Effect of bond tangency/gap on the phase behaviour of athermal polymer packings

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Abstract
We present results from extensive Monte Carlo simulations on dense and nearly-jammed packings of chains of hard spheres of uniform size [1]. Through a robust chain-connectivity-altering algorithm we are able to simulate chain lengths of 1000 spheres within modest computational time. Local environment and similarity to specific crystal structures are gauged through the crystallographic element norm (CCE) metric [2]. We study the role of bond constraints on the packing efficiency and structural characteristics of polymer assemblies: by increasing the bond tolerance (bond gaps) we observe accelerated crystal nucleation and growth which in turn lead to a wealth of ordered morphologies [3]. In their majority crystals structures with bond gaps are significantly different from the random hexagonal close packing which prevails in the strict tangent limit [4,5]. In general, bond tangency shifts the occurrence of the phase transition to higher packing densities compared to monomers [6] and to chains with bond gaps. Based on these findings using simple geometric arguments we explain the role of rigid and flexible constraints in the phase behavior of general atomic and particulate systems.

References


Figures

Figure 1: System snapshot of 54-chain hard sphere system of average chain length \( N = 1000 \) with bond gaps. Hcp- and fcc-like spheres are shown in blue and red, respectively. Sites with fivefold local symmetry are shown in green.