

Mechanisms for correlated surface diffusion of weakly bonded dimers

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We propose a model for the potential energy of a dimer on a surface that allows to identify the relevant reaction paths for diffusion and assess the favored path as the result of a competition between gain of potential energy due to the atom surface interaction and loss of elastic energy due to stretching of the dimer bond. We show that atoms forming weakly bonded dimers tend to diffuse via individual jumps although they remain bound to each other during the process, giving a rationale for the correlated piecewise diffusion observed on Si(001). For dimer equilibrium lengths smaller than the surface periodicity, the model predicts the not yet considered diffusion path that we call pinched diffusion with a contraction of the dimer bond length. Determination of the few parameters of the model requires only a study of the interaction of a single atom with the surface and of an isolated dimer instead of the complex potential energy of a dimer on a surface.

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I. INTRODUCTION

The diffusion of single atoms and small clusters on surfaces is an important step during crystal growth and thin layer formation. Scanning tunneling microscopy (STM) and the recently developed atom tracking STM techniques^{1,2} allow to follow the kinetics of a surface feature with high time resolution and have given detailed information on the motion of Si and Ge dimers along the rows and troughs of the reconstructed Si(001) (Refs. 3–8) and Ge(001) (Ref. 9) surfaces. Fast diffusion has been observed along the rows,⁸ and *ab initio* calculations¹⁰ for this quasi-one-dimensional situation indicate that the dimer diffuses not as a rigid unit but rather one atom at a time, a process called piecewise diffusion. An intriguing aspect of piecewise diffusion is the intermediate step in which the two atoms can be separated by as much as twice the equilibrium distance, as if the dimer were dissociated.^{11,12} However, on the basis of density functional calculations of Ge and Si dimers on Si(001) that give piecewise diffusion along the rows as the most favorable path, Lu *et al.*¹⁰ pointed out that, although in the intermediate step the dimer atoms do not have a direct bond between them, they do have a strong correlation between them. To emphasize this finding, Lu *et al.* call this diffusion mode correlated piecewise diffusion, rather than just piecewise diffusion.

We propose a simple model potential to describe the energetics of a dimer on a periodic substrate that gives a rationale for this diffusion mode. The potential is constructed as sum of a periodic modulation, describing the interaction between each dimer atom and the substrate, and of a Morse potential, describing the interatomic dimer interaction. This potential yields a potential energy surface (PES) very similar to that resulting from density functional calculations¹⁰ and can describe both rigid and piecewise diffusion. We show that, within our model, correlation during piecewise diffusion is due to a soft interatomic dimer bond that makes that the two atoms are still bonded even when they are separated by two lattice sites. On the basis of only a few parameters, namely the diffusion barrier of a single atom, the periodicity of the substrate, the equilibrium distance and binding energy

of an isolated dimer, one can easily identify which diffusion path will be more favorable. The few parameters of the model could be either measured experimentally or calculated *ab initio* for a given system once and for all. This calculation would be much simpler than calculating the full PES of a dimer onto a surface, and could easily be generalized to more dimensions and larger clusters. The model can also be of use to gain insight on the effect of external electric fields^{6,13–15} on the chosen diffusion path. Furthermore, we find also a not yet considered mechanism where the dimer diffuses by contracting its bond. This diffusion mode, that we call pinched diffusion, becomes favored when the interatomic dimer distance becomes smaller than the periodicity of the substrate.

The paper is organized as follows. In Sec. II we introduce our model potential for a dimer interacting with a surface, in Sec. III we describe the resulting PES and calculate the diffusion paths for varying strength of the interatomic interactions and for different ratios of the dimer equilibrium bond length to the surface periodicity. Finally in Sec. IV we summarize our results and outline the perspectives of this work.

II. MODEL POTENTIAL OF DIMER-SURFACE INTERACTION

We consider a homonuclear dimer composed of two mutually interacting atoms with masses m and coordinates x_i ($i=1,2$), moving on a one-dimensional (1D) substrate. The interaction of each atom with the substrate, $V_{\text{sub}}(x_i)$, is modeled by a periodic modulation of the form

$$V_{\text{sub}}(x_i) = \frac{1}{4} V_0 \left[1 + \cos\left(2\pi \frac{x_i}{a}\right) \right], \quad (1)$$

where a is the lattice constant of the substrate. The potential V_{sub} varies between 0 and $V_0/2$, so that the effective barrier for two noninteracting atoms is V_0 . The sinusoidal potential V_{sub} may be thought of as given by an ordered array of atoms in a crystalline surface. This approximation, which amounts to taking only the first Fourier component with wave vector

