

DY 13: Crystallization, Nucleation and Self Assembly II (joint session CPP/ DY)

Time: Monday 15:45–18:30

Location: PC 203

DY 13.1 Mon 15:45 PC 203

Estimation of crystal nucleation barriers from Monte Carlo simulations — ●ANTONIA STATT^{1,2}, PETER VIRNAU², and KURT BINDER² — 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 V with particle number N at a density exceeding the onset density of freezing may exhibit phase coexistence between a crystalline nucleus and surrounding fluid. Using a 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. There is neither a need to precisely locate the interface nor to compute the (anisotropic) interfacial tension [1]. As a test case, a soft version of the Asakura-Oosawa model [2] for colloid polymer-mixtures is treated. While our analysis is appropriate for crystal nuclei of arbitrary shape, we find the nucleation barrier to be compatible with a spherical shape, and consistent with classical nucleation theory.

[1] A. Statt, P. Virnau and K. Binder, PRL 2014 (in press)

[2] M. Dijkstra, R. van Roij and R. Evans, Phys. Rev. E 59, 5744-5771, 1999

DY 13.2 Mon 16:00 PC 203

Nano-Dewetting in Colloidal Crystal Drying — ●MULDA MULDARISNUR and FRANK MARLOW — MPI für Kohlenforschung, 45470 Mülheim an der Ruhr, Germany

The drying of colloidal crystals is connected with a continuous shrinkage process [1]. However, several minutes after starting the drying, the system seems to take a breath before it shrinks monotonously until its final state after about one day. This short period we call "v"-event because of the shape of the curve characterizing the lattice constant: a decrease followed by a counter-intuitive increase which ends after one hour. This event is found in time-dependent optical spectra. It is assigned to the start of a nano-dewetting process occurring at the colloidal particles.

[1] M. Muldarisnur and F. Marlow, Observation of Nano-Dewetting in Colloidal Crystal Drying, Angew. Chem. Int. Ed. 2014, 53 (33), pages 8761-8764

DY 13.3 Mon 16:15 PC 203

Solidification fronts in supercooled liquids: how rapid fronts can lead to disordered glassy solids — ●ANDREW ARCHER¹, MORGAN WALTERS¹, UWE THIELE², and EDGAR KNOBLOCH³ — ¹Department of Mathematical Sciences, Loughborough University, Loughborough, LE11 3TU, UK — ²Westfälische Wilhelms-Universität Münster, Institut für Theoretische Physik, Wilhelm-Klemm-Str. 9, 48149 Münster, Deutschland — ³Department of Physics, University of California at Berkeley, Berkeley, CA 94720, USA

We determine the speed of a crystallization/solidification front as it advances into the uniform liquid phase after it has been quenched into the crystalline region of the phase diagram, for systems of soft particles. We calculate the front speed by assuming the system can be treated using dynamical density functional theory (DDFT). There are two mechanisms by which the front can advance, depending on whether the liquid state is linearly stable or not. When linearly unstable, the front speed can be calculated by applying a marginal stability criterion. As the solidification front advances, the density profile behind the advancing front develops density modulations, whose wavelength λ is a dynamically chosen quantity. For shallow quenches, λ is close to that of the crystalline phase and so well-ordered crystalline states are formed. However, when the system is deeply quenched, λ can be quite different from that of the crystal, so the solidification front naturally generates disorder in the system. Significant rearrangement and aging must subsequently occur for the system to form the regular well-ordered crystal that corresponds to the free energy minimum.

