

# Molecular dynamics study of the behavior of a single long chain polyethylene on a solid surface

H. X. Guo, X. Z. Yang, and T. Li

*Polymer Physics Laboratory, Center for Molecular Science, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080 China*

(Received 3 August 1999; revised manuscript received 1 December 1999)

A molecular dynamics simulation has been used in exploring the behavior of a single long chain polyethylene (PE) on a solid surface. We have established how varying the intermolecular (polymer-surface) van der Waals (vdW) interaction force effects the structural and dynamic properties of the polymer chain. For a high intermolecular vdW force, the starting PE chain adsorbs on to solid surface, and develops into a stretched monolayerlike structure. However, for a low intermolecular vdW force, segments in the PE chain avoid the surface and fold into a compact lamellalike structure. However, for a moderate intermolecular vdW force, the PE chain forms into a polylayerlike structure where stems align parallel to the surface. Unlike the short chain molecules, the overall conformations developed by the long chain PE possess a degree of intramolecular (intrachain) order. In addition to these, we have systematically analyzed the changes in components of the square of the radius of gyration parallel and orthogonal to the surface, as well as the intermolecular and intramolecular vdW energy of the PE chain when it transforms to monolayerlike, lamellalike, and polylayerlike configurations. Results show that the structural change is in phase with the variation of parallel and orthogonal components of the square of the radius of gyration, and has a corresponding relation with the intermolecular and intramolecular vdW energy. The intermolecular vdW force drags the PE chain lying on the surface and stretching into a loose monolayer. The intramolecular vdW force, rather than any of the other intramolecular interactions, drives the PE chain folding into a compact, ordered lamella.

PACS number(s): 83.20.Jp, 61.41.+e, 36.20.Ey

## I. INTRODUCTION

The behavior of polymers on a solid surface is an area of theoretical and experimental interest. Obtaining detailed microscopic level information on the surface conformation and dynamics of polymers could greatly aid the improvement of existing polymer materials and the development of new ones. However, detailed structural changes of polymers on solid surfaces are difficult to investigate experimentally. Recently, rapidly developed computer simulations opened new avenues for such investigations. People have used the Monte Carlo (MC) method to study the adsorption of polymers on a solid surface [1–7]. Besides the MC method, molecular dynamics (MD) simulation is also a standard theoretical tool. MD simulation is not only capable of providing the same type of information as generated from MC simulations but can also demonstrate a detailed microscopic transition behavior. In addition, the MD simulation makes no assumption about harmonic or collective motion, and is the only practical way to probe the time and temperature dependent behaviors in a system of interest. At present, people began to use the MD method to study the adsorption of polymers on a solid surface [8]. Results show that the MD method can simulate the entire adsorption process. However, all these computer simulations, that contribute to the study of adsorption process, are not concerned about how the polymers behave under various polymer-surface interaction forces. In addition, in these simulations, the chain length is always limited below 150 segments. The obtained adsorbed structure has a low degree of intrachain order. Sundararajan and Kavassalis [9] have used a MD simulation to examine the chain-folding phenomenon of a single-polyethylene (PE) chain in vacuum. They found that at a torsional barrier of 2 kcal/mol the minimum chain length requirement for the for-

mation of a stable ordered folded-chain lamella is 150 CH<sub>2</sub>. This is because for a chain with a length above 150 CH<sub>2</sub> units, the intrachain van der Waals (vdW) energy is low enough to compensate for the increase in energy owing to torsion and bond-angle deformations in the fold. For polymers on a solid surface, with the increase of chain length, compared with the polymer-surface interaction force the intrachain vdW interaction increases. So for long chain polymers on a solid surface, their conformational changes will be not like those of the short ones. Furthermore, in these simulations, one segment of the starting chain is usually anchored to a surface site. Such an initial conformation is considered as a serious limitation for modeling the physically adsorbed polymer.

In this paper, we use the MD method to simulate the behavior of long chain polymers on a solid surface. We wish to establish how varying the polymer-surface vdW force affects the structural and dynamic properties of long chain polymers on a solid surface. At the same time, we wish to identify the influence of the intrachain vdW force on the structural and dynamic properties of long chain polymers on a solid surface. Therefore, we have to discuss the relation between the structural transition and the polymer-surface interaction energy and the intrachain vdW energy. In order to understand the behavior of polymers on a solid surface in detail, as well as to reduce the expensive computer simulation time, we, like other authors [1,2,7,8], focus our attention on a single chain on the surface. Such chain studies are extremely useful in understanding and elucidating the behavior of many chains on the surface. All these investigations, were concerned with the effect of polymer-surface interaction. Thus, like in Refs. [7,8], we neglect the solvent effect. Such a simulation corresponds to a polymer chain in a solid-vacuum interfacial environment.

## II. MODEL

Our physical model consists of a single long flexible PE chain with length more than 200 CH<sub>2</sub> units (each CH<sub>2</sub> group is treated as a united atom) near an impenetrable, homogeneous solid surface. In a MD simulation, the long chain PE will develop into a thermodynamically stable structure on the solid surface. The specific initial conformation used is unimportant, because its memory will be lost during the simulation. Therefore, in this paper, the initial configuration at a given chain length is selected at random without an overlapping of the nonbonded atoms. As mentioned above, one of our objectives is to study the effect of the polymer-surface vdW interaction force on the behavior of the PE long chain. To reduce the expensive time consumption in calculating the polymer-surface vdW force, we assume that the solid substrate is made up of carbon atoms and can be divided into two-dimensional, infinite, uniform layers parallel to the surface. The surface is located in an infinitely extended  $x$ - $y$  plane at  $z=0$ . For a chain atom at  $(x_i, y_i, z_i)$ , it will interact with substrate atoms located within the area of  $\pi[R_{\text{cutoff}}^2 - (z_i + kl)^2]$  in the  $k$ th layer. Here  $x_i$ ,  $y_i$ , and  $z_i$  are the Cartesian coordinates of chain atom  $i$ ,  $R_{\text{cutoff}}$  is the cutoff distance for the nonbonded interaction, and  $R_{\text{cutoff}}=9 \text{ \AA}$ ;  $k$  is the number of layers,  $k=0,1,\dots,[(R_{\text{cutoff}}-z_i)/l]$ ,  $l$  is the layer spacing, and  $l=4 \text{ \AA}$ . For further simplification, we ignore the corrugation of the surface and assume that within layers the substrate atoms are homogeneously distributed with a fixed area number density of carbon atoms,  $n$ . Subsequently, the polymer-surface vdW energy based on the pairwise 6–12 Lennard-Jones interaction can be expressed as

$$\begin{aligned} \mathcal{E}_{\text{vdW}} &= \sum_{i=1}^N \sum_{k=0}^{(R_{\text{cutoff}}-z_i)/l} 2\pi n \varepsilon \left[ \int_0^{\sqrt{R_{\text{cutoff}}^2 - (z_i + kl)^2}} \frac{\sigma^{12}}{[\tau_k^2 + (z_i + kl)^2]^6} - 2 \frac{\sigma^6}{[\tau_k^2 + (z_i + kl)^2]^3} \right] \tau_k d\tau_k \\ &= \sum_{i=1}^N \sum_{k=0}^{(R_{\text{cutoff}}-z_i)/l} \pi n \varepsilon \left[ \frac{\sigma^{12}}{5(z_i + kl)^{10}} - \frac{\sigma^6}{(z_i + kl)^4} - \frac{\sigma^{12}}{5R_{\text{cutoff}}^{10}} + \frac{\sigma^6}{5R_{\text{cutoff}}^4} \right] \end{aligned} \quad (1)$$

