

CPP 19: Crystallization, Nucleation and Self-Assembly

Time: Tuesday 9:30–13:00

Location: MER 02

Invited Talk

CPP 19.1 Tue 9:30 MER 02

Multiscale Model of Flow-Induced Crystallization in Polymers — DAVID NICHOLSON, MARAT ANDREEV, CHENMAY GANGAL, and •GREGORY RUTLEDGE — Massachusetts Institute of Technology, Cambridge, MA USA

The structure and properties of a semicrystalline polymer depends sensitively on both its chemico-physical nature and the way it is processed. Flow-induced crystallization (FIC) is one such coupled phenomenon. Models of FIC in polymers must account for the effect of flow on crystallization kinetics, but also the effect of evolving crystallinity on the rheology of the flowing polymer melt. For the first part, atomistic nonequilibrium molecular dynamics (NEMD) simulations are used to characterize the nucleation of a new crystal phase from the polymer melt under homogeneous flow conditions. The kinetics of nucleation are characterized using a mean first-passage time analysis, and a model based on the orientational ordering of Kuhn segments is proposed. For the second part, a variation of the discrete slip-link model (DSM) is used for the rheology of entangled polymer melts that accounts for partial crystallinity through the introduction of crosslinked *bridge* and/or *dangling* segments between developing crystallites, combined with a suspension model to reflect the stiffening associated with a growing crystal phase. This dual-network/suspension model describes well the evolution of both viscoelasticity and crystallinity for a number of linear low-density polyethylenes, and affords a deeper understanding of the essential physics that underlie the coupling between fluid mechanics and phase change.

CPP 19.2 Tue 10:00 MER 02

Polyethylene crystallization induced by a solution-prefolded nucleus — •TIMUR SHAKIROV and WOLFGANG PAUL — University of Halle, Halle, Germany

We present results of molecular dynamics simulations of an under-cooled polyethylene melt. We simulate a system of 2000 chains of 150 monomers each with the PYS force-field [1]. To initiate crystallization we insert in the melt a small two-chain nucleus (which we pre-fold in the vacuum) and cool down the system to 280 K. The crystalline lamella forms around the inserted nucleus during the cooling process and grows further at constant temperature. We characterize the growing crystallite by its average diameter (typical linear size in the cross-section perpendicular to the crystal director) and the height of the lamella (the averaged size along the crystal director). Both, diameter and height of lamella, grow during the entire simulation (~ 900 ns at the final temperature). A saturation of the growth is observed only as the crystallite reaches the surrounding spontaneously formed crystallites. Our analysis of the chain kinetics in the inner volume of the crystallite shows remaining chain mobility along the chain director. The distribution of short-time displacements of the inner-crystalline monomers has signatures of discrete jumps of a single bond length along the director of the crystal.

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

CPP 19.3 Tue 10:15 MER 02

How to grow semicrystalline lamellae in MD simulations — WILLIAM FALL^{1,2}, JÖRG BASCHNAGEL¹, OLIVIER LHOST³, and •HENDRIK MEYER¹ — ¹Institut Charles Sadron, CNRS UPR22 and Université de Strasbourg, France — ²LPS Université Paris-Saclay, Orsay, France — ³TotalEnergies One Tech Belgium, Zone Industrielle C, 7181 Feluy, Belgium

To investigate the influence of short chain branches in the crystallization of high molecular weight polyethylene (PE) we adapted a united monomer model for molecular dynamics simulations. We showed recently that a small fraction of branches allows to control the lamellar thickness in the semicrystalline structures [*Macromol* 55 (2022) 8434]. This work is extended to bidisperse mixtures of highly entangled C₄₀₀₀ and C₄₀₀ with different branch distributions mimicking industrial PE morphologies. A self-seeding protocol is presented which allows to simulate the growth of well aligned lamella, and analyse morphological features. We thank TotalEnergies for funding and GENCI/IDRIS (Orsay) and CAIUS/HPC centre (Strasbourg).

