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Anisotropic diffusion of *n*-butane and *n*-decane on a stepped metal surface

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The diffusion of single *n*-butane and *n*-decane molecules on a model stepped surface, Pt(655), and on a corresponding flat surface, Pt(111), is investigated using molecular-dynamics simulations and anisotropic united atom model. The surface step on Pt(655) causes the alkane molecules to adsorb on the lower terrace in all-trans conformations with their long molecular axes adjacent and parallel to the step edge, and to diffuse anisotropically along the surface step via a constant wiggly motion without rotation or marked deviation from the parallel adsorption configuration. At relatively high temperatures, the alkane molecules can temporarily break away from the step edge but cannot migrate across the step edge in either the downstair or upstairs direction. In comparison with the diffusion on Pt(111), the diffusivity of *n*-decane is reduced by the surface step but its diffusion barrier is hardly affected. In the case of the shorter *n*-butane, however, the surface step significantly reduces the diffusion energy barrier and gives rise to higher diffusion coefficients at lower temperatures. Important implications of the simulation results are discussed. © 2005 American Institute of Physics. [DOI: 10.1063/1.1949170]

I. INTRODUCTION

The diffusion of alkane molecules on metal surfaces is of great importance and broad interest. From a technological standpoint, this diffusion system concerns a number of important surface rate processes (e.g., heterogeneous catalytic reactions and thin-film growth). Fundamentally, this system has also been used as a model system to study the surface diffusion of chain molecules¹⁻³ that have rich, complex behaviors but yet to be fully understood. In general, an adsorbate at or near a solid surface diffuses through a multidimensional potential-energy surface (PES) that results from the interplay between the adsorbate's internal degrees of freedom and external interaction with the surface. Surface diffusion is therefore very strongly influenced by the characteristics of the adsorbate and of the substrate surface. By comparison with simple adatoms, alkanes and similar chain molecules possess many internal degrees of freedom that can create significantly different PESs and result in diverse and interesting diffusional behaviors on solid surfaces.¹⁻⁴ Surface defects also play a critical role in surface diffusion in that they alter not only the physical structure of a surface but also the topographical features of the resultant PES. They have indeed been shown to bring about new diffusion mechanisms and pathways not seen on smooth surfaces.⁵⁻⁸ Since surface defects can be expected to be an intrinsic part of the surface structure on grounds of entropy, they could affect and sometimes even mask many surface rate processes. A detailed understanding of the influence of surface defects on surface diffusion as well as on other surface phenomena is therefore necessary in order to interpret experimental data more accurately and utilize differently structured surfaces more effectively.

Surface steps are one of the most abundant and most influential surface defects. Even the best manufactured single-crystal surfaces to date have steps separated by distances less than a few hundred angstroms.⁷⁻⁹ As one-dimensional microscopic structures that divide a surface into terraces of different heights, surface steps break the isotropy of the surface structure and introduce anisotropic characteristics into PES and into various surface phenomena and rate processes. Experimental studies⁷⁻¹² have indeed demonstrated that the presence of surface steps can cause unique and sometimes overwhelmingly anisotropic surface diffusion. Relevant theoretical analyses¹³⁻¹⁵ and simulation studies¹⁵⁻¹⁹ also provided substantial fundamental insight and elucidation in this respect. However, the majority of these studies considered either single atoms or very simple molecules as diffusing adsorbates and employed relatively simplistic models. Much less effort has been made to understand the effect of surface steps on the important diffusion system of alkanes on metal surfaces. Experiments using laser-induced thermal-desorption (LITD) techniques showed that the diffusion coefficient of *n*-butane on a stepped ruthenium surface is significantly higher in the direction parallel to the step edge than in the perpendicular direction.²⁰ In addition, as the surface coverage increases, the diffusion coefficient of *n*-butane was found to increase on the stepped ruthenium surface.²¹ Despite the success, these LITD experimental measurements have been considered to have limited resolution of the underlying diffusion mechanisms under a very low surface coverage and at a molecular level, due to their integral, nonlocal nature.²²