$\varepsilon$  and  $\sigma$  are the arithmetically averaged polymer-surface Lennard-Jones parameters.  $\tau_k$  is the projection of position of the chain atom  $i$  onto the  $k$ th layer. Hentschke [10] compared the adsorbed carbon atom-graphite basal plane vdW energy under conditions of including the corrugation of the surface and neglecting the corrugation effect within layers. Results show that there is little difference between the two cases, such that the corrugation effects produce a weak contribution to the polymer-surface vdW energy. Equation (1) approximates to the true polymer-translation symmetry surface vdW energy. As we know, the polymer-surface vdW force is equal to  $-\nabla \mathcal{E}_{\text{vdW}}$ . Under these assumptions, the polymer-surface vdW force is dependent on  $z_i$  and  $n$ . Obviously, for the same initial configuration, by varying the number density of the substrate carbon atom, we can vary the polymer-surface interaction force. In this case, a solid with a high carbon atom number density corresponds to material which has a high

polymer-surface interaction force, which the PE chain is strongly attracted to. Conversely, a solid with a low carbon atom number density corresponds to that material which has a low polymer-surface interaction force, which the PE chain easily wiggles away from. In this paper, in order to compare the different conformations developed by the long and short chain molecules, we have also simulated the behaviors of short chain molecules with length below 100 CH<sub>2</sub> units on a solid surface.

The configuration energy for the model PE chain is given as a sum of the intrachain (intramolecular) interaction energy and the polymer-surface (intermolecular) vdW energy calculated using the *Dreiding II* force field,

$$\mathcal{E} = E_{\text{stretch}} + E_{\text{bend}} + E_{\text{torsion}} + E_{\text{vdW}} + \mathcal{E}_{\text{vdW}}. \quad (2)$$

The first four terms describe the intramolecular interaction including bond stretching, bond angle bending, and torsion, as well as the nonbonding vdW interaction. The intramolecular vdW interaction is also calculated by the pairwise 6–12 Lennard-Jones interaction. Through out our simulation, we employ the NVT ensemble. A constant temperature of 300 K is attained using Nosé-Hoover method. The equation of motion is solved by the leapfrog Verlet algorithm with a time step of 0.001 or 0.0002 ps. The relaxation constant for the heat bath variable is 0.1 ps. The calculations are performed using ourselves designed MP2 molecular dynamics simulation software in a PC. Although the long chain PE is capable of developing into a thermodynamically equilibrium structure on a solid surface, the time scale for such process is prohibitively long. For example, in Ref. [5], King and Cosgrove indicated that well in excess of  $10^6$  moves would be required before a 49-segment chain could reach something approximating true thermodynamic equilibrium in a MC simulation. For a chain with a length below 1000 CH<sub>2</sub>, the thermodynamic equilibrium conformation can be obtained in our MD simulation. However, for a chain with a length above 4000 CH<sub>2</sub>, attainment of the true thermodynamic equilibrium becomes rather difficult or even impossible due to our limited computer resources. Therefore, in this paper all the simulations are run until the chain approximates or reaches its equilibrium structure, i.e., until the simulated chain lost its memory of the initial configuration, and running the program further resulted in no discernable changes in the structural properties and energy beyond natural fluctuations.

In the present work, to determine the position of a PE chain relative to the surface, we calculate the polymer center of mass along the  $z$  direction  $z_{\text{cm}}$ . To characterize the anisotropic configuration of the polymer, components of square of the radii of gyration in directions parallel  $s_{\parallel}^2$  and perpendicular  $s_{\perp}^2$  to the surface were calculated:

$$s_{\parallel}^2 = \frac{1}{N} \left( \sum_{i=1}^N (x_i - x_{\text{cm}})^2 + (y_i - y_{\text{cm}})^2 \right), \quad (3)$$

$$s_{\perp}^2 = \frac{1}{N} \left( \sum_{i=1}^N (z_i - z_{\text{cm}})^2 \right), \quad (4)$$

where subscript cm stands for the polymer center of mass. To describe the conformation of a polymer at a surface, we

consider the content of local conformations known as trains, loops, and tails. Trains are consecutive segments in contact with the surface, loops lie between trains and extend away from the surface, and tails are series of segments at the chain ends that are not in contact with the surface.

### III. RESULTS AND DISCUSSION

We have simulated the behavior of PE chains with a length above 200  $\text{CH}_2$  units on a solid surface, with various carbon atom number densities. It is found that with the variation of the intermolecular vdW force, the polymer exhibits different configurations and dynamic properties. However, irrespective of whatever structure is formed, compared with the intermolecular and intramolecular vdW energy the contributions from bond stretching, bond angle bending, and torsion to the configuration energy are lower than 40%. Changes in the configuration energy, as well as the total energy (configuration energy and kinetic energy), are in phase with the intramolecular or the intermolecular vdW energy. The intramolecular vdW force rather than any of the other intramolecular interactions drives the PE chain folding into a compact, ordered lamella. The intermolecular vdW force drags the PE chain lying on the surface, and stretches it into a loose monolayer. Simulations with a starting conformation corresponding to the rotational isomeric state (RIS) or all-trans distribution, and simulations with explicit hydrogens as opposed to the united-atom approximation of the  $\text{CH}_2$  groups, led to similar results. In the following subsections, we describe the behavior of the long chain PE on a solid surface according to the relative magnitude of the intermolecular vdW force.

#### A. For a low intermolecular vdW force

Figure 1 shows the sequence of conformations at various times, for a starting amorphous PE chain with 4004  $\text{CH}_2$  units on the solid surface with a low carbon atom number density. Obviously, the chain is not attracted to the surface, but folds into a compact lamellalike structure. Simulations on the other long chains with different initial configurations, as seen in Fig. 2, also produced this kind of lamella. These obtained lamellae not only possess a deformed close-packed hexagonal symmetry, but also display both adjacent and non-adjacent foldings of the chain. The distance between the stems in lamella varies from 4.4–5.2  $\text{\AA}$ , similar to the inter-chain packing distance in the crystal structure of PE. The structural characteristics of the lamellae revealed by our simulations are in agreement with the MD simulation results of Sundararajan and Kavassalis [9,11]. However in the case of short chains, the phenomenon of stable chain folding is not observed.

