CPP 29: Crystallisation, Nucleation and Self assembly

Time: Wednesday 15:00–18:45 Location: C 243

Topical Talk CPP 29.1 Wed 15:00 C 243

Observation of kinks and antikinks in colloidal monolayers driven across ordered surfaces — •Thomas Bohlein[1,2], Jules Mikhael[1], and Clemens Bechinger[1,2] — [1]2. Physikalisches Institut, Universität Stuttgart, Germany — [2]Max-Planck-Institut für Intelligente Systeme, Stuttgart, Germany

Friction between solids is responsible for many phenomena like earthquakes, wear or crack propagation. Unlike macroscopic objects which only touch locally due to their surface roughness, spatially extended contacts form between atomically flat surfaces. They are described by the Frenkel-Kontorova (FK) model which considers a monolayer of interacting particles on a periodic substrate potential. In addition to the well-known stick-slip motion such models also predict the formation of kinks and antikinks which largely reduce the friction between the monolayer and the substrate. Here, we report the direct observation of kinks and antikinks in a two-dimensional colloidal crystal which is driven across different types of ordered substrates. We show that the frictional properties only depend on the number and density of such excitations which propagate through the monolayer along the direction of the applied force. In addition, we also observe kinks on quasicrystalline surfaces which demonstrates that they are not limited to periodic substrates but occur under more general conditions.

Topical Talk CPP 29.2 Wed 15:30 C 243

2D and 3D assembly of polymer-coated gold nanoparticles — •Matthias Karg — Department of Chemistry, University of Bayreuth, Bayreuth, Germany

The assembly of metal nanoparticles into superstructures with mm or even cm dimensions is a challenging scientific task.

We coated gold nanoparticles with cross-linked polymer shells resulting in core-shell particles with well-defined structures[1]. The polymer shells are composed of poly-N-isopropylacrylamide (PNIPAM), which is a thermoresponsive material. Due to these shells, the effective particle volume of the nanoparticles is increased significantly. This allows reaching high volume fractions with comparably low particle numbers.

Crystallization was observed over a broad range of particle concentrations at room temperature[2]. Upon an increase in temperature, the PNIPAM shells shrink and the overall particle volume fraction decreases. This causes melting of the crystals in a certain concentration range. Upon cooling, crystallization occurs again, once a critical volume fraction is reached. These melting/recrystallization processes were observed to occur with very high reproducibility as will be demonstrated in this contribution. This unique behaviour is interesting for applications in sensing and optics since it presents a new pathway towards the controlled preparation of large-scale 'nanocrystal-doped' photonic crystals.

[1] M. Karg, S. Jaber, T. Hellweg, P. Mulvaney, Langmuir 2011, 27, 820 [2] M. Karg, T. Hellweg, P. Mulvaney, Adv. Funct. Mater. DOI: 10.1002/adfm.201101115

CPP 29.3 Wed 16:00 C 243

Lattice orientation, defects, and optical diffraction of opal-type photonic crystals — •Mulda Muldarisnur, Parvin Sharifi, and Frank Marlow — Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany

A systematic investigation on SEM images reveals that the capillary deposition method (CDM) [1] results in opal films with specific orientations which are interesting photonic crystals [2]. The orientation of the (111) fcc plane parallel to substrate is typical for many opals. However, opal orientation in respect to the growth direction is specific for a certain class of growth methods and indicates a decisive influence of the suspension flow during opal formation. The nearly perfect surface and the oriented lattice allows the existence of two crystal parts (intergrowths) having a certain misfit. The lattice misfit induces disordered boundaries and defects. We found that scattering by these and other defects can be described using Mie-like scattering. Recent angle-resolved transmission measurements and microscopic observations support the existence of two fcc domains in CDM-made opals. We observe well-resolved high-order diffraction peaks indicating opals with high quality. We can very well describe the rich features in the angle-resolved spectra by using the kinematical diffraction theory. Furthermore, intensity variation with angle can be described by using a simplified dynamical diffraction theory.

References: [1] H.-L. Li, W. Dong, H.J. Bongard, F. Marlow, J. Phys. Chem. B 109, 9939 (2005). [2] M. Muldarisnur and F. Marlow, J. Phys. Chem. C 115, 414 (2011).

