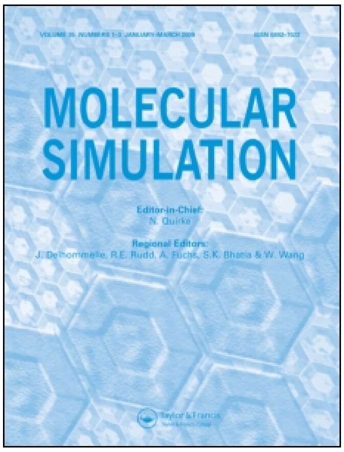

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Molecular Dynamics Study of the Structural Formation of Short Chain Molecules: Structure and Molecular Mobility

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MOLECULAR DYNAMICS STUDY OF THE STRUCTURAL FORMATION OF SHORT CHAIN MOLECULES: STRUCTURE AND MOLECULAR MOBILITY

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By carrying out molecular dynamics simulations of 100 short chain molecules, each of which consists of 20 CH_2 groups, we show that the orientationally ordered structure is formed at low temperature by a sudden cooling from a random configuration at high temperature. The essentially extended chains form a monolayer structure. The ratio of the lattice constants a/b takes the hexagonal value $\sqrt{3}$ at 400 K and decreases as the temperature decreases. From detailed analysis of the local orientational order, it is found that the growth of the local ordered clusters proceeds *in a stepwise fashion*. From the analysis of the molecular mobility, we find that the longitudinal chain motion increases dramatically with increasing temperature while the transverse chain motion is not sensitive to the temperature variation.

Keywords: Chain molecule; structural formation; bond-orientational order; molecular mobility; molecular dynamics simulation

1. INTRODUCTION

Since polymer chains show diverse static and dynamical structures, they have various mechanical and thermodynamical properties. Among them, *n*-alkanes (C_nH_{2n+2}) are chain molecules with simple chemical structure and are believed to be model materials for the chain molecules. Thus the study of the behavior of *n*-alkanes plays an important role in understanding more

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*Corresponding author. Tel.: 81-572-58-2561, Fax: 81-572-58-2668, e-mail: fujiwara@toki.theory.nifs.ac.jp complex chain molecules such as liquid crystals and lipid membranes. The crystal structure of the rotator phase of *n*-alkanes has been extensively studied by experiments, theoretical analyses and computer simulations from physical, chemical and biological interests. Doucet *et al.* [1, 2] showed the phase diagram of *n*-alkanes as a function of the chain length n ($18 \leq n \leq 26$) by X-ray experiments. They found that the structure of the rotator phase of the odd-numbered *n*-alkanes is different from that of the even-numbered *n*-alkanes [1, 2]. The rotator phases are classified into two types: the R_{I} phase and the R_{II} phase. The R_{I} phase has a bilayer structure with orthorhombic subcell. In the R_{I} phase, the ratio of the lattice constants a/b varies rapidly with the decrease of temperature from the hexagonal value $\sqrt{3}$ to the ordinary orthorhombic value of about 1.5. The R_{II} phase has a trilayer structure with hexagonal subcell. The ratio a/b in the R_{II} phase takes the hexagonal value $\sqrt{3}$. As the temperature increases, the phase transition proceeds as shown in Table I.

TABLE I Phase transitions of *n*-alkanes for various values of n ($18 \leq n \leq 26$). Arrows indicate phase transitions from a low-temperature phase to a high-temperature phase

n	*Phase*
18, 20	crystal → liquid
19, 21	crystal → R_{I} → liquid
22, 24, 26	crystal → R_{II} → liquid
23, 25	crystal → R_{I} → R_{II} → liquid

Structures and molecular motions in the rotator phases of *n*-alkanes have been studied by Monte Carlo simulations [3–6] and molecular dynamics simulations [7–9]. In these simulations, the initial configuration of short chain molecules was the ordered crystal structure. Esselink *et al.* [10] and Takeuchi [11] carried out molecular dynamics (MD) simulations of crystallization of *n*-alkanes using periodic boundary conditions.

