

Free-energy effects in single-molecule polymer crystals

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Abstract

The paper presents extensive MD simulations of the crystallization process of a single polyethylene chain with $N = 500$ monomers. It is shown that the folding process involves intermediate metastable crystalline states, in analogy with the experiments, and ends up in a equilibrated, i.e. not kinetically selected, lamella with ten stems of approximately equal length, arranged into a regular, hexagonal pattern. The free-energy landscape is presented and the different energy and entropy contributions. the latter mostly due to surface rearrangements, discussed.

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1 Introduction

Folded states of chain-like macromolecules like crystalline polymers are under current intense study. One key issue is if their morphologies are thermodynamically or kinetically controlled. Kinetic factors are believed to set the growth rate of polymer crystals as well as the thickening of folded macromolecules [1,2]. While this is a safe conclusion for long chains (polymers), where large entropic barriers hamper the conformation changes leading to structures which are e.g. partially crystalline, it may be questioned for shorter chains (oligomers) which are less impeded. Relevant to the better understanding of the crystallization of chain molecules is also the observation of the transient phases that convert them to more stable forms during the folding process of *n*-alkanes [3]. This behaviour may be seen as a manifestation of 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 conformation but prefers to reach intermediate stages having the closest free-energy to the initial state [4,5]. The crystalline state of polymers is very different from that of other materials because of the need to arrange in an ordered way a large number of monomers linked to each other sequentially. This results in a wide range of possible hierarchical morphologies where the basic unit is the lamella, which is a few hundred Ångstrom thick [1,2]. The backbone of a single polymer chain, which is several thousand Ångstrom long, is folded inside the lamella to form the so-called stems; these are perpendicular to the basal surfaces of the lamella where the loops connecting the stems are localized [2]. Recently, numerical simulations showed that single-chain polymer crystals are equilibrated, i.e. the state corresponds to the minimum of the free-energy and

is not kinetically selected. [5–8]. The present paper reports on a study, carried out by Molecular-Dynamics (MD) algorithms, of the energy and the entropy contributions to the free-energy of single-chain crystals of polyethylene (PE).

2 Numerical methods

The behaviour of a single PE chain with $N = 500$ monomers in solution has been studied by means of a united-atom model [5,6]. The solvent is mimicked by suitable friction and random forces acting on the monomers. The local interactions set the bond length distance, the bond angle, and the torsional barrier defined for every quadruplet of adjacent beads. Fig. 1 plots the dihedral torsional energy. Pair of beads not interacting by any of the preceding potentials interact via a Lennard-Jones (LJ) potential. The dynamics is described by a Langevin equation which is integrated by means of the velocity Verlet algorithm with time step $\Delta t = 10^{-3}$. Further details are given elsewhere [6]. **The time and temperature units are given by $t^* = 2.21$ ps and $T^* = 56.3$ K.** All the results are presented in terms of reduced units. The single-molecule crystal melts at $T_m = 11 \pm 0.2$ in the limit of vanishing heating rate [7]. Several runs have been performed after a previous equilibration at $T_{eq} = 15$; the final temperature $T_f = 9$ is reached via different thermal histories to test possible memory effects [6]. The latter were also investigated by preparing a sample in the “all-trans” fully-extended conformation and isothermally annealing it at $T = 9$.

3 Results

The kinetics of the crystallization process depends on the chain conformation. The nucleation may involve either the whole chain or separate portions merging at later times by reeling in their connector [5,8]. Following different paths, along which metastable intermediate crystalline structures with different number of stems are assembled and restructured, the molecule comes to a final crystalline structure, where the chain is folded with ten stems. As an example of a transition between two metastable crystals, Fig.2 shows the sliding motion of two stems on the crystal surface leading to their disappearance. In all the crystalline structures the stems have approximately the same length and are arranged into a regular, hexagonal pattern. The final stable crystal is independent of the thermal history [5]. The crystals present a rod-like shape, being characterized by the three moments of inertia I_i , $i = 1, 2, 3$ with $I_1 > I_2 > I_3$. The principal axis corresponding to I_1 denotes the X axis.

