

CPP 4: Crystallization, Nucleation and Self Assembly I

Time: Monday 9:30–12:30

Location: ZEU 114

CPP 4.1 Mon 9:30 ZEU 114

Self-assembly of quasicrystals in colloid-polymer mixtures — ●ERDAL C. OĞUZ, MATTHIAS SANDBRINK, and MICHAEL SCHMIEDEBERG — Heinrich-Heine-Universität Düsseldorf

By combining lattice sum calculations and Monte Carlo computer simulations, we investigate the stability of quasicrystals in colloid-polymer mixtures. In our model, the colloidal interactions are dictated by a repulsive Yukawa potential, whereas the presence of polymers yield an attractive depletion force between them. Hence, we obtain an isotropic pair interaction potential with multiple length scales that we use to support the two incommensurate length scales of the desired quasicrystalline structures. By minimizing the corresponding lattice sums, we determine the ground-state phase diagram ($T=0$) and we search for parameter sets where the system prefers quasicrystalline ordering rather than any other crystalline structure, i.e., we explain what polymer concentration, what depletion length, and what density are needed to grow quasicrystals with a given symmetry. For comparison and in order to extend the ground-state calculations to finite temperatures, we perform Monte Carlo computer simulations of our system. Therefore, our calculations and simulations explain how colloidal building blocks in experiments have to be designed in order to achieve the self-assembly of intrinsic colloidal quasicrystals.

CPP 4.2 Mon 9:45 ZEU 114

Testing nucleation theory for collidal crystals from estimates for the Laplace pressure in the fluid — ●ANTONIA STATT, PETER VIRNAU, and KURT BINDER — Institut für Physik, JGU Mainz

We use a soft extension of the well-known effective Asakura Oosawa model [1] to study phase coexistence of a crystal "droplet" surrounded by liquid with Monte Carlo Simulations. 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 new created interface. The enhancement of the pressure in the surrounding liquid in comparison to the coexistence pressure, the so-called Laplace pressure, can be measured via the virial theorem [2]. With this we are able to compare the predictions of the classical nucleation theory without suffering from ambiguities occurring when one needs a microscopic identification of the crystalline droplet.

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

[2] D. Deb, A. Winkler, P. Virnau and K. Binder, J. Chem. Phys. **136**, 134710, 2012

CPP 4.3 Mon 10:00 ZEU 114

Guided assembly of nano-particles exploiting forces induced by 3D confinement — ●STEFAN FRINGES¹, COLIN RAWLINGS¹, HEIKO WOLF¹, URS DUERIG¹, MADHAVI KRISHNAN², and ARMIN KNOLL¹ — ¹IBM Research, 8803 Rüschlikon, Switzerland — ²Institute of Physical Chemistry, University of Zurich, 8057 Zurich, Switzerland

It has been shown previously that charged nanoparticles can be stabilized in a static nano-fluidic slit due to the formation of the electric double layer. By shaping the topography of the confining interfaces, a trapping potential is established for the nanoparticle, which overcomes the Brownian motion and traps the nanosized object for several hours [1]. Here we demonstrate a mechanical setup capable of controlling the confining surfaces with sub-nanometer precision. By controlling the slit height, the strength of the trapping potential is directly controlled. The shape of the potential is also defined by the shape of the topography, which is carved out of a thermally decomposable polymer film by 3D thermal Scanning Probe Lithography (tSPL) [2]. The potential landscape is experimentally determined by observation of the particle motion at high frame rates using Interferometric scattering imaging. The undissociated polymer surface has a lower energy barrier for direct contact. We demonstrate that this energy barrier can be overcome at small separations, where the van der Waals force dominates providing stable deposition. In addition, the particles can be transferred to the substrate of choice by thermal decomposition of the polymer film.

[1] Krishnan et al., Nature 467, 692-695, 2010

[2] D. Pires, A.W. Knoll et al., Science 328(5979), 732-735, 2010

CPP 4.4 Mon 10:15 ZEU 114

Real-Time Observation of Non-Classical Protein Crystallization Kinetics — ●ANDREA SAUTER¹, GUDRUN LOTZE², FAJUN ZHANG¹, and FRANK SCHREIBER¹ — ¹Universität Tübingen, Institut für Angewandte Physik — ²European Synchrotron Radiation Facility, F-38043 Grenoble Cedex 9, France

We present a real-time study of protein crystallization for beta-lactoglobulin in the presence of CdCl₂ by small angle X-ray scattering (SAXS) and optical microscopy. In the presence of CdCl₂ both classical and non-classical crystallization can be found depending on the concentration of protein and salt. A phase diagram region can be identified in which real-time SAXS demonstrates the existence of an intermediate state prior to crystallization that cannot be explained by classical nucleation theory. It shows as a minimum at 0.48 nm⁻¹ and a maximum at 0.7 nm⁻¹ which become visible in the scattering curves after several minutes. With time, this new feature becomes more pronounced. In the next step, Bragg peaks appear and the position of the minimum shifts towards larger q values. The minimum regresses again and in the end, only the contribution of the Bragg peaks is left. It can be concluded that an amorphous intermediate structure forms before crystallization starts and is consumed later by the growing crystals. Evolution and kinetics of the two components can be followed in real-time by X-ray scattering and microscopy.