The purpose of this paper is to clarify the mechanism of the structural formation of short chain molecules at the molecular level. To this end, we carry out the MD simulations of isolated short chain molecules and analyze the formation process of the orientationally ordered structure and the molecular motion in the obtained ordered structure.

2. MODEL AND METHOD

The present computational model is the same as that used in the previous work on the structural formation of chain molecules [12, 13]. The model chain molecule consists of a sequence of CH_2 groups, which are treated as united atoms (united atom approximation). The mass of each CH_2 group is 14 g/mol. The united atoms interact *via* the bonded potentials (bond-stretching, bond-bending and torsional potentials) and the non-bonded potential (12–6 Lennard-Jones potential). The atomic force field used here is the DREIDING potential [14]: (i) the bond-stretching potential,

$$V_{\text{stretch}}(d) = k_d(d - d_0)^2/2, \tag{1}$$

where d_0 is the equilibrium bond length and d is the actual bond length, (ii) the bond-bending potential,

$$V_{\text{bend}}(\theta) = k_\theta(\theta - \theta_0)^2/2, \tag{2}$$

where θ_0 is the equilibrium bond angle and θ is the bond angle between three adjacent atoms, (iii) the torsional potential,

$$V_{\text{torsion}}(\phi) = k_\phi\{1 - \cos(3\phi)\}/2, \tag{3}$$

where ϕ is the dihedral angle formed by four consecutive atoms, and (iv) the 12–6 Lennard-Jones potential between atoms separated by more than two bonds along the same chain and between atoms in different chains,

$$V_{LJ}(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6], \tag{4}$$

where r is the distance between atoms. The values of all the potential parameters are listed in Table II.

The numerical integrations of the equations of motion are performed using the velocity version of the Verlet algorithm [15]. We apply the Nosé-Hoover method in order to keep the temperature of the system constant [16–18]. The integration time step and the relaxation constant for the heat bath variable are 0.001 ps and 0.1 ps, respectively. The cutoff distance for the

TABLE II Potential parameters used in our simulation [14].

Parameter	*Value*	*Unit*
d_0	0.153	nm
θ_0	1.2310	rad
k_d	70000	kcal/nm$^2\cdot$mol
k_θ	100	kcal/rad$^2\cdot$mol
k_ϕ	2.0	kcal/mol
ε	0.1984	kcal/mol
σ	0.36239	nm

Lennard-Jones potential is 10.5 Å. The chain molecules are exposed to vacuum and there is no box to confine them. The total momentum and the total angular momentum are taken to be zero in order to cancel overall translation and rotation of chains. The root-mean-square fluctuations of the extended system Hamiltonian in our simulation are between 0.01% and 0.1% for 2×10^6 time steps (2 ns). The MD simulations are carried out by the following procedure. At first, we provide a randomly distributed configuration of 100 short chain molecules, each of which consists of 20 CH_2 groups, at high temperature ($T = 700\,K$). It is then quenched to $T = 400\,K$ and subsequently it is cooled stepwise to $T = 100\,K$ with the rate of 100 K/ 2000 ps. The cooling history is schematically depicted in Figure 1.

3. SIMULATION RESULTS

3.1. Chain Configuration

We show, in Figure 2, the chain configurations viewed along the *b*-axis at various times ($t = 1, 120, 180, 230, 300$ and 2000 ps) obtained by our MD simulations at $T = 400\,K$. The *a*, *b* and *c* axes respectively correspond to the crystalline *a*, *b* and *c* axes in the orthorhombic system. From Figure 2, we

