

Transient and equilibrated single-molecule crystals of polyethylene: Molecular-dynamics studies of the lamellar fold length

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Abstract

A united-atom model of polyethylene (PE) has been studied by molecular-dynamics simulations to investigate the conformations of transient and equilibrated single-molecule PE crystals. It is shown that, in spite of the wide differences in the number and the length of the stems forming the ordered structures, the average length of the loops connecting the stems is nearly constant.

Key words: folding process, polymer crystals

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1 Introduction

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 [1–4]. 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 foldings are localized.

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Different processes in polymer crystallization are known [1,2]. Here, we are interested in the *primary homogeneous nucleation* of single-molecule crystals in dilute solutions. Very few groups have challenged the experimental study of single-molecule single crystals [5–7]. This motivated several simulation works [8–18]. In particular, for a united-atom model of polyethylene (PE) it was found that the equilibrium chain conformation of single-molecule crystals is folded [8,9,18]. Differently, the general consensus is that for *multi-chain* crystallites the global minimum of the free-energy corresponds to the extended conformation of the single chain [19]. The equilibrium or kinetically-selected conformation of the single chain is reached by the reorganization of the folded structure involving changes in the number of stems μ [3,9,18]. This yields transient states which are in general of difficult characterization [20]. This behaviour may be seen as a *microscopic* 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 [21].

A key feature of the lamella is the folding region where the loops connecting two different stems are located. Both the experimental [3] and the numerical [17,18] works pointed out the sharpness of the loops connecting the different stems. This paper presents novel evidence about the loop structure gained from molecular-dynamics (MD) simulations on a united-atom model of PE. Surprisingly, it is found that the average number of segments per loop λ is constant for a wide variety of transient and equilibrated crystal structures. The paper is organized as follows. In Sec.2 the numerical methods are presented. The results are presented and discussed in Sec.3. Conclusions are summarized in Sec.4.

2 Numerical methods

The simulations deal with the behaviour of a single PE chain with $N = 500$ monomers in solution. The solvent is mimicked by suitable friction and random forces acting on the monomers. The chain is described as a sequence of beads, where each bead represents a single methylene CH_2 group. No distinction is made between internal methylene CH_2 groups and terminal methyl CH_3 groups in order to obtain a slight improvement in efficiency [10]. For long chains this approximation is fair. The local interactions shaping the chain are defined by the potentials

$$U_{\text{bond}}(r) = k_r(r - r_0)^2 \quad (1)$$

$$U_{\text{angle}}(\theta) = k_\theta(\cos \theta - \cos \theta_0)^2 \quad (2)$$

$$U_{\text{torsion}}(\phi) = k_1(1 - \cos \phi) + k_2(1 - \cos 2\phi) + k_3(1 - \cos 3\phi) \quad (3)$$

$U_{\text{bond}}(r)$ is a harmonic spring potential defined for every couple of adjacent beads, r being their distance and r_0 the equilibrium bond length. $U_{\text{angle}}(\theta)$ is defined for every triplet of adjacent beads, θ being the angle between the corresponding bonds and θ_0 its equilibrium value. Finally, $U_{\text{torsion}}(\phi)$ is defined for every quadruplet of adjacent beads and ϕ is the dihedral angle between the planes defined by the corresponding three adjacent bonds. Pairs of beads not interacting by any of the preceding potentials interact by means of a Lennard-Jones potential

$$U_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (4)$$

with a cutoff radius $r_{\text{cut}} = 2.5\sigma$. The set of parameters of the above force field are taken from ref. [22] (see table 1). The force field enforces the local stiffness of the chain yielding a Kuhn segment length $\ell_k \cong 1.2$ [1,2,18], corresponding to segments with about four beads. Therefore, the polymer is sketched as a succession of about $N_k = 125$ rigid segments. The corresponding time and temperature units are given by $t^* = 2.21$ ps and $T^* = 56.3$ K. All the results will be presented in terms of reduced units. For the set of parameters listed in Table 1 the single-molecule crystal melts at $T_m = 11 \pm 0.2$ in the limit of vanishing heating rate [22,9].