In order to obtain fundamental insight and a detailed understanding of the effect of surface steps on alkane diffusion on metal surfaces, this work examines surface diffusion of single alkane molecules on a stepped surface and on a corresponding flat surface using molecular-dynamics (MD)

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simulations. A relevant intriguing phenomenon unveiled by recent studies of alkane and chain molecules on flat surfaces is a crossover of diffusion dynamics as chain length increases.^{1,2,4,23} It would be interesting and important to know if similar crossover behavior also exists in alkane diffusion on stepped surfaces. To shed light on this matter, two alkanes of appropriately different chain lengths are considered in this work. The MD method, in general, is less coarse-grained and better suited to study systems where atomic-scale characteristics are important and complex. It has proven to be instrumental in providing a fundamental understanding of alkane diffusion on flat solid surfaces.^{1–3,23–25} However, MD simulation studies employing genuine stepped surfaces have been quite rare. Instead, small surface stripes or surface islands²⁶ have been used to provide effects similar to those of surface steps. Without proper precautions, these alternatives are likely to subject an adsorbed molecule to simultaneous interactions with and direct influence from more than one surface step, which could alter the results sought by this work. The major difficulty associated with incorporating genuine stepped surfaces in MD simulations lies in the necessary implementation of periodic boundary conditions which are seemingly uneven on stepped surfaces. A method to overcome this difficulty has been successfully applied to treat a regularly stepped surface in one of our recent studies²⁷ and also employed in the present work. The model stepped surface adopted here is the (655) surface of a face-centered-cubic (fcc) metal. It has regularly spaced steps separated by sufficiently wide terraces so that the influence of the aforementioned artifacts can be avoided. A detailed description of the stepped fcc(655) surface and the treatment of its periodic boundary conditions is presented in Sec. II.

II. SIMULATION MODELS AND METHOD

The fcc(655) surface can also be labeled as fcc(s)-[11(111)×(100)] in step notation.²⁸ As indicated by the more explicit step notation and by its ball model shown in Fig. 1(a), the fcc(655) surface comprises of (111) terraces that are 11 rows wide and (100) steps that are single-atom high. It is thus a vicinal surface with respect to the flat fcc(111) surface which is one of the most commonly used surfaces in relevant studies. In fact, the fcc(655) surface can be obtained by deliberately miscutting fcc(111) by an angle of 5.05° which is the angle between the two surface normal vectors, namely, [655] and [111]. In this study, the simulation unit cell consists of one (111) terrace and one (100) step. A slab of five layers is used to represent fcc(655) and 264 (11×24) atoms are used to represent one layer. Surface atoms in the top three layers move in accordance with the interaction forces acting on them. The fourth layer is treated as a heat bath layer to control temperature via a Gaussian thermostat method.²⁹ Atoms in the bottom layer are fixed to their equilibrium lattice positions to represent the crystal bulk and provide a structural template for the layers above. To implement periodic boundary conditions in the presence of surface steps and terraces of different heights, the model slab was rotated around the step ridge (*y* axis) by the same angle of 5.05° to make even the boundaries in the *x* direction

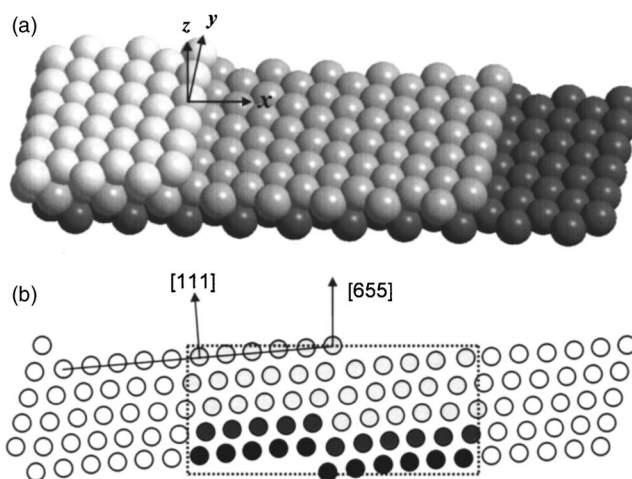


FIG. 1. (a) A ball model of the stepped fcc(655) surface and the coordinate system used in this work. (b) Schematic side view of the fcc(655) surface. The arrows indicate the normal vectors that define the fcc(655) surface and the fcc(111) terrace. The dotted rectangle represents the simulation unit cell, where the heat-bath layer and the template layer are represented by gray and dark circles, respectively.

