Entropy-driven phase transition in dense packings of athermal chain molecules

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Abstract

The random or ordered packing of objects has been in the spotlight of research since early times. How spheres, cubes, disks, whether oranges, candies or molecules, stack up when poured into a vessel is an intriguing problem with a wide range of practical applications in colloids, engineering, biology, materials and polymer science. Hard spheres constitute the simplest, nontrivial model which captures interactions based exclusively on the concept of excluded volume; as such it is amenable to analytic approaches. Simulations on crystallization in monomeric hard-sphere packings were first presented back in 1950s in the works of Wood and Jacobson [1] and Alder and Wainwright [2]. Given that athermal systems do not incur into energetic gains or penalties upon configurational transitions, entropy is the driving force for phase transition (crystallization) [3,4]. It is now well established that given sufficient time, crystal nucleation and growth can be naturally observed in monomeric hard-sphere assemblies at all packing densities above the melting point [5].

While the disorder-order transition and the corresponding crystal nucleation and growth are readily observable in simulations of monoatomic hard spheres the modeling of the corresponding process in dense packings of hard-sphere chains (macromolecules) remained, until recently, elusive. Whether the chain connectivity and the related holonomic constraints completely halt, partially frustrate or even do not affect at all, athermal crystallization remained a controversial topic.

In the present contribution we employ extensive Monte Carlo (MC) simulations, based on chain-connectivity-altering algorithms, to generate and successively equilibrate random (disordered) packings of freely-jointed chains of tangent hard spheres of uniform size [6]. Through this modeling approach thousands of statistically uncorrelated configurations of the simulated chain systems are generated at concentrations ranging from very dilute up to the close vicinity of the maximally random jammed (MRJ) state [7] within modest computational time [8].

The degree of ordering (crystallization) is monitored by means of the characteristic crystallographic element (CCE) norm [9], a strictly monotonic and structure-discriminating measure of order based on the point symmetry group of the local environment of a site. The CCE norm has been shown to sensitively and quantitatively detect changes in local ordering, while identifying the emerging ordered structure with high specificity [9]. Once applied to the athermal polymer packings the CCE norm revealed that in the absence of any external influence the hard-sphere chains were observed to systematically and spontaneously crystallize at all packing densities above 0.56 [10]. Furthermore, the observed phase transition appears to be insensitive to variations in chain length and polydispersity, and the crystallinity of the established stable phase increases with increasing concentration [11].

By far the most salient feature of the crystal polymer structures is the presence of a randomly stack-faulted, layered morphology with a single stacking direction (Fig. 1). Thus, incipient nucleus consists of parallel, two-dimensional layers of either hexagonal close packed (hcp) or face center cubic (fcc) character in random alternation.

To understand better the driving mechanism and the entropic origins of the phase transition we study the rearrangement of local free volume around each site. Here, local density is determined as the reciprocal of the volume of the corresponding Voronoi polyhedron. It is shown that local free volume becomes more spherical and more symmetric through the phase transition. In turn, ordered sites are able to explore their local vicinity more efficiently increasing their mobility. Thus, there is a significant increase in translational entropy which drives the nucleation and growth of crystals.

Finally, we discuss some recent simulation findings on the effect of the intensity of the holonomic constraints (here in the form of bond lengths) on the ability of chains to crystallize at packing densities near the melting transition.

Current insights from athermal polymer crystallization can shed light on the role of entropy in chemically more complicated phenomena like protein folding and crystallization in the bulk and under confinement.

References

[1] W. W. Wood and J. D. Jacobson, J. Chem. Phys. **27** (1957) 1208.
[2] B. Alder and T. Wainwright, J. Chem. Phys. **27** (1957) 1208.

