CPP 9: Crystallization, Nucleation and Self-Assembly II

Time: Monday 15:00–17:15   Location: H 2032

CPP 9.1   Mon 15:00   H 2032

Branches, Tie Chains and Entanglements in Bimodal Polyethylene Single Crystals under Uniaxial Tensile Strain — WILLIAM S. FALL[1], JÖRG BASCHNAGEL[2], and •HENDRIK MEYER[2] — [1]Laboratoire de Physique des Solides - UMR 8502, CNRS, Université Paris-Saclay, 91405 Orsay, France — [2]Institut Charles Sadron - UPR22, CNRS, Université de Strasbourg, France

Short chain branched, bimodal polyethylene resins are relatively resistant to failure, due to their base material strength, when compared to other unimodal or linear compounds. The relationship between molecular level architecture and the mechanical properties of bimodal, branched PE resins is however relatively poorly understood. Using coarse-grained molecular dynamics simulations and a united-monomer model of PE, single well-aligned multi-lamella PE crystals are grown [1], using self-seeding and drawn to mimic uniaxial tensile testing. During deformation, the crystallinity, tie-chain and entanglement content are continuously monitored and correlated with the stress-strain curves obtained and mechanical properties. In addition, the dependence of all metrics on the rate of deformation and direction of drawing are also investigated, such a study is only possible due to the well-aligned PE crystals utilized here [1]. The elastic modulus of well-aligned PE crystals is strongly dependent on the direction of deformation. In the equivalent multi-domain systems, grown by continuous-cooling, such trends are almost completely hidden.

[1] Fall, W. S.; Baschnagel, J.; Benzerara, O.; Lhost, O.; Meyer, H. ACS Macro Letters 2023, **12**, 808-813.

CPP 9.2   Mon 15:15   H 2032

n-Alkanes on graphite-like substrate: Flat-histogram Monte Carlo investigation of prefreezing — •TIMUR SHAKIROV — University of Halle, Halle, Germany

In this investigation, we explore the prefreezing phenomenon [1], characterized by the formation of a thermodynamically stable thin frozen layer in polymer melts on substrates, occurring at temperatures above the bulk crystallization temperature. We consider short n-alkanes [2] in contact with graphite-like substrates. Employing flat-histogram Monte Carlo simulations [3,4], we analyze the influence of the interaction strength between the polymer and the substrate with a graphite-like lattice structure. Our research estimates the prefreezing temperature's dependence on the substrate-polymer attraction strength, providing a possibility to determine the minimal interaction threshold for prefreezing and estimating its asymptotic behavior at extremely strong attraction. The flat-histogram techniques enable a model-independent estimation of the system's free energy landscape. The outcomes of this study are compared against phenomenological theory [1] of prefreezing transition.

[1] O. Dolynchuk, M. Tariq, T. Thurn-Albrecht, J. Phys. Chem. Let. 10 (2019) 1942-1946.

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

[3] F. Liang et al, J. Am. Stat. Assoc. 102 (2007) 305-320.

[4] T. Shakirov, Comp. Phys. Commun. 228 (2018) 38-43.

CPP 9.3   Mon 15:30   H 2032

How to distinguish crystal symmetries in coarse-grained computer simulations of polymer crystallization in melts? — •EVGENIIA FILIMONOVA, TIMUR SHAKIROV, and VIKTOR IVANOV — Martin-Luther-University Halle-Wittenberg, Halle (Saale), Germany

We report on our recent developments in comprehensive analysis of crystalline structures arising during crystallization in polymer melts. Using flat histogram Monte Carlo simulations of a coarse-grained model, we obtain a very large number of (partially) crystalline conformations for low energies. We faced with the problem of distinguishing between different crystalline symmetries using the traditional well-known analysis based on bond order parameters, first suggested by Steinhardt and later improved by many authors, especially due to thermal noise. Additionally, some deformations of symmetries appear to be caused by inavoidable finite size effects. We have developed a new approach to calculate the bond order parameters using improved averaging of coordinates of particles, including a new method for visualization of local crystalline ordering on small scales. As a result, we were able to observe the coexistence of domains with different local crystalline symmetries, which had not previously been reported in the literature.

CPP 9.4   Mon 15:45   H 2032

Nucleation patterns of polymer crystals analyzed by machine learning models — •ATMIKA BHARDWAJ[1,2], JENS-UWE SOMMER[1,2], and MARCO WERNER[1] — [1]Institut Theorie der Polymere, Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Strasse 6, 01069 Dresden, Germany — [2]Institute für Theoretische Physik, Technische Universität Dresden, Zellescher Weg 17, 01062 Dresden, Germany

We employ unsupervised machine learning algorithms to investigate conformation patterns during polymer crystallization from undercooled melts using simulation data obtained from coarse grained molecular dynamics simulations. Our focus is on data-driven techniques that establish decision boundaries to detect the crystalline state of individual monomers without any prior knowledge, as opposed to classical methods that position these boundaries based on the analysis of stem length distributions [C. Luo and J.-U. Sommer, *Macromolecules* **44** (2011), 1523]. We utilize self-supervised auto-encoders to compress local conformation fingerprints of individual monomers. We show that the compressed fingerprints are organized in a lateral map that can be associated with the degrees of conformation and orientation order in the monomer's environment. The Gaussian mixture model allows to distinguish the crystalline from the amorphous phase by identifying a dense region within that map that reflects the reduced degrees of freedom. The high specificity of the method allows us to uncover the intricate temporal patterns related to crystalline order, even before any clear indications of the transition became evident in thermodynamic properties, such as specific volume.