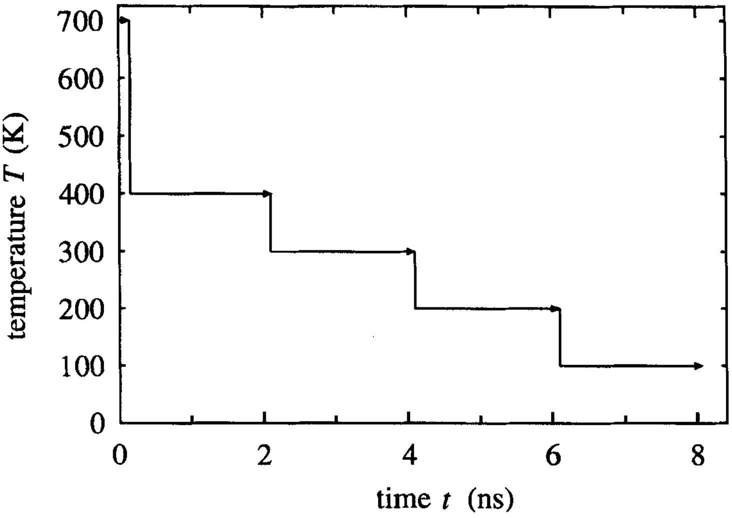

FIGURE 1 Schematic explanation of the cooling process. The cooling rate is 50 K/ns.

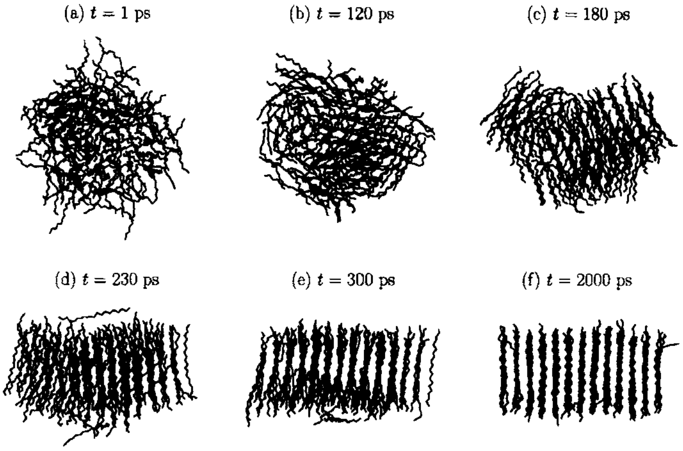

FIGURE 2 The chain configurations of 100 short chain molecules for $T = 400$ K viewed along the *b*-axis. (a) $t = 1$ ps, (b) $t = 120$ ps, (c) $t = 180$ ps, (d) $t = 230$ ps, (e) $t = 300$ ps and (f) $t = 2000$ ps.

find the following features: (i) In the early time ($t = 1$ ps), the configuration of chain molecules is *random*. (ii) With the elapse of time, the local orientationally-ordered regions (clusters) grow in several positions ($t = 120$, 180 and 230 ps) and at last they coalesce into a large cluster ($t = 300$ ps). (iii) At $t = 2000$ ps, a highly ordered structure is formed.

3.2. Local Orientational Order

In order to investigate the growth process of the local orientational order, we introduce the concept of a "*cluster*" as a bunch of local orientationally-ordered chains [10, 13]. The definition of a cluster is as follows. Two chain molecules belong to the same cluster if the following two conditions are satisfied: (i) $|\mathbf{r}_c^i - \mathbf{r}^j{}_c| < r_0$ and (ii) $\alpha_{ij} < \alpha_0$, where $\mathbf{r}_c^i$ is the position vector of the center of mass of the i-th chain, α_{ij} is the angle between the principal axis with the smallest moment of inertia of the i-th chain and that of the j-th chain and satisfies $0 \leq \alpha_{ij} \leq \pi/2$. In our calculations, we set $r_0 = 1.5\sigma$ and $\alpha_0 = 10°$. We show, in Figure 3, the largest cluster size s at $T = 400$ K as a function of time. It can be seen from this figure that the growth of the clusters proceeds *stepwise*. From the analysis of clusters, it is found that the clusters grow in a stepwise fashion because the growth of clusters proceeds through coalescence of them [13]. The stepwise behavior is also found in the global bond-orientational order parameter [13].

