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Micro Processes Study on Structure Change in N-Pentadecane Thin Film Adsorbed on Substrate: A Molecular Dynamics Simulation

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Abstract

It is experimentally found that adsorbed thin film consists of chain molecules changes its structure when it is heated at temperature lower than the melting point; but the molecular micro processes are remaining unknown; here we investigated the micro processes of structure change in n-pentadecane thin film adsorbed on substrate by use of molecular dynamics simulation. We found that, at temperature 200K (lower than the melting point), the isotropic amorphous thin film becomes a crystalline thin film in which molecule chains parallel to the substrate with relaxation time of about 12000ps; however, at temperature 290K (also lower than the melting point), the thin film structure changed essentially, the molecule chains changed their orientation from parallel to the substrate becomes nearly perpendicular to the substrate with relaxation time of about 5000ps.

Keywords: Structure change, N-alkane, Thin film, Substrate, Molecular dynamics simulation.

Contents

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1. Introduction

Composite materials and their manufacturing methods had become a very important field with the increment demand of functional materials by the end of last century [1]. Development of thin film adsorbed on substrate for industry and medical treatment have been attracting much attention; and the functional materials consist of organic long chains used for living body are the topical subjects [2-6]. All of the functions of the functional materials are closely depend on the manufacturing technology of the composite materials [1, 2, 7, 8]. Among the manufacturing processes, one of the key process is to control the formation of the interfacial (or surficial) phase of two kind materials， and its fundamental is the mechanism of the interfacial interaction between the substrate and the adsorbed thin film [2, 9-12]. In order to improve the function of the composite materials, the atomic and the molecular micro processes should be known clearly [13-15]. However, at the present, the composite materials are manufactured by controlling the composite conditions (temperature, pressure, proportion of components, etc.), then examine the functions of the composited material; if the functions are not satisfied to the demand, then adjust the composite conditions and manufacture again [16-19]. Therefore, many molecular micro processes of the manufacturing are remaining unknown. To our knowledge, there has been no report on the study of molecular micro processes of structural change in adsorbed long chain thin film.

In the present work, our purpose is to investigate the molecular micro processes of structural change in *n*-pentadecane thin film adsorbed on substrate. For the molecules in the *n*-pentadecane thin film, we adopt a conventional united atom model of *n*-alkane taking the valence angle bending and the dihedral angle rotation as well as the C–C bond stretching ; it is the same as our previous works [20, 21]. For the substrate, in order mainly to show the attractive property, here we consider a flat substrate without atomistic scale structures [22].

2. Model and Simulation Method

2.1. Molecular Model

The molecule is assumed to be composed of CH_2 and CH_3 groups. These groups interact with each other via bonded potentials (*e.g.* bond stretching, bond-angle bending, and dihedral-angle distortion) and non-bonded van der Waals potential. The atomic force field used in the simulation consists of, (i) the C-C bond-stretching potential

$$U_{stretch}(l) = \frac{1}{2} k_b (l - l_0)^2 , \qquad (1)$$

Where *l* is for the C-C bond length and *l0* is its equilibrium value, (ii) the potential for the bending of C-C-C bond angle θ

$$U_{bend}(\theta) = \frac{1}{2} k_\theta (\cos\theta - \cos\theta_0)^2 , \qquad (2)$$

Where θ0 is the equilibrium bond angle, (iii) the torsion potential

$$U_{torsion}(\phi) = k_\phi \sum_{n=0}^{5} a_n \cos^n \phi , \qquad (3)$$

where *Φ* is the dihedral angle formed by four consecutive carbon atoms, and (iv) the 6-12 Lennard-Jones potential between united atoms separated by more than three bonds along the chain and between the atoms in different chains,

$$U_{LJ}(r) = \begin{cases} 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}(r < r_c) \\ \\ 0 \ (r > r_c) \end{cases} , \qquad (4)$$

Table-1. Values of the parameters used in our simulation.[a]