15 min. break

CPP 9.5   Mon 16:15   H 2032

Influence of Cross-Linking and Deformation on Polymer Crystallization and Melting — HUZAIFA SHABBIR[1], MICHAEL LANG[1], •MARCO WERNER[1], and JENS-UWE SOMMER[1,2] — [1]Institut Theorie der Polymere, Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany — [2]Institute für Theoretische Physik, Technische Universität Dresden, Germany

We investigate the influence of the degree of cross-linking and deformation on polymer crystallization and melting behavior by means of molecular dynamics simulations. The crystallization and melting are carried out in constant strain conditions. Different properties such as specific volume, crystallinity, orientation order, and stress are studied as a function of temperature. These properties serve as key indicators, offering insights into both the microscopic and macroscopic behavior of the polymer system during the processes of crystallization and melting. Our simulation data confirms that deformation in the melt induces a pre-alignment of polymer chains in the direction of deformation, acting as a driving force for early crystallization in the deformed system. Additionally, we observe that higher degrees of deformation lead to an increase in stem length within the system, consequently higher temperatures are required for complete melting. The crystallinity exhibits an increasing and decreasing behavior in response to higher degrees of deformation and cross-linking, respectively. These findings have implications for tailoring material properties through controlled deformation and cross-linking, offering opportunities for the design of polymers with programmed mechanical response.

CPP 9.6   Mon 16:30   H 2032

Characterisation of the different polymorphs of syndiotactic polystyrene using data-driven methods — •ATREYEE BANERJEE[1], TRISTAN BEREAU[2], and JOSEPH F. RUDZINSKI[1,3] — [1]Max Planck Institute for Polymer Research, Mainz, Germnay — [2]Heidelberg University, Germany — [3]Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin

Syndiotatic polysterene (sPS) exhibits complex polymorphic behaviour, resulting in rugged free energy landscapes (FELs). Enhanced sampling methods have the potential to remedy to explore the rugged FEL with prior knowledge of collective variables (CVs) that can resolve the relevant transition pathways, typically identified through extensive physical or chemical expertise. Recently, data-driven methods have at-

tracted considerable attention for learning relevant CVs without significant a priori insight. In this work, we adapt an atomic representation used in machine learning to efficiently describe the local environment of sPS monomers. These descriptors do not require the incorporation of excessive system-specific intuition and demonstrate good transferability properties. We then investigate low-dimensional projections from methods of varying complexity: Principal Component Analysis (linear projection), Uniform Manifold Approximation, and Projection (manifold learning). These dimensionality techniques, in conjunction with clustering, provide physically meaningful polymorphic states.

CPP 9.7 Mon 16:45 H 2032

Investigating the Crystallization Behavior of Polymer Nanocomposites Through Molecular Dynamics Simulations — •Hailong Yu[1,2] and Jens-Uwe Sommer[1] — [1]Leibniz-Institut für Polymerforschung Dresden, Hohe Strasse 6, 01069 Dresden, Germany — [2]State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, 201620, Shanghai, China

Using molecular dynamics with the CG-PVA model [C. Luo and J.-U. Sommer, Computer Physics Communications 2009, 180, (8), 1382-1391] and primitive path analysis, we explored the crystallization of polymer nanocomposites with varied nanoparticle concentrations. Three systems, all employing repulsive potentials but differing in the number of nanoparticles, were examined within a matrix of long polymer chains. During crystallization, it was observed that nanoparticles migrated into interlamellar regions, aligning with the amorphous phase, as evidenced by the radial distribution function (RDF) analysis. This suggests not only the spatial confinement of nanoparticles but also their displacement from PVA's crystalline domains. These results are in agreement with recent experimental observations [K. Bornani et al., ACS Macro Letters 2022, 11, (6), 818-824]. The pure system, devoid of nanoparticles, exhibited higher crystallization temperatures and crystal ratios than nanocomposite counterparts, with consistently lower entanglement lengths during both crystallization and melting. These results show nanoparticles' crucial impact on polymer crystallization, affecting thermal behavior and structure.

CPP 9.8 Mon 17:00 H 2032

Atomic imaging of the critical nucleus size of multilayer hexagonal ice growth — •Dong Guan, Tiancheng Liang, Zixiang Yan, Li-Mei Xu, En-Ge Wang, and Ying Jiang — International Center for Quantum Materials, School of Physics, Peking University, Beijing 100871, China

Multilayer water ice growth is widespread and plays a significant role in various natural phenomena. An essential aspect of water ice growth is the elusive nature of the critical ice nucleus, attributed to its transient and delicate characteristics. We present the precise atomic size of the critical ice nucleus in hexagonal water ice (ice Ih) through the utilization of qPlus-based cryogenic noncontact atomic force microscopy (NC-AFM) equipped with a CO-terminated tip. Freezing samples during the growth process allows us to capture the intermediate structures involved in the growth of Ih ice. Our investigation reveals that pentamers and hexamers are the most prevalent intermediate structures, and their combination gives rise to the 3-5 cluster, which we define as the critical ice nucleus. Combined with density functional theory, we might show that the structure alteration of the 3-5 cluster results in the formation of a new core for Ih ice. This new core can expand by incorporating additional water molecules along its periphery. This research is the first achievement in elucidating the exact atomic structure of a critical ice nucleus in water. It provides valuable insights into the water freezing process and holds the potential for application to other nucleation processes.