The structural changes of the crystalline structures are twofold: i) changes due to the increase or decrease of the number of stems, e.g. see Fig. 2; ii) changes which leave the number of stems unaltered. The former are effectively characterized by the moment of inertia I_1 and are activated [5]. The latter, which are presented in the following, do not lead to either appreciable changes of I_1 or the internal energy and need a finer description which is beyond the purpose of the present paper. Examples of such processes are provided by the reorganizations taking place on the crystal surface. The basic process is shown in fig. 3 where two stems are seen to slide on the crystal surface while preserving their alignment with the ordered substrate. Another kind of restructuring with

no change of the number of stems is the position exchange between aligned stems, e.g. the expulsion of a stem terminated by one chain-end from the inside of the crystal, see Fig. 4. Notice that the above kinds of rearrangements leave the potential energy largely unaffected, i.e. they are entropic processes, with negligible changes of the moments of inertia. In order to characterize the reorganization of the chain, both the free energy F and the potential energy U is sampled and their average over all the available configurations correlated to the order parameter I_1 . In particular, the free energy is evaluated according to the Landau's formula $F(X) = -k_B T \ln P(X)$ where $P(X)$ is the probability to find the macroscopic order parameter with value X [9]. Figure 5 plots the free-energy landscape (FEL) at $T = 9$, the overall potential energy and its torsional and LJ contributions as functions of the largest moment of inertia of the chain I_1 . **For a given I_1 value the above quantities are the averages over all the configurations with equal I_1 assumed by the crystal during the time evolution**. Since bond angles and length exhibit negligible changes, the related energies are not considered. Chain conformations with $I_1 \lesssim 6000$ are largely disordered and also not considered. Several minima of the free energy, corresponding to well-defined metastable crystals with different number of stems, are seen. The absolute minimum corresponds to the equilibrated lamella with ten stems. Figure 5 shows that the overall potential energy exhibits minima close to the free-energy ones. The minima of the potential energy are separated by barriers as high as about $20 - 30 k_B T$. The minima of the potential energy are due to minima of both the torsional and the LJ potentials which are separated by barriers with height of about $10 - 20 k_B T$.

4 Discussion

The height of the barriers of the torsional potential in Fig. 5 is understood by noting that the disappearance of one stem implies that one loop does the same. That process needs about four $g_{\pm} \rightarrow t$ transitions [5], see fig.1, which, when completed, lead to a decrease of the torsional energy of about $4\Delta U$. Notice that, during the disappearance of the loop, the profile of the torsional potential when plotted vs. I_1 , fig.5, resembles the one of the dihedral torsional energy with about four times larger magnitude, see fig.1. During the disappearance of the loop and the stem, the chain increases the size to rearrange itself and accommodate the remaining stems in a new ordered state[7]. This provides a qualitative explanation of the contribution to the energy barriers due to the LJ potential energy, fig.5. The LJ barriers are similar in size to the torsional-potential ones. The mild tendency of the LJ potential to increase with I_1 is due to the corresponding increase of the length of the stems and, then, of the aspect ratio of the crystal.

Fig. 5 shows that the FEL barriers at $T = 9$ are much smaller than the potential-energy ones implying meaningful entropic contributions. In fact, the combinatorics of the stems and of the loops, is enough to model of the FEL landscape without the fine sub-structures due to the torsional potential [6]. Other entropic processes are identified by figs.3, 4. They do not change the number of stems and are expected to shape the FEL local minima, see Fig.5. Differently, the rearrangements leading to a change of the number of stems, and then of the loops, induce transitions between metastable crystals, see Fig.2. They are not purely entropic due to the change of both the torsional and the LJ energy.

The above processes resulting in rearrangements with or without changes in the number of stems of the single-molecule crystals represent the essential effects to be incorporated in the available coarse-grained model of FEL [6] to account for its fine structure. The procedure goes beyond the purpose of this paper and will be discussed elsewhere.

5 Conclusions

MD simulations of the crystallization of a single polyethylene chain shows that the folding process involves intermediate metastable crystalline states and ends up in a equilibrated lamella with ten stems. The free-energy landscape is presented and the different energy and entropy contributions are discussed. The latter are mostly due to surface rearrangements.

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Figure captions

Fig. 1. The dihedral torsional energy as function of the dihedral torsional angle in units of $k_B T$ with $T = 9$ in reduced units. ΔU is the energy change in a $g_{\pm} \leftrightarrow t$ transition.

Fig. 2. The disappearance of two stems and two loops (bold) by suitable sliding motion on the crystal surface. The pictures are taken at times (in reduced units): $t_A = 14800, t_B = 14900, t_C = 15000, t_D = 15200$. The cartoons below the wire-frame view sketch the rearrangements of the thick portion of the chain involved in the transition.

Fig. 3. Snake-like displacement of two stems (bold) sliding on the crystal surface. The cartoon below the wire-frame view sketches the next move of the two stems to get the optimal alignment with the ordered substrate of the inner stems (grey lines). The black dashed line is the new position of the displaced portion of the stems after the move.

Fig. 4. The expulsion of one stem terminated by a chain-end (united-atoms) by the inside of the crystal. The snapshots are taken at times (in reduced units): $t_A = 26240, t_B = 26260, t_C = 26270, t_D = 26280$. The two cartoons below the snapshots are schematic cross-sections of the ordered middle portion of the crystal at t_A and t_D . The circles denote the stems. The light-colored circle is the stem terminated by the chain-end.

