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Abstract

Entropy-Driven Phase Transition of Semiflexible Hard-Sphere Polymer Packings in Two and Three Dimensions †

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We study, at the atomic level, the behaviour of athermal, linear semiflexible polymers of tangent spheres in thin films of one-layer thickness (2-D systems) and bulk 3-D systems. We employ extensive Monte Carlo simulations [1] at progressively increased concentrations adopting the hard-sphere model to represent interactions between monomers. Extreme, plate-like confinement for thin films is realized through the presence of flat, parallel walls in one dimension with the inter-wall distance being equal to the diameter of the spherical 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 entropy-driven phase transition from initially disordered (random) to ordered (crystal) local and global structures in dense polymer packings in 2-D and 3-D systems 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]. In all cases, we identify the critical volume fraction for the phase transition and gauge the established crystal morphologies.

References

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