CPP 19.4 Tue 10:30 MER 02

Crystallization precursors in polymer melt analyzed by machine learning — •ATMIKA BHARDWAJ^{1,2}, MARCO WERNER¹, and JENS-UWE SOMMER^{1,2} — ¹Leibniz-Institut für Polymerforschung Dresden e. V., Hohe Str. 6, D-01069 Dresden, Germany — ²Institute for Theoretical Physics, Technische Universität Dresden, Zellescher Weg 17, D-01069 Dresden, Germany

Crystallization in polymers is a long-standing problem in both experimental and theoretical polymer science. The transition dynamics occurring in an under-cooled polymer melt is a local environmental phenomenon rather than a property of individual particles (or monomers) and depends on subtle conformation patterns such as entanglements between the chains. We develop machine learning (ML) methods to study this non-equilibrium thermodynamic process. Upon recognizing the relevant parameter set to explore different phases during polymer crystallization, we investigate the spatial and temporal patterns of the precursor states that determine the nucleation sites. The objective is to recognize the precursors that stimulate crystal growth before the occurrence of such development.

CPP 19.5 Tue 10:45 MER 02

How entanglements determine the morphology of semicrystalline polymers — ZEFAN WANG, MAREEN SCHALLER, ALBRECHT PETZOLD, KAY SAALWÄCHTER, and •THOMAS THURN-ALBRECHT — Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06099 Halle

Crystallization of polymers from entangled melts generally leads to the formation of semicrystalline materials with a nanoscopic lamellar morphology. Controlling this structure is key to the rational design of thermoplastic materials, but there is no consensus yet on the factors that control the thickness of the amorphous layers and therefore together with the crystal thickness the crystallinity. We here elucidate the effect of entanglements on the morphology in a series of model blends of high-molecular-weight polymers with unentangled oligomers leading to a reduced entanglement density in the melt as characterized by rheological measurements. Small-angle X-ray scattering experiments after isothermal crystallization reveal a reduced thickness of the amorphous layers, while the crystal thickness remains largely unaffected. A simple yet quantitative model without adjustable parameter is suggested, according to which the measured thickness of the amorphous layers adjusts itself in such a way that the entanglement concentration reaches a specific maximum value.

CPP 19.6 Tue 11:00 MER 02

Modelling Study of Reinforcement and Crack Formation in Strain-Crystallizing Elastomer Networks — •LENA TARRACH¹, REINHARD HENTSCHKE¹, and JAN WEILERT² — ¹Bergische Universität Wuppertal, Wuppertal, Germany — ²Covestro Deutschland AG, Leverkusen, Germany

A coarse-grained model has been developed to simulate reinforcement and crack formation in strain-crystallizing elastomer networks. This work is based on the model for strain-induced crystallization (SIC) proposed by Plagge and Hentschke [1], which here is extended for the investigation of rupture.

Generally, strain-crystallizing elastomer networks possess a higher tensile strength than non-crystallizing networks. Therefore, the force on the links, i.e. the polymer chains in the model network, is analyzed to define a critical force for their rupture. It is examined how structural parameters and parameters for the free energy of semi-crystalline links affect the tensile strength of strain-crystallizing networks compared to non-crystallizing networks. The variation of these parameters does not improve the tensile strength in both the 2D- and the 3D-case.

Thus, a critical crystallinity, which makes certain links unbreakable, is introduced to model the alignment of the polymer backbones along the stretching direction. The tensile strength of 2D- and 3D-networks is enhanced.

[1] Plagge, J. & Hentschke, R. Microphase Separation in Strain-Crystallizing Rubber. *Macromolecules* 54, 5629-5635. <https://doi.org/10.1021/acs.macromol.1c00757> (2021).