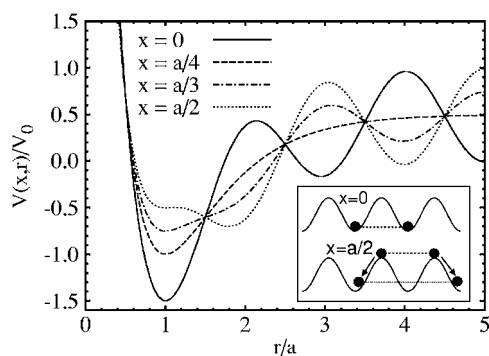


FIG. 1. Effective interatomic potential for four values of x as a function of the interatomic distance r . The parameters are $r_{\text{eq}}=a$, $w=1.5a$, $D_0=1.5V_0$. The inset shows the location of the dimer with respect to the periodic potential for $x=0$ and $x=a/2$. See text.

$2\pi/a$ of the periodic potential, is rather well justified because higher components are known to decay exponentially. Moreover it is supported by *ab initio* calculations such as those of Refs. 16 and 17.

The interaction between the two atoms forming the dimer, $V_{\text{int}}(r)$, is modeled by a Morse potential of the form

$$V_{\text{int}}(r) = D_0(e^{-2\rho(r-r_{\text{eq}})} - 2e^{-\rho(r-r_{\text{eq}})}), \quad (2)$$

where D_0 is the well depth with respect to infinite separation, and r_{eq} the equilibrium separation so that $V_{\text{int}}(r_{\text{eq}}) = -D_0$. The parameter ρ controls the width w of V_{int} , defined as the difference between the two values of r for which $V_{\text{int}}(r) = -D_0/e$, e being the base of the natural logarithm. With this definition, one can show that $w = 2.170\,077/\rho$. The force constant k , defined as the second derivative at $r=r_{\text{eq}}$, decreases for increasing width as $k = 2\rho^2 D_0$. We have chosen a Morse potential because it is considered suitable to describe molecular binding and is often used to fit *ab initio* results. The details of our results will of course depend on the chosen pair potential but the qualitative features of the diffusion paths will still be mostly related to the stiffness of the interatomic bond as discussed in Sec. III.

In terms of the center-of-mass (c.m.) and relative coordinates, $x = (x_1 + x_2)/2$ and $r = x_2 - x_1$ respectively, the total potential $V(x, r)$ describing the dimer interacting with the substrate is given by

$$V(x, r) = \frac{V_0}{2} \left[1 + \cos\left(\frac{2\pi}{a}x\right) \cos\left(\frac{\pi}{a}r\right) \right] + V_{\text{int}}(r). \quad (3)$$

The translational (x) and vibrational (r) degrees of freedom of the dimer are coupled by the product term $\cos(2\pi x/a)\cos(\pi r/a)$ in Eq. (3), so that the vibrational spectrum of the dimer depends on the position x of the c.m. on the surface. In Fig. 1, we show the r dependence of $V(x, r)$ for four values of x for a commensurate dimer ($r_{\text{eq}}=a$). As x increases from 0 to $a/2$, this effective interatomic potential broadens and becomes shallower. Moreover, a new minimum develops for $x=a/2$ and $r=1.8a$ as a result of a competition between the two potential energy contributions V_{sub} and V_{int} . In fact, as shown in the inset of Fig. 1, for $x=a/2$, and $r=r_{\text{eq}}=a$, each dimer atom is located on the top of the periodic

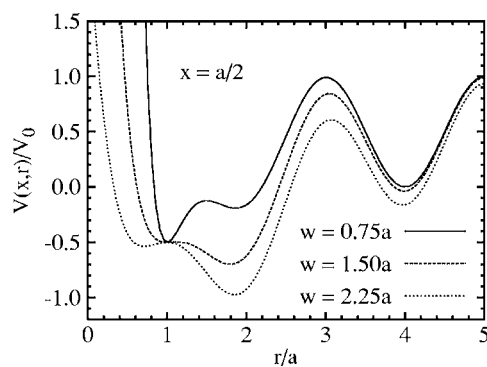


FIG. 2. Effective interatomic potentials as a function of the interatomic distance r for $x=a/2$ and for three values of the width w . The other parameters are the same as in Fig. 1.

potential so that any increase of the internuclear distance r decreases the potential energy due to the substrate V_{sub} and increases the elastic energy due to the interatomic interaction V_{int} . As a result, a new minimum for $r > a$ may appear, as shown in Fig. 2, where we plot $V(x, r)$ for $x=a/2$ and for three values of the width w . A large w leads to a deeper minimum at $r > a$ because it implies a smaller force constant and elastic energy. Conversely, for a small w (or large force constant), this minimum may lie above the minimum at $r=a$.

