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Compensating Hamiltonian method for chemical reaction dynamics: Xe desorption from Pd(100)

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We report on a method that allows us to study with molecular dynamics a chemical reaction with an activation barrier that is much higher than the thermal energy. The method leads to a new Hamiltonian with which it is possible to compute reaction rate constants, and reactive trajectories even at low temperature. The method is applied to Xe desorption from Pd(100). The desorption rate constants are compared with transition state rate constants. The mechanism of the desorption is studied, and a model is given that explains the molecular dynamics results. Conversion of lateral into normal kinetic energy during the desorption process is shown to be important.

I. INTRODUCTION

Still little is known about the dynamics of reactions of heterogeneous catalysis.^{1,2} Chemical reaction dynamics studies focus mainly on relatively simple reactions; and chemisorption studies usually deal only with energetics.³ If we want to know how a catalyst works it is absolutely necessary, as temperature is an important parameter in the outcome of catalytic processes, to know something about the behavior of adsorbed atoms.

The function of a catalyst is to reduce the activation energy of a reaction, or to open new reaction paths with low activation energies. Consequently, a study on the dynamics of a catalytic process is a study on infrequent events; the name given to processes that have to pass a bottleneck in phase space.^{4,5} This bottleneck is caused by an activation barrier that is much higher, even for a catalytic process, than thermal energies at normal reaction conditions. Although the system will often try to overcome the activation barrier, it will only very occasionally succeed.

We have used molecular dynamics (MD) in this study as this method gives the most detailed picture of the dynamics. On the time scale of the usual MD simulation, i.e., in the order of tens or hundreds of picoseconds, infrequent events practically never occur. This is not the case if one studies surface diffusion or scattering of energetic atoms from surfaces.⁶⁻⁸ We present a generalization of the compensating potential method of Grimmelmann *et al.*,⁴ which we call the compensating Hamiltonian method. It also unifies Grimmelmann's and Bennett's method.⁹ Moreover, we show that our method can be used not only to calculate statistical properties, but to study reaction mechanisms as well. The method enables the system to overcome the activation barrier.

We illustrate the method by looking at the desorption of Xe from the Pd(100) surface, as this is the simplest case of a process on a catalytic surface that involves a high activation barrier. The desorption rate constant, we find, differs on the whole little from the transition state desorption rate constant, except at low temperatures. The MD simulation tells us exactly where on the surface the Xe atom desorbes, why it desorbes, and how long the transition from an adsorbed to a desorbed Xe atom takes.

II. THEORY

A. The reaction rate constant

For completeness we present in this subsection the variational reaction rate theory on which our method is based. More details can be found elsewhere.^{4,10-14} We will have the system of an atom adsorbed on a surface in mind, but the theory can easily be extended to other systems.

We define a function S on the phase space of the system so that a point with $S(q,p) > 0$ corresponds to a system that has reacted, and a point with $S(q,p) < 0$ corresponds to a system that has not reacted. Here, q stands for all generalized coordinates, and p for the conjugate momenta. We call that part of phase space with $S(q,p) < 0$ the reactant region, and the part with $S(q,p) > 0$ the product region. The surface $S(q,p) = 0$ is called the dividing surface. We shall give examples of the function S below.

The equation

$$k = \frac{1}{Z} \int dq dp \dot{S} \Theta(\dot{S}) \delta(S) \quad (1)$$

gives the reaction rate constant. The integration is over all of phase space: ρ is the phase space density, δ is the Dirac delta function, Θ is the Heaviside step function,¹⁵ and Z is the partition function of the reactants. The delta and the step function restrict the integration to that part of the dividing surface where the system goes from reactant to product region. The factor $\dot{S}$ gives the rate with which this occurs.

Variational reaction rate theory requires that the dividing surface should minimize the reaction rate constant. A natural choice for desorption of an adatom, and indeed the one that has been used so far,⁴ is

$$S_1(q,p) = z - z_0, \quad (2)$$

where z is the normal distance of the adatom to the surface, and z_0 is the variational parameter. For canonical ensembles and adatom-surface potentials that increase monotonically beyond the potential minimum, as is the case for noble gas adsorption, the rate constant becomes minimal for $z_0 \rightarrow \infty$. This result is understandable if one realizes that for finite z_0 there are trajectories in phase space that cross the dividing surface from reactant to product region, but then recross it

back to the reactant region. In an MD simulation one can only work with finite z_0 , and a correction to Eq. (1) has to be made.⁴ We have opted instead for another dividing surface.

If we ignore thermal vibrations of the surface atoms and surface corrugation, there is no energy transfer between the surface and the adatom, and hence no desorption. The dividing surface can then be given by

$$S_2(q, p) = \frac{p_z^2}{2m} + V(z), \quad (3)$$

where m is the mass of the adatom, p_z is the conjugate momentum of z , and V is the adatom-surface potential, which, for noble gas atoms, is monotonically increasing beyond its minimum and $V \rightarrow 0$ if $z \rightarrow \infty$. A reactive trajectory for S_2 , i.e., one that starts in the reactant region at $t \rightarrow -\infty$ and ends in the product region at $t \rightarrow \infty$, also crosses the dividing surface $S_1 = 0$ for all finite z_0 . For once we have $p_z > 0$ and $S_2 > 0$, we must have $p_z > 0$ at all times, because otherwise S_2 becomes negative as $V(z) < 0$. On the other hand, there are reactive trajectories for S_1 for which $S_2 > 0$ at all times. These correspond, however, to scattering processes, and should not be taken into account.