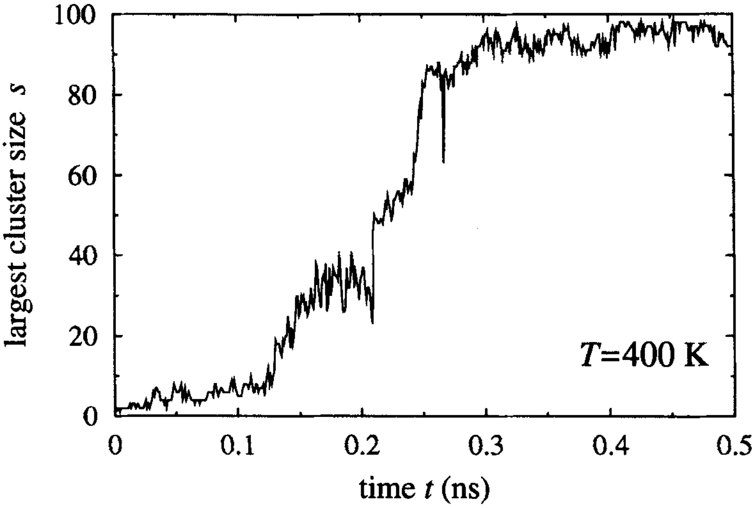

FIGURE 3 The size of the largest cluster s *versus* time t at $T = 400$ K.

3.3. Structure

Here, we study the orientationally ordered structure obtained by our MD simulation. At $T = 400$ K, since the ratio of the lattice constants a/b is equal to $1.733 \approx \sqrt{3}$, chain molecules are found to be packed hexagonally (Fig. 4). The lattice constants a and b, and the ratio a/b are plotted in Figure 5 at various temperatures. Figure 5(a) indicates that the parameter a decreases as the temperature decreases while the parameter b stays almost constant compared with the variation of a in this temperature region. The temperature dependence of the parameters a and b in our isolated short chain-molecule system is in qualitative agreement with the experimental results for the R_{I} phase of odd-numbered n-alkanes [19] and the MD calculations for the infinite chain model of n-alkanes [7]. From Figure 5(b), it is found that the ratio a/b takes the hexagonal value $\sqrt{3}$ at $T = 400$ K and decreases as the temperature decreases.

We then study the distribution of *gauche* defects. We define the *gauche* state by $| \phi | > \pi/3$, where ϕ is the dihedral angle. We plot the fraction of *gauche* states P_{gauche} *versus* bond number n_{B} in Figure 6 at various temperatures. Note that bonds with $n_{\mathrm{B}} = 1$ and $n_{\mathrm{B}} = 10$ correspond to the end bonds and the central bonds, respectively. This figure tells us that almost all the bonds are in the *trans* state at low temperatures ($T = 100$ and 200 K) while *gauche* states are excited predominantly in the chain ends at

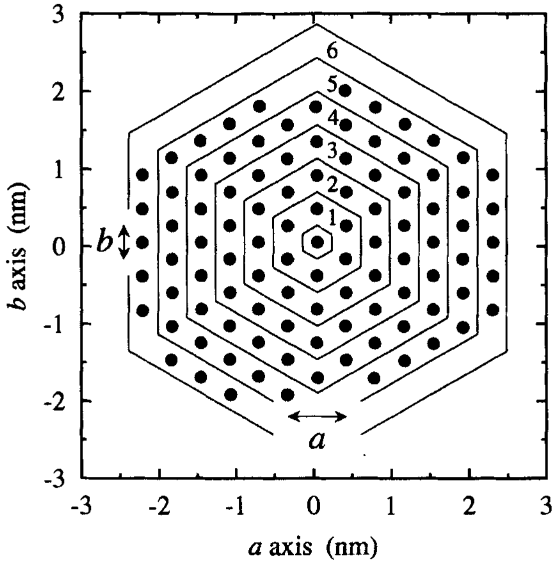

FIGURE 4 The center-of-mass positions of individual chain molecules for $T = 400\,\text{K}$ viewed along the c-axis. Hexagons are depicted in order to show a hexagonal packing of the chain molecules. A figure in each layer denotes a layer number.

