CPP 70: Crystallization, Nucleation and Self-Assembly II

Time: Thursday 15:00–18:15   Location: C 230

Invited Talk   CPP 70.1   Thu 15:00   C 230

Crystallization in melts of semi-flexible hard polymer chains: An interplay of entropies and dimensions — •Wolfgang Paul and Timur Shakirov — Institut für Physik, Martin Luther Universität, 06099 Halle

Morphology selection upon crystallization of long-chain polymers is governed by an intricate and so far unresolved interplay between thermodynamic and kinetic effects. We argue, that the thermodynamic driving forces for this phase transition can be studied looking at relatively short chains as well. For a melt of short, semi-flexible polymer chains with purely repulsive intermolecular interactions, Stochastic Approximation Monte Carlo simulations can be employed to obtain the complete thermodynamic equilibrium information. Thermodynamics is obtained based on the density of states of a simple coarse-grained model, which varies by up to 5500 orders of magnitude. We show that our polymer melt undergoes a first-order crystallization transition upon increasing the chain stiffness at fixed density. The lyotropic three-dimensional orientational ordering transition drives the crystallization and is accompanied by a two-dimensional hexagonal ordering transition in the plane perpendicular to the chains. While the three-dimensional ordering can be understood in terms of Onsager theory, the two-dimensional transition is similar to the liquid-hexatic transition of hard disks. Due to the domination of lateral two-dimensional translational entropy over the one-dimensional translational entropy connected with columnar displacements, the chains form a lamellar phase.

CPP 70.2   Thu 15:30   C 230

Free energy barriers for crystal nucleation from fluid phases — •Peter Koss[1,2], Antonia Statt[3], Peter Virnau[1,2], and Kurt Binder[1] — [1]Institut für Physik, Johannes Gutenberg-Universität Mainz, Staudingerweg 9, 55128 Mainz, Germany — [2]Graduate School of Excellence Materials Science in Mainz, Staudinger Weg 9, 55128 Mainz, Germany — [3]Princeton University, Princeton, NJ 08544, USA

A fluid in equilibrium, confined in a finite volume, with a density exceeding the onset of freezing, may exhibit phase coexistence with a crystal nucleus surrounded by liquid or a gas. Classical nucleation theory predicts that the barrier of homogeneous nucleation is comprised of two contributions, the free energy gained by the creation of a crystal droplet and the free energy loss due to surface tension of the newly created interface. We obtain the excess free energy due to the surface of the crystalline nucleus by using a computational method suitable for the estimation of the chemical potential of dense fluids. Our analysis method is appropriate for crystal nuclei of all shapes, without suffering from ambiguities occurring when one needs a microscopic identification of the crystalline droplet. We present an analysis method to determine the coexistence pressure between fluid and crystal, and the nucleation barrier for a soft version of the effective Asakura-Oosawa model at $\eta_p^r = 0.1$, 0.2 and 0.28 [1].

[1] P. Koß, A. Statt, P. Virnau, and K. Binder, Phys. Rev. E 96, 042609 (2017)

CPP 70.3   Thu 15:45   C 230

Additive modified crystallization in binary Lennard Jones system — •Bhaskar Sen Gupta, Marc Radu, and Kurt Kremer — Max Planck Instutute for Polymer Research, Mainz, Germany

Additive modified crystallization is ubiquitous in nature, e.g., during the growth of calcitic stalactites, of mollusk shells or of bone structures. Control of crystallization by additives has applications in many areas of science and technology, such as production of pharmaceuticals, semiconductors, and nonlinear optics, as well as formation of biominerals. We employ computer simulation to study the additive enhanced crystal growth in a binary Lennard Jones mixture under different scenarios. The crystal growth rate, the structure of the liquid solid interface and the interface morphologies strongly depend on the miscibility of the components. An accelerated crystal growth is observed for systems of poor solubility. We find the growth of different types of crystals and the growth dynamics depend on the structure of the interface which is determined by the solubility of the (non-crystalizing) minority component. It is also observed that the crystal growth mechanism follows the predictions of the Kardar-Parisi-Zhang theory in $2 + 1$ dimensions for well miscible Lennard Jones mixtures.

CPP 70.4   Thu 16:00   C 230

Nucleation work in the crystallization of hard spheres — •David Richard and Thomas Speck — Staudingerweg 9, 55128, Mainz, Germany

Calculating the nucleation work associated with the spontaneous formation of a nucleus from a mother phase is not an easy task. On one side, classical nucleation theory (CNT) provides an accurate framework to compute the nucleation barrier associated with two coexisting bulk phases. On the other side, it fails to describe small nuclei composed of few hundreds (or even thousand) of particles. In this study, we combine a new approach to compute free energy barriers from brute force simulations and forward flux sampling without having to sample the dissolution of the nucleus. This method is applied to study the crystallization of hard spheres. We combine results from these simulations with seeding and equilibrium droplets [1,2], and make use of the nucleation theorem to evaluate the nucleation work for a large range of supersaturations. We present a direct comparison of this method with the capillary approximation present in CNT.