Equation (1) counts every crossing of the dividing surface from reactant to product region once. This gives an upper bound to the reaction rate constant. Systems that react via multiple crossings should only be counted once, and systems that finally end in the reactant region should not be counted at all. As the S function of Eq. (3) is not obtained variationally, we have to correct Eq. (1) by splitting that part of the dividing surface with $\dot{S}(q, p) > 0$ into an area s_0 that is crossed only by trajectories that finally end in the reactant region; an area s_1 that is crossed only once from reactant to product region; an area s_2 that is crossed twice from reactant to product region (and once in the other direction), etc. The reaction rate constant is then

$$k = \frac{1}{Z} \left[\int_{s_1} + \frac{1}{2} \int_{s_2} + \frac{1}{3} \int_{s_3} + \dots \right] dq dp \rho \dot{S} \Theta(\dot{S}) \delta(S). \quad (4)$$

Equation (3) also allows us to compute the partition function Z , which is given by

$$Z = \int dq dp \rho \Theta(-S). \quad (5)$$

We note that this is not possible with Eq. (2), because then Z diverges, and the rate constant becomes zero.

B. Molecular dynamics for reactions with a high activation barrier

If we use MD to simulate a reaction, Eq. (4) can be simplified by changing to a time-averaged expression.¹⁶ We make the transformation

$$\int dq dp \rho \rightarrow \lim_{T \rightarrow \infty} \frac{1}{2T} \sum_{\text{all trajectories}} \int_{-T}^T dt \quad (6)$$

to get

$$k = \lim_{T \rightarrow \infty} \frac{1}{2T} \left[\sum_{s_1} + \frac{1}{2} \sum_{s_2} + \frac{1}{3} \sum_{s_3} + \dots \right] \times \int_{-T}^T dt \dot{S}(t) \Theta[\dot{S}(t)] \delta[S(t)] / \lim_{T \rightarrow \infty} \frac{1}{2T} \sum_{s_0, s_1, s_2, \dots} \int_{-T}^T dt \Theta[-S(t)]. \quad (7)$$

The summations are over trajectories that cross the dividing surface in s_1, s_2, s_3 , etc. We simplify this expression using

$$\delta[S(t)] = \sum_{S(t_i)=0} \frac{\delta(t-t_i)}{|\dot{S}(t_i)|}. \quad (8)$$

The summation is over all times at which the dividing surface is crossed. If we substitute this expression in Eq. (7), we obtain

$$k = \frac{N_{\text{reactive}}}{\sum_{s_0, s_1, s_2, \dots} \Delta t_{\text{reactant}}}, \quad (9)$$

where N_{reactive} is the number of reactive trajectories, and $\Delta t_{\text{reactant}}$ is the time that a trajectory is in the reactant region.

One might expect problems from the trajectories that do not cross the dividing surface, as for these $\Delta t_{\text{reactant}} \rightarrow \infty$. We assume that they form a set of zero measure in the space of all trajectories. In practice, the problem does not arise because $\Delta t_{\text{reactant}}$ is limited by the duration of the simulation. We found that it is possible to choose a duration such that an increase of it does not change the reaction rate constant.

We are interested in reactions at a specific temperature. This means that we have a canonical ensemble, and the phase space density is proportional to a Boltzmann factor,¹⁶ i.e.,

$$\rho \propto e^{-\beta H} \quad (10)$$

with $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant, T is the temperature, and H is the classical Hamiltonian of the system. Transformation (6) is only valid if we use an MD method that generates trajectories that yield canonical ensemble averages. We have used a stochastic dynamics method,¹⁷⁻¹⁹ but others are also possible.²⁰⁻²²

If the activation energy for the reaction is much higher than the thermal energy, then a simulation of the order of picoseconds will not show a reaction. Grimmelmann *et al.* have developed a simple, yet powerful, method to compute statistical properties of so-called infrequent events.⁴ We generalize here their “compensating potential” method. We replace the Hamiltonian H of our system by an effective Hamiltonian $\tilde{H}$ via

$$H = \tilde{H} + U(S). \quad (11)$$

We choose the compensating Hamiltonian U in such a way that the effective Hamiltonian $\tilde{H}$ has an activation barrier of the same magnitude as the thermal energy. Substituting Eqs. (10) and (11) into Eq. (4), we obtain

$$k = e^{-\beta U(0)} \left[\int_{s_1} + \frac{1}{2} \int_{s_2} + \frac{1}{3} \int_{s_3} + \dots \right] dq dp \tilde{\rho} \dot{S} \Theta(\dot{S}) \delta(S) / \int dq dp \tilde{\rho} e^{-\beta U(S)} \Theta(-S), \quad (12)$$

where $\tilde{\rho} \propto \exp(-\beta \tilde{H})$. Using transformation (6) with ρ replaced by $\tilde{\rho}$, and Eq. (8), we get

$$k = \frac{N_{\text{reactive}} \exp[-\beta U(0)]}{\lim_{T \rightarrow \infty} \sum_{s_0, s_1, s_2, \dots} \int_{-T}^T dt \exp\{-\beta U[S(t)]\} \Theta[-S(t)]} \quad (13)$$

The point of the compensating Hamiltonian is that now the number of reactive trajectories will be large. The reaction rate constant will still be small because of the factor $\exp[-\beta U(0)]$ in the nominator.

Replacement (6) with $\tilde{p}$ is valid if we use the effective Hamiltonian $\tilde{H}$ for the simulation. If we express the equations of motion in terms of the original Hamiltonian H , we find²³

$$\dot{q}_\alpha = \frac{\partial \tilde{H}}{\partial p_\alpha} = \frac{\partial H}{\partial p_\alpha} - \frac{dU}{dS} \frac{\partial S}{\partial p_\alpha} \quad (14a)$$

and

$$\dot{p}_\alpha = -\frac{\partial \tilde{H}}{\partial q_\alpha} = -\frac{\partial H}{\partial q_\alpha} + \frac{dU}{dS} \frac{\partial S}{\partial q_\alpha}, \quad \text{with } \alpha = 1, \dots, N. \quad (14b)$$

These equations can become very complicated. In particular, one no longer has $m_\alpha \dot{q}_\alpha = p_\alpha$, where m_α is some mass, and one cannot use numerical methods in MD developed for Newton's equations anymore.