[cf., Fig. 1(b)].²⁷ The interaction among surface atoms is modeled with a Lennard-Jones (LJ) 12-6 potential whose parameters, $\sigma_{\text{Pt}}=2.542 \text{ \AA}$ and $\epsilon_{\text{Pt}}=65.764 \text{ kJ/mol}$, were fitted to reproduce the lattice constant and cohesive energy of platinum (Pt).³⁰ The distance between two step edges is then 25.7 Å and significantly larger than the potential cutoff distance of the alkane–surface interaction discussed below. Alkane diffusion on the flat fcc(111) surface is also simulated in order to understand the effect of the surface step by comparison. The fcc(111) surface is modeled very much the same as the fcc(655) surface, except that its unit cell is rhombus-shaped and each layer has 256 (16×16) atoms.

The present work focuses on the surface diffusion of two representative alkanes: *n*-butane (C₄H₁₀) and *n*-decane (C₁₀H₂₂). In recent years there has been a renewed interest in improving the simulation potential models for alkanes.^{31,32} This work adopts the anisotropic united atom (AUA) model³¹ together with the parameters that have been further optimized by Ungerer *et al.*³³ Compared to the conventional united atom (UA) model,^{24,34} the AUA approach gives the pseudoatoms, namely, the–CH₂–and–CH₃ groups, appropriately different sizes ($\sigma_{\text{CH}_2}=3.4612 \text{ \AA}$ and $\sigma_{\text{CH}_3}=3.6072 \text{ \AA}$) and different interaction strengths ($\epsilon_{\text{CH}_2}=86.291 \text{ K}$ and $\epsilon_{\text{CH}_3}=120.15 \text{ K}$), while keeping the bending and torsion potentials similar. More importantly, the interaction sites of the nonbonded interactions between pseudoatoms are placed at the geometrical centers instead of the carbon atoms that are assumed in the UA model. This shift of interaction sites takes into account the steric effect of hydrogen atoms and gives rise to better simulation results for alkanes.³³

Since the alkane–surface interaction is considered to be physical and relatively weak, it is a proper treatment to employ pairwise interactions between surface atoms and alkane pseudoatoms. Not knowing any existing study that has extended the AUA model to the alkane/platinum system, we first set out to obtain a proper AUA-Pt interaction potential. To this end, we used the LJ 12-6 potential truncated and

corrected at $3\sigma_{\text{CH}_3\text{-Pt}}=9.2238 \text{ \AA}$, and the Lorentz–Berthelot mixing rule such that $\sigma_{ij}=(\sigma_{ii}+\sigma_{jj})/2$ and $\epsilon_{ij}=\sqrt{\epsilon_{ii}\epsilon_{jj}}$. As a result, $\epsilon_{\text{CH}_3\text{-Pt}}/\epsilon_{\text{CH}_2\text{-Pt}}=\sqrt{\epsilon_{\text{CH}_1}/\epsilon_{\text{CH}_2}}$, and the only parameter remains to be characterized is $\epsilon_{\text{CH}_3\text{-Pt}}$, or equivalently $\epsilon_{\text{CH}_2\text{-Pt}}$. We carried out MD simulations to compute the heat of adsorption for four *n*-alkanes (C_4 , C_8 , C_{12} , and C_{16}) on Pt(111) with different $\epsilon_{\text{CH}_3\text{-Pt}}$ values. Very linear fits were obtained and indicated that the contribution to the heat of adsorption from each pseudoatom was 4.79 kJ/mol when $\epsilon_{\text{CH}_3\text{-Pt}}=1300 \text{ J/mol}$, and 7.77 kJ/mol when $\epsilon_{\text{CH}_3\text{-Pt}}=1950 \text{ J/mol}$. These two values of alkane adsorption heat encompass the reported range of 5–6.5 kJ/mole of carbon unit.^{35,36} We also simulated a C_4 monolayer film on Pt(111) with $\epsilon_{\text{CH}_3\text{-Pt}}=1300 \text{ J/mol}$. The desorption energy was found to be approximately 26.3 kJ/mol, which is about 1.31 times smaller than the experimental data of 34.31 kJ/mol (Ref. 35) and prompted us to use the ratio to settle on a value of 1700 J/mol for $\epsilon_{\text{CH}_3\text{-Pt}}$. This $\epsilon_{\text{CH}_3\text{-Pt}}$ value corresponds to $\epsilon_{\text{CH}_2\text{-Pt}}=1441 \text{ J/mol}$ and an adsorption heat of approximately 6.26 kJ/mole of carbon unit. The former is slightly higher than 1300 J/mol used in similar simulation studies employing the UA model^{2,23} and the latter is within the reported range of experimental data.