Parameters	Values	Units
m (CH2)	1.4×10^{22}	kg/mol
m (CH3)	1.5×10^{22}	kg/mol
*l*0	0.152	nm
kb	3.46×10^{7}	J/nm2 mol
u 0	112.4	degree
*k*u	5.0×10^{5}	J/mol
*k*f	9.0×10^{3}	J/mol
*a*0	1.0	
*a*1	1.31	
*a*2	21.414	
*a*3	20.3297	
*a*4	2.828	
*a*5	23.3943	
ε(CH2–CH2)	500	J/mol
ε(CH3–CH2)	600	J/mol
ε(CH3–CH3)	730	J/mol
σ(CH2–CH2)	0.38	nm
σ(CH3–CH2)	0.38	nm
σ(CH3–CH3)	0.38	nm
rc	2.50	σ(CH2–CH2)
T	4.1×10^{-13}	s
Δ*t*	2.05×10^{-15}	s

[a] These parameter values were taken from Ref. Rigby and Roe [23].

where r is the distance between the atoms, and r_C is the cut-off distance chosen to be 2.5σ. In all presentations in this work, the length and the energy are expressed by the following reduced units: the unit length σ=0.38 nm, the unit energy ε= 500 J/mol. Values of all the parameters used in our simulation are, the same as those used in our previous papers [20, 21] listed in Table I.

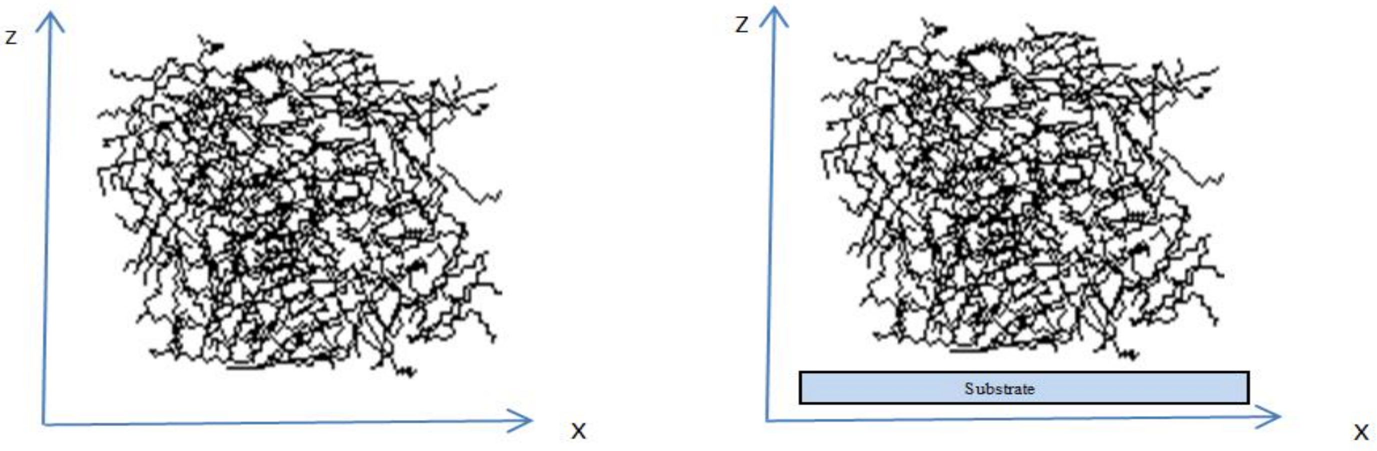
2.2. Substrate Model

It has been experimentally found that some anomalous change of molecular orientation takes place in films on a glass substrate [22] however, the micro process in molecular level remain unknown. In order to show the main attractive property only, here we consider a flat substrate without atomistic scale structures. Hence the substrate potential only depends on the distance r from the evaporated molecule to the substrate surface. Here we adopt the following conventional form given by Steele [24]:

$$\phi_{sub}(r) = \frac{2\pi K\sigma^2}{A}\left\{\frac{2}{5}\left(\frac{\sigma}{r}\right)^{10} - \left(\frac{\sigma}{r}\right)^{4} - \frac{\sigma}{3dr}\left(\frac{\sigma}{r+0.61dr}\right)^{3}\right\} \quad (r < 5r_c), \qquad (5)$$

By setting the parameters in eq.5, the substrate has the depth of the potential minimum of about 4ε, it is about one-third of the total attraction of an n-alkane crystal when {001} is the substrate surface. This is also a reasonable value for highly attractive substrate such as metals and graphite [22, 25].