[1] Seeding approach to crystal nucleation. J. R. Espinosa, C. Vega, C. Valeriani, and E. Sanz, JCP (2016). [2] Finite-size effects on liquid-solid phase coexistence and the estimation of crystal nucleation barriers. A. Statt, P. Virnau, and K. Binder, PRL (2015).

CPP 70.5   Thu 16:15   C 230

Short-polyethylene systems: On the low-temperature states of single chains and few chain aggregates — •Timur Shakirov and Wolfgang Paul — Institute of Physics, University of Halle, Halle, Germany

The phase behavior of polyethylene has been under investigation during many decades. But investigation of single-chain crystallization is a technically difficult problem. One of the reasons for this is that in the case of molecular dynamics simulations as well as in experiments, it is not so easy to distinguish thermodynamic and kinetic effects on chain folding. We here present results of a Wang-Landau type Monte Carlo simulation, which give a possibility to analyze thermodynamic equilibrium properties of a system. Our simulation study of short polyethylene chains is based on a chemically realistic united atom model [1]. Simulation results for deep-energy (or equivalently low temperature) states of single chains of different lengths demonstrate a set of various ground-state configurations: from stretched and hairpin-like configurations of short chains to a helix-like structure reeled round one of the chain's ends. Aggregates of a few chains demonstrate more complex behavior having disordered and ordered phases even for aggregates composed of a couple of chains. Corresponding low-energy configurations differ form configurations of single chains having the same length. However, with increasing chain length, single chain and aggregate morphologies become more similar.

[1] W. Paul, D. Y. Yoon, and G. D. Smith, J. Chem. Phys. 103 (1995) 1702-1709.

15 min. break

CPP 70.6   Thu 16:45   C 230

Polymorphism of syndiotactic polystyrene crystals studied by coarse-grained and atomistic simulations — •Chan Liu[1], Christine Peter[2], Kurt Kremer[1], and Tristan Bereau[1] — [1]Max Planck Institute for Polymer Research, 55128 Mainz, Germany — [2]Theoretical Chemistry, University of Konstanz, Konstanz, Germany

Syndiotactic polystyrene (sPS) has attracted both academic and industrial attention because of its complex polymorphic behavior upon crystallization. However, computational modeling of polymer crystallization is a challenging task because these processes are slow on the molecular time scale. From a combination of Coarse-grained (CG) modeling and Replica Exchange Molecular Dynamics (REMD), we study for the first time polymorphism of polymer crystals from simulations. In our work, we show that the CG model is capable to reproduce sPS crystallization at a transition temperature in good agreement with atomistic simulations. Main (alpha and beta) polymorphs found in annealing experiments occur in both atomistic and CG simulations. The CG model allows us to efficiently characterize polymorphism at a large scale.

CPP 70.7   Thu 17:00   C 230

In situ Formation and Growth Characterization of Iron Oxide Nanoparticles by Synchrotron X-Ray Scattering Techniques — •Robert Wendt[1,2], Eike Gericke[1,2], Anna Lang[2], Dragomir Tatchev[3], Giorgia Greco[1], Markus Wollgarten[4], Armin Hoell[1], Klaus Rademann[2], and Simone Raoux[1,5] — [1]Helmholtz-Zentrum Berlin für Materialien und Energie, Institute for Nanospectroscopy, DE — [2]Humboldt-Universität zu Berlin, Department of Chemistry, DE — [3]Bulgarian Academy of Sciences, Institute of Physical Chemistry, Sofia, BG — [4]Helmholtz-Zentrum Berlin für Materialien und Energie, Department of Nanoscale Structures and Microscopic Analysis, DE — [5]Humboldt-Universität zu Berlin, Department of Physics, DE

This work includes an innovative measurement setup for microwave-assisted nanoparticle syntheses which facilitates in situ investigations of pressurized colloidal solutions by allowing exact addition of precursor solution into the sealed vessel reactor and withdrawal of colloid solution at any time. Thereby, we are able to investigate and characterize the early stages from molecule to nanoparticle in a time-range of milliseconds by coupling in situ UV-Vis spectroscopy, synchrotron based Wide-Angle and Small-Angle X-ray Scattering. These in situ studies are combined with complementary ex situ methods, Transmission Electron Microscopy, Electron Energy Loss Spectroscopy and X-ray Absorption Spectroscopy. By combining these results, we provide concepts for formation and growth mechanisms of iron oxide nanoparticles which were synthesized by microwave-assisted solvothermal routes.

CPP 70.8   Thu 17:15   C 230

Tracking the reaction and film formation dynamics during in situ polymerization of polythiophene thin films — •Jenny Lebert[1], Eva Maria Kratzer[1], Stephan Pröller[1], Oliver Filonik[1], Philippe Fontaine[2], and Eva M. Herzig[3] — [1]TU München, Munich School of Engineering, Herzig Group, 85748 Garching, Germany — [2]Synchrotron SOLEIL, 91192 Saint Aubin, France — [3]Universität Bayreuth, Physikalisches Institut, Herzig Group - Dynamik und Strukturbildung, 95440 Bayreuth, Germany

Native polythiophene belongs to the class of conjugated, semiconducting polymers which become conductive upon doping and therefore offer a broad range of potential applications in organic electronics. While polythiophene itself is insoluble, it is possible to obtain solution-processed thin films by employing an in situ polymerization technique.

