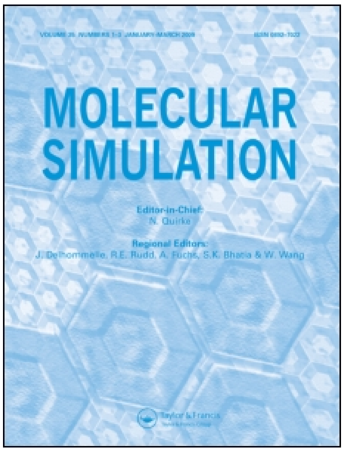

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MOLECULAR-DYNAMICS SIMULATION OF THE SURFACE DIFFUSION OF *n*-ALKANES ON Pt(111)

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In the present study, the equilibrium adsorption and the dynamics of surface diffusion in a model of ethane and *n*-butane on a Pt(111) surface were simulated with molecular dynamics. At low temperatures, we found that both admolecules adsorb in a specific binding site. Through analysis of the trajectories, several features of the dynamics were resolved. At low temperature, we observed that diffusion occurs through a nearest-neighbor hopping mechanism involving both lateral rotation and axial translation. At high temperatures, the admolecule makes multiple-site hops and nonlocalized long flights. The temperature dependence of the diffusion coefficients was analyzed and was found to exhibit good Arrhenius behavior. The apparent diffusion coefficients follow trends seen in related experimental studies. In the case of ethane, a comparison between the diffusion barrier measured in the molecular-dynamics simulations and the theoretical barrier predicted by transition-state theory indicates that the simulated barrier is larger than the theoretical value. This finding is consistent with conclusions in recent studies of metal-atom diffusion on metal surfaces, where it was found that systems with low corrugation exhibit a non-unique relationship between the dynamical diffusion barrier and the potential-energy-surface topology.

KEY WORDS: Surface diffusion, *n*-alkanes, Pt(111).

1 INTRODUCTION

Since the 1920's, when interest in crystal growth spurred interest in transport over surfaces, surface diffusion has been a topic of considerable study [1-30]. Diffusion is fundamental to a number of surface rate processes of technological interest. For instance, the progress of catalytic-surface reactions is influenced by the mobility of adspecies. Surface diffusion is also important in determining the morphology of thin films and, hence, its role in technologies involving coating, adhension, tribology, and deposition is also significant.

Despite its prominence in a wide variety of interfacial phenomena, the body of knowledge of surface diffusion has been limited primarily to the study of atoms. In recent years, a few experimental studies have began to probe the diffusion dynamics of adsorbed molecules [16, 19, 21-26]. Although studies up to this point have been directed towards measuring surface diffusion coefficients, which provide an overall characterization of transport, there has been some speculation regarding novel mechanistic behavior that may characterize molecular adsorbates [21-26]. Unlike atoms, molecules have both internal and rotational degrees of freedom. The role of these features in diffusion is not well understood. With recent advances in experimental techniques, such as scanning-tunneling-microscopy, it has become possible to resolve the internal structure of adsorbed molecules [31] and to follow dynamical details of surface diffusion [8,9]. Hence, the capacity to resolve unique features of diffusion is increasing and raises the exciting possibility for new discoveries in a potentially rich and interesting area.

Molecular simulation techniques have long been recognized for their ability to provide insight to the microscopic phenomena underlying the macroscopic behavior of condensed-matter systems. Details of molecular diffusion that are difficult to probe experimentally can be thoroughly studied with Monte Carlo methods, molecular-dynamics simulations, and related techniques. In our work, we have been using these methods in one of the first extensive theoretical efforts to gain insight to the diffusion dynamics of adsorbed molecules [30–33]. Our studies have focused on the diffusion dynamics of *n*-alkanes on metal, single-crystalline surfaces. Related experimental studies [22–26] have probed the diffusion dynamics of short chain (C3–C6) *n*-alkanes on Ru(001). *N*-alkanes form a homologous series, ranging from methane, which is small, symmetrical, and can perhaps be regarded as atom-like, to polythylene, a basic macromolecule. It is hoped that some of the results of these studies can be applied to enhance understanding of the mobility of adsorbed polymers. Two questions of central interest in our studies are: What are the mechanisms of chain molecule diffusion? and How might the diffusion be described theoretically? It is likely that the answers to these questions depend on factors such as the length of the chain, the temperature, the concentration of surface molecules, etc. Our work up to this point has focused on the diffusion of single adsorbed chain molecules. In this paper, we summarize the results of some of these studies [30–33].

