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Molecular dynamics simulation of chains mobility in polyethylene crystal

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The mobility of polymer chains in perfect polyethylene crystal was calculated as a function of temperature and chain length through Molecular dynamics in united atom approximation. The results demonstrate that the chain mobility drastically increases in the vicinity of the phase transition from the orthorhombic to quasi-hexagonal phase. In the quasi-hexagonal phase, the chain mobility is almost independent on temperature and inversely proportional to the chain length.

Mechanical properties of semi-crystalline polymers below the melting temperature are strongly governed by morphology of crystallites that depends on how the melt was prepared and treated. Polymer crystallites can undergo a variety of structural phase transitions that is a subject of extensive studies. Polyethylene (PE) is widely used as a "model system" for high-crystallinity polymer [1]. At normal conditions (room temperature and atmospheric pressure), the PE crystal is in orthorhombic [2] or monoclinic phase [3]. The PE crystals undergo phase transition to quasi-hexagonal phase at elevated pressure (more than 400 MPa) and temperature ($> 520\,\mathrm{K}$) [4–6].

Quasi-hexagonal phase has been found in numerous diverse polymeric systems [7]. One common property of the quasi-hexagonal polymeric phase is some degree of conformational disorder, either in the main chain or in the side groups or in both. Compared with the ordered crystalline state, there is a high degree of molecular mobility, with the chain performing both rotational and translational motion. Translational chain mobility enables easy formation of extended chain crystals in polymers that exhibit the quasi-hexagonal phase; isothermal extension of the initially folded chains has been shown to occur in the quasi-hexagonal phase [7]. The PE chains in both monoclinic and quasi-hexagonal crystals are parallel to each other. However, the monomers of the chain in monoclinic phase predominantly belong to the same plane, while the monomers of the chain in quasi-hexagonal phase are randomly oriented. Therefore, the

chains in quasi-hexagonal phase form close packing of rods [7].

Diffusion rate of PE chains in quasi-hexagonal phase was measured experimentally in Ref. [6] using proton spin-lattice relaxation experiments and significant increase in the rate of chain diffusion from about 10^{-12} (orthorhombic phase) to $10^{-9}\,\mathrm{cm^2/s}$ (quasi-hexagonal phase) was observed. The molecular dynamics modeling and understanding of the atomistic mechanisms of high chains mobility in the quasi-hexagonal phase is the purpose of the current work.

The LAMMPS software package [8] was utilized for molecular dynamics simulations. Polyethylene chains were modeled in united atom version of Dreiding forcefield [9]. The Nose–Hoover style thermostat and barostat were used in these calculations [10]. The modeled samples were comprised of 64 polyethylene chains with 36, 100, and 200 carbon atoms in each chain. The simulations were performed in periodic boundary conditions in all directions. The chains were made "infinite" via binding the last carbon atom of each chain with the first carbon atom of the closest image of the same chain in c-direction. We used orthorhombic phase of PE crystal as an initial state of our simulations. The front and side views of the initial configuration of the modeled sample with 100 carbon atoms in each chain are shown in Fig. 1a. After initial geometrical optimization of the system, the Molecular dynamics (MD) trajectory was run in NPT ensemble. We use below the relative temperature, τ, normalized by the Lennard-Jones interaction constant, ε; $\tau = T/\varepsilon$.
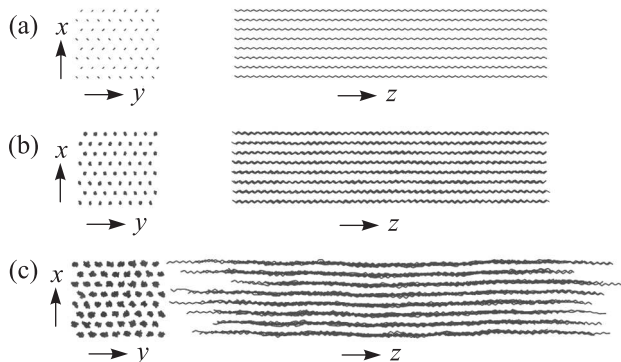

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Fig. 1. Crystalline sample. (a) – Orthorhombic phase, $\tau = 0$. (b) – Monoclinic phase, $\tau = 3$, $t = 1$ ns. (c) – quasi-hexagonal phase, $\tau = 5$, $t = 1$ ns

Fig. 2. Temperature dependencies of the elementary cell dimensions ratio b/a and the probability density range of setting angle

