MAR12-2011-000595

Abstract for an Invited Paper
for the MAR12 Meeting of
the American Physical Society

Understanding entangled polymers: What we can learn from athermal chain packings[1]

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The study of random and ordered packings (from atoms and colloidal particles to sand grains) has been the focus of extensive research. This is not surprising since an understanding of the mechanisms that control morphology and packing is the key to the design and synthesis of novel "smart" materials and functionalities. In particular, the study of packings of chain molecules presents challenges but also insights which are absent in monatomic systems and further allows for a direction comparison with them. In this contribution we give an overview of our work on very dense and nearly jammed packings of athermal polymers. We show that chain molecules can be as efficiently and as densely packed as monatomic analogs up to the same maximally random jammed state. We also show that an exact correspondence can be established between the statistical-mechanical ensembles of packings of monatomic, and chain systems, which yields insights on the universality of jamming. By studying the effect of concentration on polymer size and on the underlying network of topological hindrances we precisely identify the distinct universal scaling regimes and the corresponding exponents. An unsuspected connection, valid from dilute up to very dense assemblies, is established between knots (of intermolecular origin) and entanglements (intermolecular constraints). We finally show that, against expectations, entropy-driven crystallization can occur in dense systems of athermal polymers once a critical volume fraction is reached. Such phase transition is driven by the increase in translational entropy: ordered sites exhibit enhanced mobility as their local free volume becomes more spherical and symmetric. Incipient nuclei develop well defined, stack-faulted layered crystal morphologies with a single stacking direction. The ordering transition and the resulting complex morphologies are analyzed, highlighting similarities and differences with respect to monatomic crystallization.

[1]We acknowledge support by the Spanish Ministry of Science and Innovation (MICINN) through project "Ramon y Cajal" and by MICINN and Comunidad de Madrid through project "I3."