

CPP 9: Crystallization, Nucleation and Self Assembly II

Time: Monday 15:00–18:00

Location: ZEU 260

Invited Talk

CPP 9.1 Mon 15:00 ZEU 260

Self-assembly of soft colloids into meso-, para-, and quasicrystals — ●STEPHAN FOERSTER¹, ALEXANDER EXNER¹, SABINE ROSENFELDT¹, PETER LINDNER², and JAN PERLICH³ — ¹Physikalische Chemie I, Universität Bayreuth, Germany — ²Institut Laue Langevin (ILL), Grenoble, France — ³HASYLAB/DESY, Hamburg, Germany

Soft colloids interact via soft potentials and often are internally structured. At high volume fractions this leads to the formation of mesocrystals, paracrystals and quasicrystals. [1,2] We show how multi-body interactions, multiple length scales and defects decisively control self-assembly at high volume fractions. Neutron- and synchrotron X-ray diffraction are used to reveal the formation of these structures in-situ.

References: [1] S. Fischer, A. Exner, K. Zielske, J. Perlich, S. Deloudi, W. Steurer, P. Lindner, S. Förster, Colloidal quasicrystals with 12-fold and 18-fold diffraction symmetry, Proc. Natl. Acad. Sci. 108 (2011) 1810. [2] A. Exner, S. Rosenfeldt, S. Fischer, P. Lindner, S. Förster, Defect accommodation in nanostructured soft crystals, Nanoscale 2013, in press

CPP 9.2 Mon 15:30 ZEU 260

The Flexible Rare Event Sampling Harness System (FRESHS) — KAI KRATZER¹, JOSHUA BERRYMAN², AARON TAUDT¹, JOHANNES ZEMAN¹, and ●AXEL ARNOLD¹ — ¹Institut für Computerphysik, Universität Stuttgart, Germany — ²Theory of Soft Condensed Matter, University of Luxembourg, Luxembourg

Nucleation is a rare event that is computationally expensive to study in brute force computer simulations. Special sampling techniques can reduce this effort. We present the Flexible Rare Event Sampling Harness System (FRESHS), an open source software framework (<http://www.freshs.org>) that provides Forward Flux Sampling (FFS) and Stochastic Process Rare Event Sampling (S-PRES), which are two such methods well suited to study nucleation events.

Several features of FRESHS make its application particularly easy. FFS or S-PRES only require an order parameter that describes the progress of the rare event and allows to split the transition into milestones or interfaces. Our FFS implementation features automatic interface placement, which ensures optimal flux through all interfaces without the need of expert knowledge. ‘Ghost’ runs overcome the computational bottleneck of waiting for the last trial simulation when advancing to the next interface. FRESHS can steer popular Molecular Dynamics codes such as GROMACS, LAMMPS or ESPResSo, and other software can be attached through a simple plugin system. Our framework allows for checkpointing and flexible analysis already during runtime, and is suitable for single workstations up to large compute clusters.

CPP 9.3 Mon 15:45 ZEU 260

Modelling the structure of tubular J-aggregates using MD-simulations and MD-based calculations of exciton spectra — ●JÖRG MEGOW¹, STEFAN KIRSTEIN¹, MERLE RÖHR², MARCEL SCHMIDT AM BUSCH³, ROLAND MITRIĆ², THOMAS RENGER³, JÜRGEN P. RABE¹, and VOLKHARD MAY¹ — ¹Humboldt-Universität zu Berlin, Deutschland — ²Julius-Maximilians-Universität, Würzburg, Deutschland — ³Johannes Kepler Universität, Linz, Österreich

Tubular J-aggregates composed of amphiphilic cyanine dyes have been studied in [1,2]. Two different approaches were used to build a molecular model of the structure: First, a theoretical model based on absorption spectra and on orientations of transition dipoles was translated into real arrangements of molecules [1]. Second, molecules were packed to reproduce best a structure model based on high resolution cryo-TEM [2]. For the first time now, molecular dynamics (MD) simulations of the aggregates in solution together with MD-based calculations of optical spectra are utilized to study the structure of the system. MD simulations of both structure models show that the model of [1] is unstable, while the model that is consistent with [2] is stable during MD simulation. Based on the simulations, Frenkel exciton spectra for both structure models have been computed. It will be shown that a detailed calculation of the energy transfer coupling, including screening effects, allows for a reasonably good description of the absorption spectrum also for the second structure model.