The equations of motion were integrated using the Verlet algorithm^{37,38} in conjunction with the SHAKE algorithm^{38,39} to constrain the C–C bond length at 1.535 Å and to allow the use of 3 fs as the time step. For each alkane on Pt(655) and Pt(111), we started our simulations from the lowest temperatures and with all-trans initial conformations. To proceed to the next higher temperature, a number of final configurations at the end of production runs at the previous lower temperature were selected as initial conditions. At least five different temperatures were probed for each combination of alkane and surface, and more than 20 separate MD simulations were performed for each temperature in order to obtain proper statistics for the results presented here. Every MD simulation was equilibrated first prior to a production run of 200 000 time steps (600 ps). The equilibration criteria included the average temperature, the magnitude of temperature fluctuations, and interaction potential energies.

III. RESULTS AND DISCUSSION

In order to have sufficient surface mobility for reasonable statistics, the lowest temperatures used to study surface diffusion of *n*-butane and *n*-decane in this work were 75 and 100 K, respectively. The other temperatures probed for *n*-butane are 100, 125, 150, and 175 K, and for *n*-decane 125, 150, 175, 200, 225, and 250 K. For comparison purposes, we plot representative center-of-mass trajectories of *n*-butane on Pt(111) at different temperatures in Fig. 2. It is apparent and also consistent with existing studies^{2,23} that the diffusion mechanisms of *n*-butane on flat metal surfaces include hops and long flights. The latter mechanism is known to be characteristic of chain molecules diffusing on structured surfaces and occurs due to the difficulty in simultaneously fitting a chain of atoms into proper positions.^{2,3,23} The hopping mechanism is important only at very low temperatures, while long flights contribute predominantly to surface diffusivity at

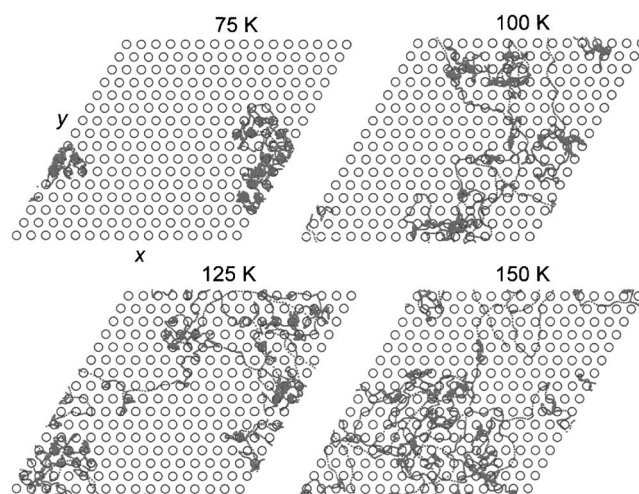


FIG. 2. Representative center-of-mass trajectories of *n*-butane on Pt(111). The open circles represent the first-layer surface atoms.

higher temperatures. Although not shown here, similar trajectories and findings but smaller diffusivities have been observed for *n*-decane on Pt(111) in this study.