We have found two special cases of interest where this is not so. The first is

$$U(S) = U[q_1 - q_1^{(0)}], \quad (15)$$

where $q_1^{(0)}$ is a constant, and

$$H = \sum_{\alpha=1}^N \frac{p_\alpha^2}{2m_\alpha} + V(q_1, \dots, q_N). \quad (16)$$

If we substitute Eqs. (15) and (16) into Eq. (14), and eliminate the momenta, we find

$$m_1 \ddot{q}_1 = -\frac{\partial V}{\partial q_1} + \frac{\partial U}{\partial q_1} \quad (17a)$$

and

$$m_\alpha \ddot{q}_\alpha = -\frac{\partial V}{\partial q_\alpha}, \quad \text{for } \alpha = 2, \dots, N. \quad (17b)$$

We also have $m_\alpha \dot{q}_\alpha = p_\alpha$ for $\alpha = 1, \dots, N$. This is the case that Grimmelmann *et al.* treat.⁴ Equation (17a) is the origin of the name compensating potential.

The second special case is

$$U(S) = \tau S \quad (18a)$$

and

$$S = \frac{p_1^2}{2m_1}, \quad (18b)$$

where τ is a constant. Substituting Eqs. (16) and (18) into Eq. (14), we get

$$\frac{m_1}{1-\tau} \ddot{q}_1 = -\frac{\partial V}{\partial q_1} \quad (19a)$$

and

$$m_\alpha \ddot{q}_\alpha = -\frac{\partial V}{\partial q_\alpha}, \quad \text{for } \alpha = 2, \dots, N. \quad (19b)$$

We now have $m_1 \dot{q}_1 = (1-\tau)p_1$, and $m_\alpha \dot{q}_\alpha = p_\alpha$ for $\alpha = 2, \dots, N$. It is possible to extend this case to more than one momentum. Compensating Hamiltonians like Eq. (18) can yield Bennett's method.⁹ Both special cases can also be combined; the next section shows an example. So the compensating Hamiltonian method unifies Grimmelmann's and Bennett's methods.^{4,9}

We can use Eq. (11) to compute the expectation value of any quantity. For a canonical ensemble we find

$$\langle X \rangle_H = \frac{\langle X e^{-\beta U} \rangle_{\tilde{H}}}{\langle e^{-\beta U} \rangle_{\tilde{H}}}, \quad (20)$$

where X is an arbitrary function of the coordinates and conjugate momenta. The angular brackets stand for statistical averages, and the indices give the Hamiltonian with which these averages must be computed. The expression for the reaction rate constant forms really a special example of Eq. (20).

C. The reaction mechanism

Although the effective Hamiltonian $\tilde{H}$ generates reactive trajectories, because of the changed dynamics, they are quite useless if we want to know the mechanism of the reaction. For this we need to generate trajectories with the original Hamiltonian H . This is normally accomplished by starting the trajectory at the saddle point of the potential energy surface in configuration space. There is, however, no reason why all reactive trajectories should pass through the saddle point. Moreover, for cases like adsorbed noble gasses, there is no such saddle point.

We solve the problem by starting trajectories at the dividing surface in phase space, and by sampling the starting points with the probability for finding the system at such a point. This probability is given by a Boltzmann factor and, including normalization, is given by

$$P = \frac{\exp(-\beta H)}{\int dq dp \exp(-\beta H) \delta(S)}. \quad (21)$$

All reactive trajectories have to cross the dividing surface, and the problem that remains to be solved is how to generate the probabilities. We do this within MD also by using the compensating Hamiltonian method. If we substitute Eq. (11) into Eq. (21) we find

$$\begin{aligned} P &= \frac{\exp(-\beta \tilde{H}) \exp[-\beta U(0)]}{\int dq dp \exp(-\beta \tilde{H}) \exp[-\beta U(S)] \delta(S)} \\ &= \frac{\exp(-\beta \tilde{H})}{\int dq dp \exp(-\beta \tilde{H}) \delta(S)} = \tilde{P}. \end{aligned} \quad (22)$$

This means that the probability of finding the system at a certain point on the dividing surface is the same for the original and the effective Hamiltonian, which leads then to the following method to generate reactive trajectories. We start the simulation in the reactant region with the effective Hamiltonian $\tilde{H}$, and continue the simulation until the dividing

surface is crossed. At that moment we switch to the original Hamiltonian H , and integrate the equations of motion forwards and backwards. Finally, we reverse the backward-integrated part and put it before the forward-integrated part. The trajectory we thus obtain is a representative trajectory of the ones we looked for.

At the moment the system crosses the dividing surface, we have $\dot{S} > 0$ for the simulation with the effective Hamiltonian $\tilde{H}$. If we switch to H this does not change because

$$\dot{S} = \{S, H\} = \{S, \tilde{H}\} + \{S, U(S)\} = \{S, \tilde{H}\}, \quad (23)$$

where the curly brackets are Poisson brackets.²³ However, it is possible that a trajectory that is found as described above is not reactive, because it recrosses the dividing surface, and has to be discarded. Fortunately, this does not mean that trajectories that are reactive for H are generated then with the wrong probability, as the *relative* probabilities with which they are generated does not change by discarding the nonreactive trajectories.

III. COMPUTATIONAL DETAILS

We simulated the desorption of one Xe atom from a Pd(100) surface with the generalized Langevin formalism in the form developed by Tully.¹⁹ We used a third-order Beeman algorithm for the numerical integration.^{24,25} Time steps were 8 fs. A simulation consisted of 4 ps to equilibrate the system, and then a maximum of 80 or 120 ps during which the Xe atom could desorb. The system was simulated for 4 ps more after it had crossed the dividing surface to check for recrossings. Most of the recrossings took place within 1 ps after the initial crossing. When computing reaction mechanisms we integrated 4 ps forwards and 8 ps backwards with the original Hamiltonian H from the point at

which the dividing surface was crossed. We used at least 100 simulations for the rate constants, and 500 simulations for the reaction mechanism at each temperature and parameter τ (see below). The Pd(100) surface was represented by a cluster of 17 atoms: 12 atoms in the first and 5 in the second layer (see Fig. 1). As the Xe atom diffuses over the surface, the simulation added and deleted Pd atoms to the cluster, as described by Tully,¹⁹ as soon as the Xe atom left the square in Fig. 1.