Although we started from the orthorhombic phase, the transition into the monoclinic phase occurred within 50 ps from start of MD simulation at the temperatures below $\tau = 4.5$. The snapshot (front and side view) of the sample configuration at temperature $\tau = 3$ and time $t = 1$ ns after initial time moment is shown in Fig. 1b. The monomers of individual chains predominantly belong to one plane. Thermal motion results in fluctuations of the monomer near the chain plane, as seen at the front view of Fig. 1b, and in the transverse waves that are observed at the side view Fig. 1b. The transition into the quasi-hexagonal phase was observed at the temperature above $\tau = 4.5$. The snapshot (front and side view) of the sample configuration at temperature $\tau = 5$ and time $t = 1$ ns after initial time moment is shown in Fig. 1c. The monomers in quasi-hexagonal phase are randomly oriented although the chains in the crystal are parallel to each other on the average. The transverse waves are also observed in quasi-hexagonal phase at the side view of Fig. 1c.

The ratio of the elementary crystal cell dimensions transversal to the chain direction, b/a, is equal to $\sqrt{3} \approx 1.732$ in the quasi-hexagonal phase. Calculated b/a averaged through MD trajectory in NPT ensemble as a function of temperature is presented in Fig. 2. The transition from monoclinic to quasi-hexagonal phase occurs in the temperature range from $\tau = 4$ to 4.5 Lennard-Jones units as seen in Fig. 2. The transition manifests itself in the abrupt change of the system sizes in transversal directions, which indicates the change of the chain packing in the crystal. The ratio $b/a = 1.732$ stated above the transition temperature implies the quasi-hexagonal packing of the chains. Qualitatively similar dependence of b/a on temperature for PE crystal was obtained in united atom molecular dynamic simulation in [11] (see Fig. 1 therein). Minor quantitative differ-
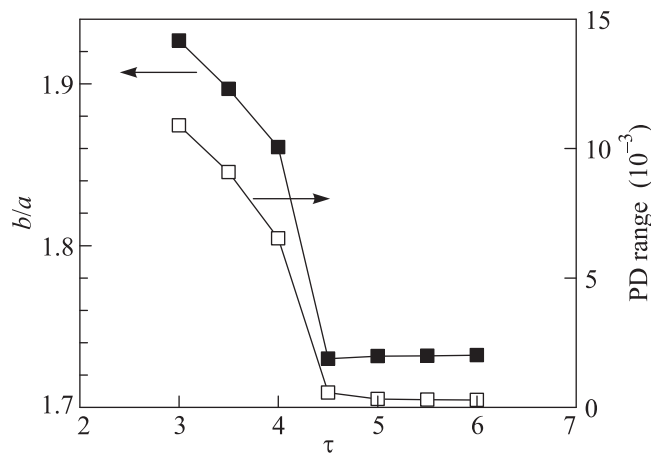
ences between Fig. 2 of this paper and Fig. 1 in [11] are caused by the difference in force fields used in this work and in [11].

To study the orientation order in the phases the distribution of the setting angle was calculated following [11]. The distribution of the setting angle is a sum of δ-functions in totally orientation ordered phase and is a constant in disordered phase. The local setting angle α is defined for each atom as follows. For each bond angle formed by three neighboring atoms in one chain, a bisector vector is constructed, which is multiplied by $(-1)^n$ (n is the number of an atom in the chain). The angle α is the angle between the x-axis and the projection of this vector onto xy-plane. The distributions of setting angle for three temperatures are shown in Fig. 3. Qualitatively, Fig. 3 looks similar to Fig. 2 in [11]. The
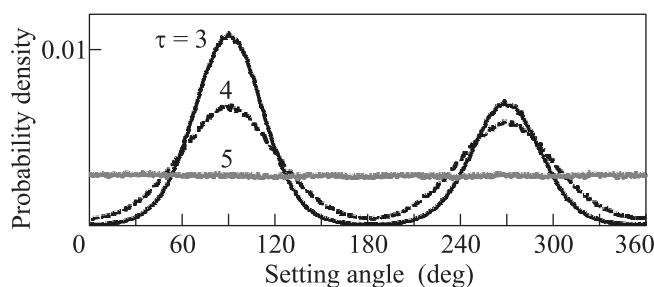

Fig. 3. Local setting angle distribution function for three temperatures

quantitative differences should be attributed to the difference of the employed force fields.

In monoclinic phase ($\tau = 3$ and 4), the setting angle is distributed near $\alpha = 0°$ and $180°$ and the width of distribution decreases with decrease of temperature.

In quasi-hexagonal phase ($\tau = 5$), the distribution of setting angle is uniform that indicates the loss of orientation order. For quantitative characterization of uniformity of the setting angle distribution, we utilized the range of distribution. The range is equal to the maximal value of the setting angle minus the minimum value of the setting angle. For totally inform distribution the range is equal to zero. The range of the setting angle distribution as a function of temperature is plotted in Fig. 2. The range tends to zero simultaneously with tending of b/a to 1.732, i.e. when the crystal undergoes the phase transition to the quasi-hexagonal phase. That indicates the vanishing of the orientation order of monomers at the phase transition to the quasi-hexagonal phase.