2.3. Preparation of Isotropic Melt Initial State



(a) (b)

Figure-1. Isotropic melt initial state. (a) Isotropic melt n-pentadecane molecules; (b) The isotropic melt n-pentadecane molecules are put on the substrate.

An initial crystalline sample was composed of 400 *n*-pentadecane molecules, and it has no interaction with the substrate. In order to prepare an isotropic melt initial state, the initial sample was heated with a low temperature ramping rate, and is relaxed at 500K which is well higher than the melting point but lower than the evaporation temperature. After sufficient long relaxation time of about 10,000ps, the isotropic melt source is completed [Fig.1 (a)], then it is put on the substrate described above. Thus the isotropic melt initial state is prepared [Fig.1 (b)]. There are periodic condition in x and y axis directions.

3. Results and Discussions

3.1. Orientation of Molecules in the Thin Film at Lower Temperature (200K)

(1) Starting from the initial state, Figure 1 (b), we first quenched the initial state at temperature 200K. with about 12800ps relaxation, the isotropic amorphous thin film becomes a crystalline thin film in which molecule chains parallel to the substrate; the snapshot of the crystalline thin film is shown in Figure-2 (d).

(2) Process of the structure change in the thin film at temperature 200K is shown in Figure-2 (a), (b) and (c).

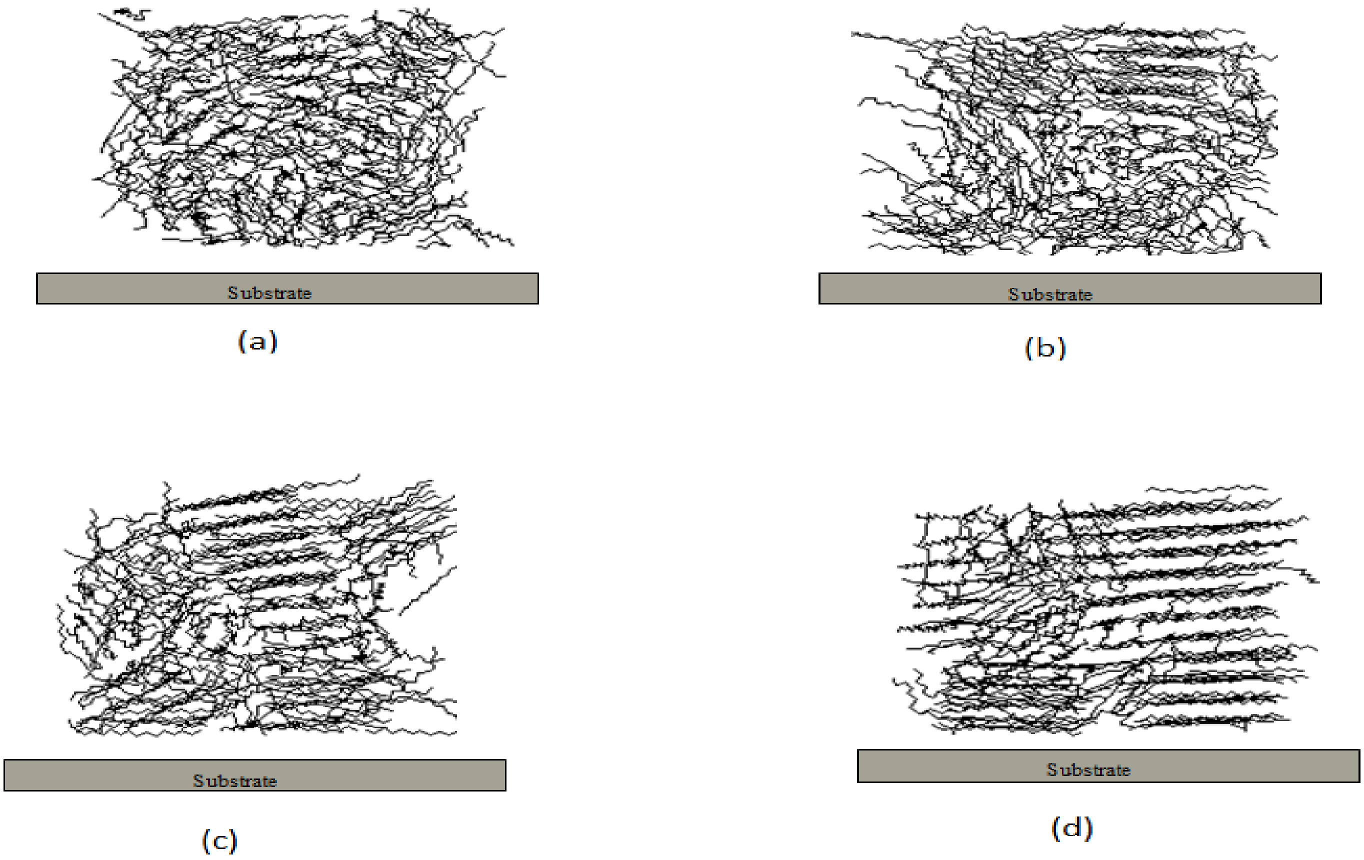


Figure-2. The micro processes of structure change in the n-pentadecane thin film from isotropic melt initial state becomes a crystalline state. (a) The snapshot after 1600ps relaxation from the isotropic melt initial state. (b) The snapshot after 4000ps relaxation. (c) The snapshot after 8000ps relaxation. (d) The snapshot after 12800ps relaxation.

3.2. Orientation of Molecules in the Thin Film at Higher Temperature (290K)

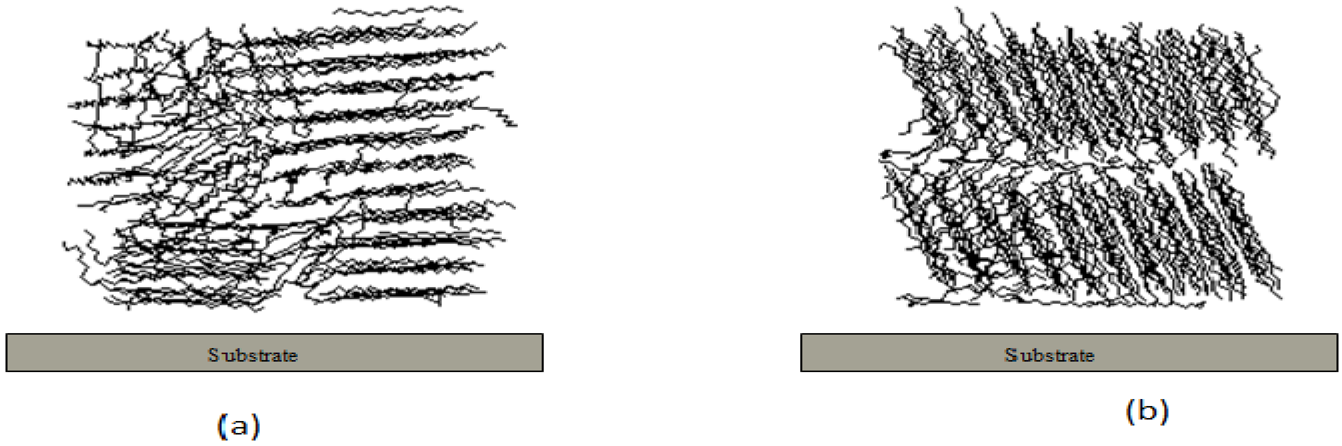


Figure-3. The essential structure change of n-pentadecane thin film. (a) The molecule chains parallel to the substrate at temperature 200K. (b) The molecule chains perpendicular to the substrate at temperature 290K.

