

Molecular Dynamics Study of the Adsorption Behavior of Normal Alkanes on a Relaxed α -Al₂O₃ (0001) Surface

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Adsorption behavior of two normal alkanes (C₁₁ and C₂₀₀) with explicit hydrogens on a relaxed α -Al₂O₃ (0001) surface at 150 °C was studied using classical molecular dynamics (MD) simulation along with the use of the COMPASS force field. Prior to the MD simulations, first principle density functional theory (DFT) calculations were carried out to relax the alumina (0001) surface that was created by cleaving the corresponding crystal structure. It was found that orientation of the adsorbed segments and the number of carbons adsorbed seem to be insensitive to the chain length. The computed adsorption energy per mole of adsorbed CH₂ agrees well with those obtained from inverse gas chromatography measurements. Also, both simulation and experimental results showed that the adsorption energy decreased with increasing chain length. It was observed that molecular planes containing the skeletal carbons of the alkane segments that formed the first adsorption layer tend to orient parallel to the alumina surface, regardless of chain length. However, there existed a small amount of C₁₁ segments adopting the perpendicular orientation. For both C₁₁ and C₂₀₀, the average distance between the neighboring adsorbed segments was determined to be 4.6 Å which is slightly lower than the distance between two adjacent normal alkane molecules in their crystalline form but is equal to the interatomic distance between the aluminum atoms in the surface layer of the alumina surface. The present work suggests that both the orientation and adsorption energy of normal alkanes on the alumina (0001) surface depends on whether the surface is relaxed or not.

1. Introduction

Adsorption of chainlike molecules on solid surfaces has intrigued many researchers as the process is relevant to a wide range of practical applications such as colloidal suspensions, lubricants, coatings, paints,¹ polymer molding, surface modification of medical implants,² etc. More recently, the subject has attracted additional interest in the field of nanoparticle synthesis because behavior of chainlike molecules, used as a dispersant, influences significantly the shape and size and, therefore, the properties of inorganic colloidal nanocrystals synthesized in an organic environment. This increasing attention is simply attributed to the potential applications of such nanoparticles in biomedical applications (e.g., drug delivery). It is obvious that behavior of chainlike molecules adsorbed on solid surfaces with drastically different chemical characteristics from themselves would not be the same as that on organic surfaces. To obtain desired properties of systems containing such interfaces, it is imperative to obtain molecular level insights into the spatial arrangement and intermolecular interactions of the chainlike molecules at such “organic–inorganic” interfaces. In this regard, atomistic level simulation techniques have a great potential for providing us with the insights needed.

Molecular dynamics (MD) simulation has been routinely applied to study structure and dynamic behavior of chainlike molecules in their bulk and thin film states over the past few decades with considerable success. However, great challenges still exist for studying interactions between organic molecules and inorganic solid surfaces by molecular dynamics. One major stumbling block is that most existing force fields cannot predict

the structure of solid substrates accurately as such force fields are not optimized for inorganic materials. Another problem is that, since the relaxation time scales of most inorganic substrates of interest (e.g., metals or metal oxides) and those of chainlike molecules differ by several orders of magnitude, this makes classical MD simulation infeasible for equilibrating both the organic and inorganic parts of the system simultaneously. It is worth noting that Monte Carlo (MC) simulation works no better as an alternative approach than MD simulation in this regard.³ To simplify the calculations, uniform metal surface models are usually employed in most of these MD simulations because structures of these metal surfaces are simple and well characterized by experiments. On the other hand, adsorption of chainlike molecules onto heterogeneous surfaces (such as those of metal oxides) is poorly understood, even though most of the applications involve such systems. At present, the only computational chemistry technique that would be able to precisely predict the structure and relaxation dynamics of metal oxides is the density functional theory (DFT) first principle calculations.^{4–6} Nevertheless, it is infeasible to perform MD simulation using such an ab initio approach for systems containing chainlike molecules interacting with metal oxide surfaces as the computational cost is prohibitively high. For instance, Dkhissi et al. carried out quantum mechanical calculations on the grafting of chain organosilane compounds on SiO₂-hydroxylated solid surfaces; unfortunately, only one single molecule with a few alkyl chains could be studied.⁷ In general, coarse grained models are employed to represent chainlike molecules by using united atoms to represent repeat units, which could have different chemical composition, in a given chain molecule,^{1,8,9} and DFT calculations are performed to determine the interactions between such united

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atoms and the uniform metal surface of interest. The resultant interaction energy will then be used for performing MD simulation.^{8,9} Obviously, this approach only works for highly coarse-grained chains and simple inorganic surfaces. Therefore, detail local packing of the adsorbed segments could not be obtained.