For the Pd-Pd interactions we have used a harmonic potential of the form

$$\phi_{ij} = \frac{\lambda_{NN}}{2} [(\mathbf{u}_i - \mathbf{u}_j) \cdot \hat{\mathbf{r}}_{ij}]^2 + \frac{\mu_{NN}}{2} \{(\mathbf{u}_i - \mathbf{u}_j)^2 - [(\mathbf{u}_i - \mathbf{u}_j) \cdot \hat{\mathbf{r}}_{ij}]^2\} \quad (24a)$$

for nearest neighbors, and

$$\phi_{ij} = \frac{\lambda_{NNN}}{2} [(\mathbf{u}_i - \mathbf{u}_j) \cdot \hat{\mathbf{r}}_{ij}]^2 \quad (24b)$$

for next-nearest neighbors.²⁶ In these equations the $\mathbf{u}$'s are displacements, and $\hat{\mathbf{r}}_{ij}$ is the unit interatomic vector. The parameters λ_{NN} , μ_{NN} , and λ_{NNN} have been fitted using elastic constants.²⁶ The coupling with the so-called ghost particles has been fitted to the bulk Debye temperature for the second-layer atoms, and to the surface Debye temperature for the first-layer atoms.¹⁶ As the force constant for displacements parallel to the surface is much higher than for displacements in the normal direction, we have used a modified surface Debye temperature for parallel displacements. We have used a 12-6 Lennard-Jones potential for the Xe-Pd interaction,^{27,28}

$$v_{\text{Xe-Pd}}(R) = \epsilon \left[\left(\frac{R_0}{R} \right)^{12} - 2 \left(\frac{R_0}{R} \right)^6 \right], \quad (25)$$

with R_0 the equilibrium distance for PdXe, and ϵ the bond strength. We have fitted this form to the adsorption energies of Xe on Pd(100), Pd(110), and Pd(111).²⁹ Table I shows the numerical values for the interaction parameters and the experimental data to which they have been fitted.

As dividing surface we have used

$$S = \frac{p_z^2}{2m_{\text{Xe}}} + V_C(z), \quad (26)$$

where m_{Xe} is the mass of the Xe atom, z its normal coordinate, p_z the normal conjugate momentum, and V_C a potential shown in Fig. 2. Except for small z , the dividing surface separates the bonded and nonbonded trajectories if the potential energy of the Xe atom would equal the potential energy of a Xe atom along a fourfold axis, at the same normal distance and with all Pd atoms at their equilibrium positions. We have changed V_C for small normal distances, because otherwise for large values of the parameter τ in Eq. (27) the Xe atom could go subsurface. This change has a negligible effect on the rate constants, as the dividing surface is not crossed when the normal coordinate of Xe is small, and the partition function Eq. (5) gets only extra contributions from the region where H is large and $\exp(-\beta H)$ very small.

The compensating Hamiltonian we have used is

FIG. 1. The cluster used in the simulation. Solid circles are first-layer atoms; dashed circles second-layer atoms. The square is the area in which the Xe atom can be found (see the text).

TABLE I. Potential parameters and experimental results (respectively, elastic constants c , Debye temperatures θ , and adsorption energies E_{ads}) to which they have been fitted.

	Experiment	Fit	Reference
c_{11}	221 GPa	221 GPa	30
c_{44}	70.8 GPa	70.8 GPa	30
c_{12}	171 GPa	171 GPa	30
λ_{NN}/k_B		30 530 K $\text{\AA}^{-2}$	
μ_{NN}/k_B		- 3530 K $\text{\AA}^{-2}$	
λ_{NNN}/k_B		2070 K $\text{\AA}^{-2}$	
θ_{bulk}	273 K	269–273 K	31, 32
$\theta_{\text{surface}}^{\perp}$	142 K	142 K	31, 32
$\theta_{\text{surface}}^{\parallel}$	194 K	193–194 K	
$E_{\text{ads}}(110)/k_B$	5130 K	5193 K	29
$E_{\text{ads}}(100)/k_B$	4730 K	4579 K	29
$E_{\text{ads}}(111)/k_B$	4180 K	4267 K	29
ϵ/k_B		683 K	
R_o		3.194 $\text{\AA}$	

$$U(S) = \tau S, \quad (27)$$

with $0 \leq \tau < 1$. The Hamiltonian of the system is given by

$$H = \sum_{\alpha=1}^N \frac{p_{\alpha}^2}{2m_{\alpha}} + V_{\text{Pd}} + V_{\text{Xe-Pd}}, \quad (28)$$

where V_{Pd} is the potential depending only on the displacements of the Pd atoms and $V_{\text{Xe-Pd}}$ is the Xe–Pd interaction potential. The equations of motion for the Pd atoms are

$$m_{\text{Pd}} \ddot{q}_{\alpha} = - \frac{\partial V_{\text{Pd}}}{\partial q_{\alpha}} - \frac{\partial V_{\text{Xe-Pd}}}{\partial q_{\alpha}}. \quad (29a)$$

For the Xe coordinates, except the normal coordinate when the effective Hamiltonian $\tilde{H}$ is used, the equations are

$$m_{\text{Xe}} \ddot{q}_{\alpha} = - \frac{\partial V_{\text{Xe-Pd}}}{\partial q_{\alpha}}, \quad (29b)$$

FIG. 2. Potential energy curves (in K) for the Xe atom at one-, two-, and fourfold sites (denoted by, respectively, 1, 2, and 4), and the potential in the compensating Hamiltonian (denoted by C) as a function of the normal distance to the surface (in $\text{\AA}$).

and for the normal coordinate of Xe with the effective Hamiltonian $\tilde{H}$ the equation is

$$\frac{m_{\text{Xe}}}{1-\tau} \ddot{z} = - \frac{\partial V_{\text{Xe-Pd}}}{\partial z} + \tau \frac{\partial V_C}{\partial z}. \quad (29c)$$

Equation (13) for the desorption rate constant becomes

$$k = \frac{N_{\text{des}}}{\lim_{T \rightarrow \infty} \sum_{s_0, s_1, \dots} \int_{-\tau}^T dt \exp[-\beta \tau S(t)] \Theta[-S(t)]}, \quad (30)$$

where N_{des} is the number of trajectories that yield a desorbed Xe atom.

