Crystallization and Glass Transition of Polymers Interacting with the Square-Well Potential

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Crystallization in general atomic and particulate systems is of paramount importance in the development of novel materials with enhanced characteristics. Its understanding, especially at the molecular level, is thus critical to connect atomic structure with the macroscopic behaviour of the end material. Despite of its relevance and the ever-growing body of published literature, there are still numerous unsolved questions around the crystallization of complex macromolecular systems, especially since chain crystals are formed under special processing conditions and confer unique properties to the corresponding systems. In the present work, we employ Monte Carlo simulations to study the phase behaviour of linear, freely jointed chains whose spherical monomers interact through the pair-wise Square Well (SW) potential [1]. Compared to the typical, excluded-volume, Hard Sphere (HS) model, the SW potential allows the systematic study of how intensity and range of interactions affect the phase behaviour. A wide variety of different structures are obtained by varying the model parameters: from amorphous clusters to well-ordered ones, consisting of virtually perfect FCC, HCP, HEX and BCC crystals. When critical values of both interaction parameters are met, clusters form fivefold-rich local structures leading effectively to vitrification. We further study the cluster formation under dilute conditions and the short- and long-range structure of polymer chains. Present results allow the systematic comparison between the energy-driven crystallization in SW systems and entropy-driven crystal nucleation of athermal polymers [2] and the behaviour of chemically more complex macromolecules [3]. Such insights can help the design of novel colloidal and granular polymers with short-range attraction.

REFERENCES

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[2] Karayiannis, N.C; Foteinopoulou K; Laso M. Entropy-driven crystallization in dense systems of athermal chain molecules. Phys Rev Lett. 2009;103(4):045703.
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FIGURES

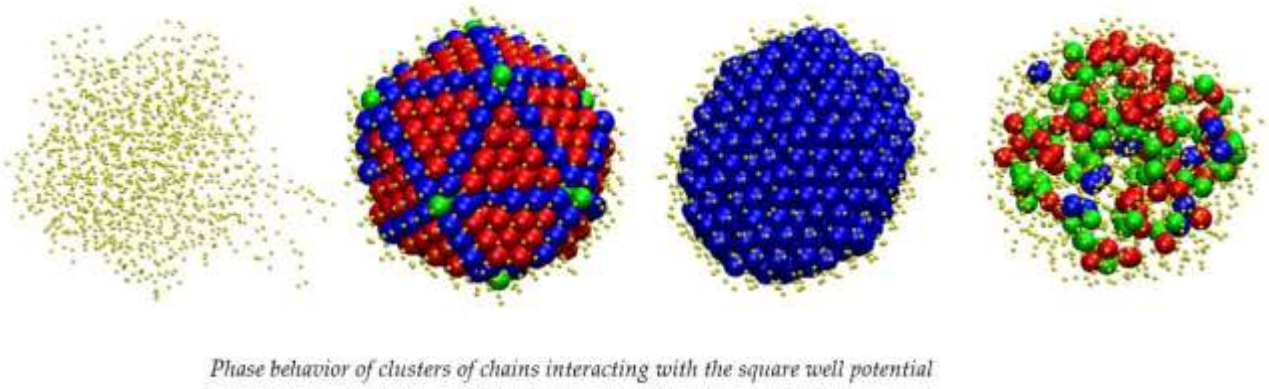

Figure 1: Snapshots of several system configurations at the end of the simulations. Monomers are color-coded according to its similarity to given crystal structures.