The dynamics is described by the Langevin equation

$$\ddot{\mathbf{r}}_i = -\nabla_i U - \Gamma \dot{\mathbf{r}}_i - \mathbf{W}_i \quad (5)$$

where \mathbf{r}_i denotes the position vector of the i -th bead, $\nabla_i U$ is the sum the internal forces acting on it, $\Gamma \dot{\mathbf{r}}_i$ is the frictional force and \mathbf{W}_i is a gaussian noise:

$$\langle \mathbf{W}_i(t) \cdot \mathbf{W}_j(t') \rangle = 6\Gamma k_b T \delta_{ij} \delta(t - t') \quad (6)$$

The friction and the random forces account for the solvent and set the temperature via the proper fluctuation-dissipation theorem. Eq.5 is integrated by means of the velocity Verlet algorithm with time step $\Delta t = 0.001$ [23,24].

The runs are performed according to the following protocol: seventeen random chain conformations are initially equilibrated at $T_{eq} = 15$ for at least ten times

Table 1
Parameters of the force field.

Parameter	Value	
	reduced units	SI units
ϵ	1	0.112 kcal/mol
σ	1	4.04 Å
m	1	14.03 g/mol
Γ	1	0.455 Hz/mol
k_r	51005	350 kcal/mol Å ²
r_0	0.38	1.53 Å
k_θ	535.71	60 kcal/mol
θ_0	109°	109°
k_1	26.96	3.02 kcal/mol
k_2	-5	-0.56 kcal/mol
k_3	23.04	2.58 kcal/mol

the time needed for the self correlation function of the end-to-end vector to vanish. The equilibrated chain does not exhibit any local orientational order. The final temperature $T_f = 9$ is reached via instantaneous direct quenches $T_{\text{eq}} \rightarrow T_f$. The data are collected immediately after the quench. Memory effects were also investigated by preparing a sample in the “all-trans” fully-extended conformation and isothermally annealing it at $T = 9$.

3 Results and discussion

For all the thermal histories, the nucleation starts either globally (Fig.1: top) or in distinct sites (Fig.1: bottom), as previously noted [9]. Anyway, at later times a single ordered structure is systematically observed which undergoes structural changes leading to transient crystalline structures with different number of stems μ . We characterize here the latter regime only and neglect the very early stage. The final crystalline state, i.e. the one reached at long times, is found to be independent of the thermal history and, more specifically, to correspond to the free-energy global minimum [18] in agreement with previous results on shorter chains at the same $T_f = 9$ [8,9]. The number of stems of the final crystalline state is $\mu = 10$. A tomography of that state is presented in fig.2. The tomography of the transient crystalline states does not reveal marked differences apart from the number of stems μ and the number of

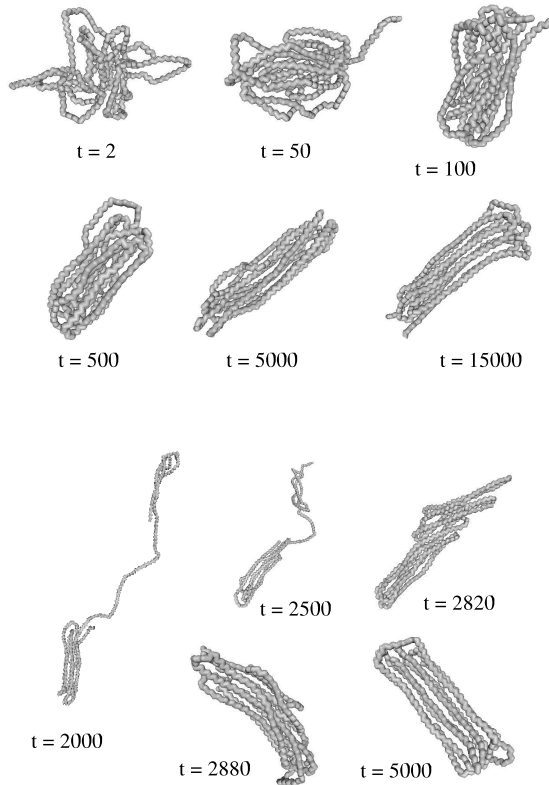


Fig. 1. Wire-frame snapshots of the crystallization of a single polyethylene chain with $N = 500$ monomers for two different initial states: chain equilibrated at $T_{eq} = 15$ and quenched at $T_f = 9$ (top); chain initially in the fully-stretched configuration (all-trans) and isothermally annealed at $T = 9$ (bottom). For the latter case note the presence of initial distinct nucleation sites merging at later times.

Kuhn segments m belonging to each stem.