2 MODEL

The system is comprised of Pt surface atoms and a single ethane or *n*-butane adsorbate. In modeling the Pt(111) surface, a five-layer, rhombic slab, which contained 26 atoms per layer, was utilized. The Pt–Pt interaction was modeled using a Lennard-Jones (6–12) potential with parameters σ_s and ε_s from Halicioglu *et al.* [34] and a cut-off radius of $2.5\sigma_s$. The Lennard-Jones potential provides computational economy and has been found to represent the surface phonon spectrum of fcc(111) metals with reasonable accuracy [35–37]. Atoms in the top three layers followed Newton's equation of motion. The equations were integrated using the Verlet algorithm [38] with a time step of one femtosecond. The fourth-layer atoms were maintained isothermal by means of the Gaussian thermostat method [39–41]. The equations of motion for these atoms are given by

$$\dot{\boldsymbol{p}}_i = -\nabla_{r_i} U - \xi \boldsymbol{p}_i, \tag{1}$$

where $\boldsymbol{p}_i$ is the momentum of atom *i*, *U* is the potential energy, and ξ is a quantity akin to a friction coefficient that is adjusted at each time step to constrain the instantaneous kinetic temperature to a desired value. The integration scheme for atoms in the fourth layer and the determination of ξ was done via a method proposed by Brown and Clarke [42]. Atoms in the fifth layer were fixed to the equilibrium platinum crystal-lattice positions to provide a structural template for the atoms above. Periodic boundary conditions were applied in the x and y direction parallel to the surface.

The alkane admolecule was modeled with the united-atom (UA) model developed by Ryckaert *et al.* [43, 44], in which methyl and methylene groups are represented by a single interaction center located at the position of each carbon atom. The UA model has been used to accurately represent both adsorbed [45–48] and fluid-phase [49–55] alkanes in several studies. The potential energy of the molecule U is given by the sum of the intramolecular potential energy U_{intra} and the molecule-surface interaction U_{ms}. A sketch indicating relevant contributions to the intramolecular potential is shown in Figure 1. Since the C—H stretching and the H—C—H bond-angle bending modes (both of which occur at high frequencies relative to other internal modes) are eliminated by the UA approximation, the remaining contributions to the intramolecular potential energy come from C—C stretching, C—C—C bond-angle bending, and torsion about non-terminal C—C bonds. The high-frequency (~ 1000 cm^{-1} [56]) C—C stretch was neglected by constraining the carbon–carbon bond length to its fluid-phase equilibrium value. The bond-angle bending and torsional modes have the lowest frequencies at approximately 420 cm^{-1} and 200 cm^{-1}, respectively [56], and were considered in modeling *n*-butane. The intramolecular potential energy for *n*-butane was given by the sum of contributions from these two modes, i.e., by

$$U_{\text{intra}} = U_b + U_t, \tag{2}$$

where U_b is the energy for C—C—C bending and U_t is the energy change upon torsion about the central C—C bond. The bond-angle bending potential had a harmonic form suggested by van der Ploeg and Berendsen [57], given by

$$U_b(\theta_i) = \frac{1}{2} k_b (\theta_i - \theta_0)^2. \tag{3}$$

Here, θ_i is the angle of the ith C—C—C bond, θ_0 is the equilibrium angle, and k_b is constant. The potential energy for torsion U_t was modeled by a six-term cosine

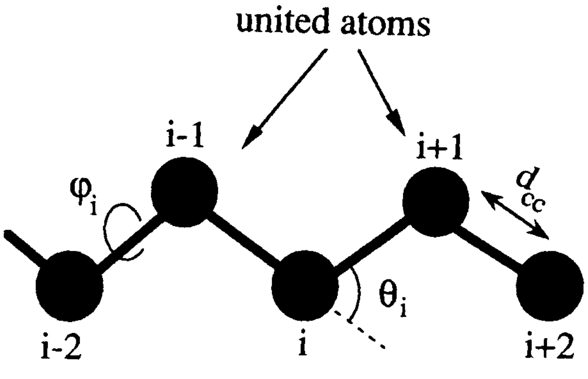


Figure 1 The UA model for an alkane chain. θ is the bending angle and φ is the torsion angle. The intramolecular potential of the chain is a function of these bending and torsion angles.

expansion [43] of the form

$$U_t(\varphi) = \sum_{l=0}^{5} a_l(\cos\varphi)^l, \tag{4}$$

where φ is the dihedral angle.