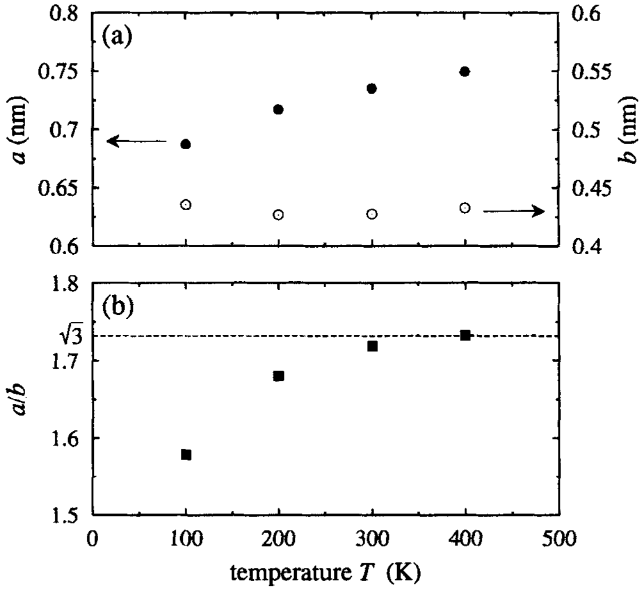

FIGURE 5 (a) Lattice constants a and b, and (b) the ratio a/b *versus* temperature T. A dashed line indicates the hexagonal value $\sqrt{3}$.

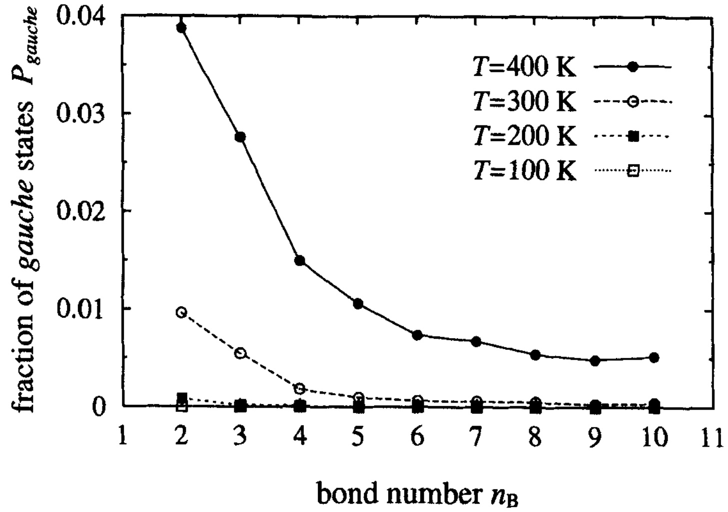

FIGURE 6 The fraction of the *gauche* states P_{gauche} *versus* bond number at various temperatures.

$T = 300$ and 400 K. This feature is in qualitative accord with the experimental results for n-$C_{21}H_{44}$ [20] and the MD results [7]. It should be noted that *gauche* states are excited even in the chain interiors at $T = 400$ K.

3.4. Molecular Mobility

In this section, we investigate the molecular motion at various temperatures. In order to measure the extent of the molecular motion of chain molecules, we define the average fluctuations along individual axes in each layer l as

$$\Delta a(l) = \left\{ \sum_{m \in l\text{-th layer}} \frac{1}{n_l} \langle (a_c^m - \langle a_c^m \rangle)^2 \rangle \right\}^{1/2}, \tag{5}$$

$$\Delta b(l) = \left\{ \sum_{m \in l\text{-th layer}} \frac{1}{n_l} \langle (b_c^m - \langle b_c^m \rangle)^2 \rangle \right\}^{1/2}, \tag{6}$$

$$\Delta c(l) = \left\{ \sum_{m \in l\text{-th layer}} \frac{1}{n_l} \langle (c_c^m - \langle c_c^m \rangle)^2 \rangle \right\}^{1/2}, \tag{7}$$