Figure 3 shows parallel and orthogonal components of the square of the radius of gyration versus time, when the above long chain with 4004  $\text{CH}_2$  units develops into a lamella. Figure 4 plots its intramolecular interaction energy (including bond stretching, bond angle bending, torsion, and vdW), intermolecular vdW energy, configuration energy, and total energy as functions of time. It is apparent that under the condition of a low carbon atom number density or a low intermolecular vdW force, the intramolecular vdW energy is much lower than the intermolecular vdW energy. Contribu-

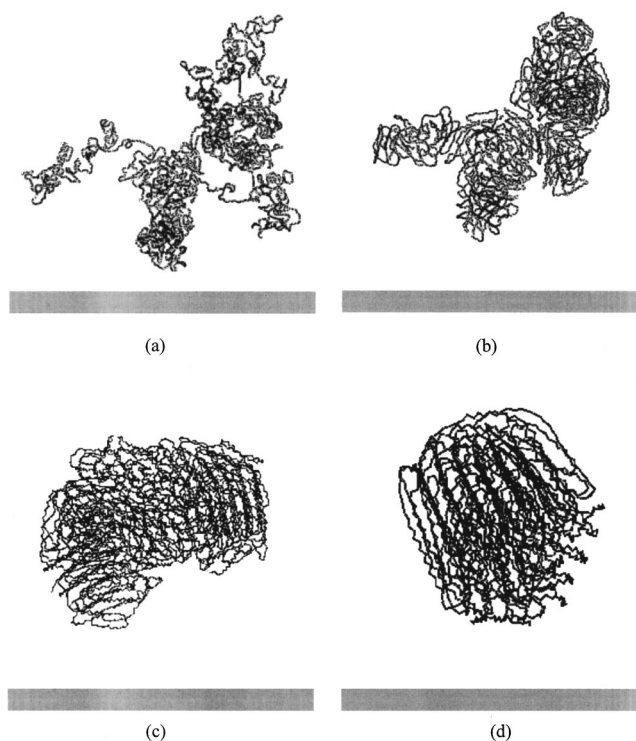


FIG. 1. Snapshots of conformations obtained from an amorphous PE chain with 4004  $\text{CH}_2$  units on the solid surface, with low carbon atom number density of  $0.01/\text{\AA}^2$  in the  $x$ - $z$  plane at (a) 0 ps, (b) 25 ps, (c) 145 ps, and (d) 980 ps.

tions from bond stretching, bond angle bending, and torsion to the configuration energy are averaged to about 38.85%. Changes in the configuration energy, as well as the total energy, are in phase with the intramolecular vdW energy. The model PE long chain evolves under the control of the intramolecular vdW force. To understand the molecular basis for the intramolecular vdW force induced folding process, we use Figs. 3 and 4 to illustrate the structure and energy

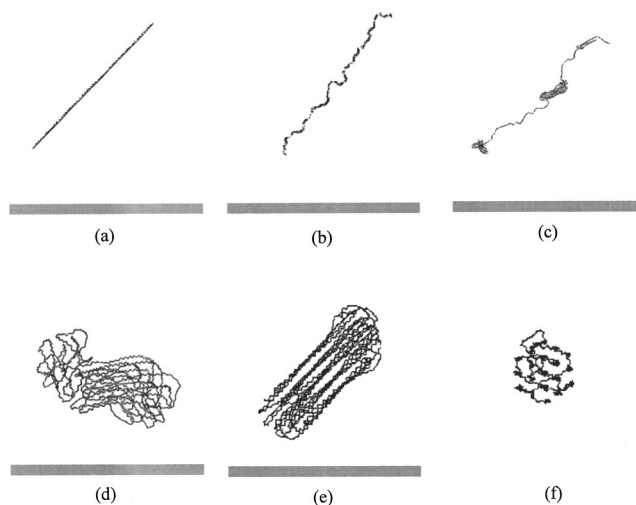


FIG. 2. Conformations extracted from a PE chain of 980  $\text{CH}_2$  units in an all-trans state on the solid surface with a carbon atom number density of  $0.01/\text{\AA}^2$  at various times. (a) 0 ps, (b) 15 ps, (c) 35 ps, (d) 130 ps, and (e) 7.83 ns in the  $x$ - $z$  plane, and (f) 7.83 ns along the stem direction.

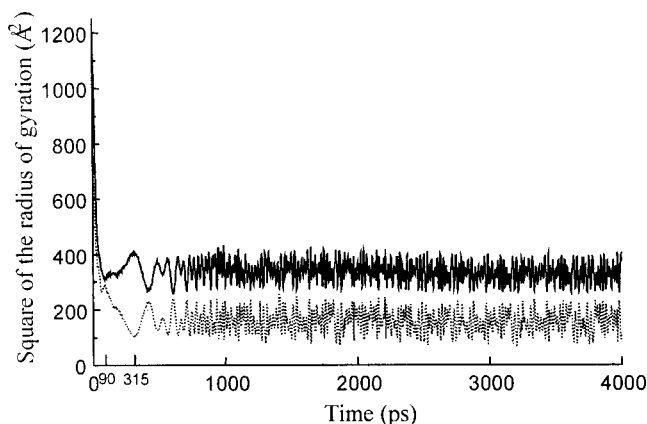


FIG. 3. Time evolution of the parallel (solid line) and perpendicular (dotted line) components of the square of the radius of gyration when an amorphous PE chain of 4004  $\text{CH}_2$  units forms into the lamella.

transitions when the long chain PE forms into a lamella. For the starting amorphous chain, within the first 90 ps, as shown in Fig. 1(b), segments condense into local folded domains in which the vicinal sequences of trans bonds aggregate together. Therefore,  $s_{\parallel}^2$  and  $s_{\perp}^2$  first decrease dramatically with time. As we know, outside the equilibrium distance the intramolecular vdW energy is an increased function of the inter-nonbonding-atom distance. The more compact the chain conformation, the nearer the distance between non-bonding atoms, and the more speedy the reduction of the intramolecular vdW energy. During this local folding process, segments initially near the surface leave the surface [Fig. 1(b)]. Like the intramolecular vdW energy, the intermolecular vdW energy outside the equilibrium distance is an increased function of distance between the segment and the surface. With segments leaving the surface, the intermolecular vdW energy rises quickly to its plateau value at 0 kcal/mol. Then, within the next 225 ps the local folded domains coalesce into a lamellalike structure, as seen in Fig. 1(c). This coalescence leads to a contraction in the  $z$  direc-