The interaction of the alkane admolecules with the Pt(111) surface was modeled using a Lennard-Jones (6–12) potential with pairwise-additive intractions between the united atoms and the Pt surface atoms. Regarding the molecule-surface parameters, σ_{ms} was obtained, using the Lorentz-Berthelot mixing rules [58], from the average of σ_s for the Pt–Pt interaction and σ_m for the fluid-phase, Lennard-Jones interaction between united atoms [43], i.e.,

$$\sigma_{ms} = \frac{\sigma_m + \sigma_s}{2}. \tag{5}$$

This estimate gave $\sigma_{ms} = 3.231$ Å. The value of $\varepsilon_{ms}/k_B = 156.36\,\mathrm{K}$ was chosen to approximately match the experimental heat of adsorption for *n*-butane on Pt(111) of 8.2 kcal/mol [59]. The potential was truncated at a distance of $2.5\,\sigma_{ms}$.

The equations of motion for molecules with intramolecular constraints (e.g., fixed bond lengths) must properly account for the rigid-body motion. In the approach used here, the "method of constraints" [44, 55, 60, 61], Newton's equation of motion is given an additional term which accounts for the constraint forces. For a chain having n united atoms with position vectors $\{\mathbf{r}_i\}$ $(i = 1, n)$, the set of l holonomic constraints can be written as

$$\sigma_i(\mathbf{r}) = (\mathbf{r}_{i+1} + \mathbf{r}_i) - d_{cc}^2 = 0, \tag{6}$$

where d_{cc} is the equilibrium length of the carbon–carbon bond. The Lagrange equation of motion for united atom i of mass m_i is given by

$$m_i\ddot{\mathbf{r}}_i = -\nabla_{r_i} U - \sum_{k=1}^{l} \lambda_k \frac{\partial\sigma_k}{\partial \mathbf{r}_i}. \tag{7}$$

Here $\{\lambda_k\}$ $(k = 1, l)$ is a set of Lagrange multipliers requiring that the solution of Eq. (7) satisfies the constraints of Eq. (6). The first term on the right-hand side of Eq. (7) is the force arising from the gradient in the potential energy of the molecule ($U = U_{\mathrm{intra}} + U_{ms}$), while the second may be attributed to forces constraining the C—C bond length. The equations of motion were integrated using the Verlet algorithm [38] with a time step of one femtosecond. The integration was a two-step procedure in which the equations were first integrated without constraint forces and then corrected to satisfy the constraints exactly. The second step involved determining the Lagrange multipliers, which were treated as parameters. At each time step, these were obtained from the SHAKE algorithm of Ryckaert, Ciccotti, and Berendsen [61]. The SHAKE algorithm is an iterative procedure, which is terminated when the bond-length constraints are satisfied to within some tolerance τ, with

$$\tau > \frac{|d_{cc} - |\mathbf{r}_i - \mathbf{r}_{i+1}||}{d_{cc}}. \tag{8}$$

The choice of τ affects energy conservation as well as the number of iterations required for the convergence of SHAKE. A value of $\tau = 10^{-7}$ was used in this study. Values smaller than this result in a significant increase in the convergence time for the SHAKE algorithm with only marginal gains in the degree of energy conservation [62].

Simulations were run in the temperature range of 15–125 K for ethane and 50–175 K for *n*-butane. For each temperature, twenty simulations, each with a length of 500 ps., were run to obtain trajectory data. Each run consisted of an equilibration phase, in which the velocities of all particles were adjusted to achieve the desired temperature, followed by a simulation run. In all of the results reported here, the average temperature of the molecule was within one percent of the desired temperature. The trajectory results were analyzed to study several static and dynamical aspects of the adsorption, as discussed below.