III. DIFFUSION MECHANISMS

The two-dimensional (2D) PES, given by $V(x, r)$, is shown in Fig. 3. Figures 1 and 3 provide a complete description of the 2D PES, a periodic arrangement of barriers along x and a potential well with a periodic tail in r , of period twice the period in x . The adsorption sites, i.e., the sites of lowest potential energy on the 2D PES, are located at $x=na$ and $r=a$, where n is an integer. In Fig. 3 they are indicated as A1 and A2.

A dimer can diffuse on the surface from A1 to A2 via many different diffusion paths with a probability that decreases exponentially with the maximum energy required, so that only few paths must be considered at low temperatures. Among the diffusion paths, a reaction path is defined as the path that connects A1 to A2 via local minima separated by saddle points (barriers),¹⁸ as shown in Fig. 3. The reaction path is then constructed as the sequence of segments following the steepest descent from the saddle points into the local minima.

There are two reaction paths connecting the adsorption sites A1 and A2. The first one is the path A1-S3-A2, along which the dimer moves as a rigid unit with $r=r_{\text{eq}}$. The second reaction path, A1-S1-M-S2-A2, corresponds to piecewise diffusion. Because the dimer bond almost doubles for this case, after the jump of the first atom, it is often assumed that along this path the dimer dissociates and reforms afterwards.^{8,10} In our model, due to the new minimum in $V(x, r)$ shown in Figs. 1 and 2, the dimer is still well bound and not at all dissociated, even when r is almost $2r_{\text{eq}}$. We believe that this is the chemical mechanism behind the correlated piecewise diffusion.

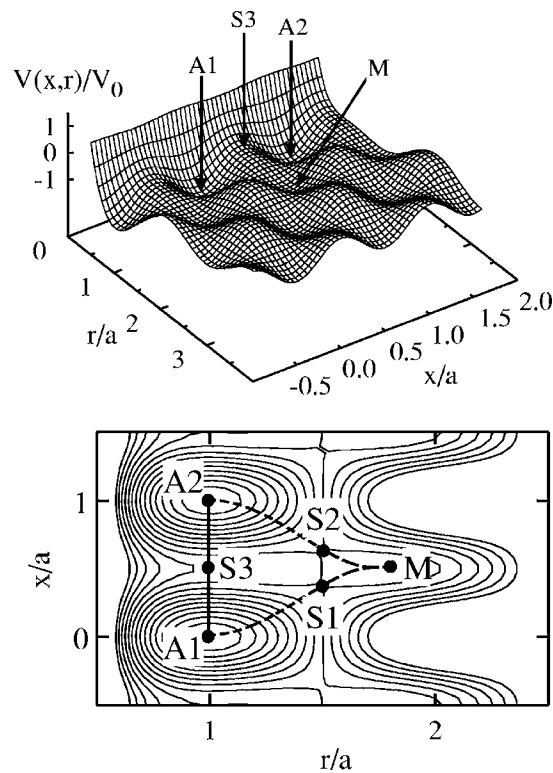


FIG. 3. Surface plot (upper panel) and contour plot (lower panel) of the 2D PES of $V(x,r)$ [Eq. (3)] with all parameters as in Fig. 1. In both plots A1 and A2 are the adsorption sites, M a local minimum and $S3$ a saddle point. Shown only in the contour plot are saddle points $S1$ and $S2$. The reaction path A1-S3-A2 corresponds to rigid diffusion, A1-S1-M-S2-A2 to piecewise diffusion. The contour spacing is in $0.1V_0$.