Alumina surface plays an important role in many technological areas simply because alumina (e.g., α - Al_2O_3) is frequently used as catalysts and catalyst supports. Also, alumina constitutes part of a naturally occurred material: clay. In addition, owing to oxidation reaction, aluminum surfaces are always covered by a layer of alumina, thereby determining the surface and interfacial properties of aluminum. Despite the importance and relevancy of alumina surface to many applications, few achievements have been obtained in the experimental investigations on the structure and chemistry of alumina surface even in recent years. This is because it is very challenging to prepare a clean and well-defined alumina surface experimentally. Since molecular simulation can be performed on a well defined alumina surface, this, in turn, provides an effective alternative for exploring surface phenomena of alumina surfaces in a well-controlled manner. The key issue here is whether one can generate proper alumina surfaces computationally or not. This, in fact, can be accomplished by extending DFT calculations that yield correct α - Al_2O_3 crystal structure to alumina surfaces.^{4,5}

Claire et al. investigated the short chain hydrocarbon adsorption and the subsequent water penetration through a hydrocarbon film on a α - Al_2O_3 (0001) surface.¹⁰ The surface model they employed to run MD simulation was cleaved directly from the default crystal structure of α - Al_2O_3 listed in a commercial software Cerius² structures library and no further treatment was made. However, since atoms in the surface layers of α - Al_2O_3 would experience a rather different environment than in the bulk, it is necessary, in our view, to "correct" the atomic structure of the surface before MD is carried out. In this work, we therefore propose to relax the alumina surface using DFT calculations before the MD study. In this way, equilibration of the alumina surface by the MD simulation is not required. After the relaxation, positions of all alumina surface atoms will then be fixed and classical MD simulation will be carried out with the deposition of the chainlike molecules of interest onto the surface. Nonetheless, data for un-relaxed alumina (0001) surface will be also presented to illustrate the importance of relaxation. Normal alkanes at two fairly different chain lengths (C_{11} and C_{200}) will be used. The rationale that MD simulation can be performed using such a strategy is that the frequency of the vibration of the aluminum-oxygen bond (on the order of femtoseconds) is by far much faster than that of the relaxations of the alkane chains of interest (on the order of nanoseconds).^{5,11} To characterize the adsorption behavior of the normal alkanes, orientations and adsorption energy at 150 °C were determined.

2. Simulation Models and Methods

2.1. Relaxation of α - Al_2O_3 (0001) Surface using Density Functional Theory (DFT). It is well-known that molecules near a surface adopt a rather different intermolecular packing from those in the bulk state as such molecules are at a higher free energy state. For solids, surface atoms would undergo a so-called geometry optimization process (i.e., relaxation) by which the atoms move to the lowest free energy state. Since most solid substrates of interest are of inorganic in nature, classical force fields are not adequate for such a relaxation process. Rather, use of the ab initio approach is more appropriate. Computationally, the relaxation process is performed on structures that

are created by cleaving the corresponding crystal.¹² In this work, the relaxation approach of Ruberto et al. will be applied to the α - Al_2O_3 (0001) surface.¹² Here, the bulk structure of the alumina crystal was obtained from an inorganic crystal library of a commercial software so-called Materials Studio (see Figure 1a). The crystal is composed of "sandwich" like layers of aluminum and oxygen atoms (see Figure 2). Each layer (considered to be a repeat unit) contains three sub-layers of atoms in which two are made up of Al atoms, whereas the sub-layer in between the two Al sub-layers is made up of oxygen atoms. The repeat unit is believed to be nonpolar (i.e., no net charges).¹² α - Al_2O_3 (0001) surface was initially obtained by cleaving the alumina bulk structure at an Al terminated plane at a chosen depth. The rationale of cleaving the crystal at an Al terminated plane is that electrostatic considerations as well as classical and quantum mechanical calculations indicate that the most favorable (0001) surface of α - Al_2O_3 is terminated by a single plane of Al atoms.^{4,10}

Slabs consisting of different numbers of repeat units were constructed to investigate the effect of the thickness of slab on the relaxation geometry of the surface atoms. This is accomplished by calculating the surface energy of the slabs based on the concept of "cleavage energy" or separation energy E_{sep} ,¹² the energy needed to cleave one infinite crystal into two separate infinite crystals, each of which has one surface. It is worth noting that the separation energy is essentially equal to the surface energy of the slab created in our simulation as two surfaces are created in the cleaving process. The vacuum section in between the two surfaces of the model was set to 15 Å, which ensured that interactions between two neighboring slabs could be ignored.¹² Since such surfaces are symmetric, the surface energy E_s could be obtained as

$$E_s = E_{\text{sep}}/2 \quad (1)$$

The separation energy could be obtained as

$$E_{\text{sep}} = E_{\text{cell}}(n) - nE_b \quad (2)$$

where

$$E_b = E_{\text{cell}}(n) - E_{\text{cell}}(n-1) \quad (3)$$

E_b is the bulk binding energy of one repeat unit. $E_{\text{cell}}(n)$ is the calculated total energy of a slab with n repeat units. The method to calculate surface energy here was believed to be more consistent than a separate bulk crystal calculation, due to the fact that the value of E_{sep} at sufficiently large n would converge, thus ensuring the independence of E_{sep} on the slab thickness.¹² In fact, when the slab is thick enough, both surfaces of the slab would be fully relaxed with identical spacing while the repeat units in the middle of the slab resemble that in the bulk. Relaxation of the slabs with different numbers of repeat units was carried out using the CASTEP code available in Materials Studio, a first principle calculation code developed based on the DFT. Exchange and correlation were treated with generalized gradient approximation (GGA)–PW91. Ionic cores were represented by ultrasoft pseudopotentials. A kinetic energy cutoff of 340 eV was used, and the k -point sampling mesh separation was set to 0.05 Å⁻¹.