IV. RESULTS AND DISCUSSION

A. The desorption rate constant

The parameter τ in Eq. (27) is not yet specified. Although the desorption rate constant is independent of the parameter, to obtain good statistics with a minimum of effort its choice is important. The adsorption energy of the Xe atom on the cluster is $E_{\text{ads}}/k_B = 3756$ K, so that for temperatures of $T \approx 1000$ K and above, no compensating Hamiltonian is needed ($\tau = 0$). Below these temperatures too many and too long simulations are needed with $\tau = 0$ to obtain reliable results. If τ is chosen too large, the effective mass in the normal direction becomes large, and it takes a long time to obtain equilibrium. As we start with a zero-velocity Xe atom, we then find too small values for the desorption rate constant. Calculations of the desorption rate constants for a one-Pd-atom cluster at $T = 200$ K as a function of τ show that there is a range of about 0.4 in τ where the results do not change significantly. For the 17-Pd-atom cluster we found that $(1-\tau)E_{\text{ads}}/k_B T$ should be between 3 and 5. We have used $\tau = 0.95$ at $T = 50$ K, 0.90 at 100 K, 0.75 at 200 K, 0.60 at 300 K, and 0.30 at 500 K.

Figure 3 shows the desorption rate constant as a function of temperature. It also shows a comparison with the transition state desorption rate constant. We have obtained this constant by assuming a free motion in two dimensions for the transition state, and for the adsorbed state hindered diffusion parallel and harmonic oscillations normal to the surface. The classical transition state desorption rate constant then becomes^{33,34}

FIG. 3. Desorption rate constants (k in s^{-1}) from the simulations (circles), fit of Eq. (31) to these constants (solid line), and the transition state results (dashed line).

$$k_{TS} = \nu I_0^{-2}(\beta V) \exp[-\beta(E_{ads} - 2V)], \quad (31)$$

where ν is the frequency for vibrations normal to the surface, $2V$ is the barrier for diffusion, E_{ads} is the adsorption energy, and I_0 is a modified Bessel function of order zero. Using the Xe-Pd interaction potential of the simulations, we get: $\nu = 1.55 \times 10^{12} \text{ s}^{-1}$, $2V/k_B = 890 \text{ K}$, and $E_{ads}/k_B = 3756 \text{ K}$. The barrier $2V$ is the difference between the adsorption energies for the four- and the twofold site. The alternative would be to use the coefficient of the second term in the Fourier expansion of the Xe-surface potential.^{35,36} The difference between the transition state desorption rate constant and that of the simulation is small; on the scale of Fig. 3 it is hardly visible. The difference is largest for low temperatures. This seems natural as at these temperatures the Xe atom moves away from the surface relatively slow, so that the Pd atoms can recapture the Xe atom, whereas transition state theory assumes a configuration of no return. In contradistinction, Tully has found that larger deviations occur at high temperatures, which he ascribes to a smaller sticking probability at those temperatures.^{19,37} This difference may be due to his use of microreversibility. Whereas adsorption trajectories tend to cluster around fourfold sites, desorption trajectories do not. Our small difference is still surprising though, because it implies that, although the motions of the Pd atoms cause the desorption, details of these motions are not very important. In particular, Eq. (31) contains only parameters that depend on the Xe-Pd interaction, but none that depend on the Pd-Pd interaction.

As transition state theory gives a good approximation, one may try to obtain ν , V , and E_{ads} by fitting Eq. (31) to measured rates. We tested this by fitting Eq. (31) to the rate constants derived from the simulations. We found $\nu = 7.64 \times 10^{11} \text{ s}^{-1}$, $2V/k_B = 1284 \text{ K}$, and $E_{ads}/k_B = 3784 \text{ K}$. The fit is very sensitive to variations of E_{ads} , but not to those of ν and V . The last 10% decrease of the root-mean-square deviation of $\log k$ was accompanied by a decrease of ν of 25% and an increase of V of 35%.

From the fit to the desorption rate constant we have calculated the activation energy

$$E_{act} \equiv -\frac{\partial \ln k}{\partial \beta} \quad (32)$$

and the preexponential factor

$$\nu_0 \equiv k \exp(\beta E_{act}). \quad (33)$$

They are shown in Fig. 4. The activation energy is less than the adsorption energy as the Xe atom can desorb from positions on the surface where it is weaker adsorbed. This is especially true for high temperatures. From Eq. (31) it follows that for $T \rightarrow 0$ the activation energy becomes equal to the adsorption energy. For $T \rightarrow \infty$ it becomes equal to $E_{ads} - 2V$. The preexponential factor is about 10^{13} s^{-1} , a factor often used in the analysis of thermodesorption spectra, but it varies with temperature. For low temperatures it seems to approach a straight line as a function of $1/T$. Indeed, we find from Eq. (31)

$$\nu_0 \rightarrow \left[\frac{2V}{k_B T} - \frac{1}{2} \right] \frac{\pi \nu}{e}, \quad (34)$$

if $T \rightarrow 0$. The reason why ν_0 diverges at low temperatures is

FIG. 4. Activation energy (in K) (left ordinate; solid curve), and preexponential factor (in 10^{13} s^{-1}) (right ordinate; dashed curve) from the fit to the desorption rate constants.

that the barrier for diffusion gives a factor T in the partition function of the adsorbed Xe atom, which is absent from the partition function of the transition state. For $T \rightarrow \infty$ we find $\nu_0 \rightarrow \nu$. Figure 5 shows a thermodesorption spectrum for low coverages that we have calculated using the desorption rate constants derived from the simulations. The agreement with the experimental thermodesorption spectra for Xe on Pd(111)²⁹ is good. The lower adsorption energy of our cluster, with respect to the infinite surface, compensates for the lower adsorption energy of Pd(111), with respect to Pd(100). For Xe on Pd(110), the peaks are at somewhat higher temperature, as expected.³⁸ We have not found a thermodesorption spectrum for Xe on Pd(100).