Fig. 5. From the top to the bottom: the free-energy landscape (FEL) at $T = 9$, the overall potential energy and its torsional and Lennard-Jones contributions as function of the largest moment of inertia of the chain I_1 . The labels indicate the number of stems μ of the metastable crystals corresponding to the free-energy minima.

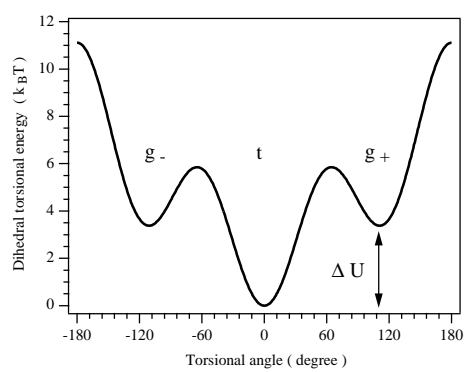


FIGURE 1

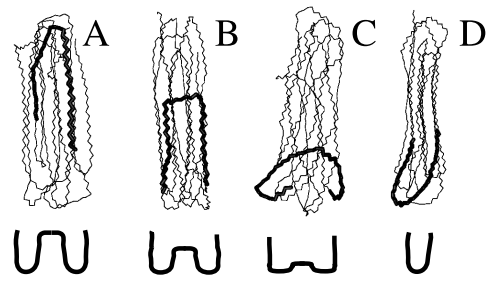


FIGURE 2

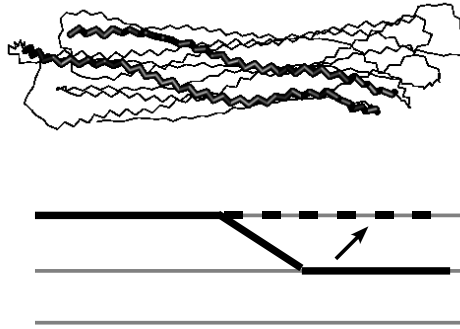


FIGURE 3

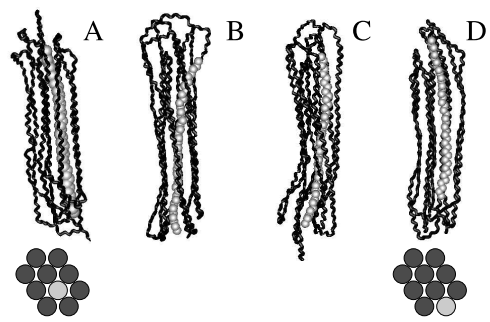


FIGURE 4

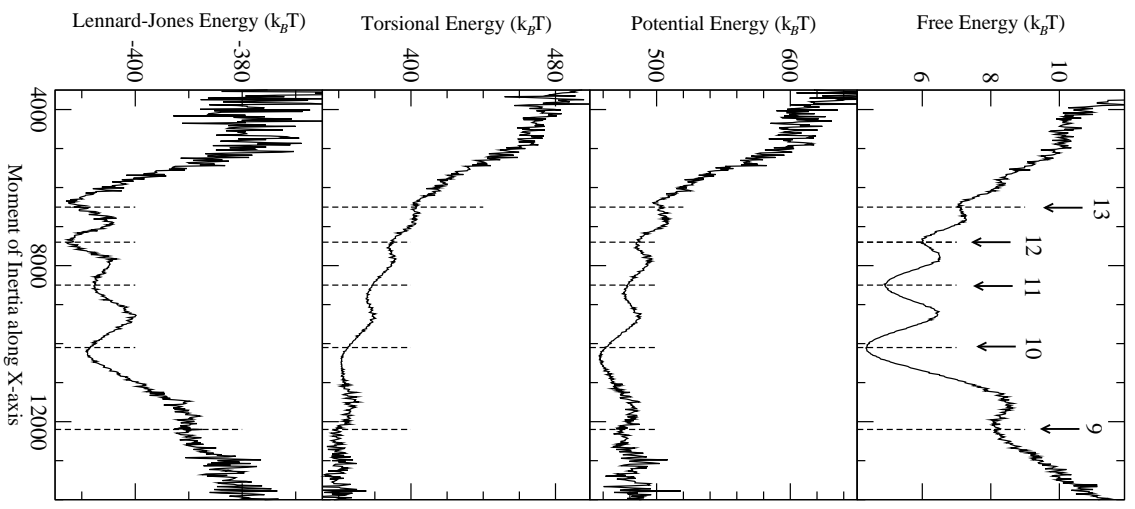


FIGURE 5