2.2. Molecular Dynamics (MD) Simulation. MD simulations were carried out with the use of commercial software Materials Studio. The COMPASS force field was employed to describe the atomic interactions between the normal alkanes and α - Al_2O_3 (0001) surface. COMPASS is an ab initio force field

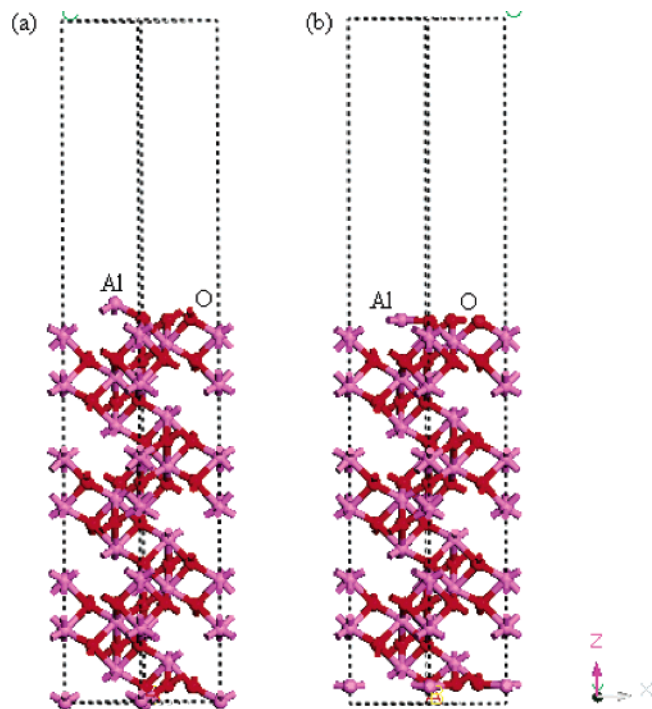


Figure 1. Hexagonal vacuum slab of α - Al_2O_3 (0001) surface (a) before relaxation and (b) after relaxation.

optimized for condensed-phase applications. Simulation results have shown that it can make accurate predictions of structural, conformational, cohesive, and other physical properties for a wide range of substances.¹³ The expressions used in this force field are presented in Table 1.¹⁴ The functions include two categories of energy terms: valence terms which include diagonal and off-diagonal cross-coupling terms and nonbonded interaction terms. As can be seen from the table, owing to the complexity of the expressions, a large number of parameters are used. For clarity, not all parameters are listed here (however, they can be found easily from ref 14). Rather, we chose to show only the Lennard-Jones parameters that were used in the present work (see Table 2). It is worth noting that we used the sixth order combination law to calculate the cross Lennard-Jones parameters. The van der Waals interaction has a cutoff distance of 9.50 Å with a spline width of 1.00 Å and a buffer width of 0.50 Å. Long-range corrections were also applied for the effects

of cutoff and splining. Here, it should be pointed out that interactions between aluminum and oxygen atoms in alumina were described as nonbonded. Similarly, van der Waals (vdW) energy and Coulombic energy terms describe the interactions between atoms in the alkanes and those in the alumina surface. However, charges of the atoms in the alkane chains were ignored in simulation. Therefore, vdW energy was the only one accounted for the interactions between the normal alkanes and relaxed alumina surface. The rationale for ignoring the partial atomic charges of alkanes is based upon the belief that alkane molecules near the organic–inorganic interface should carry relatively small partial atomic charges as these molecules are nonpolar in their bulk state. It is worth noting that most of the alkane molecules used in the model were far from the interface. Considering the additional computational times that are required for handling such charges, we felt justified not to include them in the calculations. Nonetheless, the computed adsorption energy (see Results and Discussion), which agrees fairly well with experiment, supports such an approach.

Two explicit normal alkane models (i.e., hydrogen atoms were modeled explicitly), one consisting of 40 chains each with 11 backbone carbons (C_{11}) while the other a single chain of 200 backbone carbons (C_{200}), were used in the present work. Using the experimental density of the normal alkanes at 150 °C (0.6396 (C_{11}) g/cm³ and 0.7706 (C_{200}) g/cm³),¹⁵ thin film initial structures were constructed in such a way that the simulation cells were periodic only in two dimensions (i.e., x and y directions here). It is worth noting that the density of the inner region of these thin films was equal to that of the corresponding bulk material and interfacial regions on both sides of the thin films with a width of less than 10 Å was present. Each thin film alkane model was assembled with a supercell of alumina surface slab with surface area of 313.82 Å² (lattice parameters $a = 19.036$ Å, $b = 19.036$ Å; $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 60^\circ$). It should be noted that similar results were obtained when systems with larger simulation cells were used and that the alkane thin film structures were energy minimized using a convergence criterion of 0.1 kcal/mol Å and equilibrated before they were assembled with the alumina surface slab. Figure 3a shows the resulting structure for C_{200} above the supercell of alumina surface slab. Following the energy minimization, MD simulation was carried out at 150 °C. As mentioned, the relaxation behavior of the alumina surface is much faster than that of the alkanes; therefore,