B. The mechanism for desorption

Figure 6 shows how the energy of the Xe atom changes on average 2 ps before to 1 ps after the dividing surface is crossed. The trajectories have been computed with the method described in Sec. II C. Although they have been computed much further back in time, only a part is shown, because most changes only occur just before desorption. This means that the desorption process in itself is very fast. The period

FIG. 5. Simulated thermodesorption spectrum. Temperature increase is 3 K s^{-1} .

FIG. 6. Total energy (a), potential energy (b), normal kinetic energy (c), and lateral kinetic energy (d) (all in K) of the Xe atom from 2ps before to 1ps after the dividing surface is crossed. In all cases averages over 500 simulations are shown at, curves from top to bottom, $T = 1000, 500, 300, 200, 100$, and 50 K.

for a vibration of the Xe atom normal to the surface at low temperatures is 645 fs. From Fig. 6 then follows that desorption is caused by a single hard collision with the surface. Consistent with this picture is that the energy of the Xe atom increases first in the normal kinetic energy, and is then gradually converted into potential energy. At lower temperatures it takes the system longer to cross the dividing surface after that collision, as the energy transfer is smaller. We also note that almost immediately after the dividing surface is crossed there is no more energy transfer between the surface and the Xe atom.

The variations in the lateral kinetic energy T_{lat} are very remarkable. At equilibrium we should find for the statistical average $\langle T_{\text{lat}} \rangle = k_B T$. Just before the dividing surface is crossed $\langle T_{\text{lat}} \rangle$ is much higher, however. Apparently, there is a slow accumulation of lateral kinetic energy, which is converted into normal kinetic energy thus helping the desorption. The effect is more important at low temperatures. Table II shows the same effect. When the temperature is lowered a Xe atom that diffuses over the surface spends more time at energetically favorable sites. The site preference for desorption changes, however, much slower. This implies that before desorption already some energy has been transferred to the Xe atom.

Figure 7 shows the distribution P_θ of the angle between the surface normal and the direction into which the Xe atom desorbes; i.e., the desorption angle. It is defined as

$$P_\theta(\theta) = \int d\mathbf{w} P_f(\mathbf{w}) \delta \left[\theta - \arccos \left(\frac{w_z}{\sqrt{w_x^2 + w_y^2 + w_z^2}} \right) \right], \quad (35)$$

where P_f is the distribution for the velocities $\mathbf{w}$ at $t \rightarrow \infty$. We

have not divided P_θ by $\sin \theta$ as is often done. With our definition we get a distribution with a maximum that shifts with temperature. This is clearer, we think, than a change in the slope of the distribution that is obtained without the factor $\sin \theta$. As a reference Fig. 7 shows a $\cos \theta$ distribution ($\sin \theta \cos \theta$ with our definition). As will be shown below this distribution is obtained when the Xe atom desorbes isotropically and the thermal energy is much smaller than the adsorption energy. We see that at low temperatures the peak in the distribution shifts to smaller angles. We will show below that this too can be explained by the conversion of lateral into normal kinetic energy.

We also checked if the kinetic energy of the Xe atom after desorption was Boltzmann distributed, and, if so, if the temperature was the same as that of the surface. Table III shows the results. For a Boltzmann distribution we should find for the normal T_{nor} and lateral kinetic energy T_{lat} ;

$$\langle T_{\text{nor}} \rangle / k_B = T/2, \quad (36a)$$

$$\langle T_{\text{lat}} \rangle / k_B = T, \quad (36b)$$

$$\Delta T_{\text{nor}} / k_B = T/\sqrt{2}, \quad (36c)$$

TABLE II. Site distributions for diffusion (left numbers) and desorption (right numbers). The sites are defined as Voronoi cells.

T (K)	Fourfold		Twofold		Onefold	
∞	0.25		0.50		0.25	
1000	0.37	0.25	0.47	0.51	0.16	0.25
500	0.49	0.27	0.40	0.49	0.11	0.25
200	0.83	0.28	0.16	0.51	0.02	0.21
100	0.98	0.44	0.02	0.43	0.00	0.13
50	1.00	0.70	0.00	0.25	0.00	0.05

FIG. 7. The desorption angle distribution P_θ at $T = 1000$ K (a) and at $T = 100$ K (b). The bars are binned simulation results. The solid curves are results from the DTN model. In (a) the deflection angle $\alpha = 53.8^\circ$, and in (b) $\alpha = 84.1^\circ$. The area of the bars and under the curves is the same. The dashed curves depict a $\cos \theta$ distribution [$\sin \theta \cos \theta$ with the definition of Eq. (35)].

and

$$\Delta T_{\text{lat}}/k_B = T, \quad (36d)$$

where Δ stands for the standard deviation. The normal kinetic energy distribution corresponds to a temperature that is much higher than the surface temperature. Moreover, it is certainly not Boltzmann. The lateral kinetic energy distribution may be Boltzmann, but at low temperatures it is characterized by a temperature that is lower than the surface's. Again, this points to the conversion of lateral into normal kinetic energy. In what follows we will present a model that explains the results above.