Invited Talk

DY 13.4 Mon 16:30 PC 203

Spontaneous symmetry breaking in 2D: Kibble-Zurek mechanism in colloidal monolayers at finite cooling rates — SVEN DEUTSCHLÄNDER, GEORG MARET, and ●PETER KEIM — Universität Konstanz

The Kibble-Zurek mechanism describes the evolution of defects and domains when a system is forced through a phase transition with spontaneously broken symmetry. It describes Higgs field in the early universe shortly after the Big Bang or condensed matter systems like quenched quantum fluids. For a system with second order phase transition, the domain structure naturally arises when it is cooled at a finite rate. Since diverging correlation length are accompanied with critical slowing down, the system has to fall out of equilibrium for any non-zero rate; At this so called fall out time the correlation length is frozen out before the transition can take place globally. Within this picture, we investigate the non-equilibrium dynamics in a soft-matter analogue, a two-dimensional ensemble of colloidal particles which in equilibrium obeys the Kosterlitz-Thouless-Halperin-Nelson-Young melting scenario with continuous phase transitions. The ensemble is exposed to finite cooling rates of the pair-interaction parameter (being an inverse system temperature) at very different rates from deep in the isotropic fluid into the polycrystalline phase. We analyse defect configurations as well as the evolution of orientationally ordered domains quantitatively via video microscopy and show that their frozen-out length scale follows an algebraic decay as function of the quench rate as predicted by the Kibble-Zurek mechanism.

15 min. break.

DY 13.5 Mon 17:15 PC 203

Molecular Dynamics Study of Colloidal Quasicrystals — ●HEIKO G. SCHOBERTH, HEIKE EMMERICH, and THOMAS GRUHN — Lehrstuhl für Material- und Prozesssimulation, Universität Bayreuth, D-95440 Bayreuth

Quasicrystals are of continuous interest due to their fascinating fundamental properties and their potential applications like advanced photonic materials. In the last years colloidal quasicrystals have been found in solutions with spherical polymer core-shell micelles [1]. Fundamental aspects have been investigated in theoretical studies in which the core-shell micelles are represented with a step-potential, in which the core-core interaction is modeled by infinite repulsion while the shell-shell interaction is modeled by a plateau at constant height ϵ and width λ [2]. The real interaction of the micelles is a continuous function which is more smeared out at the core and shell boundaries. Therefore, we perform coarse-grained molecular dynamics simulations to investigate the influence of the potential shape on the self-assembling structure. Varying the parameters we study systematically the phase diagram finding domains with 6-,10-,12-,24-fold symmetries. With increasing smoothness of the potential the phase diagram changes qualitatively and the geometry of the phase boundaries gets more regular.

[1] Fischer S. et al., PNAS, 108, 1810-1814 (2011)

[2] Dotera T. et al., Nature, 506, 208-2011 (2014)

DY 13.6 Mon 17:30 PC 203

Real-time study of multi-step nucleation in protein crystallization — ●ANDREA SAUTER¹, FELIX ROOSEN-RUNGE², FAJUN ZHANG¹, GUDRUN LOTZE³, ROBERT M. J. JACOBS⁴, and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen — ²Institut Laue-Langevin, Grenoble, France — ³European Synchrotron Radiation Facility, Grenoble, France — ⁴Department of Chemistry, University of Oxford, UK

We present a real-time study of protein crystallization of bovine β -lactoglobulin in the presence of the divalent salt CdCl_2 using SAXS and optical microscopy. Monitoring the crystallization kinetics, we demonstrate a multi-step crystallization mechanism particularly focusing on the role of the metastable intermediate phase (MIP). In the first step, an intermediate phase is formed, followed by the nucleation of crystals within the intermediate phase. In the next step, this intermediate phase is consumed by nucleation and slow growth and the crystals are exposed to the dilute phase. At this stage, the number of crystals stays nearly constant, whereas the crystals grow rapidly due to access to the free protein molecules in the dilute phase. The results suggest that increasing the salt concentration near the transition zone *pseudo-c*** reduces the energy barrier for both the MIP and crystal nucleation. The observed kinetics can be well described using a rate-equation model based on a clear physical multi-step picture. This real-time study not only provides direct evidence for a multi-step

process for protein crystallization, but also elucidates the role and the structural signature of the MIP in the non-classical process of protein crystallization.