Unrelaxed			Relaxed		
Nonpolar repeat unit			Relaxation magnitude		
<div style="display: flex; align-items: center;"> <div style="writing-mode: vertical-rl; transform: rotate(180deg); margin-right: 5px;">Nonpolar repeat unit</div> <div style="display: flex; flex-direction: column; align-items: center;"> <div>— Al —</div> <div>— O — O — O —</div> <div>— Al —</div> <div>— O — O — O —</div> <div>— Al —</div> <div>— O — O — O —</div> <div>— Al —</div> <div>— O — O — O —</div> <div>— Al —</div> <div>— O — O — O —</div> </div> </div>	Interlayer distances		Interlayer distances		
	(0.84 Å)		(0.08 Å)		
	(0.84 Å)		(0.83 Å)		
	(0.49 Å)		(0.27 Å)		
	(0.84 Å)		(1.01 Å)		
	(0.84 Å)		(0.88 Å)		
	(0.49 Å)		(0.44 Å)		
	(0.84 Å)		(0.84 Å)		
	(0.84 Å)		(0.79 Å)		
	(0.49 Å)		(0.55 Å)		
	(0.84 Å)		(0.80 Å)		
	(0.84 Å)		(0.84 Å)		

Figure 2. Nonpolar structure of α - Al_2O_3 (0001) surface containing ten repeat units before and after relaxation. However, only the top four repeat units are shown. The atomic layers that are perpendicular to the alumina (0001) surface, interlayer distances, the relaxation magnitude in percentage, and the nonpolar repeat unit for building the surface are shown.

TABLE 1: Functional Forms used in the COMPASS Force Field¹³

Interaction		Equation
Valence terms	Bond energy	$E_b = \sum_b [k_2(b-b_0)^2 + k_3(b-b)^3 + k_4(b-b)^4]$
	Angle energy	$E_\theta = \sum_\theta [k_2(\theta-\theta_0)^2 + k_3(\theta-\theta_0)^3 + k_4(\theta-\theta_0)^4]$
	Torsion energy	$E_\phi = \sum_\phi [k_1(1-\cos\phi) + k_2(1-\cos 2\phi) + k_3(1-\cos 3\phi)]$
	Out-of-plane angle	$E_\chi = \sum_\chi k_2\chi^2$
	Cross-coupling terms	$E_{cross} = \sum_{b,b'} k(b-b_0)(b'-b_0') + \sum_{b,\theta} k(b-b_0)(\theta-\theta_0)$ $+ \sum_{b,\phi} (b-b_0)[k_1 \cos\phi + k_2 \cos 2\phi + k_3 \cos 3\phi]$ $+ \sum_{\theta,\phi} (\theta-\theta_0)[k_1 \cos\phi + k_2 \cos 2\phi + k_3 \cos 3\phi]$ $+ \sum_{\theta,\theta'} k(\theta'-\theta_0')(\theta-\theta_0)$ $+ \sum_{\theta,\theta',\phi} k(\theta-\theta_0)(\theta'-\theta_0') \cos\phi$
Nonbond terms	Coulombic interaction	$E_{coul} = \sum_{i,j} \frac{q_i q_j}{r_{ij}}$
	Van der Waals energy	$E_{vdW} = \sum_{i,j} \epsilon_{ij} [2(\frac{r_{ij}^0}{r_{ij}})^9 - 3(\frac{r_{ij}^0}{r_{ij}})^6]$

TABLE 2: Lennard-Jones Parameters Used to Describe Nonbonded Interactions between Various Atomic Species¹²

<i>i</i>	<i>j</i>	ϵ_{ij} (kJ/mol)	γ_{ij}^0 (Å)	<i>i</i>	<i>j</i>	ϵ_{ij} (kJ/mol)	γ_{ij}^0 (Å)
Al	Al	2.361	3.500	O	C	0.485	3.749
Al	O	1.480	3.566	O	H	0.238	3.354
Al	C	0.752	3.698	C	C	0.259	3.854
Al	H	0.405	3.261	C	H	0.113	3.526
O	O	0.936	3.627	H	H	0.096	2.878

atoms in the relaxed α -Al₂O₃ (0001) surface were fixed during the MD simulations. The Nose canonical method along with the velocity-Verlet algorithm and a time step of 1 fs was used for generating the MD trajectories.¹⁶ Simulations were carried out up to a time period as long as 18 000 ps to ensure adequate equilibration of the alkane chains near the alumina surface. Different initial alkane conformations were used to test the reproducibility of the simulation.

The adsorption energy E_{ads} is defined as the energy difference between the system with a thin film of normal alkane chains in close contact with the relaxed alumina surface ($E_{PE+surf}$) and the systems consisting of the alkane chains only E_{PE} , and of a clean, relaxed alumina surface E_{surf} in their pure form:⁶