Unlike on the flat Pt(111) surface, the configurations and conformations of adsorbed alkanes on Pt(655) could be significantly influenced by the anisotropic surface steps. It is thus a desirable precaution to place the initial position of an alkane molecule above the alkane–Pt(655) interaction range and assign to it a small downward velocity and different orientations with respect to the step edge. As the alkane molecule approaches the surface, its interaction with the atomistically structured surface triggers configurational relaxation including translational and rotational motions, and guides the exploration of the potential-energy surface. Regardless of initial orientation, the final configuration of adsorbed *n*-butane and *n*-decane on Pt(655) was found to be alkane molecules at the bottom of the step edge on the lower terrace in all-trans conformations with their long molecular axes adjacent and parallel to the step edge (cf., Fig. 3). This should not be a surprise since the surface step creates a region of higher coordination number to provide stronger adsorption sites, and since the parallel configuration and all-trans con-

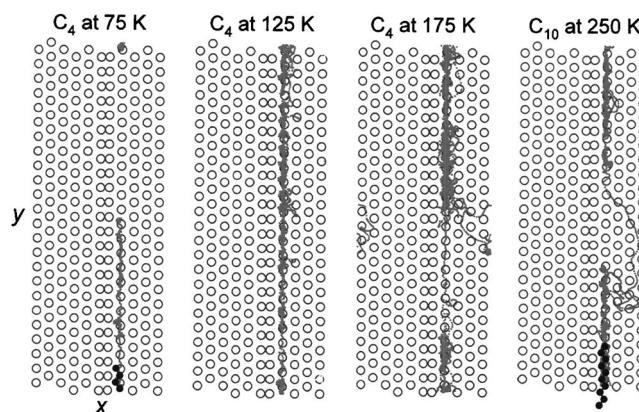


FIG. 3. Representative center-of-mass trajectories of *n*-butane and *n*-decane on Pt(655). The open circles represent the first-layer surface atoms defined in Fig. 1(b) and the dark circles represent the equilibrium configurations of adsorbed *n*-butane and *n*-decane.

formation maximize the contact between the step edge and the alkane molecules. It is worth noting that even with an initial orientation across the step edge, the relatively small *n*-butane and *n*-decane molecules can still quickly rotate and migrate on the terrace to reach the step sites and attain the parallel configuration. The parallel configuration of the adsorbed alkanes is responsible for the anisotropic diffusion dynamics seen on the stepped surface presented below. Whether large chain adsorbates having more structural flexibility exhibit the same behavior or not on the stepped surface would be an interesting and relevant question.

Figure 3 shows some representative center-of-mass trajectories on the stepped Pt(655) surface for *n*-butane at 75, 125, and 175 K, and *n*-decane at 250 K. In sharp contrast with the same molecules on the flat Pt(111) surface (cf., Fig. 2), diffusion on the stepped surface is clearly anisotropic and mostly along the step edge. In particular at low temperatures, surface diffusion of *n*-butane and *n*-decane on Pt(655) is strictly one dimensional. As the temperature increases, the alkane molecules become less strongly bound to the step due to higher thermal energy and eventually are able to break away from the step at relatively high temperatures. Such a breakaway is a temporary event in our simulation systems because the strong interaction from the step tends to recapture the alkane molecules and because the elevated energy barrier located at the edge of the step,^{20,21,26,27} generally known as the Ehrlich–Schwoebel barrier,⁴⁰ prevents the alkane molecules from descending to a lower terrace. We remark that the breakaway of adsorbates from the surface step could become a long-lasting or virtually permanent event when the temperature is very high and/or the terrace is very wide.