CPP 4.5 Mon 10:30 ZEU 114

Growth of nanoparticles - from milliseconds to hours — ●TORBEN SCHINDLER, MARTIN SCHMIELE, TILO SCHMUTZLER, THAER KASSAR, and TOBIAS UNRUH — Lehrstuhl für Kristallographie und Strukturphysik, Friedrich-Alexander-Universität Erlangen Nürnberg, Staudtstr. 3, 91058 Erlangen

Zinc oxide is a promising semiconductor material, which shows interesting optical and electronic properties on the nanoscale and makes it a promising candidate for many applications, e.g. solar cells. However, detailed knowledge about the kinetics of nucleation and growth of the nanoparticles is crucial for a targeted production.

The nanoparticles are synthesized by simply mixing a precursor and an alkaline solution. The growth of the nanoparticles can be studied using in-situ time-resolved small angle X-ray scattering (SAXS). A stopped flow device at a synchrotron SAXS instrument enabled us to determine the size of the nanoparticles as early as 5 ms after the synthesis, with which we could detect a strong increase of the particle diameter especially within the first 200 ms. In addition, an unexpected behavior was observed using triethylamine as alkaline solution. The particle diameters are fluctuating on a ms-timescale during the ripening process. These findings will be presented with additional absorption spectroscopy studies to describe the time- and temperature-dependent ripening process of differently synthesized ZnO nanoparticles from milliseconds to hours.

CPP 4.6 Mon 10:45 ZEU 114

Triply-intergrown distorted 3D nets: A new tricontinuous equilibrium morphology in copolymeric systems — ●MICHAEL G. FISCHER^{1,2}, LILIANA DE CAMPO², STEPHEN T. HYDE², and GERD E. SCHROEDER-TURK¹ — ¹Institut für Theoretische Physik I, Friedrich-Alexander Universität Erlangen-Nürnberg, Staudtstr. 7, 91058 Erlangen, Germany — ²Dept. of Applied Mathematics, Research School of Physics and Engineering, The Australian National University, Canberra ACT 0200, Australia

Copolymeric self-assembly provides an efficient route to the formation of ordered 3D nanostructures. The most complex equilibrium structure in diblock copolymer melts is the core-shell Gyroid based on the intergrowth of two continuous network domains. Adaptation of the molecular architecture is a strategy to achieve different phases, such as kaleidoscopic columnar phases in star-shaped triblock terpolymers. However, the formation of phases based on more than 2 network domains has not yet been reported in copolymer melts. We show that a triply-periodic tricontinuous structure based on the intergrowth of three nets is a stable equilibrium phase of star-shaped triblock copolymers when an extended core is introduced into the molecules. We use self-consistent field theory to confirm the geometric intuitions why the introduction of the core leads to the formation of this new phase. Its effect is a change in the relative importance of interface tension

between the three polymeric species and entropic chain stretching to the free energy. This phase is the first tricontinuous network phase in copolymer melts, which has long-range crystalline order but low symmetry.

15 min. break

CPP 4.7 Mon 11:15 ZEU 114

An in situ GISAXS study of BCP thin films during annealing in neutral and in selective solvent vapors — •ILJA GUNDEL^{1,2}, XIAODAN GU², ALEXANDER HEXEMER¹, and THOMAS RUSSELL² — ¹Lawrence Berkeley National Laboratory, Berkeley, USA — ²University of Massachusetts, Amherst, USA

Solvent vapor annealing (SVA) is a means to achieve lateral order of block copolymer (BCP) microdomains in thin films but the underlying mechanism of the ordering process is ill-understood. Here, we used real time in situ grazing-incidence small-angle x-ray scattering (in situ GISAXS) to investigate the ordering of BCP microdomains as solvent vapor was added or removed. We systematically studied the influence of the amount of swelling and solvent removal rate on the lateral order of BCP microdomains in neutral and selective solvent vapors, respectively. In case of neutral solvent vapor larger grain sizes were observed at higher swelling while for selective solvent vapor high swelling induced changes in the packing of microdomains. The effect of solvent removal on the degree of lateral order was studied by deswelling films at different removal rates. Here, we observed a substantial deterioration of lateral order of microdomains in selective solvent vapor that is significantly stronger than in neutral solvent vapors, where the fastest solvent removal rate even allowed to freeze in the ordered microdomain structure of the swollen BCP film.