$$E_{ads} = -E_{PE+surf} + E_{PE} + E_{surf} \quad (4)$$

3. Results and Discussion

3.1. Relaxation of α -Al₂O₃ (0001) Surface. Structures of α -Al₂O₃ (0001) surface before and after relaxation are depicted in panels a and b in Figure 1, respectively. Similar to what earlier DFT studies showed,^{4,6,12} it was observed that the outmost layer of Al atoms and the O atoms right underneath such a layer lie in nearly the same plane. Our calculated spacings in between the first six layers of atoms (4 Al layers and 2 O layers) were -90% , -1.2% , -45% , $+20\%$, and $+4.8\%$ (see Figure 2). Other research groups obtained similar simulation results. In particular, results of Lodziana et al. are -85% , $+3.2\%$, -45% , $+20\%$, and $+4.8\%$, respectively,⁶ and those of Hass et al. for the spacings in between the first five layers are -82% , $+7\%$, -52% , and $+25\%$, respectively.⁴ Besides, review of calculated surface relaxations of α -Al₂O₃ (0001) surface could be found in the paper of Sun et al.¹⁷ UV photoelectron spectroscopy (UPS) and meta-stable impact electron spectroscopy (MIES) measurements showed that spacing between the first and second layers of the surface atoms ranges from -63% to -68% .^{18,19} It is worth noting that MIES techniques are only sensitive to the topmost surface atoms. The discrepancy between the simulation and experimental results was attributed to the difficulty associated with preparing well defined alumina surfaces experimentally.⁴ Nevertheless, the important point here is that both computational

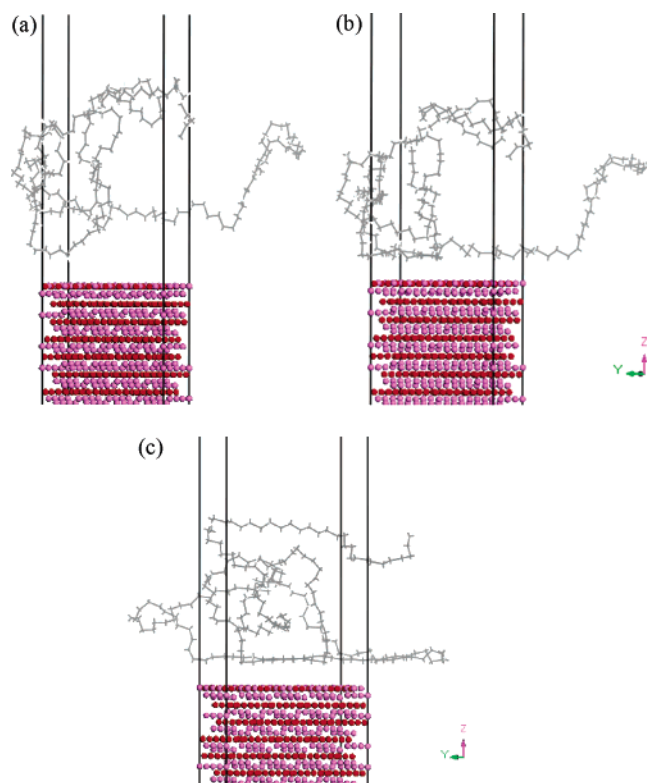


Figure 3. Conformations of C₂₀₀ at different simulation times: (a) before energy minimization; (b) after energy minimization (0 ps); (c) 18 000 ps.

TABLE 3: Computed Surface Energies of Relaxed α -Al₂O₃ (0001) Surfaces Containing Different Numbers of Repeat Units by DFT Calculations

<i>n</i>	<i>E</i> _{cell} (eV)	<i>E</i> _b (eV)	ΔE_b (eV)	<i>E</i> _s (J/m ²)
3	-4318.0600			
4	-5758.1752	-1440.1152		0.9323
5	-7198.5731	-1440.3979	-0.2827	1.3935
6	-8638.9837	-1440.4106	-0.0127	1.4194
7	-10079.3670	-1440.3833	0.0273	1.3526
8	-11519.7712	-1440.4042	-0.0209	1.4309
9	-12960.1811	-1440.4099	-0.0057	1.4309
10	-14400.5760	-1440.3949	0.0150	1.3758

and experimental results illustrate that surface atoms of α -Al₂O₃ (0001) surface do relax. This reinforces our belief that adsorption study should be done on a relaxed rather than unrelaxed surface. Here, it should be remarked that we performed the relaxation calculations due to our belief that it is relevant to the adsorption of alkane chains on the alumina (0001) surface. It does not mean that our calculations are better than the previous studies.

The surface energy values calculated by DFT for slabs containing different numbers of repeat units are listed in Table 3. It can be seen from the table that the relaxed surfaces with six or more repeat units satisfy the convergence criterion of $\Delta E_b < 0.05$ eV.¹² In addition, the fluctuation of ΔE_b seems to be fairly random, not showing a specific oscillating pattern at all. This means that repeat units in the interior of a slab containing more than six repeat units (i.e., nine sub-layers of surface atoms on each side of the slab) would have a structure that resembles that of the bulk. However, to ensure a good description of the relaxation effect of the surface atoms on the adsorption behavior of normal alkanes, relaxed alumina slabs composed of ten repeat units were used in the subsequent MD calculations. The average surface energy averaging over the slabs with six to ten repeat units was determined to be 1.40 J/m², which is slightly lower than the DFT results of Ruberto