3 RESULTS AND DISCUSSION

At a temperature of 15 K for ethane and 50 K for *n*-butane, the adsorption is localized to a single "site" over the entire simulation period (500 ps.). The minimum-energy binding conformations of ethane and *n*-butane are shown in Figures 2(a) and 2(b), respectively. These were the only conformations observed when adsorption was localized. In both cases, we have independently determined the minimum-energy conformations via Monte Carlo methods [32, 33]. Both molecules lie "flat" with their molecular axes parallel to the surface. As shown in Figure 2(a), the center of mass of the ethane molecule is located above a bridge site between two surface Pt atoms with each of the two united atoms residing close to a three-fold site on the surface. Figure 2(b) shows the two degenerate binding configurations for the same position of the center of mass of *n*-butane. Similar to ethane, the adjacent united atoms also reside close to three-fold sites with the center of mass over a bridge site. Bond-angle bending of *n*-butane was found to be negligible and the molecule was found to be in the trans

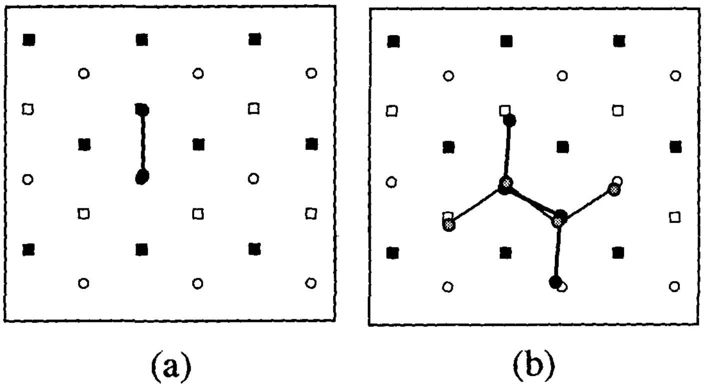

(a) (b)

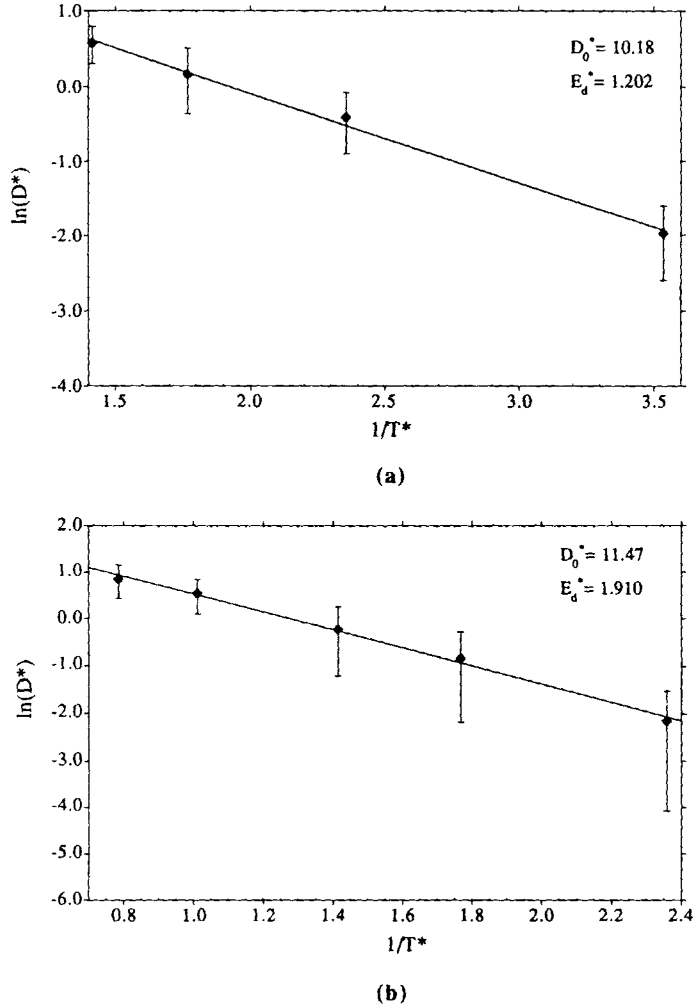
Figure 2 The minimum-energy binding conformations of ethane **a** and *n*-butane **b**. ■ Represents first-layer Pt atoms; □ represents second-layer Pt atoms; ○ represents third-layer Pt atoms; ●–● represents the alkane chain.

conformation for greater than 99% of the time at all temperatures probed. Our observations for both molecules are consistent with findings from low-energy electron diffraction [63] and infrared spectroscopy [64] studies of *n*-alkanes on Pt(111).