[3] L. Onsager, Ann. N. Y. Acad Sci. **51** (1949) 627.
[4] D. Frenkel, H. N. W. Lekkerkerker and A. Stroobants, Nature **332** (1988) 822.
[5] M. D. Rintoul and S. Torquato, Phys. Rev. Lett. **77** (1996) 4198.
[6] N. C. Karayiannis and M. Laso, Macromolecules **41** (2008) 1537.
[7] S. Torquato, T. M. Truskett and P. G. Debenedetti, Phys. Rev. Lett. **84** (2000) 2064.
[8] N. C. Karayiannis and M. Laso, Phys. Rev. Lett. **100** (2008) 050602.
[9] N. C. Karayiannis, K. Foteinopoulou and M. Laso, J. Chem. Phys. **130** (2009) 074704.
[10] N. C. Karayiannis, K. Foteinopoulou and M. Laso, Phys. Rev. Lett. **103** (2009) 045703.
[11] N. C. Karayiannis, K Foteinopoulou, C. F. Abrams and M. Laso, Soft Matter **6** (2010) 2160.

Figures
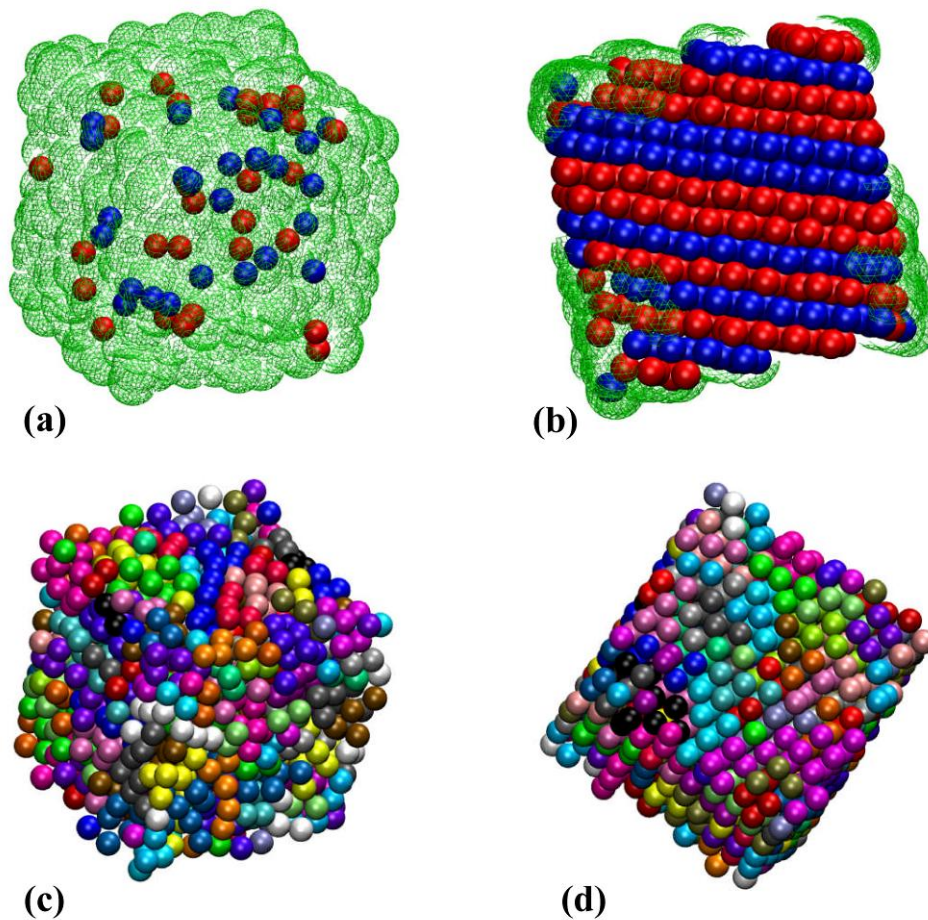
Figure 1. System configurations at (a) early stage of simulation (amorphous packing), and (b) late stage where the majority of sites possess a highly ordered local environment. Blue and red colored spheres correspond to sites with fcc-like and hcp-like local order, respectively. (c) and (d) same as in (a) and (b) but all sites are colored according to the parent chain [10].