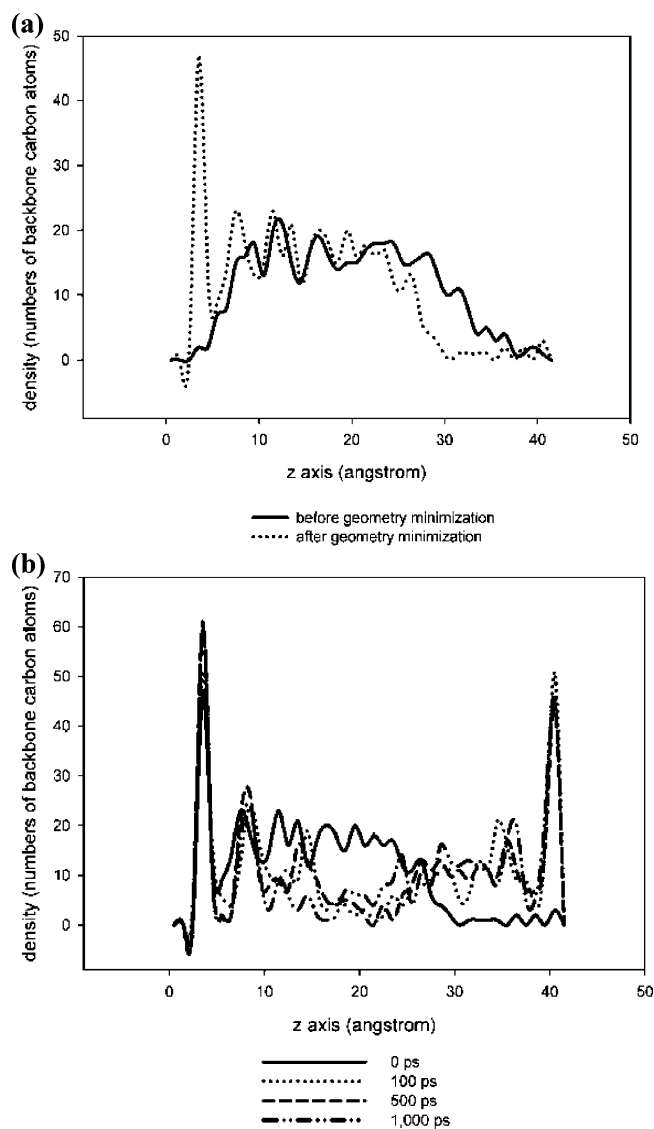


Figure 4. Density distribution profile of C₁₁ along the *z* direction (*z* being the direction perpendicular to the alumina (0001) surface) at different simulation times: (a) before and after energy minimization; (b) at different simulation times: 0, 100, 500, and 1000 ps.

et al. (1.60 J/m²), which was also determined by averaging over up to 10 repeat units.¹² We speculate that the difference in the computed average surface energy is attributed to the difference in the sizes of the systems used in respective groups.

3.2. Adsorption Behavior of Normal Alkanes (C₁₁ and C₂₀₀). It should be pointed out that prior to the MD simulations chains in both C₁₁ and C₂₀₀ thin film models were pulled significantly toward the alumina surface during the energy minimization step. In particular, there were about 47 and 30 carbon atoms (the first adsorption layer) that were in direct contact with the relaxed surface for C₁₁ and C₂₀₀, respectively. This is attributed to the fact that a relatively strong van der Waals interaction exists between atoms of normal alkanes and surface atoms of alumina.

Figures 4 and 5 show the density profiles of both C₁₁ and C₂₀₀ over the durations of the respective simulations on the same relaxed alumina (0001) surface. It is clear that during the MD simulation alkane chains (both C₁₁ and C₂₀₀) moved further toward the alumina surface. Specifically, numbers of backbone carbon atoms that formed the first nearest layer to the relaxed alumina surface increased from a value of 47 to 61 and from 30 to 41 for C₁₁ and C₂₀₀, respectively. Also layers of segments