As a major characterization of diffusion dynamics, we measured the tracer-diffusion coefficient using the Einstein equation, given by

$$\langle l^2 \rangle = 2dDt. \tag{9}$$

Here, $\langle l^2 \rangle$ is the mean-square displacement, d is the dimension of the motion (two-dimensional motion is assumed for surface diffusion), D is the tracer-diffusion coefficient, and t is time. We measured the mean-square displacement as an ensemble



(a)

(b)

Figure 3 Arrhenius plot of diffusion coefficients for ethane **a** and *n*-butane **b**. The uncertainties represent one standard deviation from the average diffusion coefficient obtained over 20 runs.

average over varying time intervals and obtained the diffusion coefficient from the slope of a plot of $\langle l^2 \rangle$ vs. t. Arrhenius plots of the dimensionless diffusion coefficient $D^* = D(m_s/\varepsilon_{ms}\sigma_{ms}^2)^{1/2}$, where m_s is the mass of a surface atom, vs. the reciprocal of the dimensionless temperature $T^* = k_B T/\varepsilon_{ms}$ for ethane and *n*-butane are shown in Figures 3(a) and 3(b), respectively. The slope and intercept of the Arrhenius plot yield an Arrhenius activation energy E_d and prefactor D_0 for a diffusion coefficient of the form predicted by transition-state theory, given by

$$D = D_0 \exp(-E_d/k_B T). \tag{10}$$

From the Arrhenius plots, we obtain $D_0 = 0.016 \pm 0.001\,\mathrm{cm}^2/\mathrm{s}$ and $E_d = 0.42 \pm 0.02$ kcal/mol for ethane and $D_0 = 0.018 \pm 0.001\,\mathrm{cm}^2/\mathrm{s}$ and $E_d = 0.59 \pm 0.02$ kcal/mol for *n*-butane. The uncertainties reported here are one standard deviation in a linear, least-square fit of the data in Figures 3 to equation (10). A measure of the relative strengths of the normal and parallel components of the molecule-surface potential is given by the corrugation ration Ω, where Ω is given by

$$\Omega = E_d/E_{\mathrm{des}}. \tag{11}$$

Here, E_{des} is the activation energy for desorption. In this study, we found $\Omega = 0.09$ for ethane and 0.07 for *n*-butane.

In a related experimental study [22] Brand *et al.* studied the diffusion of short-chain (C3—C6) *n*-alkanes on Ru(001) using laser-induced thermal desorption (LITD). In that study, the diffusion barrier was found to be a linearly increasing function of chain length, while the preexponential factor was constant and independent of chain length [22]. Although we cannot, at this point, distinguish whether the barrier is a linear function of chain length, the preexponential factors, which are essentially the same for both ethane and *n*-butane, do follow the experimental trend. It should be noted that the diffusion coefficient that we obtain for *n*-butane is larger than the experimental diffusion coefficient [22] over the temperature range studied. Possible reasons for this discrepancy are discussed in detail elsewhere [30]. Undoubtedly, the quantitative capability of a model, assuming united atoms and a semi-empirical potential, is limited. However, the capacity of LITD to resolve the motion of a single adsorbate on a perfect crystalline surface is also limited, and, in systems probed with more than one technique, the LITD results usually provide an upper bound [16] on the diffusion barrier. At this stage of our understanding, much theoretical and experimental progress is needed to obtain a thorough understanding of *n*-alkane adsorption on smooth metal surfaces.

Representative center-of-mass trajectories from simulations run of ethane at 25 K, 50 K, 75 K, and 125 K and *n*-butane at 75 K, 100 K, 125 K and 175 K are shown in Figures 4 and 5, respectively. As shown in Figure 4, at 25 K, the diffusion of ethane occurs through nearest-neighbor hops. At 50 K, ethane begins to make multiple-site hops and nonlocalized long flights. For *n*-butane, the molecule exhibits multiple hops from one binding site to another at 75 K, with a hop length which is often greater than two unit cells. In the molecular-dynamics simulation study by Dobbs *et al.* [29] of the diffusion of CO on Ni(111), as many as 65% of the hops extended over more than two unit cells. Our results fit an emerging trend which seems to indicate that molecules exhibit a greater propensity for multiple-site hopping than atoms (see below). Decreasing localization of adsorption and greater motion between sites can be seen with

