CPP 14: Crystallization, Nucleation and Self Assembly I

Time: Tuesday 9:30–13:00 Location: H39

CPP 14.1 Tue 9:30 H39

Protein clustering as a precursor of crystallization — •Fajun Zhang[1], Andrea Sauter[1], Marcell Wolf[1], Felix Roosen-Runge[1], Michael Sztucki[2], Roland Roth[3], and Frank Schreiber[1] — [1]Institut für Angewandte Physik, Universität Tübingen — [2]ESRF, Grenoble, France — [3]Institut für Theoretische Physik, Universität Tübingen

Protein clusters are normally considered as a major impurity for growth of high quality single crystals. Here we show that pre-assembled protein clusters formed via cation bridging can serve as a building block of crystallization. Globular proteins, human serum albumin and beta-lactoglobulin have been crystallized from solution in the presence of multivalent metal ions. These negatively charged globular proteins undergo a reentrant condensation phase behavior [1]. Crystallization near phase boundaries follows different mechanisms [2]. DLS and SAXS reveal the formation of protein clusters near both phase boundaries. Real time SAXS measurements demonstrate that protein clusters act as precursors of nucleation with a reduced energy barrier [3]. Crystallographic analysis provides direct evidence of the crystal structure and cation binding sites [2]. Although the binding sites do not necessarily form the crystal lattice, they enhance interactions between protein contacts. The limited binding number (2-4) ensures the flexibility of proteins within clusters, which is crucial for the conformation relaxation during nucleation. [1] F. Zhang, et al. Phys. Rev. Lett. 2008, 101, 148101. [2] F. Zhang, et al. J. Appl. Cryst. 2011, 44, 755. Soft Matter 2012,8, 1313. [3] F. Zhang, et al. Faraday Discuss. 2012, 159, 313.

CPP 14.2 Tue 9:45 H39

Structural evolution of a dense liquid phase in protein solutions — •Andrea Sauter, Fajun Zhang, and Frank Schreiber — Universität Tübingen, Institut für Angewandte Physik

Liquid-liquid phase separation (LLPS), the reversible transformation from a homogeneous into a protein rich and a protein poor phase, can be regarded as the equivalent of a gas-liquid transition. Here we present a study of the structural evolution of LLPS in solutions of beta-lactoglobulin (BLG) in presence of YCl_3. This system was subject of our research before [1,2] and has turned out to be a good model system for two-step crystallization. Selected samples were prepared at 35°C, above their critical temperature T_c of ca 20°C. When quenched to 5°C, the solution phase separates. Using SANS and SAXS, we followed the evolution of structures at different length scales. We use protein clusters based on the crystal structure to calculate theoretical scattering curves and compare them to the measured data. The results suggest the hierarchy of protein clusters to change with temperature and time. Comparison between initial and later measurements shows an increase at low q (clusters), at $1.8\,\mathrm{nm}^{-1}$ (dimer formfactor) and several intermediate q regions and a simultanous decrease in others. A decrease of the monomer-monomer correlation peak at $2.2\,\mathrm{nm}^{-1}$ suggests the mobility of monomers within clusters to be changed in this process. The mobility of proteins within clusters and their relaxation are crucial for nucleation, so these findings will help the understanding of two-step crystallization. [1] F. Zhang et al., J. Appl. Cryst. 44, 2011, 755-762; [2] F. Zhang et al., Faraday Discuss. 159, 2012, 313-325.

CPP 14.3 Tue 10:00 H39

Entanglement Related Memory Effect in Primary Nucleation of Polymers — •Chuanfu Luo[1] and Jens-Uwe Sommer[1,2] — [1]Leibniz-Institut für Polymerforschung Dresden, Germany — [2]Technische Universität Dresden, Germany

Polymer crystallization is a non-equilibrium process and highly dependent on the thermal history. In self-seeding experiments a polymer melt is prepared by melting semi-crystalline polymer for a short time, followed by a subsequent cooling process, which can result in strong position and orientation- correlations of the resulting crystals with the previously crystalline regions [1-2]. The origin of such a memory effect is still unclear. We found indications that this memory effect is related to the state of entanglement in the melt which is still incompletely re-entangled during the heating period. By using MD simulations combined with primitive path analysis (PPA)[3], we reproduced self-seeding effects in simulations and we can show that crystallization and in particular self-seeding is directly correlated with the entanglement state of the melt. Also, we show that self-seeding takes place even for the case that all individual chains are in the molten state before cooling. [1]A. Mamun et al., Macromolecules 40, 6296-6303 (2007) [2]J.-J. Xu et al., Nature Mater. 8, 348 (2009) [3]R. Everaers et al., Science 303, 823-826 (2004)