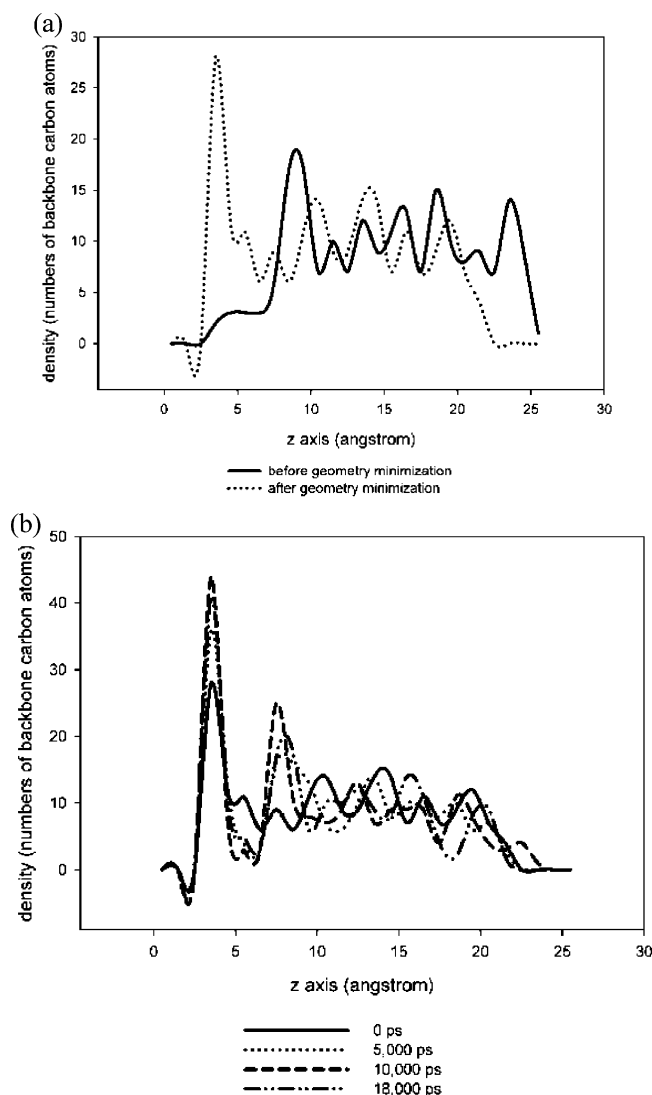


Figure 5. Density distribution profile of C₂₀₀ along the *z* direction (*z* being the direction perpendicular to the alumina surface) at different simulation times: (a) before and after energy minimization; (b) at different simulation times: 0, 5000, 10 000, and 18 000 ps.

away from the surface also moved toward the surface with a change of numbers of atoms involved. Examination of the time dependence of the density profiles of the alkane models shows that the layers of carbon atoms that are near the surface require less time to reach equilibrium number density values, whereas the far ones moved slowly into a multilayer structure. This is consistent with the fact that interactions between alkane atoms and alumina surface atoms are much stronger than those between atoms among the alkane chains.¹⁰

The separation between the first nearest layer of alkane chains and the outmost surface aluminum atoms is about 3.5 Å for both C₁₁ and C₂₀₀ cases. This result is exactly the same as what Claire et al. obtained for the interactions between an alumina surface and butane, octane, and dodecane chains.¹⁰ This equilibrium separation is simply a result of the balance between repulsive and attractive vdW forces experienced by all of the atoms involved in such an interfacial region. It should be noted that all the backbone carbon atoms in the first nearest layer adopt mostly *trans* conformation. However, what is interesting to note is that our simulation results show that the molecular planes of the adsorbed alkane segments prefer to orient parallel rather than perpendicular to the substrate surface, as shown in Figures 3 (side view) and 6 (top view). The results of Claire et al., for

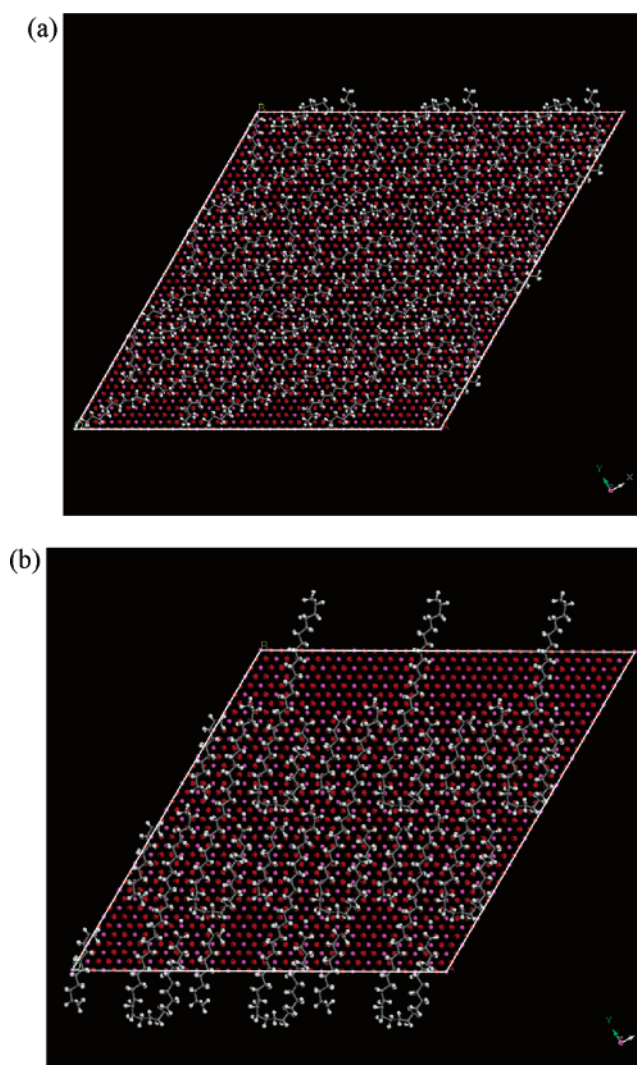


Figure 6. Orientation of the molecular axes of the first adsorption layer of (a) C₁₁ and (b) C₂₀₀ (images shown correspond to a 3 × 3 supercell of the original simulation cells). As shown, the molecular axes of the adsorbed alkane segments tilt communally to a small angle with respect to the lattice boundaries signified by the white rhombus.

which they used united atom models and an unrelaxed alumina surface at a much lower temperature (100 K), showed perpendicular orientation.¹⁰ However, in the case of C₁₁, a small fraction of molecular planes exhibited the perpendicular orientation. In general, if adsorbed segments adopt a configuration by which the molecular planes formed by the corresponding skeletal carbons are perpendicular to the surface, there will exist a peak splitting pattern with two peaks separated by about 0.9 Å in the density profile.²⁰ Such a splitting peak feature was not observed in our data (see Figures 4 and 5).