15 min. break

CPP 19.7 Tue 11:30 MER 02

New experimental setup to analyze structure formation in thermoplastic polymer melts — ●ANNA KATHARINA SAMBALE¹, ERIC EUCHLER¹, REGINE BOLDT¹, KAI UHLIG¹, LAURA NEUMANN¹, KONRAD SCHNEIDER¹, MATTHIAS SCHWARTZKOPF², STEPHAN ROTH^{2,3}, and MARKUS STOMMEL^{1,4} — ¹Leibniz-Institut fuer Polymerforschung, Dresden, Germany — ²Deutsches Elektronen Synchrotron DESY, Hamburg, Germany — ³KTH Royal Institute of Technology, Stockholm, Sweden — ⁴Technical University Dresden, Dresden, Germany

The microstructure of semi-crystalline thermoplastics is significantly influenced by the processing procedure and its parameters. Inhomogeneous shear and extensional flow fields occurring during processing can cause constraints to the chain conformations, which in turn lead to altered crystallization behavior. Although the influence of crystallization kinetics on the properties of the most commonly used polymers is considered to be sufficiently known, (local) conditions and parameters in commercially used melt processing technologies are not fully understood. We recently started to develop a new experimental setup to study structure formation in polymers induced by melt processing. The first results on the crystallization processes in quiescent polymer melts under isothermal conditions investigated by X-ray scattering measurements will be presented. In particular, time- and temperature-dependent crystallization of polylactic acid (PLA) and isotactic polypropylene (iPP) with different crystallization rates were examined and proved the concept of the experimental setup.

CPP 19.8 Tue 11:45 MER 02

The missing billions in hard sphere nucleation — SAHANA KALE, NIDHI JOSHI, and ●HANS JOACHIM SCHÖPE — Universität Tübingen, Institut für angewandte Physik, Auf der Morgenstelle 10, 72076 Tübingen

Crystal nucleation in colloidal hard spheres is a longstanding research topic in colloidal science. Light scattering experiments as well as simulations have been carried out to determine key parameters characterizing the nucleation process and to get a microscopic picture of the fluid to crystal transformation. In these studies, results both differ and agree with each other. It is still unclear whether the large disagreement in the nucleation rate densities between the experiments and simulations are of physical nature or result from different data analyses. Using laser-scanning confocal microscopy and polarization microscopy we study crystal nucleation in colloidal hard spheres. The used systems have been characterized with extreme care to allow for meaningful comparison with other experiments and simulations. We present high quality data of the nucleation rate density and key parameters describing crystal nucleation. Analyzing the nucleation process we conclude that classical nucleation theory fails.

CPP 19.9 Tue 12:00 MER 02

Non-metallic quasicrystals minimize sphere packing energy — ●MARTIN DULLE¹, VLADISLAVA FOKINA¹, THOMAS GRUHN², and STEPHAN FÖRSTER¹ — ¹Forschungszentrum Jülich, Jülich, Germany — ²Universität Bayreuth, Bayreuth, Germany

Quasicrystals are a peculiar state of order, which is fundamentally different from classical ordered crystalline states. Discovered in 1982 for metal alloys, they have in recent years also been reported for an increasing number of non-metallic materials.

Using MD-simulations we calculate the phase diagram of soft repulsive core/shell particles and find stability regions for seven different octagonal, decagonal, dodecagonal and icosahedral quasicrystals. We compare the structure and stability region of the dodecagonal phase with experiments on different polymer and nanoparticle systems and find quantitative agreement. We identify a new high density dodecagonal phase in a large number of reported non-metallic quasicrystalline systems including polymers, mesoporous silica, surfactants, BaTiO₃, TaTe and MnCrNiSi. All remaining reported non-metallic quasicrystals can be related to the other simulated quasicrystal types.

We geometrically derive all respective tilings and show how in-plane quasicrystalline order is combined with axial periodic order via the realization of certain gyro-elongated bipyramids. This geometrical arrangement minimizes sphere packing energy for certain length scale ratios and particle densities, irrespective of the absolute length scale, the type of interactions and chemical constituents.