It is important to emphasize that in our simulations we did not observe any alkane molecule migrating “upstairs” or “downstairs” across the surface steps within the probed temperature ranges. Between these two routes of perpendicular diffusion, the former “step-up” diffusion is known to be even more difficult than the latter “step-down” diffusion for physisorbed adsorbates^{20,27,40,41} because the adsorbates experience deep potential-energy minima near the bottom of the step edge but have no capability to execute the atomic-exchange mechanism that has been shown to facilitate the diffusion of strongly bound metal adatoms ascending a surface step.^{11,17} Our simulation results thus indicate that under a very low surface coverage, the existence of the surface step effectively inhibits the surface transport of C₄–C₁₀ alkane molecules in the direction perpendicular to the step edge. However, as the surface coverage reaches a monolayer or multilayer level, the adsorption sites at the surface steps and on the terraces become saturated with adsorbates, which can open up new pathways for faster surface diffusion and perpendicular diffusion across the surface steps.^{20,21,41} Under these circumstances of high surface coverage, the anisotropy of surface diffusion can still persist but become less profound.^{20,21,41} Therefore, when applying different experimental and modeling methods to study anisotropic surface diffusion on stepped surfaces, proper attention should be

paid to distinguish and recognize the suitability of the characteristic surface coverage as well as time and length scales inherent in the methods.

A closer examination of the alkane trajectories on Pt(655) and computer animations reveal that the surface step promotes a diffusion mechanism quite different from those on the flat Pt(111) surface. Specifically, the alkane molecules adjacent to the surface step translate themselves through a constant wiggly motion with their long molecular axes closely parallel to the step edge. Rigid-body rotation becomes prohibitive due to the energy penalty associated with breaking the parallel adsorption configuration, and long flights yield to shorter continual slides because it is less difficult for the surface step than the terrace sites to accommodate a chain of atoms concurrently. In a sense, a type of one-dimensional “channeled” diffusion is induced by the surface step. An important implication of this anisotropic diffusion behavior is that surface steps can be used as an effective means to transport physisorbed molecules in a specific direction across a surface. We can reasonably expect this use of stepped surfaces to hold up to a relatively high surface coverage.

The influence of the surface step on alkane surface diffusion can be further characterized quantitatively by examining tracer diffusion coefficient. To this end, the Einstein relation is used in this study. On the flat Pt(111) surface, the center-of-mass displacements in the lateral *x* and *y* directions are equivalent and hence both used for better statistics,

$$D = \lim_{t \rightarrow \infty} \frac{\langle [x(t+t_0) - x(t_0)]^2 + [y(t+t_0) - y(t_0)]^2 \rangle}{4t}. \quad (1)$$

Statistical mechanically, Eq. (1) can be separated into and taken as an average of two equivalent diffusion coefficients in the *x* and *y* directions. On the stepped Pt(655) surface, the diffusion coefficient is practically zero in our simulations in the *x* direction that is perpendicular to the step edge, so only the *y* displacement is used to calculate *D* for a fair comparison and for reduced noise in the calculated mean-square displacement,

$$D = \lim_{t \rightarrow \infty} \frac{\langle [y(t+t_0) - y(t_0)]^2 \rangle}{2t}. \quad (2)$$

The thermal dependence of the tracer diffusion coefficients was studied using Arrhenius plots presented in Fig. 4. The diffusion energy barriers extracted from the Arrhenius plots are summarized in Table I. We first compared our results to Pt(111) a similar study²³ using the conventional UA model and a smaller value for $\epsilon_{\text{CH}_3\text{-Pt}}$. The diffusion coefficients and energy barriers, in particular those of *n*-butane, were found to scale well with those reported in the previous study²³ and accord with the $\epsilon_{\text{CH}_3\text{-Pt}}$ ratio. Interestingly, the influence of the surface step on alkane surface diffusion was found to change appreciably over a relatively small range of chain length. While the surface step on Pt(655) slows down the diffusivity of the longer *n*-decane molecule, it appears to hardly affect the diffusion energy barrier. On the other hand, the surface step significantly reduces the diffusion energy barrier for the smaller *n*-butane molecule and yields higher