CPP 14.4 Tue 10:15 H39

Effect of the Crystalline α_c-Process on the Morphology of Semicrystalline Polymers: a Comparative SAXS- Study on Poly-ϵ-Caprolactone and Polyethyleneoxide — Anne Seidlitz, Thomas Thurn-Albrecht, •Ruth Bärenwald, and Kay Saalwächter — MLU Halle-Wittenberg, 06120 Halle (Saale)

Semi-crystalline polymers can be classified into two different types, depending on the presence (α_c-mobile) or absence (crystal-fixed) of the α_c-relaxation, which provides mobility to the chains in the crystals. Starting from a hypothesis of Boyd, that all polymers with a high crystallinity are α_c-mobile while all polymers with a low crystallinity are crystal-fixed, we investigated the morphology of polyethyleneoxide as a polymer with mobile crystalline chains and poly-ϵ-caprolactone as a polymer with fixed chains. We performed small-angle X-ray scattering experiments and developed a simulation based on the paracrystalline model to derive quantitative morphological information from the SAXS data. Clear differences between the structure of PEO and PCL were observed. For PCL the crystalline thickness d_c is well defined, while the amorphous thickness d_a displays a broad distribution. PEO shows a small, well defined d_a and a broad thickness distribution of the crystalline lamellae.This confirms a different mode of structure formation. The crystalline lamellae in PEO, where thickening begins already at the growth front, can reorganize during crystallization until a minimal d_a, possibly reflecting a locally equilibrated entanglement structure, is established. For PCL no thickening of the initially formed lamellae is possible and the amorphous parts are randomly filled.

CPP 14.5 Tue 10:30 H39

10-nm structure formation induced by crystallization in P3HT/PCBM blends — •Alessandro Sepe[1], Peter Kohn[1], Zhuxia Rong[1], Kai H. Scherer[1], Michael Sommer[2], Peter Müller-Buschbaum[3], Richard H. Friend[1], Ullrich Steiner[1], and Sven Hüttner[1] — [1]Cavendish Laboratory, University of Cambridge, Cambridge, UK — [2]Institute of Macromolecular Chemistry, University of Freiburg, Freiburg, Germany — [3]Lehrstuhl für Funktionelle Materialien, Physik-Department, TU München, Garching, Germany

Structural characterisation of novel semiconducting polymers is of great importance to the development of new materials for organic electronic applications. The solubility and aggregation of [6,6]-phenyl C61butyric acid methyl ester (PCBM) within a polymer matrix is of great interest for the development of fullerene based organic photovoltaic cells. Our study aims at methodically investigating the loading of a polymer with PCBM. For our investigation a specially synthesized mono-disperse regio-regular poly-(3-hexylthiophene-2,5-diyl) (P3HT) is used. The relative crystallinity of P3HT has been directly related to the nucleation density for PCBM aggregation. A combination of small, wide and grazing incident angle X-ray scattering techniques is used to track PCBM within the polycrystalline superstructure of P3HT. We have found the solubility limit of PCBM in amorphous P3HT domains, whereas, above this limit, it segregates out. Our results show that the crystallization of P3HT with crystal sizes in the range of 10 nm sets one of the length scales in the phase separation process.

CPP 14.6 Tue 10:45 H39

Heterogeneous Nucleation in Epitaxially Crystallized Polyethylene on Graphite — •Ann-Kristin Löhmann, Thomas Henze, and Thomas Thurn-Albrecht — Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, Germany

We investigate the interface between a polymer melt and a crystalline substrate to get a more microscopic understanding of heterogeneous nucleation.

As a model system we studied crystallization and melting in thin epitaxially crystallized LLDPE films on graphite by high temperature AFM measurements. Upon heating above the melting temperature the polymer film starts to dewet and leaves a thin (only few nanometres) ordered film of polyethylene with a temperature dependent thickness behind. This ordered layer at the polymer-substrate interface shows the same lamellar structure as the semicrystalline film at lower temperatures. The thickness of the ordered layer and as a consequence the dewetting of molten polymer is reversible. The temperature dependence of the stabilized layer can be described by a phenomenological thermodynamic theory [1].

In this epitaxial system a stabilized ordered layer completely wets the substrate at temperatures above the bulk melting point and acts as a nucleus for crystallization, thus explaining the unusual lamellar structure of the crystalline film observable at room temperature.

