Bond disorder, frustration and polymorphism in the spontaneous crystallization of a polymer melt

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ABSTRACT

The isothermal, isobaric spontaneous crystallization of a supercooled polymer melt is investigated by molecular-dynamics simulation of an ensemble of fully-flexible linear chains. Frustration is introduced via two incommensurate length scales set by the bond length and the position of the minimum of the non-bonding potential. Marked polymorphism with considerable bond disorder, distortions of both the local packing and the global monomer arrangements is observed. The analyses in terms of: i) orientational order parameters characterizing the global and the local order and ii) the angular distribution of the next-nearest neighbors of a monomer reach the conclusion that the polymorphs are arranged in distorted Bcc-like lattices.

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1. Introduction

Crystallization plays an important role in many areas of different scientific fields, ranging from biology to engineering and physics. Still, many microscopic details of the phenomenon are unknown, despite the abundance of related results both experimental and theoretical [1–11]. In particular, polymeric liquids are systems in which the structural features, namely the chain connectivity, cause serious hindrance to the homogeneous crystallization of the sample. In silico simulations of such systems provide great insight on this problem and have proven to be an invaluable tool in the analysis of the crystallization under controlled conditions [3]. Many simulations have been performed aiming at observing the crystallization of polymers and characterizing the structural order reached by the crystalline sample under various conditions [12–20]. Recently, Monte Carlo (MC) simulations of polymer melts made by linear chains of tangent hard-sphere monomers [21–23], i.e. with bond length *equal* to monomer diameter, have been performed to study spontaneous crystallization. The resulting crystallized structures have been interpreted as a distribution of the most densely packed structures:

face-centered cubic (Fcc) and hexagonal close packed (Hcp) lattices. Hcp and Fcc were selected as ideally ordered structures because they are known to be the primary competing alternatives in dense systems of hard spheres in the presence of a single length scale [21]. MC simulations, differently from Molecular Dynamics (MD) simulations, may fail to account for the arrest into metastable intermediate phases [22] which hinder the evolution towards the thermodynamically stable phase [24]. MD simulations of a polymer melt of chains with soft monomers, promoting the crystallization by equal bond length and equilibrium non-bonded separation, have been performed with the aim of comparing the crystalline structures obtained by cooling down to zero temperature with the highly packed Fcc and Hcp lattices [25,26]. Still, the route towards the closest packing of polymers is hindered by allowing length-scale competition of the bonding and the non-bonding interactions, as recently proven in a MD study of the crystallization triggered by confinement due to Fcc walls, where structures similar to body-centered cubic (Bcc) are observed [27].

Polymorphism, the presence of different crystal structures of the same molecule, is a well-known phenomenon in molecular crystals [28]. In particle systems the crystal structure depends on the steepness of the repulsive part of the interacting potential with hard and soft repulsions favoring Fcc and Bcc ordering respectively [29]. To date, the selection mechanism of polymorphs is elusive. One widely used criterion is the Ostwald step rule, stating that in the course of transformation of an unstable, or metastable state, into a stable one the system does not go directly to the most stable

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conformation but prefers to reach intermediate stages having the closest free energy to the initial state [24,28,30,31]. Alternatives are reported [32].

In this work the isothermal *spontaneous* crystallization of an unbounded polymeric system is studied via MD simulation of *fully-flexible* linear chains, i.e. bond-bending and bond-torsions potentials are not present. The emphasis is on the global and local order of the crystalline phase with respect to the pristine supercooled liquid where crystallization started. To this aim, specific order parameters will be used for their characterization [33,34]. A distinctive feature of the model is the presence of two *different* length scales, namely the bond length b and the distance σ^* where the minimum of the non-bonding potential, the Lennard-Jones (LJ) pair potential, is located. It is known that the competition of two incommensurate length scales favors frustration in the self-assembly of ordered structures from an initial disordered state, like in molecular crystallization [35]. Frustrated crystallization of polymers has been reviewed [36]. The role played in the crystallization behavior (including its absence) by frustration, where there is an incompatibility between the preferred local order and the global crystalline order, has been highlighted [37]. We expect different responses to frustration from the putative crystalline structures at finite temperature, i.e. Fcc, Hcp and Bcc lattices. In fact, not all the atoms in the first neighbors shell of a Bcc lattice are at the same distance, as in the Fcc and Hcp lattices. It is known that the mechanical stability of the Bcc structure is lower than in closed packed structures as Fcc [29].