TABLE III. Average kinetic energy and standard deviation in normal and lateral direction after desorption (in K). The simulation results (left numbers) as well as the results from the DTN model (right numbers) are shown. The right-most column gives the deflection angles that are used in the DTN model.

T (K)	$\langle T_{\text{nor}} \rangle / k_B$		$\Delta T_{\text{nor}} / k_B$		$\langle T_{\text{lat}} \rangle / k_B$		$\Delta T_{\text{lat}} / k_B$		α
1000	943	869	899	892	1021	1001	1016	1000	0.0°
500	475	451	446	454	480	479	497	374	61.5°
300	300	281	262	282	282	281	281	214	67.4°
200	216	192	161	192	170	170	167	120	72.7°
100	141	99	86	99	56	55	58	33	80.7°
50	109	50	60	50	24	24	26	14	83.9°

The model, which we call deflection to normal (DTN) model, is based on the following assumptions.

- (i) The desorption is caused by a single collision.
- (ii) Before this collision the velocity distribution of the Xe atom is a Boltzmann distribution with the same temperature as the surface.
- (iii) After the collision the normal component of the velocity changes, because normal kinetic energy is converted into potential energy. No corrugation is felt.
- (iv) The total kinetic energy of the Xe atom does not change at the collision, and the lateral component of the velocity is only tilted over a so-called deflection angle α towards to surface normal.

Assumptions (i) and (iii) follow directly from the results of our simulations. Assumption (ii) seems to contradict Fig. 6(d) as the lateral kinetic energy is clearly much larger than $k_B T$. We have to realize, however, that we averaged in Fig. 6(d) only over trajectories that lead to desorption. We shall show below that this higher lateral kinetic energy is one of the consequences of our model.

Assumption (iv) is central to DTN. The physical idea of the model is that when the Xe atom moves parallel to the surface at low temperatures it collides with diffusion barriers (surface corrugation), and is scattered in the direction of the normal. The angle of the velocity with the surface normal decreases hence the name of the model. At high temperatures it can move relatively easily over those barriers. The deflection angle α is therefore expected to be larger at lower temperatures. We note that we have neglected the energy transfer from the surface to the Xe atom that can be seen in Fig. 6(a). It turns out that, although this transfer is important, and although we do find discrepancies because we neglect it, the trends in the results of the simulation are surprisingly well reproduced by the DTN model.

The velocity $\mathbf{u}$ after the collision is related to the velocity $\mathbf{v}$ before the collision via

$$u_x = v_x \cos \alpha, \quad (37a)$$

$$u_y = v_y \cos \alpha, \quad (37b)$$

and

$$u_z = \sqrt{v_z^2 + (v_x^2 + v_y^2) \sin^2 \alpha}. \quad (37c)$$

The velocity distribution P_i before the collision is given by

$$P_i(\mathbf{v}) \propto \exp \left[-\frac{m_{\text{Xe}} \mathbf{v}^2}{2k_B T} \right] \Theta(-v_z), \quad (38)$$

where we introduced the step function because the Xe atom has to move towards the surface. The velocity distribution P_m just after the collision is then given by

$$\begin{aligned}
 P_m(\mathbf{u}) &= \int d\mathbf{v} P_i(\mathbf{v}) \delta(u_x - v_x \cos \alpha) \delta(u_y - v_y \cos \alpha) \\
 &\quad \times \delta \left[u_z - \sqrt{v_z^2 + (v_x^2 + v_y^2) \sin^2 \alpha} \right] \\
 &\propto \frac{u_z}{\sqrt{u_z^2 - (u_x^2 + u_y^2) \tan^2 \alpha}} \exp \left[-\frac{m_{\text{Xe}} \mathbf{u}^2}{2k_B T} \right] \\
 &\quad \times \Theta(u_z) \Theta \left[u_z^2 - (u_x^2 + u_y^2) \tan^2 \alpha \right]. \quad (39)
 \end{aligned}$$

After the collision the Xe atom has to move away from the

surface. This decreases the normal component of the velocity. The final velocity $\mathbf{w}$ is related to $\mathbf{u}$ via

$$w_x = u_x, \quad (40a)$$

$$w_y = u_y, \quad (40b)$$

and

$$\frac{1}{2}m_{\text{Xe}}w_z^2 = \frac{1}{2}m_{\text{Xe}}u_z^2 - E_{\text{ads}}. \quad (40c)$$

The final velocity distribution P_f becomes

$$P_f(\mathbf{w}) = \int d\mathbf{u} P_m(\mathbf{u}) \delta(w_x - u_x) \delta(w_y - u_y) \delta(w_z - \sqrt{u_z^2 - 2E_{\text{ads}}/m_{\text{Xe}}}) \\ \propto \frac{w_z}{\sqrt{w_z^2 + 2E_{\text{ads}}/m_{\text{Xe}} - (w_x^2 + w_y^2)\tan^2\alpha}} \exp\left[-\frac{m_{\text{Xe}}\mathbf{w}^2}{2k_B T}\right] \Theta(w_z) \Theta[w_z^2 + 2E_{\text{ads}}/m_{\text{Xe}} - (w_x^2 + w_y^2)\tan^2\alpha]. \quad (41)$$

With this distribution we can compute all properties that we have also obtained from the simulations by the evaluation of appropriate integrals.