where $\mathbf{r}_c^m = (a_c^m, b_c^m, c_c^m)$ is the position vector of the center of mass of the m-th chain, n_l denotes the number of chain molecules involved in the l-th layer, $\langle \cdots \rangle$ represents the time average between 1500 and 2000 ps and the zeroth layer corresponds to the central chain. In Figure 7, we show the average fluctuations Δa, Δb and Δc as a function of the layer number l at various temperatures. From Figures 7(a) and 7(b), we find that the transverse chain motion is not so dependent on the temperature variation. By contrast, it is found from Figure 7(c) that the longitudinal chain motion increases dramatically as the temperature increases. It is also found that the transverse chain motion as well as the longitudinal chain motion increases remarkably in the outer three layers ($l = 4$, 5 and 6). This finding is in good agreement with the results of MC simulations on *n*-alkanes by Yamamoto *et al.* [5,6].

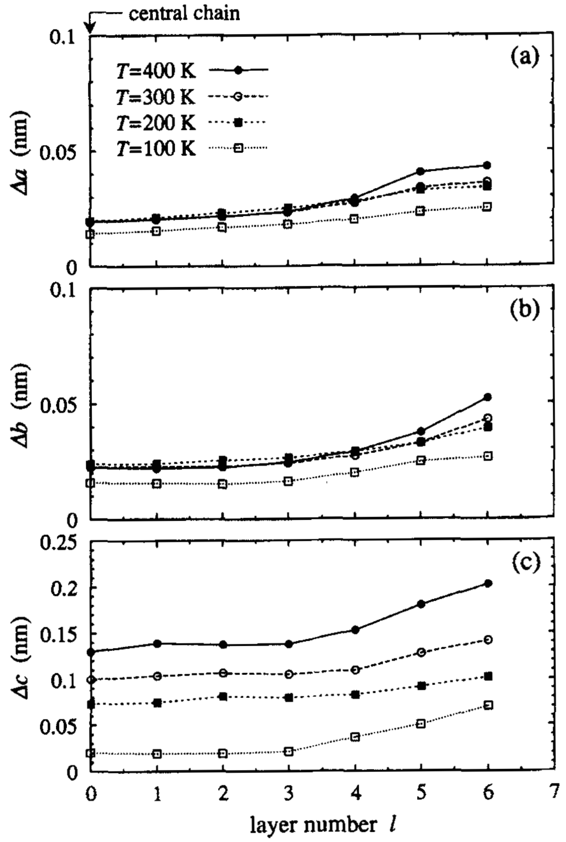

FIGURE 7 Average fluctuation (a) along the *a*-axis Δa, (b) along the *b*-axis Δb and (c) along the *c*-axis Δc *versus* layer number at various temperatures.

4. SUMMARY AND DISCUSSION

By carrying out MD simulations of 100 short chain molecules and analyzing the growth process of clusters and the molecular motion, we have obtained the following results:

(1) The orientationally ordered structure is formed at low temperature by cooling from a random configuration at high temperature.
(2) The ratio of the lattice constants a/b decreases from the hexagonal value $\sqrt{3}$ at 400 K as the temperature decreases.
(3) The local orientationally-ordered clusters grow in a *stepwise* fashion.
(4) The *gauche* defects are located predominantly in the chain ends.
(5) The longitudinal chain motion increases dramatically as the temperature increases.
(6) The chain motion increases remarkably in the outer three layers.

In the analysis of the ordered structure, the stacking of layers is not taken into account because the obtained orientationally-ordered structure is a monolayer structure. It seems reasonable to suppose that the reason why the obtained structure is not a lamella structure but a monolayer structure is that the system size is too small. We should carry out the MD simulation of much more chain molecules in order to investigate the effect of stacking on the structure.

In our simulation, the ordered structure is obtained even at very high temperature. We may say that the reason for this is that the torsional energy difference between the *trans* and the *gauche* states in the DREIDING potential is larger than that in the real *n*-alkanes.

From our MD simulations, we may say that the united atom approximation is good enough to study the structure and the translational motion qualitatively. However, our preliminary results on the rotational motion of chains show that the united atom approximation is not enough. The hydrogen atoms must be incorporated explicitly in order to study the rotational motion.

For the future work, we will carry out MD simulations of long chain molecules in order to investigate the effect of the entanglement on the structural formation.

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