A preliminary characterization of the crystallized chains is provided by the inertia tensor of the transient and the final crystalline configurations. The principal axes $\{\mathbf{1}, \mathbf{2}, \mathbf{3}\}$ are ordered according to the magnitude of the corresponding eigenvalue. As an example, for the final crystalline state with $\mu = 10$ the average values are $\langle I_1 \rangle = 10097 \pm 58$, $\langle I_2 \rangle = 9885 \pm 51$, $\langle I_3 \rangle = 1148 \pm 11$. Since $\langle I_1 \rangle \gtrsim \langle I_2 \rangle \gg \langle I_3 \rangle$, the ellipsoid of inertia of the crystal exhibits approximate cylindrical symmetry around the $\mathbf{3}$ axis, as it may be seen by visual inspection (Fig. 2).

In order to analyze the crystal structure one defines the monomer distribution function $\rho(\mathbf{r})$ as

$$\rho(\mathbf{r}) = \frac{1}{N} \sum_{i=1}^N \langle \delta(\mathbf{r} - \mathbf{r}_i^{(\text{cm})}) \rangle \quad (7)$$

where $\mathbf{r}_i^{(\text{cm})}$ is the position of the i -th bead with respect to the center of mass of the chain and the brackets denote a suitable average. In particular, one

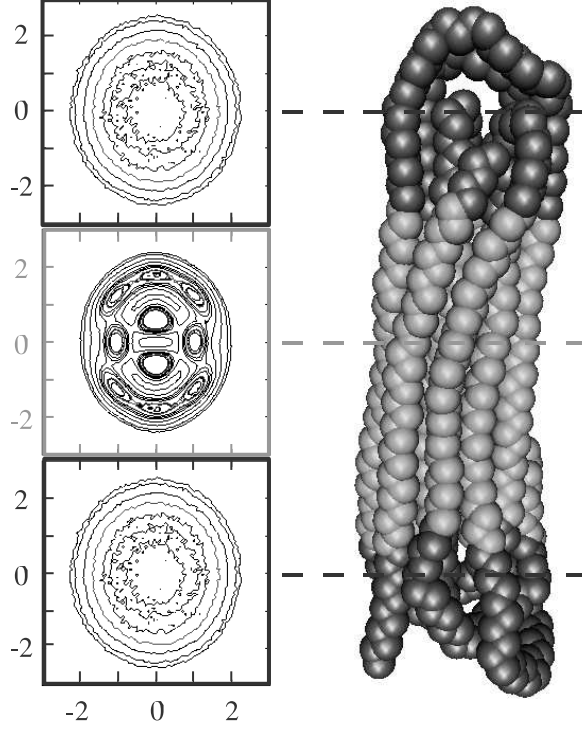


Fig. 2. Tomography of the crystal state with a number of stems $\mu = 10$. The azure zone is the stem region (the region comprised between the two maxima in the curve for $\mu = 10$ in Fig.3) . The red zones are the two caps. The left-side column plots the averaged density profiles in the cross sections marked by the dashed lines. Note the absence of ordered structures on the crystal surface and the two caps.

defines the quantity

$$N_{\parallel}(x^3) = N d \times \int \rho(x^1, x^2, x^3) dx^1 dx^2 \quad (8)$$

where $d = 0.31$ is the distance along the chain backbone between two adjacent beads of the fully-extended chain and x^k is the projection of \mathbf{r} along the k -th principal axis. The quantity $N_{\parallel}(z)$ denotes the average number of intersections of the chain with the plane at $x^3 = z$, namely a plane perpendicular to the approximate cylindrical symmetry $\mathbf{3}$ axis.

Figure 3 plots the quantity $N_{\parallel}(z)$ for all the observed transient and final crystalline structures averaged over all the thermal histories. For each crystal structure labelled by the number of stems μ , three different regions of $N_{\parallel}(z)$ are seen: the central stem region where $N_{\parallel}(z) \simeq N_{\parallel}(0) = \mu$; the transition region around the two peaks of $N_{\parallel}(z)$, where the average orientation of the stems departs from the $\mathbf{3}$ axis, and the end region where the stems join each other by forming loops. The flatness of $N_{\parallel}(z)$ in the central region follows from its highly ordered structure (see Fig. 2). Figure 3 makes it also apparent the small size of the two crystal caps. In fact, for the final crystalline state

