, RWTH Aachen, D-52056 Aachen, Germany

Our work aims at the production of microgel strings, rods and meshes via crosslinking of well-defined particle arrays. Wrinkled substrates are prepared by oxidization of stretched Polydimethylsiloxane (PDMS). Subsequently, microgels of N-vinyl caprolactam/Acetoacetoxy ethylmethacrylate (VCL/AAEM) and N-isopropylacrylamide/N-vinylcaprolactam (NIPAAm/VCL) are spin-coated onto these surfaces thereby forming self-assembled structures within the wrinkle grooves. We consequently transfer those pre-aligned particles onto flat silicon wafers to create periodic nanostructures covering large surface areas up to 3 x 3 cm, as confirmed by GISAXS measurements. UV irradiation of the assembled particles yields microgel chains with variable widths of 500- 2000 nm and lengths up to 27 microns which are tunable by altering the wavelength of the PDMS wrinkles. Due to the thermoresponsiveness of VCL/AAEM colloids anisotropic contraction can be induced, which leads to possible applications as sensors and actuators. By using light or electrosensitive microgels and considering their biocompatibility even more applications, such as synthetic muscle fibers, appear feasible.

CPP 28.5 Wed 16:15 C 130

Core size effects on the rotation and stability of dipolar clusters in rotating magnetic field — •Ayan Ray and Thomas M. Fischer — Institut für Experimentalphysik, Universität Bayreuth, 95440 Bayreuth, Germany.

We report on the rotation of colloidal clusters of non magnetic holes and of mixtures of paramagnetic beads with non magnetic holes in a ferrofluid in a rotating external magnetic field. The precession angle of the external field is a control parameter determining the stability of the cluster. Clusters become locally unstable when the local precession angle reaches the magic angle. Cluster shape dependant depolarization fields lead to a deviation of the local from the external precession angle such that close to the external magic angle different cluster shapes might coexist. For this reason cluster transitions are weakly or strongly first order transitions. If the transition is weakly first order a critical speeding up of the cluster rotation is observed. No speeding up occurs for strongly first order cluster transitions with hysteresis. The strength of the first order transition is controlled by the size of the core of the cluster.

CPP 28.6 Wed 16:30 C 130

Well-defined colloidal clusters by combined chemical and topographical templating — •Christoph Hanske[1], Alexander Wittemann[2], and Andreas Fery[1] — [1]Physical Chemistry II, University of Bayreuth, Germany — [2]Physical Chemistry I, University of Bayreuth, Germany

Assemblies of colloidal particles are promising building blocks for future lab-on-a-chip devices such as sensors. Recently, we have introduced the creation of large-scale ordered arrays of particles using wrinkled elastomers (1, 2). These wrinkled stamps are accessible by the systematic exploitation of buckling instabilities without any lithographic steps. By placing a wrinkled stamp onto a droplet of colloidal suspension, liquid filled channels are formed confining the particles. Due to capillary forces close packed arrays are formed during drying. While the procedure is applicable to a wide range of particles, successful colloidal assembly strongly depends on interfacial properties. In this contribution we concentrate on the influence of the wettability of both the stamps and the substrates on the deposition process. Furthermore, local variations of the wettability can be achieved by microcontact printing. Combing such chemically patterned substrates with topographical templating in wrinkles allows us to create colloidal clusters in highly regular arrangements.

1. Lu, C.; Möhwald, H.; Fery, A. Soft Matter 2007, 3, 1530-1536.

2. Schweikart, A.; Fortini, A.; Wittemann, A.; Schmidt, M.; Fery, A. Soft Matter 2010, 6 (23), 5860-5863.

15 min break

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Smart Microgel Capsules and Model Colloids Tailored by Droplet-Based Microfluidics — •Sebastian Seiffert — Helmholtz Zentrum Berlin, F-I2 Soft Matter and Functional Materials, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