[1] M. Heni and H. Löwen, Phys. Rev. Lett. 85, 3668-3671 (2000)

CPP 14.7 Tue 11:00 H39

Real-time GISAXS-study of DIP thin film growth — •Christian Frank[1], Jiří Novák[1], Rupak Banerjee[1], Stefan Kowarik[2], Alexander Gerlach[1], and Frank Schreiber[1] — [1]University of Tübingen, Auf der Morgenstelle 10, 72076 Tübingen, Germany — [2]Humbold University of Berlin, Newtonstr. 15, 12489 Berlin, Germany

We present a real-time *in situ* grazing incidence small angle X-ray scattering (GISAXS) study on growth of diindenoperylene (DIP) [1] thin films on SiOx substrates at various growth rates and substrate temperatures. DIP is a typical candidate for an active material in organic photo-voltaic and device applications. It is therefore important to understand how different growth parameters influence the evolution of the thin film morphology. By employing high brilliance synchrotron radiation and most recent CCD-area detectors we were able to monitor specular [2] and diffuse growth-oscillations simultaneously and in real-time. While the specular scattering contains information about crystallinity and morphology perpendicular to the sample surface, GISAXS data reflect also the lateral correlation lengths of surface features of thin films [3]. In this way we are able to monitor formation and coalescence of molecular islands during the layer-by-layer growth and the transition to the 3-D growth.

[1] A. C. Dürr et al., *Phys. Rev. Lett.* **90** (2003), 016104; [2] S. Kowarik et al., *Eur. Phys. J. Special Topics* **167** (2009), 11; [3] S. K. Sinha et al., *Phys. Rev. B* **38** (1988), 2297

15 min. break

CPP 14.8 Tue 11:30 H39

Melting Temperature and Crystal Growth Rate in Liquid Mixtures — •Konstantin Koschke[1], Davide Donadio[1], Hans Jörg Limbach[2], and Kurt Kremer[1] — [1]MPI Polymer Research, Mainz, Germany — [2]Nestlé Research Center, Lausanne, Switzerland

Crystallization of liquids is of uttermost interest for many disciplines, including materials, atmospheric and food science. The introduction of additives in solution allows the control of the key thermodynamics and kinetics parameters of crystallization, namely the transition temperature and the growth rate. Here we investigate the basic principles of crystallization of solutions by computing the melting temperature and simulating crystal growth of Lennard-Jones binary mixtures, by equilibrium and non-equilibrium molecular dynamics (EMD - NEMD) simulations. Both melting temperatures and growth rates are computed exploiting the two-phase method at equilibrium and non-equilibrium conditions, respectively. The effect of hydrophobic and hydrophilic solutes at low concentrations ($< 3\%$) is analyzed, scanning systematically size and concentration. Our MD simulations allow us to connect macroscopic thermodynamic and kinetic observables, such as phase coexistence temperature and crystal growth rate, to the microscopic structure of the solutions and to microscopic processes occurring during crystal growth.

CPP 14.9 Tue 11:45 H39

Influence of Organic Ligands on ZnO Nanoparticle Formation via in-situ XRD — •Mirijam Zobel — Lehrstuhl für Kristallographie und Strukturphysik, Universität Erlangen

Organic ligands are used in solvent-based sol-gel processes to synthesize monodisperse, metal oxide nanoparticles for semiconductor industry. The ligand type and chemistry have a decisive influence not only on the particle size, but also on the structure and kinetics during the nucleation. Using high-energy synchrotron radiation, it is possible to study this nucleation in-situ via x-ray wide angle diffraction, even in salt solutions with very low concentration (30 mM). Our model system zinc oxide exhibits a precursor structure of the metal salt, which is stable for several hours and exists both without and in presence of additional ligands, e.g. dimethyl-L-tartrate or pentantrione. Addition of an alkali results in an instantaneous transformation into larger precursor structures, which - after a further ligand-specific ripening time - again spontaneously start to nucleate to approx. 2 nm nanoparticles. This final nucleation of the particles surprisingly takes several hours. Here we report for the first time that such an in-situ high-energy x-ray wide angle diffraction experiment with synchrotron radiation is possible and that it reveals the phase formation and the growth of nanoparticles within organic solvents. By deducing the pair distribution function and hence the structure of the different phases present, more profound structure analysis can subsequently be carried out.