As mentioned above, 61 and 41 backbone carbon atoms were found in the first adsorption layer for C₁₁ and C₂₀₀, respectively, at their equilibrium state, and no more carbon atoms could enter into this layer during the last portions of the MD simulations, indicating that there exists a saturation carbon density. When the above values (61 and 41) are expressed as per unit area basis, the saturated carbon densities are 12.4 and 13.1 carbons per 100 Å² for C₁₁ and C₂₀₀, respectively. The results suggest that the saturation carbon density of alkanes is insensitive to their chain length. However, it is interesting to note that, for both C₁₁ and C₂₀₀, the average distance between the skeletal carbons of two neighboring adsorbed segments and that between the first and second layers of the adsorbed segments is about

TABLE 4: Computed Adsorption Energies of C₁₁ and C₂₀₀ Adsorbed on Relaxed and Unrelaxed Alumina (0001) Surfaces

normal alkane	alumina surface	adsorption energy (kJ/mol)	adsorption energy per mol of CH ₂ (kJ/mol)
C ₁₁	relaxed	2264 ± 31	5.15 ± 0.07
	unrelaxed	1929 ± 32	4.38 ± 0.07
C ₂₀₀	relaxed	919 ± 12	4.60 ± 0.06
	unrelaxed	745 ± 26	3.73 ± 0.13

4.6 Å and 4.0 Å, respectively. These values are slightly lower than the corresponding intermolecular spacings, which are 4.8 and 4.2 Å, respectively, in alkane (octadecane) crystals as determined by X-ray diffraction at a much lower temperature (note that our simulation temperature was 150 °C).²¹ This observation implies that the region that consists of the first two layers of adsorbed segments possesses a much higher density than that of the bulk to maximize the surface atoms interactions. Another interesting observation is about the position of the adsorbed backbone carbon atoms. The separation between an outmost surface aluminum atom and its secondary neighboring aluminum atoms in the same (0001) surface is found to be about 4.8 Å, which is comparable to the distance between two neighboring adsorbed segments in the first nearest layer (4.6 Å). A previous experimental study on the adsorption of alkane on a graphite surface by Rabe and Buchholz showed that the distance between the second from the next carbon rows in graphite amounts to 4.26 Å and that the distance between two alkane segments with perpendicular orientation is about 4.2 Å.²¹ These authors latter performed simulations and confirmed this orientation and proposed that it is the commensuration of the adsorbed alkane chains with the graphite substrate that results in the perpendicular orientation of the molecular planes of skeleton carbons relative to the graphite surface.²² It seems that, in our case, the commensuration of the adsorbed alkane segments (with explicit hydrogens) with the alumina (0001) surface induces the parallel orientation. Another observation was that the molecular axes of the adsorbed alkane segments seem to tilt communally to a small angle (25 degrees) with respect to the lattice boundaries of the substrate surface (see Figure 6) which was not observed in the case when the alumina (0001) surface was not relaxed (data not reported here).

3.3. Adsorption Energy of Alkanes (C₁₁ and C₂₀₀). Heats of adsorption of *n*-alkanes on alumina surface evaluated by inverse gas chromatography are 39.28, 46.02, 54.38, and 57.99 kJ/mol for *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane, respectively.²² Expressed in the unit of per mole of CH₂ group, the corresponding values are 7.86, 7.68, 7.77, and 7.25 kJ/mol, respectively. Table 4 summarizes our computed adsorption energies of C₁₁ and C₂₀₀ on the relaxed and unrelaxed α -Al₂O₃ (0001) surface. Compared our computed value of 5.15 kJ/mol ± 0.07 with the corresponding extrapolated value of 6.64 kJ/mol for C₁₁ based upon the aforementioned experimental values, the agreement is reasonably good considering the fact that the COMPASS force field is not optimized for these systems and that inverse gas chromatography measurements normally carry uncertainties of 3–5%. Nonetheless, the trend that the adsorption energy decreases with the increasing chain length of alkane was reproduced. On examination of the data for the unrelaxed alumina (0001) surface (see Table 4), it was found that the adsorption energies are much lower, up to 20%, than those of the relaxed systems. This is somewhat expected as locations of Al and O layers would determine the configuration of the alkane molecules near the alumina surface, leading to differences in the interaction energy.

4. Concluding Remarks

For the first time, we have combined the density functional theory (DFT) calculations and classical molecular dynamics (MD) simulations to investigate the adsorption behavior of two normal alkanes (C₁₁ and C₂₀₀) on a relaxed alumina (0001) surface. DFT ab initio calculations were carried out first to fully relax the alumina surface, and the positions of all the aluminum and oxygen atoms in the relaxed alumina (0001) surface were fixed during the subsequent classical MD simulation. It was found that relaxation of the alumina surface plays an important role in determining the configuration of the adsorbed alkane segments. Our simulation results show that molecular planes of the alkane segments in the first adsorption layer prefer to orient parallel rather than perpendicular to the substrate surface, which may be due to the commensuration of the adsorbed alkane segments with the aluminum atom rows in the substrate surface. Also, the molecular axes of the adsorbed alkane segments seem to tilt communally to a small angle (25°) with respect to the aluminum atom rows. However, this is not the case for the unrelaxed alumina (0001) surface. The adsorption energies were calculated to be 5.15 kJ/mol and 4.60 kJ/mol per CH₂ group for C₁₁ and C₂₀₀, respectively.

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