The distribution P_θ is obtained by substitution of Eq. (41) into Eq. (35). Figure 7 shows a comparison with simulation results. The deflection angle α is chosen so that the simulation results and the DTN model have the same median; i.e., $\alpha = 53.8^\circ$ at $T = 1000$ K, 70.7° at 500 K, 75.7° at 300 K, 78.8° at 200 K, 84.1° at 100 K, and 86.7° at 50 K. As expected the deflection angle increases when the temperature is lowered. The DTN model gives peaks that are somewhat sharper than those of the simulation. Except at very high deflection angles, the distribution P_θ in DTN almost equals $\sin\theta \cos\theta$. The peak shifts to lower angles more easily by increasing the deflection angle at high than at low temperatures. There are actually two parameters that determine the shape of P_θ ; the deflection angle α and the adsorption energy E_{ads} . For $\alpha = 0$ and $E_{\text{ads}} = 0$ we have $P_\theta \propto \sin\theta$. This is the case where the final velocity distribution P_f is Boltzmann. For $\alpha = 0$ and $E_{\text{ads}}/k_B T \rightarrow \infty$ we find $P_\theta \propto \sin\theta \cos\theta$. At $T = 1000$ K and $T = 500$ K we are near this limit, even though the deflection angle α seems to be large. Actually, the medians are 47.1° at $T = 1000$ K and 43.9° at 500 K. We only obtain peaks for desorption angles $\theta < 45^\circ$ when the deflection angle becomes very large. As $E_{\text{ads}}/k_B T$ becomes larger, the deflection angle must also become larger to given the same peak position.

Figure 8 shows how $\langle T_{\text{nor}} \rangle$, $\langle T_{\text{lat}} \rangle$, ΔT_{nor} , and ΔT_{lat} change as a function of the deflection angle at $T = 1000$ K. At lower temperatures, $\langle T_{\text{nor}} \rangle$ and ΔT_{nor} become more and more constant, with value $k_B T$. The shape of $\langle T_{\text{lat}} \rangle$ and ΔT_{lat} remains the same, but the bump shifts to higher values of the deflection angle. Table III shows the best fit of DTN to $\langle T_{\text{nor}} \rangle$ and $\langle T_{\text{lat}} \rangle$. The deflection angles are in reasonable agreement with the ones we have obtained before. The model clearly predicts the non-Boltzmann character of T_{nor} , and the fact that $\langle T_{\text{nor}} \rangle$ is higher than $k_B T/2$. It also shows that $\langle T_{\text{nor}} \rangle/k_B T$ and $\Delta T_{\text{nor}}/k_B T$ increase as the temperature decreases, although not so much as in the simulation. This effect can be ascribed to E_{ads} . When $E_{\text{ads}}/k_B T$ is small, we find Eqs. (36a) and (36b). At high temperature $\langle T_{\text{lat}} \rangle$ and ΔT_{lat} are predicted very well. At low temperature DTN predicts non-Boltzmann character with $\langle T_{\text{lat}} \rangle > \Delta T_{\text{lat}}$, as the

deflection angle increases. The model, however, does show that $\langle T_{\text{lat}} \rangle$ and ΔT_{lat} become lower than $k_B T$ at low temperatures. We thus find that the normal component of the velocity is determined by E_{ads} , and the lateral components by the deflection angle.

We finally want to look at the average lateral kinetic energy before the collision that leads to desorption. We therefore integrate the Boltzmann distribution of Eq. (38) only over desorbing trajectories; i.e., over the region $v_z^2 + (v_x^2 + v_y^2)\sin^2\alpha \geq 2E_{\text{ads}}/m_{\text{Xe}}$. The result is shown in Fig. 9. We see that as the integration is restricted, the average lateral kinetic energy increases when the deflection angle increases. The best values for the deflection angle are approximately $\alpha = 22^\circ$ at $T = 1000$ K, 32° at 500 K, 44° at 300 K, 53° at 200 K, 61° at 100 K, and 65° at 50 K. They are clearly smaller than the ones we have obtained before, because we have assumed in the DTN model that the energy of the Xe atom is conserved. This means that, in the DTN model, a large part of the energy that the Xe atom needs to desorb must come from the lateral kinetic energy. As can be seen in Fig. 6(a), there is also an energy transfer from the surface to the Xe atom.

FIG. 8. $\langle T_{\text{nor}} \rangle/k_B T$, $\langle T_{\text{lat}} \rangle/k_B T$, $\Delta T_{\text{nor}}/k_B T$, and $\Delta T_{\text{lat}}/k_B T$ as a function of the deflection angle α at $T = 1000$ K in the DTN model. The statistical averages are depicted by solid lines, and the standard deviations by dashed lines. The lines for T_{lat} start at 1.00 and end at 0.00. The other lines are the ones for T_{nor} .

FIG. 9. The lateral kinetic energy (in K) before desorption averaged over only those trajectories that lead to desorption in the DTN model. Curves from top to bottom depict results obtained at $T = 1000, 500, 300, 200, 100$, and 50 K.

V. CONCLUSIONS

We have chosen a dividing surface that depends on the momenta as well as the coordinates. This surface gives the same rate constant as the dividing surface, depending only on coordinates, that is obtained with variational reaction rate theory, but it is more convenient in an MD simulation. MD is a good method to study reactions. We have generalized the compensating potential method of Grimmelmann *et al.*, and have unified their and Bennett's method.⁹ Our compensating Hamiltonian method uses a function of the S function to overcome the problem of a high activation barrier. We have shown that the equations of motion need not become more difficult.

We have simulated the desorption of Xe from Pd(100) to test our method. The results are in good agreement with experiment. Our and transition state reaction rate constants are nearly the same, except at low temperatures where the reaction rate constants from the simulations are somewhat smaller. This is due to the smaller escape velocity of the Xe atom at low temperatures, which gives the Pd atoms more chance to recapture it. Desorption in the Xe/Pd(100) system finds place via one hard collision. The time between this collision and the moment the dividing surface is crossed is much shorter than the period of an oscillation of the Xe atom in the normal direction. At low temperatures this time becomes longer.

We have also used the compensating Hamiltonian method to generate reactive trajectories at low temperatures. We have studied the desorption angle distribution, the normal and lateral kinetic energy distributions, and the conversion of the energy during the desorption process. A model, called deflection to normal (DTN) model, explains the

trends in the MD results as a function of temperature. Desorption seems to take place, because, at the final collision with the surface, part of the lateral kinetic energy is converted into normal kinetic energy.

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