(1) In order to investigate the effect of higher temperature on the structure change in the thin film, the crystalline state shown in Figure-3 (a) is used as initial state (namely the Figure 2 (d)), and it is heated up continuously with temperature rising rate of about 1K/ps. As the temperature rise to 290K, the temperature rising is stopped and the sample begin to be relaxed at 290K. As the relaxing during about 5000ps, It is found that the structure of the thin film changed essentially, the molecular chains changed their orientation from parallel to the substrate (see Figure 3 (a)) becomes nearly perpendicular to substrate (see Figure 3 (b)).

(2) Representative snapshots of the structure change process at temperature 290K are shown in Figure 4. Snapshot Figure 4 (a) (namely the Figure 2 (d)) is initial state, temperature is at 200K, molecule chains parallel to the substrate. Figure 4 (b) through (h) are the middle snapshots of the change process, temperature is at 290K. Snapshot Figure 4 (i) is final state, temperature is at 290K, molecule chains perpendicular to substrate.

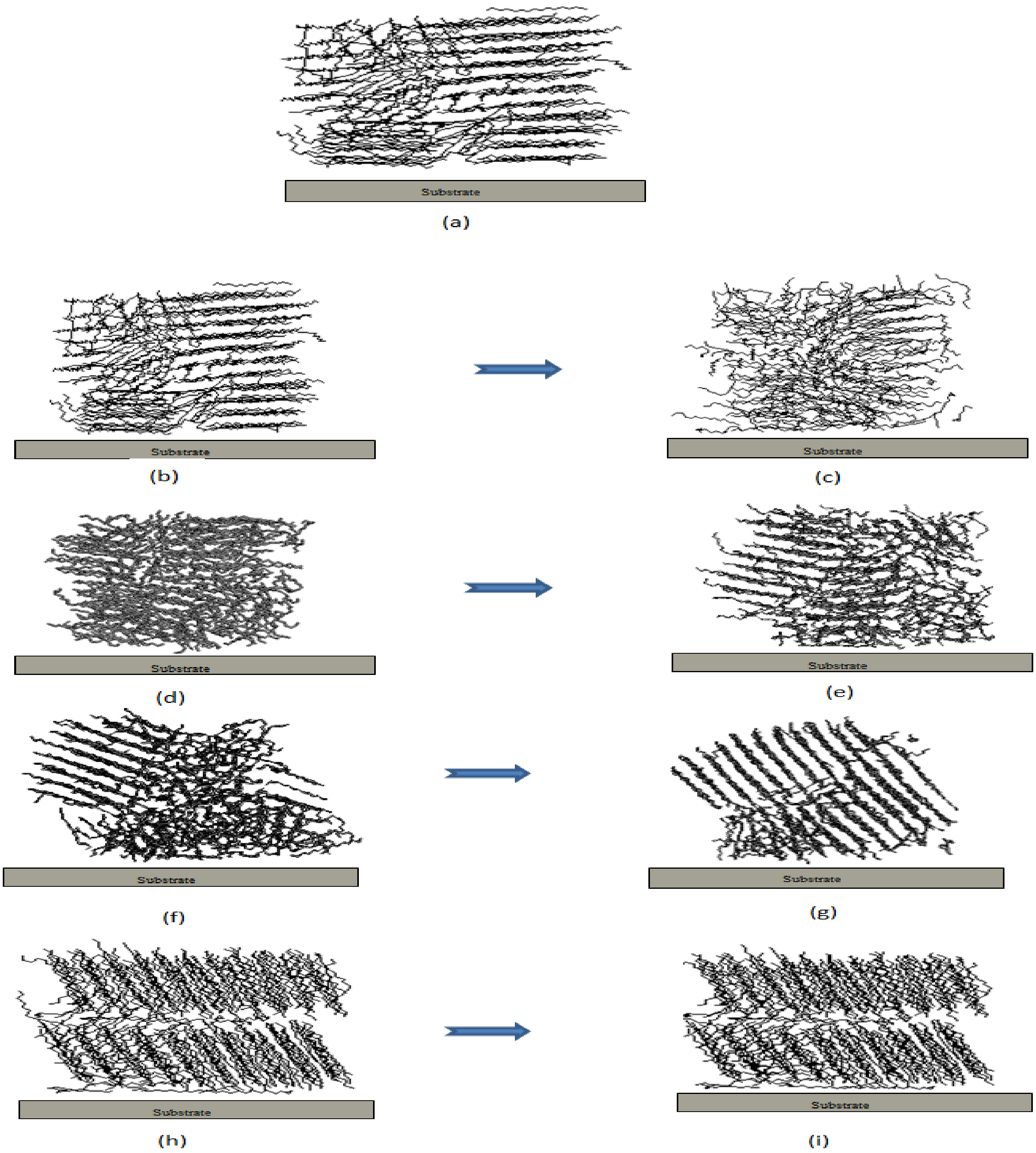


Figure-4. Snapshots of structure change in *n*-pentadecane thin film after temperature changed from 200K to 290K.
(a) Initial state, temperature 200K, molecular chains parallel to the substrate.
(b) Relaxed State of the thin film at temperature T_{relax} = 290K and relaxant time t_{relax} = 100ps.
(c) Relaxed State, T_{relax} = 290K and t_{relax} = 1600ps.
(d) T_{relax} = 290K, t_{relax} = 2400ps. (e) T_{relax} = 290K, t_{relax} = 3000ps.
(f) T_{relax} = 290K, t_{relax} = 3500ps. (g) T_{relax} = 290K, t_{relax} = 3900ps.
(h) T_{relax} = 290K, t_{relax} = 4300ps. (i) T_{relax} = 290K, t_{relax} = 4800ps.

3.3. Effect of the Substrate and the Surface

It has been shown above that the chain orientation has an outstanding change, from parallel to the substrate surface to perpendicular to the substrate surface; It occurs at temperature (both 200K and 290K) below the melting point of about 345K [21, 26, 27]. There is no such a phenomenon in bulk crystalline *n*-alkanes. This indicates that the substrate has very important effect on the structure change. This phenomenon is agreement with the results of experiment work [22].