CPP 29.4 Wed 16:15 C 243

Simulations of colliodial rods on a 2D quasicrystalline substrate — •Philipp Kählitz and Holger Stark — Institut für theoretische Physik, TU Berlin

Quasicrystals are structures with long-range positional and orientational order. However, they cannot be periodic since they possess rotational symmetries such as 5- or 10-fold axis that are forbidden for conventional crystals. These structures lead to new and unique features of matter. Therefore, a lot of effort has recently been initiated to grow atomic quasicrystals on quasicrystalline surfaces. To mimic this situation, 2D light-interference patterns have been used tostudy the phase behavior of micron-sized colloidal particles in a 2D quasicrystalline potential and new ordered phases have been identified [1,2]. This talk discusses how colloidal rods order in a quasicrystalline decagonal substrate potential. We use Monte-Carlo simulations tostudy the phase behavior of hard spherocylinders and identify, in particular, a novel decagonal phase made by clusters of aligned rods at high densities. In the low density case the behavior of the rods is similar to the previously studied hard needles [3]. We map out phase diagrams as a function of strength of the surface potential and the particle density for different rod lengths and diameters.

[1] Mikhael et al., Nature (London) 454, 501 (2008)
[2] M. Schmiedeberg and H. Stark, PRL 101, 218302 (2008)
[3] P. Kählitz and H. Stark, submitted.

CPP 29.5 Wed 16:30 C 243

Homogeneous and flat wall heterogeneous nucleation in colloids with various interaction — Andreas Engelbrecht, Markus Franke, Achim Lederer, Sara Iacopini, Richard Beyer Beyer, and •Hans Joachim Schöpe — Johannes Gutenberg-Universität Mainz, Institut für Physik, Staudinger Weg 7, 55099 Mainz, Deutschland

Understanding crystal nucleation and growth is of great interest in condensed matter physics and material science. Especially at low metastabilities crystal nucleation is dominated by heterogeneous nucleation on container walls or impurities and the competition between wall and bulk crystallization determines the microstructure of the polycrstal. Notwithstanding its relevance heterogeneous nucleation is not well understood. One promising approach to the problem is offered by the study of colloidal suspensions. In colloids the particle interactions can be experimentally adjusted to include short (hard spheres, HS) and long ranged (charged spheres, CS) repulsions as well as attractions originated by entropic forces (attractive spheres, AS). We studied the kinetics of homogeneous and wall induced heterogeneous nucleation in different colloidal model systems with various interaction (CS, HS, AS) as function of super saturation. Using light scattering as well as microscopy techniques a comprehensive analysis of the crystallization process was obtained. We can show that the competition of wall and bulk crystallization is altered significantly with the nature of the particle interaction.

15 min break

CPP 29.6 Wed 17:00 C 243

Self-assembly of amphiphilic Janus particles — •Gerald Rosenthal and Sabine H. L. Klapp — TU Berlin, Institut für Theoretische Physik, Hardenbergstr. 36 , D-10623 BERLIN, Germany

We apply molecular dynamics simulations (MDS) to investigate the structure formation of amphiphilic Janus particles in the volume phase. The Janus particles are modeled as (soft) spheres composed of a hydrophilic and hydrophobic part. Their orientation is described as a vector representing an internal degree of freedom. This model was first proposed by Somoza et al. [1]. In our study we focus on pair correlation functions, cluster characterisation and mean square displacement. We find clusters of various sizes depending on density and temperature. The cluster size distribution shows a narrower peak for higher densities at clusters of size 13, in these icosahedra particles are aligned in closed packing and therefore the number of bondings is maximised. For lower densities a variety of smaller clusters coexists. Further we calculated the aggregation temperature as function of density. In addition to this unconfined system we will compare our newest MDS results in confined geometry with our former classical density functional theory study [2], where we focused on the surface-induced ordering phenomena of such Janus particles.