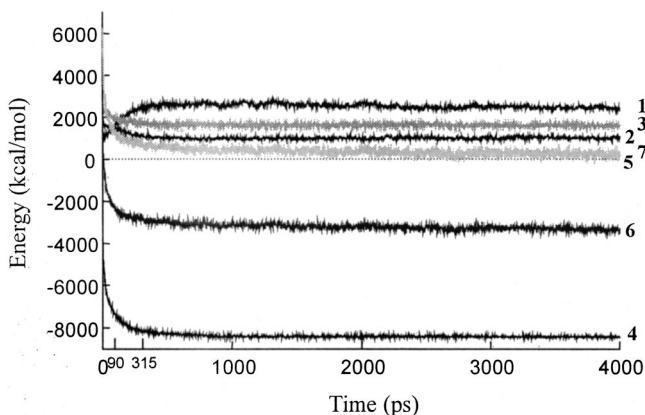


FIG. 4. Time evolution of the intramolecular interaction energy including bond stretching (labeled by 1), bond angle bending (labeled by 2), torsion (labeled by 3) and vdW (labeled by 4), intermolecular vdW energy (labeled by 5), configuration energy (labeled by 6), and total energy (labeled by 7) when an amorphous PE chain with 4004  $\text{CH}_2$  forms into the lamella.

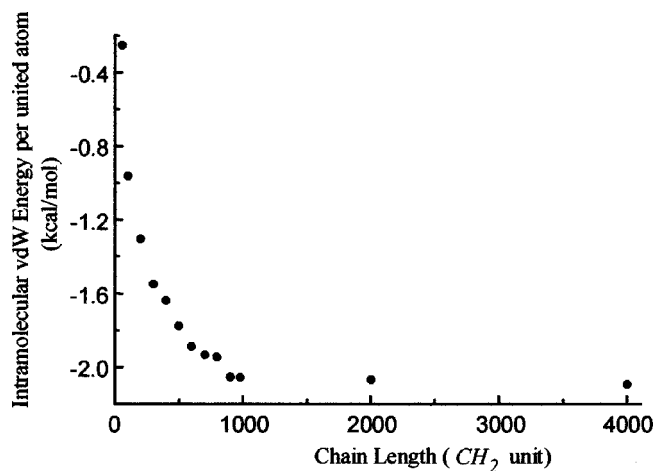


FIG. 5. Intramolecular vdW energy per united atom vs the chain length under the condition of a low number density of the carbon atom,  $0.01/\text{\AA}^2$ . The time averaged is taken between 3 and 4 ns.

tion, but expansions in the  $x$  and  $y$  directions. Therefore,  $s_{\perp}^2$  continuously reduces, but  $s_{\parallel}^2$  starts to increase. All these result in a slow decrease of the intramolecular vdW energy. Afterwards, as shown in Fig. 1(d), the lamella regulates the orientations of stems, and gradually develops into a bond orientationally ordered structure.  $s_{\parallel}^2$  and  $s_{\perp}^2$  fluctuate around each mean value, and no remarkable change is found. The intramolecular vdW energy reaches its asymptotic value. Compared with the starting amorphous configuration,  $s_{\parallel}^2$  and  $s_{\perp}^2$  of the final lamella have decreased 3.75 and 4.89 times. Obviously, the obtained lamella is a kind of compact structure. The behavior for a long PE chain with other values of the chain length is qualitatively similar. Although the order degree of the lamella produced by a long chain with 4004  $\text{CH}_2$  units is lower than that shown in Fig. 3(e), we believe that if we simulate further such an equilibrium conformation of lamella will certainly be obtained in this long chain.

As we expect, the intramolecular vdW interaction indeed increases with the chain length. In Fig. 5, we show the chain length dependence of the intramolecular vdW energy per united atom. The time average is taken between 3 and 4 ns. During this time interval the simulation system approached or attained the equilibrium state. Obviously, for the long chain, the absolute value of the intramolecular vdW energy per united atom is high. But as the chain length decreases, the value decreases at an accelerated velocity. Therefore, the shorter the chain, the smaller the contribution of the intramolecular vdW energy to the configuration energy. The non-dominating intramolecular vdW force cannot produce a stable fold. So stable chain folding is not observed in short chains. It is thus reconfirmed that the intramolecular vdW force, and not other intramolecular interactions, leads to this folded lamellar conformation.

### B. For a high intermolecular vdW force

Figure 6 shows snapshots of structural changes in an amorphous PE chain with 4004  $\text{CH}_2$  units on the solid surface, with a high carbon atom number density. We can describe the above process as follows. First, segments near the

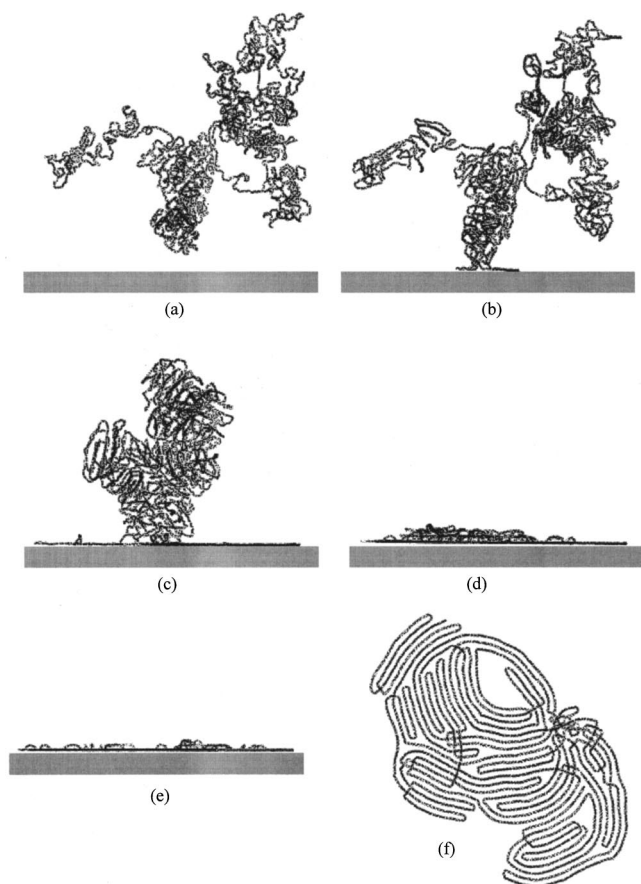


FIG. 6. Snapshots of structural changes of an amorphous PE chain with 4004  $\text{CH}_2$  units on a solid surface with a high carbon atom number density of  $0.25/\text{\AA}^2$  at various times: (a) 0 ps, (b) 5 ps, (c) 65 ps, (d) 280 ps, and (e) 6.88 ns in the  $x$ - $z$  plane, and (f) 6.88 ns in the  $x$ - $y$  plane.