The feature that the surface monolayer prefers to perpendicular to the free surface is similar to the result of our previous works [20, 21] which are studies on the surface freezing. Therefore, we think that the free surface may have important effect on the structure change in the thin film. The result as a whole is agreement with the results of other experiment and simulation works [22, 28].

4. Conclusions

We investigated micro processes of the structure change of *n*-pentadacane thin film adsorbed on solid substrate by molecular dynamics simulation. At the temperature below the melting point, we found that the *n*-pentadecane molecular chains in the crystal thin film basically have two kinds of orientations. One kind is that the molecular chains parallel to the substrate at temperature 200K, and another is that the chains perpendicular to the substrate at 290K.

These results indicate that the substrate has the effect which strongly affects the temperature dependence of structure change in the adsorbed thin film. On the other hand, because the molecules in the surficial part change their orientation to perpendicular to the substrate previous to the inner part, therefore, we think that the free surface may have important effect on the structure change in the thin film.

As a remark, we must add that the present simulation give the melting point value of about 345K of n-pentadecane, this is considerably higher than that of the experimental value of about 285K. We think this difference comes from the united atom model and from the force field adopted, as well as short duration of simulation in comparison to the typical time scale of the melting of real *n*-alkane crystals. Similar tendencies have also been observed in other simulation works [20, 21, 26, 28] References 27 and 28 show that the discrepancy is larger for longer chain alkanes and shorter chain alkanes, respectively. This may be a serious defect in our present simulation, but it also has a merit of suggesting possible temperature dependence of the structural change, and of showing possible molecular micro processes.

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