In the top panel of Fig. 4, the potential along the rigid and correlated piecewise paths is plotted for the same three values of the width w as in Fig. 2. In the lower panel of Fig. 4, the corresponding reaction paths are shown by plotting the distances traveled by each atom with respect to their initial positions. These results are very similar to those of Figs. 2 and 4 of Lu *et al.*¹⁰ of *ab initio* calculations of Ge and Si dimers on the Si(001) surface, showing that our potential can correctly describe both rigid and piecewise diffusion. What is new is that our model gives a physical insight on the factors which make rigid or correlated piecewise motion more favorable. First we examine the effect of the width (or stiffness) of V_{int} . For a larger width, or equivalently a smaller force constant, correlated piecewise motion becomes energetically more favorable. For both $w=1.5a$ and $2.25a$, the barrier for diffusion is the lowest for piecewise motion. For $w=0.75a$, however, rigid motion is more favorable. A similar effect occurs when changing the ratio D_0/V_0 which is directly proportional to the force constant k of V_{int} by $k=2\rho^2D_0$. An increase of D_0/V_0 will eventually render piecewise diffusion less favorable than rigid diffusion. Indeed, as shown in Fig. 5, increasing the ratio D_0/V_0 , increases the barrier S while bringing the local minimum M closer in energy to S . For the chosen parameters, if $D_0/V_0 > 2$, it is no longer favorable to extend the bond because the total energy required will exceed V_0 , the barrier for rigid diffusion. An external electric

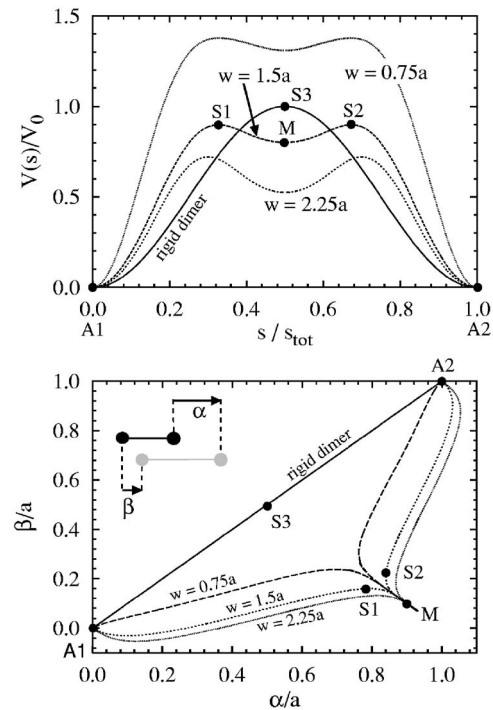


FIG. 4. Reaction paths between adsorption sites A1 and A2 of the 2D PES of Fig. 3, for three values of the width w and the other parameters as in Fig. 1. The reaction paths corresponding to correlated piecewise diffusion (broken lines) are compared with rigid diffusion (solid line). Top panel, potential as a function of the distance s along the reaction path in units of the total distance s_{tot} between the initial and final position. Bottom panel, displacement of the dimer atoms from their initial positions along the reaction path, as defined in Ref. 10 and indicated in the inset. The black circles represent the dimer atoms in their initial positions, the gray circles their positions in an intermediate state.

field could be used to change the ratio D_0/V_0 thereby changing the diffusion mode.^{6,13-15}

The previous results were calculated for $r_{\text{eq}}=a$. Last, we consider the case $r_{\text{eq}} < a$. In Fig. 6, we show the reaction paths for $r_{\text{eq}}=0.75a$. We find a new possible diffusion mode, that we call pinched diffusion, where the dimer bond gradually contracts instead of extending. As shown in Fig. 6, this diffusion path has a much lower barrier than that of correlated piecewise diffusion. To our knowledge, it has not been considered before. In particular, the *ab initio* study of Ref. 10 considered only dimer bond lengths equal to or larger than the bond length in an adsorption site.

As already noted in Sec. II the Morse potential has been chosen because it gives a good description of molecular binding and vibrational frequencies. However, the qualitative picture we have discussed would hold also for other choices of the pair potential used to describe the interatomic dimer bond. The occurrence of a lower minimum at interatomic bond lengths larger than the equilibrium value for soft force constants is a rather general feature that does not depend on the particular choice of V_{int} . The occurrence of pinched diffusion is related also to the shape of the repulsive part of the potential describing the core region and might not be favored if it is very steep.