surface anchor onto the surface, and others condense in space [Fig. 6(b)]. Afterwards, as seen in Fig. 6(c), the adsorbed segments are displaced along the surface, and drag their neighboring segments down to the surface, which bind to the surface in contiguous segments or in a train. However, the nonadsorbed segments condense further in space. Then more and more segments are dragged onto the surface. The PE chain forms into an unstable polylayerlike structure [Fig. 6(d)]. Finally, as displayed in Fig. 6(e), almost all the segments contact the surface, and stretch into a stable monolayerlike structure. No desorption occurs in the further simulation. Obviously, this is purely an adsorption process. Simulations on other long chains, as shown in Fig. 7, led to

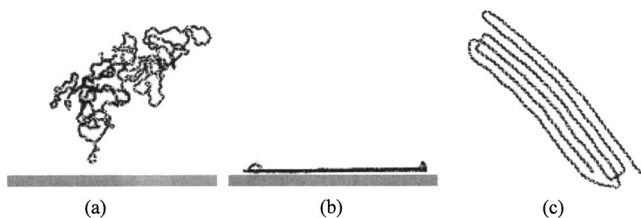


FIG. 7. Conformations extracted from an amorphous PE chain of 504  $\text{CH}_2$  units on the solid surface with a number density of the carbon atom of  $0.25/\text{\AA}^2$  at 0 ps (a) in the  $x$ - $z$  plane, and at 5 ns (b) in the  $x$ - $z$  plane and (c) in the  $x$ - $y$  plane.

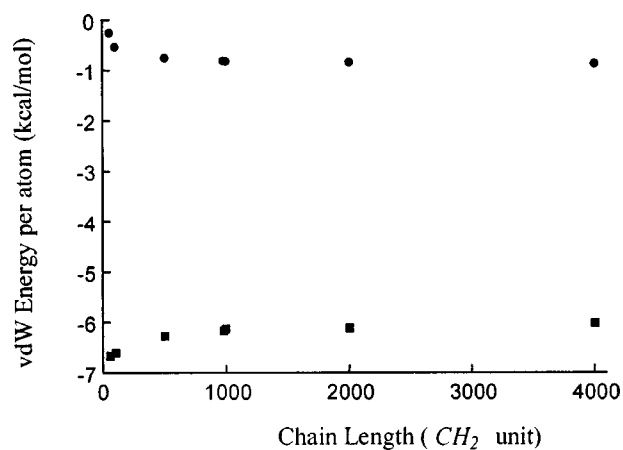


FIG. 8. The intramolecular ( $\bullet$ ) and the intermolecular ( $\blacksquare$ ) vdW energies per united atom vs the chain length under the condition of a carbon atom number density  $0.25/\text{\AA}^2$ . The time average is between 0 and 5 ns.

similar results. It is found that the monolayer developed by these long chains possesses a degree of intramolecular order. As shown in Figs. 6(f) and 7(c), adsorbed segments orient parallel to each other in patches (lamella), and form into a loose quasi-two-dimensional crystalline monolayer. The stem spacing varies from 4.3 to 5.5  $\text{\AA}$ . The ensuing structure displays both adjacent and nonadjacent foldings of the chain. However, the intramolecular order degree of monolayer produced by a chain with 4004  $\text{CH}_2$  units after a 6.88-ns-long equilibrium of the system, is lower than that of a chain with 504  $\text{CH}_2$  units after 5-ns simulation. Despite this, we believe that, if we simulate further, the long chain of 4004  $\text{CH}_2$  units will also produce such a perfect monolayer equilibrium conformation. Simulations on short chains under the same condition reveal that short chains adsorb at the surface and adopt an extended-chain conformation. Irrespective of whether the starting PE chain is long or short, most segments in the adsorbed chain are arranged in long trains; only a few segments are arranged in loops and no segments in tails. The above simulation results are basically consistent with MD simulations on  $n$ -alkanes [12–14], as well as with the experimental findings where the adsorbed  $n$ -alkanes lie flat on the surface [15].

Figure 8 illustrates the chain length dependence of the intramolecular and intermolecular vdW energies per united atom. The time average is taken between 0 and 5 ns. Evidently, as the chain length decreases, the absolute value of the intramolecular vdW energy per united atom decreases, but the absolute value of the intermolecular vdW energy per united atom increases. Therefore, the shorter the chain, the smaller the contribution from the intramolecular vdW energy to the configuration energy, and the larger the contribution from the intermolecular vdW energy to the configuration energy. Moreover, simulations under conditions of high intermolecular vdW force show that, irrespective of long or short chains, contributions from bond stretching, bond angle bending, and torsion to the configuration energy are averaged below 12.44%. So the dynamical adsorption process for short chains is completely controlled by the intermolecular vdW force, and only involves a sequential, segmental anchor and a reptilelike displacement. Chain folding does not occur.

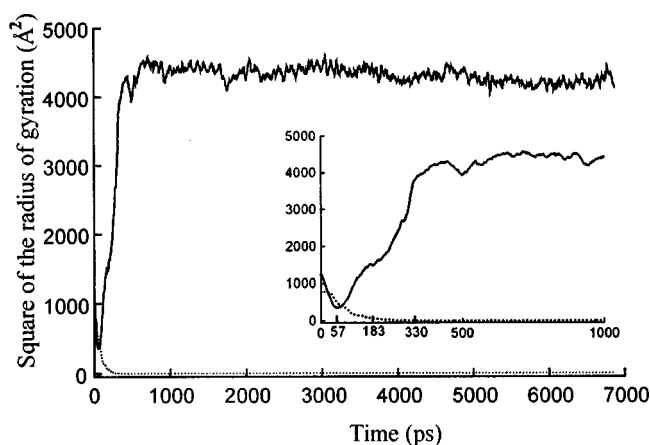


FIG. 9. Time evolution of the parallel (solid line) and the perpendicular (dotted line) components of the square of the radius of gyration when a starting amorphous PE chain with 4004  $\text{CH}_2$  units forms into a monolayerlike structure.