The paper is organized as follows: In Section 2 the polymer model is detailed and the simulation details are provided. The results are presented and discussed in Section 3. Finally, the conclusions are drawn in Section 4.
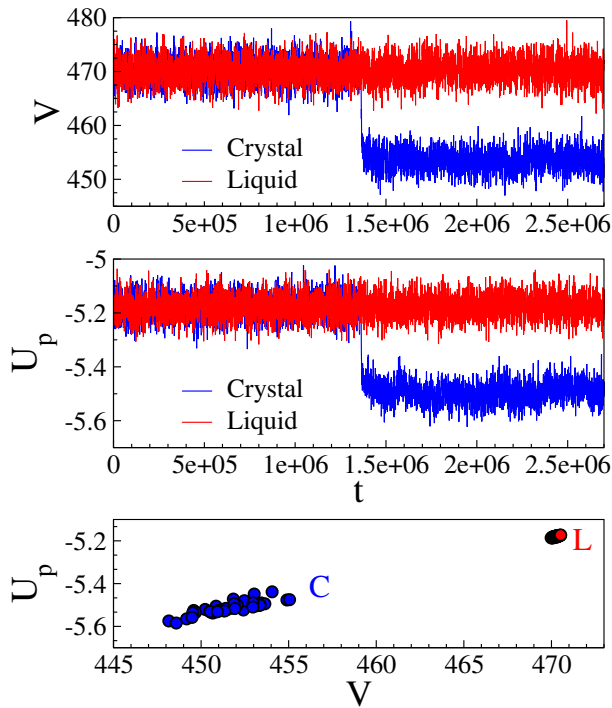
2. Methods

We consider a coarse-grained polymer model of $N_c = 50$ linear, unentangled chains with $M = 10$ monomers per chain. The total number of monomers is $N = 500$. The chains are fully-flexible, i.e. bond-bending and bond-torsions potentials are not present. Non-bonded monomers at distance r interact via the truncated Lennard-Jones (LJ) potential:

$$U^{LJ}(r) = \varepsilon \left[\left(\frac{\sigma^*}{r} \right)^{12} - 2 \left(\frac{\sigma^*}{r} \right)^6 \right] + U_{cut} \quad (1)$$

for $r \leq r_c = 2.5\sigma$ and zero otherwise, where $\sigma^* = 2^{1/6}\sigma$ is the position of the potential minimum with depth ε. The value of the constant U_{cut} is chosen to ensure that $U^{LJ}(r)$ is continuous at $r = r_c$. Henceforth, all quantities are expressed in terms of reduced units: lengths in units of σ, temperatures in units of ε/k_B (with k_B the Boltzmann constant) and time τ_{MD} in units of $\sigma\sqrt{m/\varepsilon}$ where m is the monomer mass. We set $m = k_B = 1$. The bonding interaction is described by an harmonic potential U^b [38]:

$$U^b(r) = k(r - r_0)^2 \quad (2)$$

The parameters k and r_0 have been set to $2500\varepsilon/\sigma^2$ and 0.97σ respectively [39]. Given the high stiffness of the bonding interaction, $b = 0.97 \pm 0.02$. Notice that the bond length and the minimum of the non-bonding potential are *different*, $b \neq \sigma^* \simeq 1.12$. Periodic boundary conditions are used. The study was performed in the *NPT*
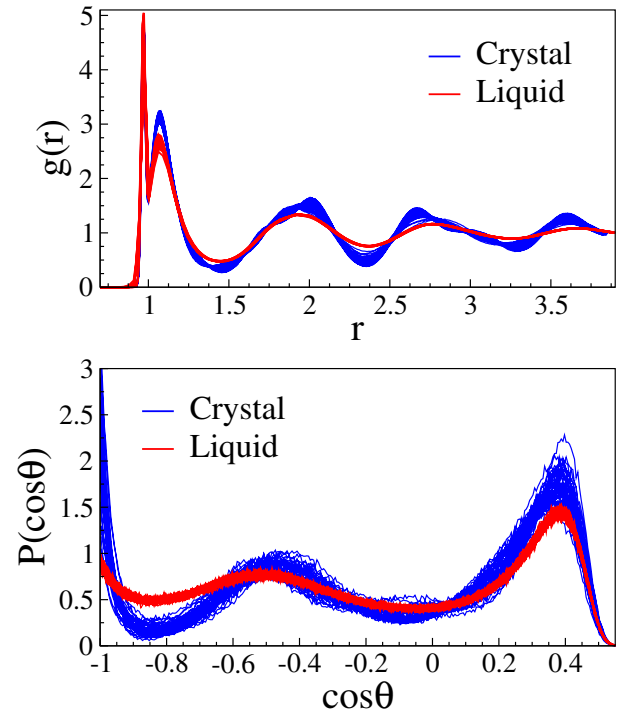

Fig. 1. Volume (top) and potential energy (middle) drops due to the spontaneous crystallization occurring in a single run (blue curve). They are compared to the typical fluctuations occurring in the metastable liquid (red curve). The bottom panel is a correlation plot between the average volume and the energy of all the crystalline (blue) and liquid (red) states under study. Note the large region spanned by the different crystalline states signaling polymorphism. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. Top: radial pair distribution function $g(r)$ of all the crystalline and liquid states. On increasing the distance r from the tagged central monomer, the first, sharp peak corresponds to the bonded monomers, whereas the other ones signal the different neighbor shells. Bottom: distribution $P(cos\theta)$ of the angle θ between adjacent bonds in a chain. The peaks occur at $\theta \approx 70°, 122°, 180°$, corresponding to three consecutive monomers which are folded - with the two non-consecutive monomers in contact $(r \sim \sigma^*)$ -, partially folded, and aligned, respectively [34]. Notice that the broad features of both $g(r)$ and $P(cos\theta)$ of the crystalline and the melt states are quite similar. Nonetheless, the ordered states exhibit sharper and, due to polymorphism, more widely distributed features than the disordered ones.