[1] A. M. Somoza, E. Chacón, L. Mederos and P. Tarazona, J. Phys.: Condens. Matter **7**, 5753 (1995)
[2] G. Rosenthal and S. H. L. Klapp, JCP, **134**, 154707 (2011)

CPP 29.7 Wed 17:15 C 243

Disentanglement during the crystallization of polymers — •Chuanfu Luo and Jens-Uwe Sommer — Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, 01069 Dresden

Long linear polymers are highly entangled in melts while they are folded and packed in crystals. Thus polymer crystallization can lead to some degree of disentanglement of the resulting semi-crystalline material. However this disentanglement process is very difficult to observe in experiments. By using molecular dynamics (MD) simulations combined with primitive path analysis (PPA)[1], we can directly reveal the structural changes of polymer chains as well as the changes of entanglement during the crystallization. The PPA can give the approximated entanglement length from the topology of an instantaneous conformation without running a long-time rheology simulation. By using PPA we analyzed the simulation results of slowly continuous cooling, annealing and self-seeding processes[2]. We show that polymers disentangle during crystallization and continue to disentangle during annealing. The changes of approximated entanglement density at different regions (crystallized Vs. melt) will also be discussed.

[1] R. Everaers et al., Science 303, 823 (2004)
[2] C.-F. Luo and J.-U. Sommer, Macromolecules 44, 1523 (2011)

CPP 29.8 Wed 17:30 C 243

Influence of electric fields on the self assembly of block copolymers in confined geometries. — •Ulrich Welling[1], Hagai Shalev[2], Yoav Tsori[2], and Marcus Müller[1] — [1]Institut für theoretische Physik, Friedrich-Hund-Platz 1, 37077 Göttingen — [2]Department of Chemical Engineering, Ben Gurion University of the Negev, Beer-Sheva, 84105, Israel

Strategies for controlling the orientation and limiting the defect density in self-assembled structures of copolymers have attracted abiding interest. Using Single-Chain-in-Mean-Field Monte-Carlo simulations and Ginzburg-Landau free-energy computations we study the influence of homogeneous and inhomogeneous electric fields on the self-assembled morphologies of symmetric, lamella-forming copolymer. We present results on the influence of an electric field on the ordering kinetics. We study the interplay between an electric field and a patterned substrate in a thin-film geometry and the relative stability of lamellar phases with different orientations that can form in a cylindric capacitor.

CPP 29.9 Wed 17:45 C 243

microphase behavior and structure of P3HT-b-PPerAcr donor-acceptor block copolymers — Gaurav Gupta[1], Peter Kohn[1], Thomas Thurn Albrecht[1], Michael Sommer[2], Ruth Lohwasser[2], and •Mukundan Thelekkat[2] — [1]Experimental Polymer Phsik, Martin Luther University Halle — [2]Applied Functional Polymers, Macromolecular Chemistry I, University of Bayreuth

Combination of electron and hole conducting organic materials for photovoltaic devices has been an area of extensive research. Short lifetime of the photo generated excitons resulting in diffusion lengths of the order of 10 nm sets a morphological requirement of having nano scale domains. The property of block copolymers to microphase separate into well defined periodic nano structures can be an ideal solution to this morphological requirement as well as for the simultaneous conduction for the dissociated charge carriers. Here we present the structural characterization of a donor *acceptor block copolymer based on side chain poly(perylene-acrylate) as electron conductor and P3HT as hole conductor. Based on scattering measurements we find a molecular weight dependence on the mechanism of microphase separation. While the lower molecular weight polymer showed a transition from a disordered melt at high temperatures to a nanostructured morphology, induced by the crystallization of individual blocks, the higher molecular weight polymer exhibited a microphase separated morphology. The latter remained intact even at low temperatures when crystallization in the individual blocks occurs.