The ensuing structure is a kind of extended-chain monolayerlike conformation. For the long chains, meanwhile, the dynamical adsorption process becomes complicated due to the presence of a relatively higher intramolecular vdW force. In order to understand the molecular basis for the intermolecular and intramolecular vdW force dependent adsorption process, variations in  $s_{\parallel}^2$  and  $s_{\perp}^2$ , as well as the intermolecular and the intramolecular vdW energies for the above amorphous long chain, are drawn in Figs. 9 and 10, respectively. Obviously, the curves of the square of the radius of gyration have a corresponding relation with the intermolecular and intramolecular vdW energy curves. According to structural and energy changes in simulations, the whole adsorption process for the long chain polymer can be divided into four stages. Here we use Figs. 9 and 10 to illustrate the structure and energy transitions at every stage. Initially, as shown in Fig. 6(a), segments in the amorphous PE chain are at least 6 Å from the surface, and the intramolecular vdW energy is about  $-3188.65$  kcal/mol, but the intermolecular vdW energy is only  $-3.01$  kcal/mol. In stage I, the PE chain evolves mainly under the control of the intramolecular vdW force. The segments fold into a compact conformation, which leads

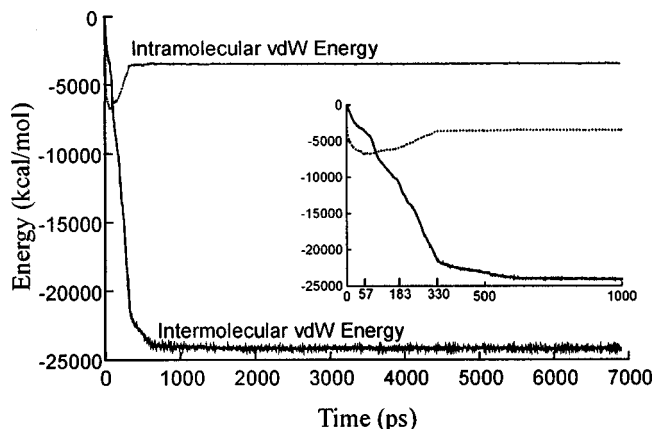


FIG. 10. Time evolution of the intermolecular (solid line) and the intramolecular (dotted line) vdW energies when a starting amorphous PE chain with 4004  $\text{CH}_2$  units forms into a monolayerlike structure.

to decrease in  $s_{\parallel}^2$  and  $s_{\perp}^2$ . Therefore, the intramolecular vdW energy first reduces with time. However, as shown in Fig. 6(b), the nonzero intermolecular vdW force always drags the near-surface segments down to the surface. When the segments are dragged to the surface, the intermolecular vdW energy decreases. After about 57 ps, the adsorption enters stage II. In stage II, the intermolecular vdW force is comparable to the intramolecular vdW force. The PE chain evolves by intermolecular and intramolecular vdW forces. As shown in Fig. 6(c), the intermolecular vdW force drags more segments down to the surface; even initially remote segments begin to approach the surface. The more segments at the surface and the nearer the distance between the segment and the surface, the quicker the decrease of the intermolecular vdW energy with time. Due to the intermolecular vdW interaction, the chain center of mass along the  $z$  direction reduces rapidly, and so does  $s_{\perp}^2$ . In addition, the intermolecular vdW force drives the adsorbed segments to adopt a stretched arrangement, and  $s_{\parallel}^2$  begins to increase with time. This eventually results in a increase of the intramolecular vdW energy with time. However, as shown in Fig. 6(c), the gradual decreased intramolecular vdW force causes some segments to fold into compact patches in space, which results in the reduction of  $s_{\parallel}^2$  and  $s_{\perp}^2$ . In this stage, the compact effect in  $s_{\parallel}^2$  is not higher than the stretched effect, so  $s_{\parallel}^2$  increases with time with fluctuations. In stage II, some segments fold in space, others approach the surface, and others stretch along the surface. This stage lasts about 126 ps. In stage III, more and more segments are adsorbed to the surface, and the intermolecular vdW energy decreases further more quickly. The intramolecular vdW force becomes larger than the intramolecular vdW force. The PE chain evolves mainly due to intermolecular vdW forces. As shown in Fig. 6(d), under the control of the intermolecular vdW force, the PE chain is dragged into an unstable, parallel, stretched polylayer. Therefore,  $s_{\perp}^2$  decreases but  $s_{\parallel}^2$  increases with time. The intramolecular vdW energy increases more rapidly with time. However, at this stage the intramolecular vdW force cannot be ignored. The intramolecular vdW interaction has the tendency to cause segments in every layer to fold into compact lamellarlike structures, which results in fluctuations in the  $s_{\parallel}^2$  curve. After 147 ps the adsorption reaches stage IV. In stage IV, nearly all the segments lie in the surface. The unstable polylayer changes into a stable monolayer due to the high intermolecular vdW force. The adsorbed monolayer folds into the ordered lamellarlike structure due to the intramolecular vdW force. Despite small scattering due to the compaction and stretching effects in conformation driven by the intramolecular and intermolecular vdW forces, curves of the  $s_{\parallel}^2, s_{\perp}^2$ , as well as intramolecular and intermolecular vdW energies become level. In further simulations, except for the intramolecular ordering, no structural transition occurs in the monolayer. The same behavior was noted in calculations on the other long chains. We thus conclude that for the long chain polymer, the adsorbing and ordering is cooperative. The adsorbed long chain strongly favors a stretched anisotropic conformation. Compared with the starting amorphous configuration,  $s_{\parallel}^2$  of the final monolayerlike structure has increased about 3.6 times. The ratio of  $s_{\parallel}^2$  to  $s_{\perp}^2$  for a final monolayer as high as 3567, has been attained.

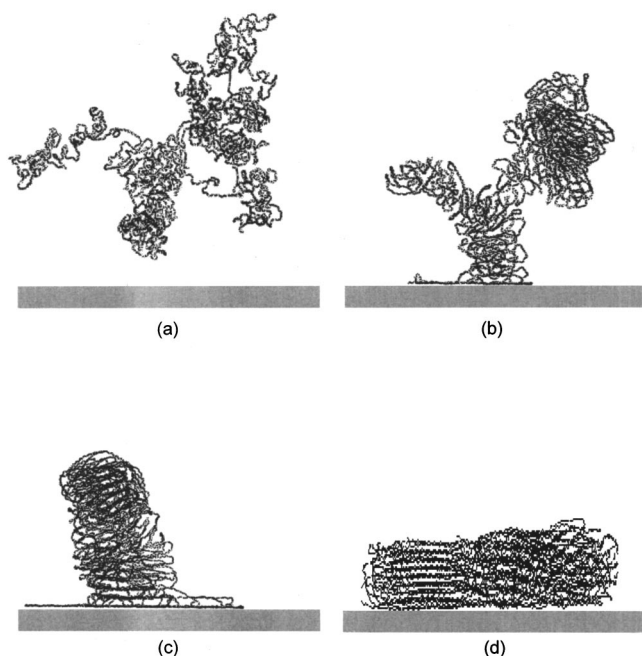


FIG. 11. Snapshots of conformations obtained from an amorphous PE chain with 4004  $\text{CH}_2$  units on the solid surface with a moderate number density of the carbon atom of  $0.15/\text{\AA}^2$ , at (a) 0 ps, (b) 30 ps, (c) 200 ps, and (d) 3 ns in the  $x$ - $z$  plane.

