Effect of Chain Stiffness on Phase Behaviour of Hard-Sphere Polymer Packings

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Abstract:

We study, at the atomic level, the packing efficiency and phase behaviour of athermal, linear semiflexible polymers of tangent hard spheres in bulk 3-D systems. We employ extensive Monte Carlo (MC) simulations [1] at progressively increased concentrations adopting the hard-sphere model to represent interactions between monomers. Chain stiffness is controlled by a tuneable potential for the bending angles whose intensity dictates the rigidity of the polymer backbone. At very high values of bending intensity, the polymer model approaches that of freely-rotated chains and bending angles sample the whole range from acute to obtuse angles, reaching the limit of rod-like polymers. We study how packing density, chain length and stiffness affect the phase transition from initially disordered (random) to ordered (crystal) local and global structures in dense polymer packings and compare against fully flexible chains and monomeric counterparts [2]. To gauge local order, we employ the characteristic crystallographic element (CCE) norm, a descriptor, which can detect and quantify, with high precision, similarity to reference crystals in general atomic and particulate systems [3,4]. Results reveal that for a given volume fraction chain stiffness significantly affects the total degree of crystallinity and the observed ordered morphologies which consist of hexagonal close packed (HCP) and face centred cubic (FCC) crystallites. Additionally, the inherent bending stiffness dictates the regime where the system transits from the initially amorphous to the stable, crystal phase.

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[4] P. Ramos, M. Herranz, K. Foteinopoulou, N. C. Karayiannis and M. Laso, *Crystals* **10**, 1008 (2020).

Biography of presenting author (should not exceed 100 words)

Daniel Martínez-Fernández studied Chemical Engineering at the Universidad Politécnica de Madrid (UPM), Spain (BSc 2018, MSc 2020). For his Master's Degree project, he joined the research group of the Laboratory of Simulation of Materials, led by Manuel Laso and Nikos Karayiannis, at the Institute for Optoelectronic Systems and Microtechnology (ISOM). Currently, he is doing his doctorate research studies at the same institution (2019–, UPM, Spain).

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