The relatively large deviation of the chains from their initial positions (Fig. 1a) in axial direction is observed in quasi-hexagonal phase (Fig. 1c) while the chains keep their initial positions in monoclinic phase (Fig. 1b). That indicates the increased chains mobility in axial direction in the quasi-hexagonal phase. For quantitative characterization of the chains mobility, we calculated the diffusion coefficient of the chain in axial direction as a function of temperature. Diffusion coefficient was calculated from MD trajectories as follows. To track the large-scale displacement of the center of mass of the chain we track the displacement of one selected atom of this chain. The axial coordinates, $z_j(t_i)$, of selected atom of each chain were recorded at each MD time step, t_i. The mean square displacement of the chains as a function of time was calculated as

$$\langle \Delta z^2(t_i) \rangle = \sum_{j=1}^{N_c} [z_j(t_i) - z_j(0)]^2, \qquad (1)$$

where N_c is the number of chains in the system.

The dependencies $\langle \Delta z^2(t) \rangle$ for three temperatures are presented in Fig. 4 for the crystal with 100 carbon atoms in each chain.

The mean square displacements in Fig. 4 were approximated by linear dependencies on time, $\langle \Delta z^2(t) \rangle = 2Dt$. Diffusion coefficient of the chains, D, is calculated from the slope of the linear trend of $\langle \Delta z^2(t) \rangle$. Calculated dependencies of D on the temperature for chain with 100 carbon atoms is plotted in Fig. 5. The range of setting angle distribution as a function of temperature is also shown in the same plot. The diffusion coefficient, D, abruptly increases in narrow region in the vicinity of the phase transition temperature from monoclinic to quasi-hexagonal phase as seen from Fig. 5. The chain mobility at the temperature $\tau = 6$ (quasi-hexagonal phase) is almost four orders of magnitude higher than that at the temperature $\tau = 4$. Diffusion coefficient, D,
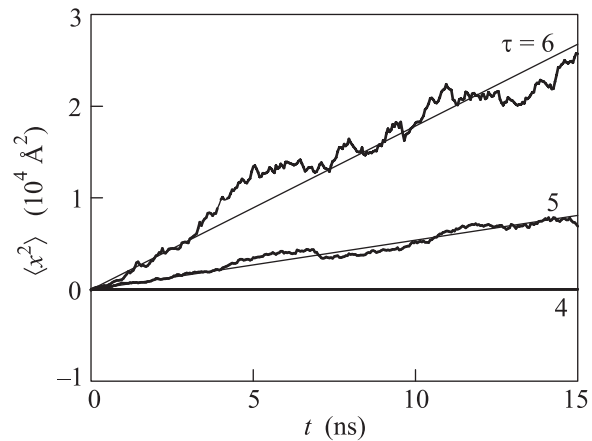

Fig. 4. Calculated from MD trajectories mean square displacements of the chains, $\langle \Delta z^2(t) \rangle$, as functions of time for several temperatures. The number of carbon atoms in the chain is 36
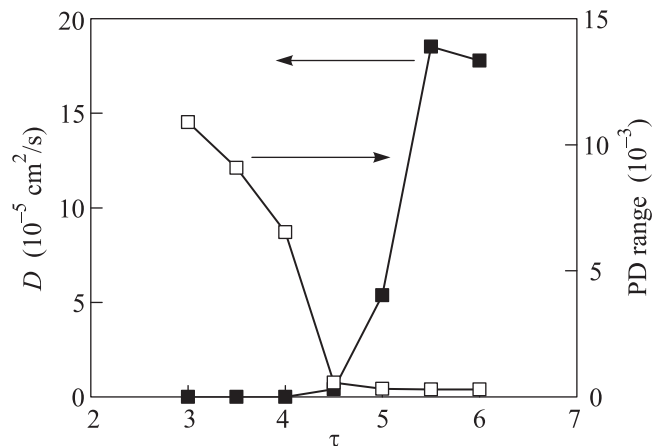

Fig. 5. Diffusion coefficient of the chains as a function of temperature

is plotted with the setting angle distribution range in Fig. 5 to emphasize the correlation between the orientation order and the chain mobility in the crystal. Thus, the MD simulation predicts that the chain mobility in PE crystal increases sharply with the vanishing of the orientation order in the crystal at the transition to the quasi-hexagonal phase.