### C. For a moderate intermolecular vdW force

Figure 11 shows conformations developed from the above amorphous long chain on a solid surface with a moderate carbon atom number density. Apparently, in this case segments fold into an ordered polylayerlike structure. In contrast with cases of high and low intermolecular vdW force, only a few segments in the polylayer make contact with the surface. Most of segments are in loops, and the length of a loop is very large. Furthermore, segments in loops fold into a parallel lamellarlike conformation, in which almost all stems are oriented parallel to the surface. As seen in Fig. 12, similar structures have also been produced by other long chains with different starting configurations. These polylayers not only possess a deformed close-packing hexagonal symmetry, they also display both adjacent and nonadjacent foldings of the chains. The distance between the layers varies from 4.4 to 5.2  $\text{\AA}$ . Simulations on short chain molecules under the same conditions reveal that adsorbing and desorbing events occur frequently, and an almost extended-chain conformation is attained.

Figures 13 and 14 illustrate  $s_{\parallel}^2$  and  $s_{\perp}^2$ , as well as the

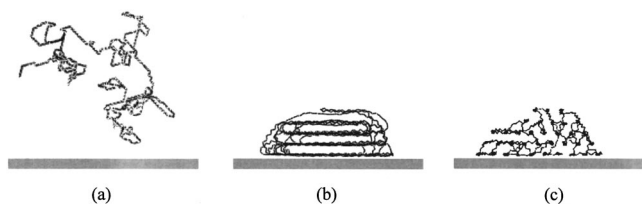


FIG. 12. Structural formation of a PE chain of 1000  $\text{CH}_2$  units with an initial RIS distribution conformation and a surface carbon atom number density  $0.05/\text{\AA}^2$  at (a) 0 ps in the  $x$ - $z$  plane, and at 5 ns (b) in the  $x$ - $z$  plane and (c) and along the stem direction.

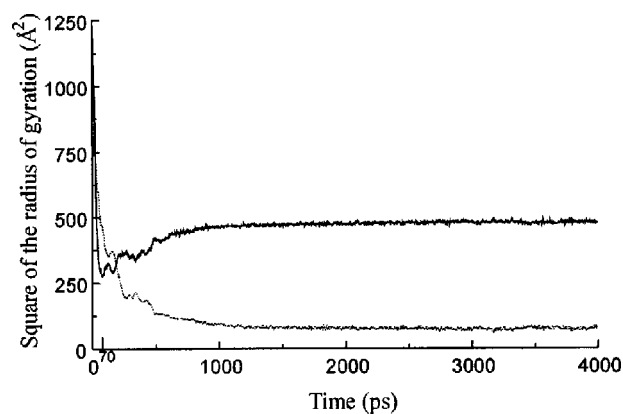


FIG. 13. The parallel (solid line) and the perpendicular (dotted line) components of the square of the radius of gyration vs time for an amorphous PE chain with 4004  $\text{CH}_2$  units under a carbon atom number density  $0.15/\text{\AA}^2$ .

intermolecular and intramolecular vdW energies versus time, when the above amorphous long chain forms into a polylayerlike structure. It is apparent that in the case of a moderate intermolecular vdW force, the PE chain evolves under the control of intramolecular and intermolecular vdW forces. Also, the intramolecular and intermolecular vdW energy curves have a corresponding relation with the square of the radius of the gyration curves. For the amorphous long chain, within the first 70 ps, the intramolecular vdW force drives the segments to fold in space [Fig. 11(b)]. The intermolecular vdW force drags the near-surface segments down to the surface [Fig. 11(b)], which has a tendency to elongate the conformation along a direction orthogonal to the surface. Therefore, as shown in Fig. 13,  $s_{\parallel}^2$  decreases rapidly with time, where the  $s_{\perp}^2$  data are noisy but still decrease speedily with time. The nearer and nearer distance between segments results in a dramatic decrease in the intramolecular vdW energy. The decreased distance between the segment and the surface, and the increased number of segments at the surface, result in a rapid decrease in the intermolecular vdW energy. Afterwards, under the cooperative effect of intramolecular and intermolecular vdW forces, the adsorbed segments stretch and fold at the surface, and the nonadsorbed segments

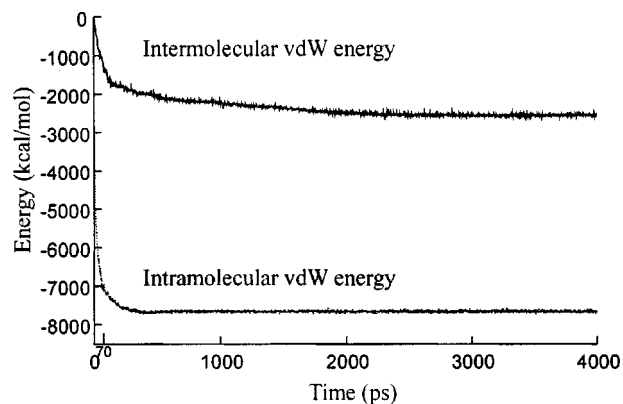


FIG. 14. The intermolecular (solid line) and the intramolecular (dotted line) vdW energies as a function of time for an amorphous PE chain of 4004  $\text{CH}_2$  units under a carbon atom number density of  $0.15/\text{\AA}^2$ .

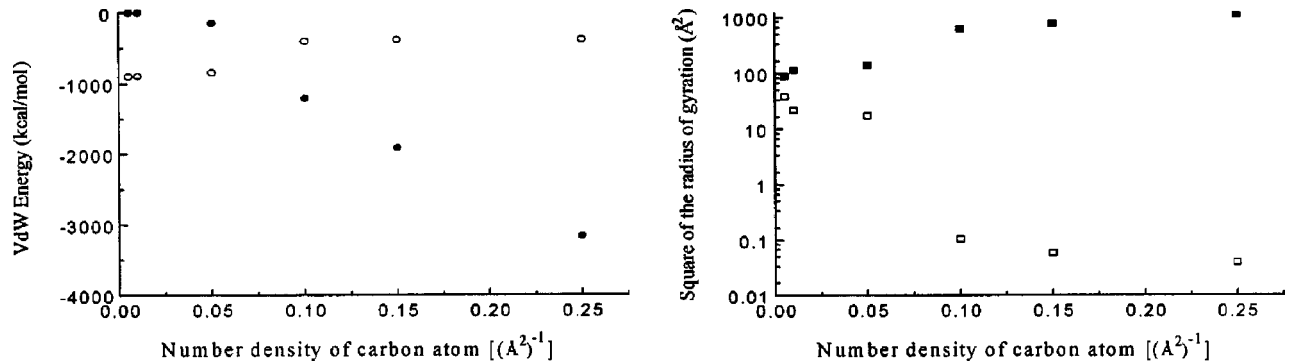


FIG. 15. The carbon atom number density dependence of (a) the intermolecular (●) and intramolecular (○) vdW energy, and (b)  $s_{\parallel}^2$  (■) and  $s_{\perp}^2$  (□) for a PE chain with 504  $\text{CH}_2$  units. The time average is taken between 4 and 6 ns.