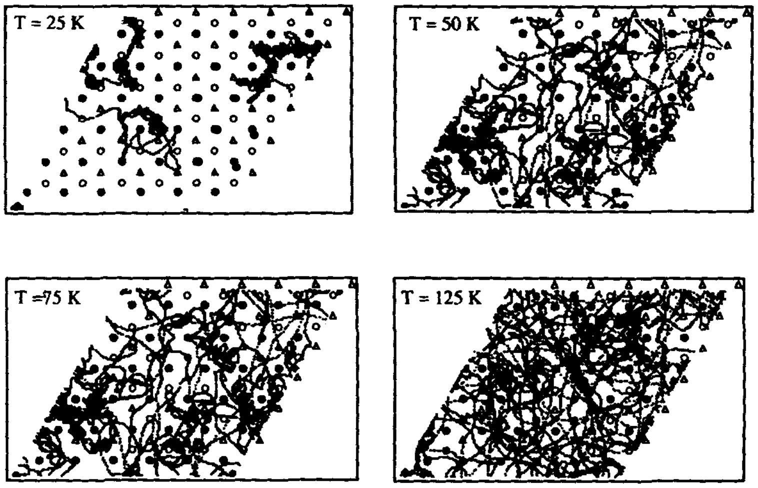


Figure 4 Two-dimensional trajectory plots for ethane at $T = 25$ K, 50 K, 75 K and 125 K. ● Represents first-layer Pt atoms; ○ represents second-layer Pt atoms; Δ represents third-layer Pt atoms.

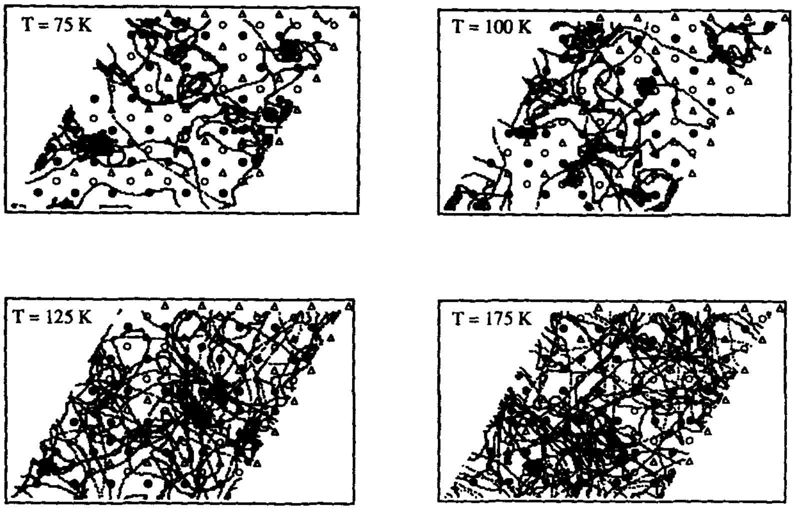


Figure 5 Two-dimensional trajectory plots for *n*-butane at $T = 75$ K, 100 K, 125 K and 172 K. ● Represents first-layer Pt atoms; ○ represents second-layer Pt atoms; Δ represents third-layer Pt atoms.

increasing temperature. At temperatures above 100 K for ethane and 125 K for *n*-butane, adsorption of the admolecule is virtually delocalized. It would seem that the adspecies-hopping model of transition-state theory, which assumes localized adsorption, is no longer valid at these temperatures.

In order to further characterize the motion of the alkane admolecules, we animated several trajectories of both ethane and *n*-butane. At high temperatures, we find that the

C—C bonds of the alkanes often directly cross over the top-layer Pt atoms through in-plane translation or swing over the surface atoms through rotation. In addition, the admolecules often move through the empty spaces of bridge sites and three-fold sites. Thus, the admolecules spend most of the time in nonlocalized long flights and multiple-site hops. At low temperatures, the adsorption is the most localized and the characteristic mechanisms of motion are the most likely to be revealed.

In much of the motion that we observed for ethane, the molecule moved between the platinum surface atoms. Such a mechanism involves both translation and in-plane rotation of the molecule. A more rigorous characterization of the diffusion mechanisms can be made by analysis of the minimum-potential-energy surface (MPES) for motion parallel to the surface. The minima on the MPES correspond to binding conformations of the molecule. Diffusion mechanisms can be obtained by sequencing molecular conformations along the minimum-energy path connecting nearest-neighbor minima. In addition, diffusion barriers can be obtained from the difference between the energies at the initial-state minimum (binding conformation) and at the maximum point along the minimum-energy path (i.e., the saddle point) connecting nearest-neighbor minima [65].