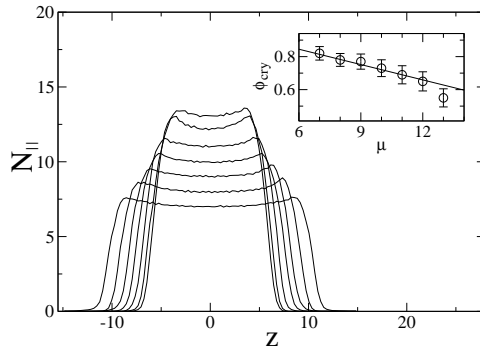


Fig. 3. The number of intersections of the chain with the plane at $x^3 = z$, $N_{||}(z)$, for the different transient and final crystalline states at $T = 9$. The number of stems $\mu = N_{||}(0)$ is in the range $7 < \mu < 13$. The crystal with $\mu = 10$ stems corresponds to the final equilibrated state. Inset: The crystalline fraction ϕ_{cry} (eq.9) vs. the number of stems μ . The superimposed line is eq.10 with $\lambda = 4.0 \pm 0.1$.

($\mu = 10$) the longitudinal size of the loops, $\Delta z \sim 3$, is fairly smaller than the crystal length $2L_c \sim 16$, where L_c is defined via the equation $N_{||}(L_c) = 1$. Notice that, since $I_3 \ll I_{\perp}$ with $I_{\perp} = (I_1 + I_2)/2 \simeq 9990$, the folded chain may be sketched as a rigid rod with length $2L$, mass N and negligible thickness. The approximation yields $L = \sqrt{3I_{\perp}/N} \simeq 7.74$, to be compared with $L_c \sim 8$. Fig. 3 also suggests that the number of monomers in the end sections does not depend in a marked way on the number of stems μ . To assess the issue, we consider the crystalline fraction ϕ_{cry} of a crystal with μ stems. ϕ_{cry} is estimated by the ratio

$$\phi_{cry} = \frac{\int_{z_{max}^1}^{z_{max}^2} N_{||}(z) dz}{\int_{-\infty}^{\infty} N_{||}(z) dz} \quad (9)$$

where z_{max}^1 and z_{max}^2 are the points where $N_{||}(z)$ reaches the maximum values. Let us assume that an average number of segments λ is located in each of the $\mu - 1$ loops connecting the stems. Then, the crystalline fraction is given by

$$\phi_{cry} = 1 - (\mu - 1) \frac{\lambda}{N_k}. \quad (10)$$

The inset of Fig. 3 shows the best-fit of ϕ_{cry} from eq.9 with eq.10 having adjusted λ . It proves that the number of segments forming the loops do not change appreciably from one transient structure to the other. At the highest number of stems (shortest crystal longitudinal size) eq.10 overestimates ϕ_{cry} suggesting that the disorder of the end sections affects the ordered part more effectively (or, alternatively, that λ increases).

Table 2
 Test of Eq.11 with $\lambda = 4$

μ	m	m^*
7	14.0	14.43
8	12.2	12.12
9	10.25	10.33
10	8.75	8.9
11	7.5	7.73
12	6.25	6.75
13	5.0	5.92

As further test of the negligible changes of λ with μ we note that the number of Kuhn segments per stem m is expressed as $m = (z_{max}^2 - z_{max}^1)/\ell_k$. On the other hand, if λ is nearly constant

$$m^* = \frac{N_k - \lambda(\mu - 1)}{\mu} \quad (11)$$

Table 2 compares m with m^* as taken from Eq.11 with $\lambda = 4$.

The above results have two main implications on the study of the free-energy landscape (FEL) of single-chain crystals. First, different models of FEL have been proposed basically assuming either long loops [9] or short loops [18]. The finding that each loop has four Kuhn segments on average supports the latter assumption which also follows from both experimental [3] and numerical studies [17]. Second, the macroscopic states of the PE single-chain crystals have been usually labelled by the (μ, m) pair, thus resulting in 3D FEL plots [9,18]. The fact that the loop size is only weakly dependent on the crystal size provides a link between the number of stems μ and the number of segments per stem m which is expressed by Eq.11. That equation paves the way to a one-dimensional representation of the FEL. The procedure is under study as well as the extension of the present results to longer chains and multi-chain crystalline structures [25].

4 Conclusions

A united-atom model of polyethylene has been studied by molecular-dynamics simulations to investigate the conformations of transient and equilibrated single-molecule PE crystals. Numerical evidence is given that, in spite of the

wide differences in the number and the length of the stems forming the ordered structures, the average length of the loops connecting the stems is nearly constant.

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