condense further and gradually slant to or align parallel to the surface. Despite small scatterings due to the compact and stretch effects in the conformation,  $s_{\perp}^2$  begins to decrease slowly, but  $s_{\parallel}^2$  begins to increase. The resultant intramolecular and intermolecular vdW energy curves begin to decrease slowly. Finally  $s_{\parallel}^2$ ,  $s_{\perp}^2$ , the intramolecular vdW energy, and the intermolecular vdW energy approach their limiting values. During this time, as shown in Figs. 11(c) and 11(d), the unstable polylayer transforms into a stable ordered polylayer. A similar behavior was observed in simulations on the other long chains.

As we defined in Sec. II, with the increase of the carbon atom number density, the intermolecular vdW force increases. Figure 15 shows the variation of the intermolecular vdW energy, the intramolecular vdW energy,  $s_{\parallel}^2$ , and  $s_{\perp}^2$  with the carbon atom number density for a PE chain with 504  $\text{CH}_2$  units. A time average is taken between 4 and 6 ns. During this time interval, equilibrium lamellarlike, monolayerlike, and polylayerlike conformations have formed. It is clear that as the carbon atom number density increases, the intermolecular vdW energy decreases, but the intramolecular vdW energy increases. The increased intermolecular vdW interaction drives more segments to attach to the surface and stretch along it. As a result, as shown in Fig. 15(b), with the increase of the carbon atom number density  $s_{\parallel}^2$  increases but  $s_{\perp}^2$  decreases. It is worth noting that like the radius of gyration, the stem length of equilibrium conformations is not only dependent on the chain length but also on the substrate carbon atom number density. For example, under a carbon atom number density of  $0.05/\text{\AA}^2$ , the stem length changes slightly from 24 to 25.5 to 28  $\text{\AA}$  as the chain length increases from 204 to 504 to 904  $\text{CH}_2$  units. However, for a chain length of 504  $\text{CH}_2$  units, the stem length increases largely from 25.5 to 68 to 101  $\text{\AA}$  as the carbon atom number density increases from  $0.05/\text{\AA}^2$  to  $0.1/\text{\AA}^2$  to  $0.25/\text{\AA}^2$ . Obviously, the stem length in the case of a low intermolecular vdW force is several times smaller than the lamellar thickness of solution-grown single crystal PE (10–20 nm). But under the case of a high intermolecular vdW force, the stem length becomes comparatively large. A detailed study of the relation between the stem length, chain length, and carbon atom number density will be pursued in a future paper.

#### IV. CONCLUSION

In this paper, we have used MD simulation to explore the behavior of a single long chain PE on a solid surface. By varying the carbon atom number density of a substrate, we can vary the polymer-surface interaction force. Simulations find that as the carbon atom number density increases, the intermolecular vdW energy and  $s_{\perp}^2$  decrease, but the intramolecular vdW energy and  $s_{\parallel}^2$  increase. For a high intermolecular interaction force, the PE chain adsorbs onto the solid surface, and develops into a stretched monolayerlike structure. However, for a low intermolecular interaction force, segments in the PE chain avoid the surface and fold into a compact lamellarlike structure. However, for a moderate intermolecular interaction force, the PE chain forms into a polylayerlike structure at the surface. During these transitions, the conformational change is in phase with the variation of the parallel and orthogonal components of the square of the radius of gyration, and has a corresponding relationship with intermolecular and intramolecular vdW energies. In addition, it is found that as the chain length decreases, the absolute value of the intramolecular vdW energy per united atom decreases, but the absolute value of the intermolecular vdW energy per united atom increases. Due to the relatively large intramolecular vdW interaction, unlike short chains the overall conformations developed by the long chains possess an intramolecular order. The intermolecular vdW force causes the PE chain to lie at the surface and stretch into a loose monolayer. The intramolecular vdW force, rather than any of the other intramolecular interactions, drives the PE chain to fold into a compact, ordered, lamellarlike structure. By identifying the effects of intermolecular vdW and intramolecular vdW forces, these simulations yield valuable insight not only into the adsorption phenomena, but also into the transition from nonadsorbed to adsorbed states.

#### ACKNOWLEDGMENT

This project has been supported by the National Natural Science Foundation of China, 863 High Technology Project and the Special Funds for Major State Basic Research Project (G1999064800).



- [1] Terence Cosgrove, Nigel A. Finch, and John R. P. Webster, *Macromolecules* **23**, 3353 (1990).
- [2] Sagrario Beltran, Herbert H. Hooper, Harvey W. Blanch, and John M. Prausnitz, *Macromolecules* **24**, 3178 (1991).
- [3] A. C. Balazs, M. C. Gempe, and Zexuan Zhou, *Macromolecules* **24**, 4918 (1991).
- [4] A. C. Balazs, C. P. Siemasko, and C. W. Lantman, *J. Chem. Phys.* **94**, 1653 (1991).
- [5] Stephen M. King and Terence Cosgrove, *Macromolecules* **26**, 5414 (1993).
- [6] Yongmei Wang and Raj Rajagopalan, *J. Chem. Phys.* **105**, 696 (1996).
- [7] K. Sumithra and A. Baumgaertner, *J. Chem. Phys.* **109**, 1540 (1998).
- [8] E. Yu. Kramarenko, P. G. Winkler, A. R. Khoknlov, and P. Reineker, *J. Chem. Phys.* **104**, 4806 (1996).
- [9] P. R. Sundarajan and T. A. Kavassalis, *J. Chem. Soc., Faraday Trans.* **91**, 2541 (1995).
- [10] R. Hentschke, *Macromol. Theory Simul.* **6**, 287 (1997).
- [11] P. R. Sundararajan and T. A. Kavassalis, *Macromolecules* **26**, 4144 (1993).
- [12] M. W. Ribarsky and Uzi Landman, *J. Chem. Phys.* **97**, 1937 (1992).
- [13] Reinhard Hentschke and Roland G. Winkler, *J. Chem. Phys.* **99**, 5528 (1993).
- [14] T. K. Xia and Uzi Landman, *Science* **261**, 1310 (1993).
- [15] J. R. Rabe and S. Buchholz, *Science* **253**, 424 (1991).