We have determined the MPES for ethane–Pt(111) and calculations for n-butane–Pt(111) are in progress [32]. Details of these calculations will be presented elswhere [32]. The MPES for ethane on Pt(111) is depicted in Figure 6(a). Due to the periodic structure of the surface, it is only necessary to consider one surface-unit cell. Our calculations show that there is one pathway for ethane motion on Pt(111). This is depicted in Figure 6(b). In the lowest-energy mechanism, characterized by a barrier of 0.14 kcal/mol, the molecule follows the sequence A—Δ—C (see Fig. 6(b)) and, in this motion, avoids the Pt atom, D. Our observation of the motion of ethane at low temperatures confirms that this mechanism is dominant.

It is interesting to compare the MPES barrier to the barrier obtained from Arrhenius analysis of the tracer-diffusion coefficients. The latter has a higher value than the MPES barrier. We tentatively attribute this finding to the influence of "dynamical corrections" to transition-state theory (i.e., multiple-site jumps and recrossings) on the diffusion. Sanders and DePristo [10] observed, in their study of metal-atom diffusion on fcc(111) metal surfaces, that the diffusion barrier obtained from molecular-dynamics simulation were larger than the barriers estimated from transition-state theory, while barriers from diffusion on more corrugated fcc(001) surfaces were comparable to theoretical estimates. The feature that they identified as the main source of the discrepancy between theory and simulation was the existence of multiple-site hops and recrossings at the transition state for simulations on the less corrugated fcc(111) surfaces. The low apparent corrugation (arising from the simulation) and the even lower actual corrugation (arising from transition-state theory) qualify our system as a "low corrugation system". Hence, our findings here corroborate those of Sanders and DePristo [10].

Similar to the mechanism for ethane, the nearest-neighbor hopping of n-butane was characterized by extensive translational and (in-plane) rotational coupling. The n-butane admolecule gradually increases the amplitude of the lateral-rotational librations until the molecule gains sufficient rotational energy to force one of the terminal united atoms to swing over a top site. Concerted, linear translational motion along the

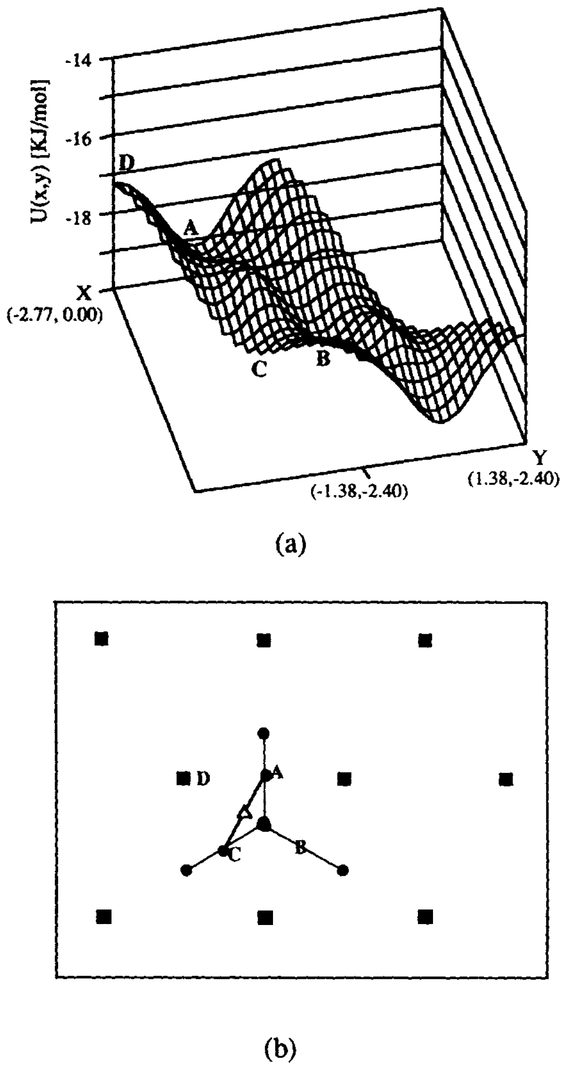
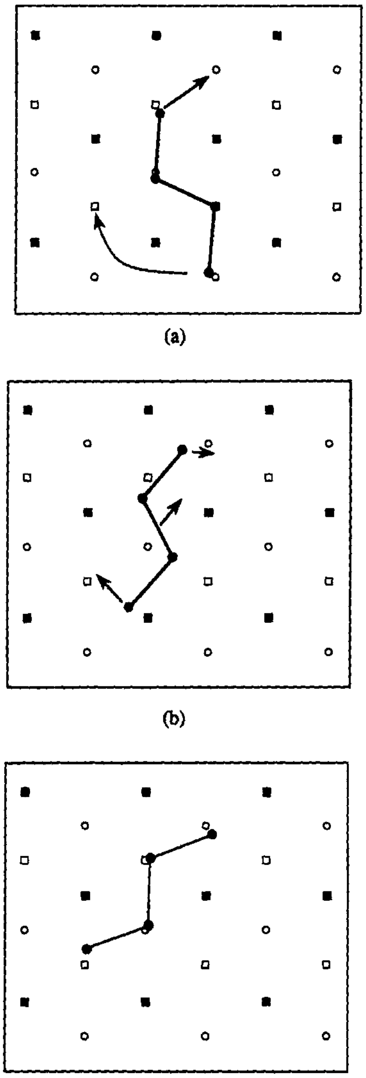