CPP 4.8 Mon 11:30 ZEU 114

Influencing molecular thin film growth with light — •LINUS PITHAN¹, HANNES ZSCHIESCHE¹, ANTON ZYKOV¹, CHRISTOPHER WEBER¹, SEBASTIAN BOMMEL², and STEFAN KOWARIK¹ — ¹Humboldt Universität, Fachbereich Physik, Berlin — ²DESY, Hamburg

The possibilities to control the orientation and structure of molecular thin films during growth are limited to very few degrees of freedom e.g. the substrate temperature and molecular deposition rate. Here we show that light can influence the molecular growth.

Vacuum deposited α -sexithiophene (α -6T) films (OMBE) tend to grow in different crystal structures. Most prominent are the low temperature (LT) and high temperature (HT) polymorphous. Both structures are found to coexist when KCl is used as substrate material, as observed by real-time x-ray diffraction studies. Using light illumination during growth we show that the coexistence can be controlled and the phase purity can be increased by eliminating the HT phase. This demonstrates the possibility to use laser illumination as new control parameter to influence organic molecular beam deposition.

CPP 4.9 Mon 11:45 ZEU 114

Switchable Properties of Smart Coatings from Polymeric Micelles Triggered by External Stimuli — •INNA DEWALD¹, JULIA GENSEL¹, JOHANN ERATH¹, EVA BETTHAUSEN², AXEL H. E. MÜLLER^{2,3}, and ANDREAS FERY¹ — ¹University of Bayreuth, Physical Chemistry II, Germany — ²University of Bayreuth, Macromolecular Chemistry II, Germany — ³Johannes Gutenberg University Mainz, Institute of Organic Chemistry, Germany

Today, many objects of our everyday life consist of coated materials indicating their growing importance in the modern era of technology.

Following this trend in recent years, formation of a variety of smart coatings using macromolecular building blocks has been demonstrated. On that account, we investigate the potential of pH-sensitive ABC triblock terpolymer micelles. The use of such colloidal particles as base material for thin films has several advantages from a material-science perspective, e.g. these building blocks can be stimulus-responsive and multi-functional on the single particle level, while coatings can be formed by simple physisorption. Using the LbL approach as pH-responsive micelles leads to coatings with novel properties, internal hierarchy and collective stimulus response of the integrated nanostructures.[1] In our work, we investigate the effects of pH on surface properties of these films [2] and explore their potential for applications as active surfaces for self-regulated bacteria release which change their surface characteristics in response to cellular metabolism.[3] 1. Gensel J. et al., Chem. Sci., 2013, 4, 325-334. 2. Gensel J. et al., Soft Matter, 2011, 7, 11144-11153. 3. Gensel J. et al., Adv. Mater., 2012, 24, 985-989.

CPP 4.10 Mon 12:00 ZEU 114

In-situ PDF study of Precursor Formation and Nucleation of ZnO Nanoparticles — •MIRIJAM ZOBEL and REINHARD B. NEDER — Lehrstuhl für Kristallographie und Strukturphysik, Universität Erlangen-Nürnberg

Most semiconductor nanoparticles are produced in sol-gel processes. For the model system zinc oxide (ZnO), abundant different synthesis strategies exist, often in organic solvents. Though the final crystalline nanoparticles are well characterized, little is known about the evolution of the crystallinity of the precursors and nanoparticles in solution. Using high-energy synchrotron radiation, we can study such nucleation processes in-situ with a 20 s time resolution, even at very low concentrations of 30 mM. To our knowledge, this is the first study of this kind. Fourier transformation of the scattering data provides us with pair distribution functions (PDF). Those mirror the distribution of interatomic distances within the sample and allow the derivation of different nanoparticle properties such as size, shape and crystallinity. Firstly, after base addition we observe metastable precursors of about 1 nm in diameter. Compared with the final wurtzite crystal structure, the PDF of the precursors show broadened peaks of the next-neighbour distances. This indicates precursor structures which possess local domains of both tetrahedral as well as octahedral arrangement. After a lag time of 100 min those precursors spontaneously nucleate to 2 nm particles, which further grow with time. We show this nucleation and growth behavior by multiphase fits of the PDFs and structural modelling of the precursor and nanoparticles.

CPP 4.11 Mon 12:15 ZEU 114

Computer simulation of heterogeneous nucleation on curved surfaces — •HENNING HÖRSTERMANN, JULIA KUNDIN, and HEIKE EMMERICH — Materials and Process Simulation, University of Bayreuth, Germany

We show how the combination of string method with the phase-field approach can be extended from simulations of homogeneous nucleation to heterogeneous nucleation. From these simulations, it is possible to directly obtain nucleation barriers for heterogeneous nucleation on arbitrary surfaces as well as information about the size and shape of the critical nucleus. We test the method by comparing the dependence of the nucleation barrier for heterogeneous nucleation on concave and convex surfaces on the surface curvature obtained from three-dimensional phase-field simulations with predictions from classical nucleation theory and find good agreement between them.