[1] D. Eisele, et al., Nature Chemistry 4, 655-662 (2012)

[2] H. v. Berlepsch et al., Chem. Phys. 285, 27-34 (2011)

CPP 9.4 Mon 16:00 ZEU 260

Relaxation of the complex heat capacity of eicosane in the metastable rotator phase. — ●CARLO DI GIAMBATTISTA, JÖRG BALLER, and ROLAND SANCTUARY — Laboratory for the Physics of Advanced Materials, University of Luxembourg

Some normal alkanes show stable and/or meta-stable polymorphisms. Understanding the process behind the formation of these structures for n-alkanes ($n \geq 20$) could yield a better understanding of the crystallization of polymers [1]. Upon cooling from the melt eicosane ($C_{20}H_{42}$) exhibits a transition to a metastable orthorhombic phase (rotator I) [2]. Upon further cooling there is a second transition to a stable triclinic structure. In this work, we investigate the metastable phase with Temperature Modulate Differential Calorimetry (TMDSC). We use stochastic temperature perturbations (TOPEM[®]-Mettler Toledo). This allows us to get a frequency dependant complex heat capacity $c_p^*(\omega)$. In the metastable rotator phase the heat capacity of eicosane becomes time dependant. In the frequency domain its complex heat capacity can be described by a temperature dependant Debye relaxator. There are two distinct temperature regions, one in which the relaxation time diverges on approaching the melting temperature and another region with an almost constant relaxation time at lower temperatures.

[1] Ungar, G. and N. Masic (1985). J. Phys. Chem. 89(6): 1036-1042. [2] Sirota, E. B., H. E. King, et al. (1993). J. of Chem. Phys. 98(7): 5809-5824.

CPP 9.5 Mon 16:15 ZEU 260

Crystallization of Charged Macromolecules using FRESHS — ●KAI KRATZER and AXEL ARNOLD — Institute for Computational Physics, University of Stuttgart, Allmandring 3, 70569 Stuttgart, DE

The investigation of nucleation, e.g. the onset of crystal growth, of proteins or colloids is demanding both in experiments and computer simulations because nucleation is a rare event. Such an event will simply not happen in the limited system sizes that can be observed experimentally or in brute force computer simulations, in particular close to the coexistence line where the energy barrier is high. However, in computer simulations this can be overcome by special simulation techniques such as Forward Flux Sampling (FFS).

Combining our parallel molecular dynamics code ESPResSo and our FFS framework FRESHS, the Flexible Rare Event Sampling Harness System, we performed computer simulations of the fluid-solid nucleation close to the coexistence line of Yukawa particles, a simple model for charged colloids. We observe a two stage nucleation process with a metastable structure forming first for a broad range of parameters and we compare to the expectations of the Classical Nucleation Theory.

15 min break

CPP 9.6 Mon 16:45 ZEU 260

Stability of crystal nuclei in poly(ϵ -caprolactone), studied by fast scanning calorimetry — ●EVGENY ZHURAVLEV, ANDREAS WURM, JÜRN SCHMELZER, and CHRISTOPH SCHICK — Universität Rostock, Institut für Physik, Rostock, Germany

Thermal stability of crystal nuclei was tested in poly(ϵ -caprolactone) at increasing temperatures. The DFSC allows controlled fast heating and cooling of the sample and determination of its heat capacity at scanning rates up to 100,000 K/s. The possibility to change the temperature so rapidly that there is no time for significant recrystallization of the crystals (or nuclei), allows successive isothermal studies of melting, reorganization and recrystallization. Comparison of isothermal crystallization with and without pretreatment at lower temperatures can be realized. The key question we are trying to answer is up to what temperature the various structures can influence on a successive crystallization after disordering. The structures range from configurations having practically unmeasurable latent heats of disordering (melting) to being clearly-recognizable, ordered species with rather sharp disordering endotherms in the temperature range from the glass transition to equilibrium melting for increasingly perfect and larger crystals. Preliminary experiments show, that the PCL nuclei, formed at 210 K (homogeneous nucleation) significantly speeds up crystallization at 250 K, but do not exist anymore at 300 K ($T_m = 343$ K).

CPP 9.7 Mon 17:00 ZEU 260

In-situ crystal thickening in semi-crystalline diblock copolymer under soft confinement — ●ROBERT SCHULZE¹, STEFAN HÖLZER², and KLAUS JANDT¹ — ¹Otto Schott Institute of Materials Research, Friedrich Schiller University Jena, Löbdergraben 32, 07743 Jena, Germany — ²Laboratory of Organic Chemistry and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstraße 10, 07743 Jena, Germany

Crystal thickening of soft-confined semi-crystalline diblock copolymers requires a rearrangement of the microdomain structure.

In the current study the crystal thickening and microdomain rearrangement of a polybutadiene-block-poly(ethylene oxide) was investigated in-situ in the bulk and on the surface of thin films by X-ray scattering and in-situ atomic force microscopy, respectively.