Figure 6 **a** The calculated minimum-potential-energy-surface (MPES) in (*x*, *y*) space for an ethane molecule on Pt(111). A, B, and C represent three nearest-neighbor binding sites. D is a first-layer Pt atom; **b** illustrates the diffusion mechanism indicated by the MPES: A—Δ—C.

molecular axis enables the molecule to move to an adjacent binding site. A three-step sequence of the mechanism, depicting a possible transition state, is shown in Figure 7. This mechanism is consistent with the suggestion by Arena *et al.* [22] that short (C3—C6) *n*-alkane motion is concerted as opposed to segmental. However, these findings are in contrast to those of Cohen and Zeiri [27, 28], which predict that the diffusion of *n*-butane should involve out-of-plane rotation about an end segment of the molecule. The edge-rotation mechanism may not have been observed for several



(a)

(b)

(c)

Figure 7 The observed lateral-rotation and axial translation nearest-neighbor hopping mechanism for *n*-butane. **a** Initial minimum-energy conformation of *n*-butane at a binding site; **b** a tentative conformation for the transition state; (c) Minimum-energy conformation at a neighboring binding site; ■ represents first-layer Pt atoms; □ represents second-layer Pt atoms; ○ represents third-layer Pt atoms; -●●- represents the alkane chain.

reasons. First, the geometry and the potential-energy-surface topology of the Pt(111) surface used here and the W(100) surface used in that study are different. We expect the W(100) surface to be more corrugated for alkane physisorption than the closely-packed Pt(111) surface. The diffusion barriers and corrugation ratios estimated by Cohen and Zeiri [27, 28] in their study are larger than the one that we find here, consistent with a more corrugated surface. It is possible, with larger barriers to translation on W(100), that out-of-plane motion and the internal modes become more important in the diffusion. The difference between two models could imply that the diffusion mechanisms of *n*-alkanes are sensitive to the structure of the surface. Finally, the temperature range of 300–1000 K considered in their study is higher than that in this study. We found, in the low-temperature range (15–175 K) probed by our study, that bond-angle bending, torsion, and motion normal to the surface were negligible. However, the temperature range of 300–1000 K in their study was much higher than that of ours. These high temperatures could allow for activation of the internal modes and greater freedom for motion normal to the surface. With faster translation at these temperatures, perhaps coupling between in-plane motion and other motions is easier. The lowest temperature probed in their study is higher than the desorption temperature of *n*-butane on Ru(001) [22] and is significantly higher than the highest temperature probed in the experimental studies of alkane diffusion [22]. Hence, the edge-rotation mechanism may not be appropriate for describing the motion of short-chain *n*-alkanes on smooth fcc(111) and hcp(001) surfaces at low temperatures. Instead, it seems more likely that the motion is concerted and rigid-rod-like, as described by our model.

CONCLUSIONS

The surface diffusion of ethane and *n*-butane physically adsorbed on Pt(111) has been simulated using molecular-dynamics over a wide temperature range. In the model for the *n*-alkanes, the UA approximation and the pairwise-additive molecule-surface potential are perhaps the most significant simplifications. Our work has corroborated results from related experimental studies [22, 63, 64] regarding the binding conformation [63, 64] and the trend of the diffusion coefficient [22] with increasing chain length. Our work has also revealed insight to the diffusion mechanisms of physically adsorbed chain molecules and their dynamical deviations from transition-state theory. Future studies will probe longer alkane chains in an attempt to uncover fundamental phenomena associated with their motion.

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