Here, we present an experimental approach of tracking both, the reaction kinetics and film formation dynamics at the same time during the film formation employing simultaneous time-resolved UV/Vis transmission spectroscopy and grazing incidence wide angle X-ray scattering (GIWAXS). With this approach, we are able to characterize the intrinsic film formation phases. This allows us to suggest which processing parameters should be adapted in order to further improve the final film characteristics.

CPP 70.9   Thu 17:30   C 230

Biomolecule-Linked Plasmonic Nanoclusters as Colloidal SERS Sensors — •Roland Paul Maximilian Höller[1], Izabella Jahn[2], Dana Cialla-May[2], Jürgen Popp[2], Munish Chanana[3], Christian Kuttner[1,4], and Andreas Fery[1,4] — [1]Leibniz Institute of Polymer Research, 01069 Dresden, Germany — [2]Leibniz Institute of Photonic Technology, 07745 Jena, Germany — [3]Institute of Building Materials, ETH Zürich, 8093 Zürich, Switzerland — [4]Cluster of Excellence Centre for Advancing Electronics Dresden and Technische Universität Dresden, 01062 Dresden, Germany

We present controlled three-dimensional nanoassemblies with core/satellite architecture as colloidally stable probes for surface-enhanced Raman scattering (SERS). Aiming at obtaining a versatile system for bioapplications with both high and robust SERS performance, we used BSA as biomolecular linker for the controlled fabrication of self-assembled nanoclusters with correlated optical and structural properties by design [1]. The SERS performance of the assembled nanoclusters was benchmarked using an aromatic low-molecular-weight model analyte (4MBA). The characteristic signals of adsorbed 4MBA were detected with high robustness. The limit of detection of 10-6 M 4MBA was determined using non-enhanced volume-Raman signals of the medium as reference [2]. For bioapplication of such nanoassemblies, the aspects of biocompatibility, cellular uptake, and biological are decisive for a rational material design.

[1] R. P. M. Höller et al., ACS Nano, 2016, 10, 5740. [2] R. P. M. Höller et al., manuscript in preparation.

CPP 70.10   Thu 17:45   C 230

Temperature-dependent IR-transition moment orientational analysis applied to thin supported films of poly-ϵ-caprolactone — •Wilhelm Kossack[1], Martha Schulz[2], Thomas Thurn-Albrecht[2], Jörg Reinmuth[1], Viktor Skokow[1], and Friedrich Kremer[1] — [1]Molecular Physics department, Peter Debye Institut für weiche Materie, University Leipzig, Linnéstraße 5, 04103 Leipzig — [2]Martin-Luther-Universität Halle-Wittenberg, Institut für Physik, FG Experimentelle Polymerphysik, 06120 Halle/Saale, Germany

Based on temperature dependent orientational infrared spectroscopy (Infrared Transition Moment Orientational Analysis), the three dimensional molecular order parameter tensors of IR-active transition dipole moments with respect to the sample coordinate system are determined during melting of Poly-ϵ-caprolcatone. Crystallinity and macroscopic order remain largely unaltered up to $T \sim 50°C$, above which they decline. This decrease reflects the melting of flat on crystalline lamellae, contributing about 34% to the crystalline material. The remaining crystallites are arranged as in two-dimensionally confined bulk-like spherulites, which melt by less than $(3\pm3)\%$. Consequently, flat on oriented lamellae are regarded kinetically favoured during confined melt crystallization, but thermo-dynamically less stable than spherulites.

CPP 70.11   Thu 18:00   C 230

Polymer self-assembly into nanoparticles through rapid solvent exchange in organic media — •Tatiana Morozova[1], Victoria E. Lee[2], Athanassios Z. Panagiotopoulos[2], Robert K. Prudhomme[2], Rodney D. Priestley[2], and Arash Nikoubashman[1] — [1]JGU, Mainz, Germany — [2]Princeton University, Princeton, USA

Polymeric nanoparticles (NP) are vital components for a wide range of applications, such as biomedical targeting and diagnostics. Recently, a new method to form monodisperse polymeric NPs was developed, which relies on the rapid micromixing of a polymer solution with a nonsolvent . Using this technique, stable NPs from hydrophobic polymer were fabricated in water without additional stabilizers. It was hypothesized that this peculiar stability might originate from electrostatic stabilization, mediated by the adsorption of hydroxide ions on the hydrophobic surface, water charge transfer effect, or possible impurities in the system. In order to elucidate the nature of the stabilization mechanism in the NP suspension, we conducted experiments using alternative organic nonsolvents instead of water, i.e. heptane and hexane. To our surprise, the polymers aggregated into stable NPs for a wide range of process parameters. We theoretically investigated possible explanations for this stability: steric, electrostatic stabilizations and conditional thermodynamic equilibrium. Our considerations suggest that electrostatic stabilization is the most likely candidate, but the source of the charge is still elusive as there are no obvious charge carriers in the system.