Initially, crystallized bulk and thin film samples were annealed at selected temperatures determined by differential scanning calorimetry. In the bulk we found a sigmoidal increase of the lamellar long period during annealing. On the thin film surface we observed that the formation of thicker lamellae results from a complex interaction between the melting of some crystalline microdomains and the thickening of the adjacent ones. Further we discovered the growth of crystalline double lamellae that consisted of non-interdigitated extended chains.

The mechanism of crystal thickening can be used to fabricate tunable nanopatterns of amphiphilic semi-crystalline diblock copolymers which are interesting e.g., in the photonics or the biomedical field.

CPP 9.8 Mon 17:15 ZEU 260

Pattern Formation in Polymer Single Crystals — HUI ZHANG¹, BIN ZHANG¹, MAXIMILIAN VIELHAUER², ROLF MÜLHAUPT^{2,3}, MORITZ BAIER⁴, STEFAN MECKING⁴, and ●GÜNTER REITER^{1,3} — ¹Institute of Physics, University of Freiburg, 79104 Freiburg, Germany — ²Institut für Makromolekulare Chemie, University of Freiburg, 79104 Freiburg, Germany — ³Freiburger Materialforschungszentrum, University of Freiburg, 79104 Freiburg, Germany — ⁴Department of Chemistry, University of Konstanz, 78464 Konstanz, Germany

Polymer crystals typically grow at conditions far from thermodynamic equilibrium, resulting in chain-folded lamellar crystals. Even in single crystals, characterized by dendritic or faceted structures with a well-defined envelope reflecting the underlying crystal unit cell, polymers are folded and thus in a meta-stable state. Systematic investigations on such crystals led to a general concept of a nucleation of secondary lamellar crystals induced by an insertion mechanism on the amorphous fold surfaces. These secondary lamellar crystals are in registry with the underlying single crystal. The dependence of the number density of secondary lamellae on the width of the side branches of the underlying crystal suggests that nucleation was controlled by the morphology of the underlying crystal which, in turn, could be tuned by crystallization temperature and film thickness. Moreover, annealing such meta-stable single crystals allowed to unveil the initial morphological framework of

a dendritic single crystal, i.e. the initial stages of growth.

CPP 9.9 Mon 17:30 ZEU 260

Tailoring diblock copolymer surface nanostructures by crystal thickening — ●ROBERT SCHULZE, MATTHIAS ARRAS, and KLAUS JANDT — Otto Schott Institute of Materials Research (OSIM), Friedrich Schiller University Jena, Löbdergraben 32, 07743 Jena, Germany

One approach to control the thickness of crystalline lamellae in the bulk is the self-nucleation experiment. But crystal thickening might be useful to tailor surface nanostructures of semi-crystalline copolymer thin films.

In this present study of a polybutadiene-block-poly(ethylene oxide), we correlate within two self-nucleation experiments, i.e., in the bulk and thin film, the calorimetric bulk properties to the resulting thin film surface nanostructures which enables the prediction of the surface nanostructure formation.

In a self-nucleation experiment, crystalline standard samples were annealed at temperatures in the melting range. Low temperature annealing promoted the thickening of crystalline lamellae on the film surface which is explained by the formation of less folded chain crystals that exhibit increased melting temperatures. Based on a theoretical analysis, we identified a functional dependence of calorimetric bulk properties on lamellar thickness which can be used to predict the lamellae thickness as a function of the annealing temperature.

We established the dual self-nucleation experiment as a powerful tool to predictably tailor surface nanostructures in the range of several nanometers.

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Evolution of Entanglement Distribution in the Growth and Melting of a Polymer Single Crystal — ●CHUANFU LUO¹ and JENS-UWE SOMMER^{1,2} — ¹Leibniz-Institut für Polymerforschung Dresden, Germany — ²Technische Universität Dresden, Germany

Many physical properties of polymers are determined by the state of entanglement, such as visco-elasticity. Another closely related topic is the crystallization and melting of polymers, in which the formation of folded chain segments are strongly related with the local entanglement states [1]. Computer simulation provides the possibility to study the changes in entanglement states during the phase transition of polymers. We developed a method to calculate the local entanglement length based on an extended primitive path analysis (PPA) [2]. We apply this method to calculate the evolution of entanglement distribution in the growth and melting of a polymer single crystal, which are achieved by large scale MD simulations. In principal, the method can be used to calculate the entanglement distribution in various conditions, such as with confinement and during dynamic processes.

[1]C. Luo and J.-U. Sommer, ACS Macro Lett. 2, 31(2013)

[2]R. Everaers et al., Science 303, 823-826 (2004)