The chain mobility in the quasi-hexagonal phase at $\tau = 6$ was calculated for four chain lengths and plotted as a function of the chain length in Fig. 6. The chain mobility in quasi-hexagonal phase is approximately inversely proportional to the chain length as seen in Fig. 6. That indicates that the chains move in perfect quasi-hexagonal crystal as a whole without activation barriers. The PE chains diffusion in the crystallites in orthorhombic/monoclinic phase via the local topological defects was studied in Refs.[12, 13] by molecular dynam-
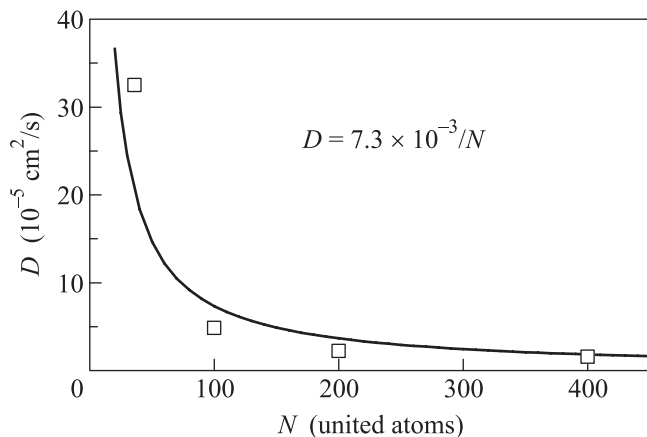
Fig. 6. Dependence of diffusion coefficient of the chains on chain length at temperature $\tau = 5$ (hexagonal phase). Solid line is a fit by dependence $D = \mathrm{const}/N$

ics simulations. The diffusion of the defects along the chain results in chain longitudinal motion in the crystallite, that is similar to reptation in polymer melt. The mechanism of the chain motion in the quasi-hexagonal phase differs from that in orthorhombic or monoclinic phases and does not involve the topological defects. The rod-like close packing of chains in the quasi-hexagonal phase indicates that the nearest chains are not sensitive to the details of the inter-chain interaction. That implies the "sliding" mechanism of the chains motion in quasi-hexagonal phase, when the chains slide relative to each other without activation barriers. The random collisions of the atoms of the chain with the atoms of the nearest chains result in viscous friction. The friction force is proportional to the chain length.

In conclusion, our MD study shows that the mobility of PE chains in the crystal increases sharply (by four orders of magnitude) at the transition of the PE crystal to the quasi-hexagonal phase, where the orientation order vanishes. The obtained results are in agreement with the experimental observation [6]. The sliding of polymer chains through the crystallites plays a key role in the so-called α_c structural transition in semicrystalline polymers with high degree of crystallinity, which is observed in dielectric relaxation measurements [14]. Besides, the understanding of the mechanism of chain mobility in crystallites can help to develop the microscopic theory of semicrystalline polymers in high-elastic state [15].

1. E. A. Zubova, N. K. Balabaev, A. I. Musienko et al., J. Chem. Phys. **136**, 224906 (2012).
2. J. A. O. Bruno, N. L. Allan, T. H. K. Barron, and A. D. Turner, Phys. Rev. B **58**, 8416 (1998).
3. T. Yemni and R. L. McCullough, J. Polym. Sci.: Polymer Physics Edition **11**, 1385 (1973).
4. D. C. Bassett, Polymer **17**, 460 (1976).
5. M. Hikosaka, K. Tsukijima, S. Rastogi, and A. Keller, Polymer **33**, 2502 (1992).
6. M. de Langen and K. O. Prins, Chem. Phys. Lett. **299**, 195 (1999).
7. G. Ungar, Polymer **34**, 2050 (1993).
8. S. Plimpton, J. Comp. Phys. **117**, 1 (1995).
9. S. L. Mayo, B. D. Olafson, and W. A. Goddard, J. Phys. Chem. **94**, 8897 (1990).
10. W. Shinoda, M. Shiga, and M. Mikami, Phys. Rev. B **69**, 134103 (2004).
11. E. A. Zubova, A. I. Musienko, N. K. Balabaev et al., Doklady Physical Chemistry **418**, 15 (2008).
12. E. A. Zubova, L. I. Manevich, and N. K. Balabaev, J. Exp. Theor. Phys. **88**, 586 (1999).
13. E. A. Zubova, N. K. Balabaev, and L. I. Manevitch, Polymer **48**, 1802 (2007).
14. R. H. Boyd, Polymer **26**(323), 1123 (1985).
15. V. V. Atrazhev, S. F. Burlatsky, D. V. Dmitriev, and V. I. Sultanov, J. Stat. Mech., P02004 (2013).