CPP 29.10 Wed 18:00 C 243

Morphological changes during annealing of polyethylene nanocrystals — •Nandita Basu[1], Anna Osichow[2], Stefan Mecking[2], and Günter Reiter[1] — [1]Physikalisches Institut, Albert-Ludwigs Universität Freiburg, Freiburg, Germany — [2]Fachbereich Chemie, Universität Konstanz, Konstanz, Germany

Polymer crystals are metastable and exhibit morphological changes when being annealed. To observe morphological changes on molecular scales we started from small nanometer-sized crystals of highly folded long-chain polymers. Micron-sized stripes consisting of monolayers or stacks of several layers of flat-on oriented polyethylene nanocrystals were generated via evaporative dewetting from an aqueous dispersion. We followed the morphological changes in time and at progressively higher annealing temperatures by determining the topography and viscoelastic properties of such assemblies of nanocrystals using AFM. Due to smallness and high surface-to volume ratio of the nanocrystals, already at 75 °C, i.e. about 60 degrees below the nominal melting point, the lateral size of the crystal coarsened. Intriguingly, this occurred without a noticeable reduction in the number of folds per polymer chain. Starting at around 110 °C, chain folds were progressively removed leading to crystal thickening. At higher temperatures, but still below the melting point, prolonged annealing allowed for surface diffusion of molten polymers on the initially bare substrate which led to the disappearance of crystals. We compared these results to the behavior of the same nanocrystals annealed in an aqueous dispersion and to bulk samples.

CPP 29.11 Wed 18:15 C 243

Two-step nucleation in protein crystallization — •Fajun Zhang[1], Andrea Sauter[1], Marcell Wolf[1], Felix Roosen-Runge[1], Baohu Wu[1], Michael Sztucki[2], Roland Roth[3], Maximilian W.A. Skoda[4], Robert M.J. Jacobs[5], and Frank Schreiber[1] — [1]Institut für Angewandte Physik, Universität Tübingen — [2]ESRF, France — [3]Universität Erlangen-Nürnberg — [4]ISIS, RAL, UK — [5]CRL, University of Oxford, UK

The attractive forces between proteins in solution are often short-ranged when compared to the size of protein, which can lead to a metastable liquid-liquid phase separation (LLPS) before crystallization. Under these conditions, the order parameters (density and structure) during protein crystal growth can be separately developed leading to a so-called 'two-step' nucleation mechanism. Here we present the results of protein crystallization in solution in the presence of multivalent counterions. It has been shown that negatively charged globular proteins undergo a reentrant condensation phase behavior [1], i.e. a phase-separated regime occurs in between two critical salt concentrations, $c^* < c^{**}$, resulting in a metastable LLPS region. Crystallization near the phase boundaries follows different mechanisms. Close to c^*, crystal growth follows the classical nucleation and growth mechanism; close to c^{**}, crystallization follows the two-step mechanism [2]. SAXS measurements demonstrate that protein clusters act as precursors for both the dense liquid phase and nucleation with a reduced energy barrier. [1] F. Zhang, et al., PRL 2008, 101, 148101; Proteins, 2010, 78, 3450. [2] F. Zhang, et al., J. Appl. Cryst. 2011, 44, 755.

CPP 29.12 Wed 18:30 C 243

Kinetics of vesicle formation: A SAXS-stopped-flow study — •Katharina Bressel[1], Michael Muthig[1], Jeremie Gummel[2], Theyencheri Narayanan[2], and Michael Gradzielski[1] — [1]Stranski-Laboratorium, Institut für Chemie, TU Berlin, Germany — [2]European Synchrotron Radiation Facility (ESRF), France

Vesicle formation processes often pass through an intermediate state of disc-like micelles that grow to a maximum size and than close to form vesicles. The driving force for the disc growth is controlled by the line tension of the disc-rim. The balance between the line tension of the discs and the bending elasticity of the vesicle bilayers determines the size and polydispersity of the initially formed vesicles.

In our study we modified the previously studied TDMAO (tetradecyldimethylamine oxide)/LiPFOS (lithium perfluorooctylsulfonate) system by addition of amphiphilic copolymers. The hydrophobic part of these copolymers is incorporated into the surfactant bilayers and is assumed to accumulate in the disc-rim and therefore lower the line tension. That leads to an increase in the maximum size of the disc-like micelles and to a slower vesicle formation. By means of the stopped-flow technique with SAXS detection we studied in situ the kinetics of the vesicle formation process. This rapid-mixing technique allows the observation of kinetic processes in the ms time range and gives excess to detailed structural information about size, shape, and polydispersity of the aggregates. We compared the analysis of these measurements to a coagulation simulation. This simulation is based on a disc growth process that follows a Smoluchowski mechanism.