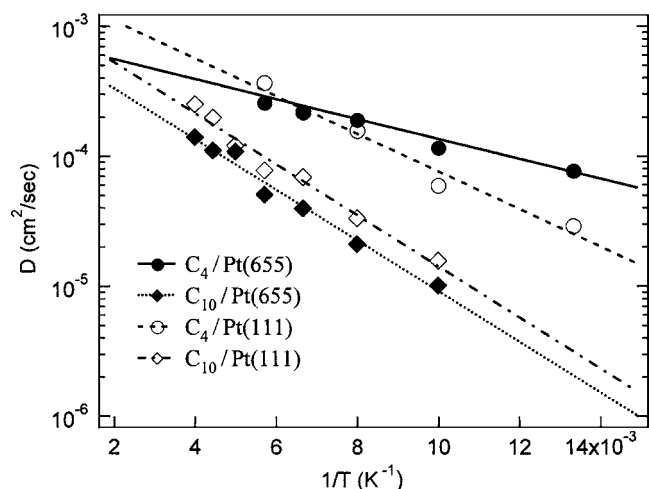


FIG. 4. Arrhenius plots of the diffusion coefficients of *n*-butane and *n*-decane on the stepped Pt(655) surface and the flat Pt(111) surface.

diffusion coefficients at lower temperatures in comparison with *n*-butane on the corresponding flat surface or terrace. It is thus suggested that the step-assisted anisotropic surface transport is particularly useful for short alkanes under low temperatures. Since the energy barrier can be related to corrugation in the PES, interaction with the surface step apparently results in a less corrugated PES for the shorter *n*-butane but little such effect for the longer *n*-decane. Detailed study of the PES and extension to longer alkanes are currently under way in order to obtain a better understanding of the emerging crossover in the diffusion dynamics of *n*-alkanes on the stepped surface.

IV. CONCLUDING REMARKS

We have extended the anisotropic united atom (AUA) model to the MD simulation of alkane/Pt interfacial system. By studying the surface diffusion of *n*-butane and *n*-decane on the stepped Pt(655) surface and on the corresponding flat Pt(111) surface, the aim of this work is to understand the effect of the surface step on alkane surface diffusion. We demonstrated that surface steps can profoundly influence adsorption configuration and diffusion dynamics of *n*-alkanes on metal surfaces by introducing prominent anisotropic features to the potential-energy surface. Specifically, the adsorption configuration of *n*-butane and *n*-decane on Pt(655) corresponds to long molecular axes adjacent and parallel to the step edge on the lower terrace in all-trans conformations. Such a configuration maximizes coordination and minimizes potential energy for alkane molecules. Due to the energy

TABLE I. Activation energy barriers for surface diffusion of *n*-butane and *n*-decane on Pt(655) and Pt(111).

Alkane	Surface	Energy barrier (kJ/mol)
<i>n</i> -butane	Pt(655)	1.363±0.099
	Pt(111)	2.776±0.263
<i>n</i> -decane	Pt(655)	3.733±0.239
	Pt(111)	3.761±0.255

penalty associated with breaking away from this parallel configuration, rotation is prohibited and the alkane molecules diffuse along the surface step by a constant wiggly motion with their long molecular axes closely parallel to the step edge. The result is an anisotropic diffusion resembling the diffusion in one-dimensionally channeled structures. Compared to the diffusion on the flat Pt(111) surface, the surface step on Pt(655) reduces the diffusivity of the longer *n*-decane molecule but hardly affects its diffusion energy barrier. However, the surface step significantly reduces the diffusion energy barrier for the shorter *n*-butane molecule and yields higher diffusion coefficients at lower temperatures. A crossover in diffusion dynamics thus appears to exist as the length of alkane chain varies.

As temperature increases, the alkane molecules become less strongly bound to and capable of breaking away from the step edge. However, such a breakaway was found to be a temporary event due to the limited width of the terrace and strong attraction from the step. In addition, the surface step can effectively inhibit the surface diffusion in the direction perpendicular to the step edge under a relatively low surface coverage. As a result, surface steps can be expected to be useful as an effective means to transport physisorbed molecules in a specific direction across a surface.

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