CPP 14.10 Tue 12:00 H39

Real time and in-situ investigations of the nucleation and diffusion during the growth of the fullerene C_{60} using X-ray scattering — •Sebastian Bommel[1,2], Nicola Kleppmann[3], Christopher Weber[2], Holger Spranger[2], Jiri Novak[4], Peter Schäfer[2], Stephan V. Roth[1], Frank Schreiber[4], Sabine H.L. Klapp[3], and Stefan Kowarik[2] — [1]Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany — [2]Institut für Physik, Humboldt-Universität Berlin, Berlin, Germany — [3]Institut für Theoretische Physik, Technische Universität Berlin, Berlin — [4]Institut für Angewandte Physik, Universität Tübingen, Tübingen, Germany

The surface morphology and the structural order during the growth of the popular organic semiconductor C_{60} were studied with simultaneous real-time and in-situ measurements of Grazing Incidence Small-Angle X-ray Scattering (GISAXS) and anti-Bragg growth oscillations during organic molecular beam deposition . For the characterization of the morphology during the growth the island density was extracted from 2D GISAXS patterns. From this we find a dependency of the island density on thickness and also temperature, i.e. 150 islands/μm^2 for 313 K and 10 islands/μm^2 for 353 K in the beginning of growth. From the anti-Bragg growth oscillations high structural order and layer-by-layer growth during the growth of multilayer films were found. From a comparison of the nucleation and the growth oscillations with the analytic Trofimov rate equations model and KMC simulations the diffusion energy and the Ehrlich-Schwoebel barrier can be estimated to be 0.5 eV and 0.1 eV, respectively.

CPP 14.11 Tue 12:15 H39

Spin Casting of Dilute Solutions to Control Nucleation and Growth — •Stefan Karpitschka, Constans Weber, and Hans Riegler — MPI für Kolloid- und Grenzflächenforschung, Potsdam, Germany

We analyze the spin casting of dilute (ideal) binary mixtures of non-volatile solutes in volatile solvents as a prototype for evaporation-controlled processes that are increasingly used to deposit specifically structured (sub)monolayers (evaporation-induced self-assembly). The first analytical description of the thinning of a volatile liquid film simultaneously subject to spinning and evaporation is presented. It shows, that the duration of a spin casting process is linked to the process parameters via power laws. A diffusion-advection model leads analytically to the equation governing the spatio-temporal evolution of the internal film composition. Its solution reveals that the solute concentration enrichment, its gradient, and its time evolution are related to the process parameters via power laws. The physics behind the power laws is uncovered and discussed [1]. This reveales universal insights into the interplay between the control parameters and their impact on the spatio-temporal evolution of the film composition of diluted mixtures. It also offers palpable guidelines to better understand and control the spin casting of non-ideal solutions. Experiments are presented which support the theoretical findings.

[1] S. Karpitschka, C. Weber, H. Riegler, PRL (2012), in revision.

CPP 14.12 Tue 12:30 H39

Nucleation and Growth of Copper Phthalocyanine from Solution — •Fatemeh Ghani and Hans Riegler — Max Planck Institute f. Colloid & Interfaces, Potsdam-Golm, Germany

Unsubstituted Metal-phthalocyanines (Pc) are excellent electron donating molecules for OSC. Usually organic solar cells with Pcs are produced by vapor deposition due to low solubility, although solution based deposition (like spin casting) is cheaper and offers more possibilities to control the structure of the film. It is necessary to find the appropriate solvents, assess the solution deposition techniques, such as dip coating, and spin castingand understand the nucleation and growth process for aggregation/precipitation and to use this knowledge to produce nanostructures appropriate for OSC. We prepared thin films of CuPc from solution in ambient air. The parameters (e.g. solution concentration profile) governing nucleation and growth are calculated based on the spin casting theory of a binary mixture of a nonvolatile solute and evaporative solvent and inter-molecular interactions.

CPP 14.13 Tue 12:45 H39

Glass transition and recristallization of alcohols in silica nanochannels — •Daniel Rau[1], Rolf Pelster[1], Tommy Hofmann[2], Dirk Wallacher[3], and Patrick Huber[4] — [1]FR 7.2 Experimentalphysik, Universität des Saarlandes — [2]Helmholtz Zentrum Berlin, Inst Complex Magnet Mat, D-14109 Berlin, Germany — [3]Helmholtz Zentrum Berlin, Dept Sample Environm, D-14109 Berlin, Germany — [4]Hamburg Univ Technol, Inst Mat Phys & Technol, D-21073 Hamburg, Germany

We studied the molecular dynamics and glass transition of n-alcohol confined in electrochemical etched silica nanochannels using broadband dielectric spectroscopy and neutron scattering. In contrast to the bulk alcohol confined alcohol exhibits a glass transition upon slow cooling but partial recrystallization occurs upon heating. This behaviour reflects the different temperature dependences of nucleation and crystal growth.