Micrometer-sized polymer gel particles can be produced with exquisite control by droplet-based microfluidics. The idea of this approach is to use emulsion droplets as templates to control the particle size, shape, and monodispersity. To extend this control towards controlling the material properties of the microgels, microfluidic templating can be combined with the use of functional, macromolecular precursors; this separates the polymer synthesis from the particle gelation and allows each to be controlled independently. It also allows complex morphologies such as hollow, anisotropic, or multi-layered microgels to be formed and complexed with additives such as drugs, colloids, or living cells. In addition to their utility for encapsulation, these microgels can serve as model systems to explore how the particle stiffness and size affect the bulk and shear elasticity of compressed particulate suspensions. While it is known that in dilute solution, the dynamics of colloidal microgels strongly dependends on the particle size, it is unclear to what extent the dynamics of microgel systems is determined by the particle size if the system is densely packed. A droplet-based microfluidic approach allows such dense-packed microgel systems to be prepared with particles of strongly varying size, revealing that the isotropic compressibility and shear elasticity of both colloidal-scale and granular-scale systems show universal, macrogel-type scaling independent of the particle size.

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How Hidden Degrees of Freedom affect Fluctuation-Theorems — •Jakob Mehl[1], Boris Lander[2], Udo Seifert[2], Clemens Bechinger[1], and Valentin Blickle[1] — [1]2. Physikalisches Institut, Universität Stuttgart, Germany — [2]II. Institut für Theoretische Physik, Universität Stuttgart, Germany

Fluctuation-theorems (FT) are one of the few exact relations, which are valid for systems driven out of equilibrium. The connection between the free energy difference and the work done to a system, known as Jarzynski equality, is certainly the most prominent example of the FT for the total entropy production Δs_{tot}. So far, experimental studies concentrated only on simple systems with one degree of freedom.

By combining paramagnetic colloidal particles and rotating laser tweezers, we study two nonequilibrium steady states, which can be coupled by an externally controlled magnetic field. Using video microscopy, we can simultaneously follow both particles' nonequilibrium fluctuations with high accuracy. As derived from stochastic thermodynamics, all degrees of freedom have to be taken into account to maintain the FT of Δs_{tot}. It is unknown whether such relations change, when only parts of the system are accessible, i.e. when in our experiment only the fluctuations of one particle are regarded. We show that for the prevailing majority of experimental cases the FT is only violated slightly, i.e. only linear correction terms contribute. For extreme situations, strong deviations are present and higher order terms are not longer negligible.

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Active Brownian Motion in Complex Environments — •Ivo Buttinoni — Universität Stuttgart, Stuttgart, Germany

Active Brownian particles are capable of taking up energy from their environment and converting it into directed motion; examples range from chemotactic cells and bacteria to artificial microswimmers. We develop a novel species of microswimmers whose active motion is due to the local demixing of a critical binary liquid mixture and can be easily tuned by illumination. Illumination causes a local heating of the caps, which induces a local asymmetric demixing of the binary mixture leading to a spatial concentration gradient across the particle. Since the heating strength is controlled by the incident light intensity, the particle's self-diffusiophoretic motion can be easily controlled. As a first step towards more realistic conditions under which such microswimmers will be employed, we study, experimentally and with numerical simulations, their behavior in patterned surroundings that present complex spatial features where frequent encounters with obstacles become important[1]. The motion of such swimmers inside mobile obstacles, i.e., passive colloids, is probed as well, showing memory effects related to the characteristics of both the passive and the active particles.

[1] G. Volpe, I. Buttinoni, D. Vogt, H.J. Kümmerer, and C. Bechinger. Microswimmers in patterned environments. Soft Matter, (7):8810{8815, 2011.

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DYNAMICAL SIGNATURE OF CRITICALITY IN COLLOIDAL HARD SPHERE LIKE FLUIDS — Markus Franke and •Hans Joachim Schöpe — Johannes Gutenberg Universität Mainz, Institut für Physik, Staudinger Weg 7, 55099 Mainz, Germany

The particle dynamics of a metastable liquid differs significantly from a liquid in the equilibrium state, giving the possibility to define the freezing point of the system of interest. Dynamic light scattering gives access to the intermediate scattering function (ISF) which measures particle number density fluctuations. Another aspect of the dynamics is the correlation of particle currents dictated by conservation of particle number density, which can be obtained by numerically differentiating the ISF. Recently it was shown that it is possible to define a dynamic freezing criterion in colloidal hard sphere systems by a careful analysis of the space time correlation function of longitudinal particle currents (CCF) [1]. We used highly cross-linked polystyrene (PS) microgel colloids dispersed in a good solvent to obtain a colloidal model system with hard sphere like interaction. We studied the dynamics of the colloidal fluid around the main structure factor peak ($1.7<qR<5$) over a wide concentration range crossing the freezing transition. Like in a PMMA hard sphere system we observe an universal scaling of the CCF for the equilibrium fluid, while deviations from this scaling were found once the suspension is in the metastable state. Furthermore it is observed that the decorrelation of the CCF becomes nonmonotonic at the structure factor peak if the fluid becomes overcritical. [1] W. van Megen, V. A. Martinez, and G. Bryant, PRL 103, 258302 (2009)