CPP 19.10 Tue 12:15 MER 02

Controlling internal structure of colloidal supraparticles

- crystalline to amorphous — ●YASHRAJ WANI¹, MELIS YETKIN², MICHAEL KAPPL², HANS-JÜRGEN BUTT², and ARASH NIKOUBASHMAN¹ — ¹Institute of Physics, JGU Mainz, Germany — ²Max Planck Institute for Polymer Research, Mainz, Germany

Colloidal supraparticles made from smaller nanoparticles (NPs) are versatile materials whose properties can be tailored through the chemistry and ordering of their constituent NPs. Such supraparticles can be scalably fabricated using solvent-drying processes that assemble NPs inside liquid droplets. In charge stabilized dispersions, the interactions can be controlled by the salt concentration, which we systematically probed in experiments and simulations. In experiments at low salt concentrations, the dried supraparticles exhibited high crystalline order, whereas amorphous structures were found at high salinity. To understand this evaporation-induced structure formation, we first determined the interaction potentials between NPs via colloidal probe atomic force microscopy and dynamic light scattering experiments. Using these pair potentials, we carried out particle-based simulations to study the aggregation behavior in detail: At low salt concentrations, the effective NP-NP interactions remained purely repulsive until the end of drying, resulting in highly crystalline supraparticles. At higher salt concentrations, however, the electrostatic repulsion became screened, leading to the formation of small NP aggregates at early stages of drying, which then eventually merged into an amorphous supraparticles.

CPP 19.11 Tue 12:30 MER 02

Unravelling the synthesis of halide perovskite nanoplatelets by SAXS — ●KILIAN FRANK¹, CAROLA LAMPE², ALEXANDER S. URBAN², and BERT NICKEL¹ — ¹Soft Condensed Matter Group and CeNS, Faculty of Physics, LMU Munich — ²Nanospectroscopy Group and CeNS, Nano-Institute, Faculty of Physics, LMU Munich

Halide perovskite nanoplatelets (NPLs) are a promising material for optoelectronic applications, such as LEDs and single photon emitters. While highly scalable and reliable ligand-assisted synthesis routes exist, a detailed structural understanding of the underlying pathways is lacking. We elucidate the processes of nucleation, growth, and superstructure assembly of CsPbBr₃ NPLs using in situ small-angle X-ray scattering (SAXS), total scattering (TS) and photoluminescence (PL) spectroscopy during the synthesis. Thereby we enable even better control of the platelet thickness on the monolayer level, and therefore of the emission wavelength, due to quantum confinement. For this purpose we built and used a specialized reaction cell for in situ synthesis at the beamlines P07 and P62 (PETRAIII, DESY, Hamburg). By SAXS analysis we follow the assembly of the constituents into a regular superstructure. In addition, we investigated the effect of post-synthetic treatment of the NPLs using the same setup to further enhance their optoelectronic properties. With our results we contribute to the development of assembly-based synthesis routes for size-tunable nanomaterials. Such materials are of particular interest to the perovskite community as building blocks for hierarchical structures.

CPP 19.12 Tue 12:45 MER 02

From protein adsorption to crystallization: a simultaneous real-time QCM-D and microscopy study — ●HADRA BANKS, FURIO SURFARO, SIMON STORZ, ANNA MAISCHBERGER, CARA BUCHHOLZ, KAI-FLORIAN PASTRYK, ALEXANDER GERLACH, and FRANK SCHREIBER — University of Tübingen, Germany

Protein crystallization is widely investigated by employing a homogeneous nucleation approach; however, it is predicted that heterogeneous nucleation is energetically more favorable [1]. Nevertheless, only few experimental studies on the nucleation of protein crystals at surfaces are available, since this is a complex phenomenon and requires surface-sensitive techniques. Here, quartz crystal microbalance with dissipation monitoring (QCM-D), a real-time surface-sensitive technique, was employed simultaneously with optical microscopy to investigate protein adsorption and crystallization at a negatively charged surface. Human serum albumin (HSA) and β -lactoglobulin (BLG), in the presence of a trivalent salt, were used as model systems for the study of heterogeneous nucleation [2]. We found that their surface behavior during crystallization exhibit complex phenomena such as wetting transition, enhanced adsorption, and layer rearrangements. The results highlight the importance of the interaction between proteins and surfaces and how this can influence protein phase behavior.

[1] J. R. Espinosa et al., *Soft Matter* 15 (47), 9625-9631, 2019

[2] O. Matsarskaia et al., *ChemPhysChem* 21 (16), 1742-1767, 2020