DY 13.7 Mon 17:45 PC 203

All-atom MD simulation of fullerene dyads in water: Exploring hydrophobic hydration — ●OLGA GUSKOVA¹, SRINIVASA RAO VARANASI^{1,2}, and JENS-UWE SOMMER^{1,3} — ¹Leibniz-Institut für Polymerforschung Dresden e. V., Theorie der Polymere, Hohe Str. 6, 01069 Dresden, Deutschland — ²University of Queensland, School of Chemical Engineering, St Lucia QLD 4072, Australia — ³Technische Universität Dresden, Institut für Theoretische Physik, Zellescher Weg 17, 01069 Dresden, Deutschland

The nanometer-sized C60 fullerene, being a boundary case between small and large hydrophobes, represents an interesting object for the investigation of hydrophobic hydration. Extensive MD simulations are performed to study the solvation of pristine fullerene and fullerene dyads as well as their self-assembly in water [1]. The solute-solvent interactions, which reflect in the structure of solvation shells, translational and orientational dynamics of water molecules near the hydrophobic C60 cage and hydrophilic side chain, the H-bond networks and their defects, as dangling -OH bonds, are described. The agglomeration behavior of fullerenes is evaluated by determining sizes of the clusters, solvent accessible surface areas, and shape parameters. [1] O. Guskova, S.R. Varanasi, and J.-U. Sommer, *J. Chem. Phys.* 141 (14), 144303 (2014).

DY 13.8 Mon 18:00 PC 203

Phase field simulations of particle capture during directional solidification of photovoltaic silicon — HEIKE EMMERICH¹, ●HENNING HÖRSTERMANN¹, JULIA KUNDIN¹, JOCHEN FRIEDRICH², MARAL AZIZI², CHRISTIAN REIMANN², ARNE CRÖLL³, THOMAS JAUSS³, and TINA SORGENFREI³ — ¹University Bayreuth, Chair of Material and Process Simulations, Bayreuth, Germany — ²Fraunhofer IISB, Erlangen, Germany — ³University Freiburg, Institute for Geosciences, Freiburg, Germany

We study the interaction between the solidification front and SiC particles present in the melt during the growth process of silicon for solar cells. Particles of a given size are pushed in front of the interface for growth velocities below a critical value and are incorporated into

the crystal for growth velocities above this value. The existing theoretical models for particle capture find a relationship between critical particle size and critical growth velocity by assuming an equilibrium between a combination of gravity, drag, lift and other forces acting on the particle in the vicinity of the interface. For silicon these models predict significantly higher critical particle sizes than observed in experiments. We use a phase field model to test if these deviations can be explained by deviations from the spherical particle shape usually assumed in the theoretical models or effects like the deformation of the interface caused by the presence of the particle. In addition to testing and adapting existing theories, we narrow down the possible underlying mechanisms by identifying relevant length scales and other properties that are required to explain the experimental results.

DY 13.9 Mon 18:15 PC 203

Crystallization kinetics in printed active layers for organic solar cells — ●STEPHAN PRÖLLER¹, FENG LIU², CHENHUI ZHU³, PETER MÜLLER-BUSCHBAUM⁴, THOMAS P. RUSSELL², ALEXANDER HEXEMER³, and EVA M. HERZIG¹ — ¹Technische Universität München, Munich School of Engineering, 85748 Garching, Germany — ²University of Massachusetts Amherst, Department of Polymer Science and Engineering, MA 01003 Amherst, Massachusetts, USA — ³Lawrence Berkeley National Laboratory, Advanced Light Source, CA 94720 Berkeley, California, USA — ⁴Technische Universität München, LS Funktionelle Materialien, 85748 Garching, Germany

Organic solar cells are a promising alternative to silicon based inorganic ones. Among other advantages like high absorption, a key advantage is the processability out of solution. This allows for printing of large area photovoltaic devices at low costs at low energy input. The morphology and crystalline properties of the active layer is of utmost importance for the functionality like exciton separation or charge carrier transport and thus for the performance of the produced devices. So far, not much is known on the crystallization kinetics of printed organic photoactive layers. Using an industrial slot-die printing process we studied the morphology evolution of a photoactive blend by in-situ X-ray scattering methods. With these experiments we are able to picture the process of crystallization of the polymer blend. We identified different stages during crystallization and propose a model for the crystal growth. This understanding is important to gain control over the morphology development of the system to improve organic solar cell performance.