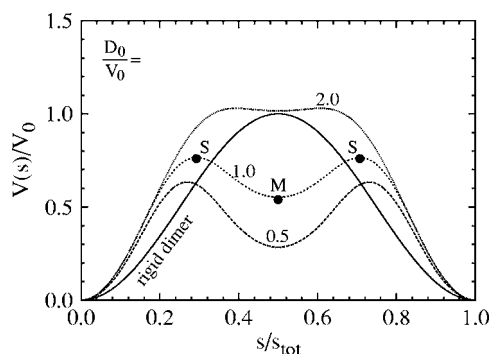


FIG. 5. The potential along the reaction paths between the adsorption sites A1 and A2 of the 2D PES of Fig. 3, for different values of the ratio D_0/V_0 and the other parameters as in Fig. 1. The reaction paths corresponding to correlated piecewise diffusion (broken lines) are compared with rigid diffusion (solid line). The potential is plotted as a function of the distance s along the reaction path in units of the total distance s_{tot} between the initial and final position. Shown only for $D_0/V_0=1.0$ are the saddle points S and local minimum M .

IV. SUMMARY AND PERSPECTIVES

In summary, we have proposed a simple, yet insightful, description of the energetics of a dimer onto a surface as resulting from the competition between gain of potential energy due to the interaction of each atom with the surface and loss of elastic energy due to stretching of the natural dimer bond length. Different diffusion paths can be evaluated and compared. We have shown that atoms forming weakly bonded dimers tend to diffuse in a piecewise fashion although they remain bound to each other during the process giving a rationale for the correlated piecewise diffusion observed on Si(001). The model predicts also a not yet considered diffusion path, the pinched diffusion, with a dimer contraction for dimer equilibrium lengths smaller than the periodicity of the substrate.

Our results can be used for different purposes. The most straightforward is to help the interpretation of *ab initio* calculations of dimers on real surfaces like those of Ref. 10. These calculations are very complex and expensive because they imply a reliable description of the surface and the calculation of the energy of very many configurations of the dimer on the surface. This means also that possible reaction paths may be missed, like the one corresponding to pinched diffusion which has not been considered in Ref. 10. However, our approach is informative in itself and could be made more accurate by determining the few parameters of the model by *ab initio* methods. This would only require a study of the interaction of a single atom with the surface and of an isolated dimer instead of the complex PES of a dimer onto a surface. It would be important to prove that indeed this approximation gives results which compare well with those

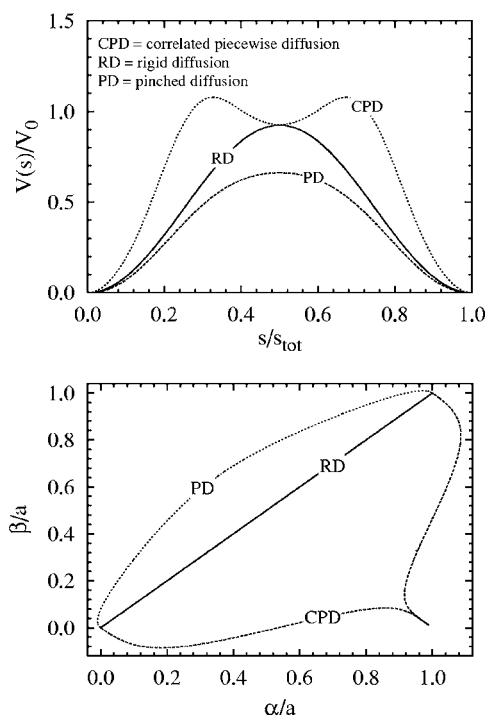


FIG. 6. Reaction paths between adsorption sites A1 and A2 of the 2D PES of Fig. 3, for $r_{\text{eq}}=0.75a$ and the other parameters as in Fig. 1. The broken lines correspond to correlated piecewise diffusion (CPD) and pinched diffusion (PD), the solid line to rigid diffusion (RD). Top panel: the potential as a function of the distance s along the reaction path in units of the total distance s_{tot} between the initial and final position. Bottom panel, displacement of the dimer atoms from their initial positions along the reaction paths, as indicated in Fig. 4.

obtained by considering the dimer onto a surface as done in Ref. 10. Mapping the problem of dimers on a surface onto the simpler one of the motion of two atoms in the potential $V(x, r)$ would make possible and would support the predictivity of studies of the diffusive dynamics by Langevin simulations.¹⁹

Last, preliminary results,²⁰ suggest that a quantum description of the dynamics of a dimer in our model potential can be influenced by the appearance of a minimum at larger dimer bond lengths and that (resonant) tunneling further enriches the diffusion process. We hope that our work will stimulate further research on this topic.

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