CPP 28.11 Wed 18:00 C 130

A Poisson-Boltzmann solution of the two-colloid problem — •Alexander Schlaich, Stefan Kesselheim, Marcello Sega, and Christian Holm — Institut für Computerphysik, Universität Stuttgart, Pfaffenwaldring 27, 70569, Stuttgart, Deutschland

The force acting between colloidal particles in ionic solutions is often modeled in terms of the nonlinear Poisson-Boltzmann equation. A solution can be obtained using standard finite element methods, however usual assumptions, like a constant surface charge density at the particle's surface or a constant surface potential, are not able to reproduce the correct potential if the typical distance becomes small such that the Debye layers overlap.

To determine these boundary conditions, we use an iterative procedure which also accounts for a jump of the dielectric constant at the particles surface. We compare our results to theoretical predictions and the results of coarse-grained molecular dynamics simulations using explicit ions. The efficient parallel implementation, using the Distributed and Unified Numerics Environment DUNE, also allows us to consider the question of pairwise additivity in the Poisson-Boltzmann description.

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Free-standing Fluid Filaments Using Star-shaped and Discotic Liquid Crystal Mesogens — •Tanya Ostapenko, Michael Morys, Alexey Eremin, and Ralf Stannarius — Otto-von-Guericke-Universität, Universitätsplatz 2, 39106 Magdeburg, Germany

Stable free-standing filaments have been formed in several mesophases of bent-core liquid crystals. Such filaments can have slenderness ratios of 1000 or more. In contrast, filaments prepared from columnar liquid crystal phases of disk-shaped molecules have slenderness ratios several orders of magnitude lower, due to the two-dimensional compressibility of the phase. From atomic force microscopy measurements, smectic filaments appear to have a corrugated structure, with composite bundles constructing the filament [1].

Recently, star-shaped oligobenzoates were synthesized [2], which form various liquid crystal columnar mesophases over a large temperature range. To date, there have been no reports on free-standing filaments prepared from such mesophases. Using a similar experimental setup to that described in [1], along with polarizing microscopy, we were able to create meta-stable filaments. We measure optical, mechanical and electrical properties of these unique systems and discuss potential applications.

[1] A. Nemes, et. al. *Phys. Chem. Chem. Phys.* **8**, 469-476 (2005).
[2] M. Lehmann, et. al. *Chem. Eur. J.* **14**, 3562-3576 (2008).

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Small Angle Scattering applied to Phospholipid stabilized

Colloidal Crystals — •Martin Schmiele, Mirijam Zobel, and Tobias Unruh — Lehrstuhl für Kristallographie und Strukturphysik, Staudtstraße 3, D-91058 Erlangen

Many routines do exist to simulate small angle scattering of dispersions of homogeneous nanoparticles, they all rely on the calculation of the particle form factor. However, dispersions of nanocrystals with long crystallographic c-axes may show Bragg peaks in the small angle range. With the existing routines, Bragg reflections can only be taken into account by heuristic models for the peak profiles. In order to compute small angle diffractograms from colloidal dispersions of nanocrystals the X-Ray Powder Pattern Simulation Analysis (XPPSA) has been developed. The XPPSA facilitates the computation of this scattering contribution directly from the crystals geometry. Application-related our group focuses on dispersions of tripalmitin nanocrystals stabilized with phospholipids in an aqueous dispersion medium. They can be considered as a representative model for many similar colloidal dispersions that are currently under discussion as potential drug delivery carrier systems. Revealing the molecular arrangement of the phospholipids at the interface between tripalmitin and the aqueous phase is vitally important to comprehend the stabilization mechanism and to control drug encapsulation. A preliminary study with the aid of the XPPSA utilizing SAXS gave no clear picture for the structure of the stabilizer layer. To remove this ambiguity, SANS experiments at different contrasts for the stabilizer layer were carried out.