

Diffusion of an adsorbed particle: Temperature dependence

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Diffusion of an adsorbed particle: Temperature dependence

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This paper completes a theoretical investigation of the motion of an atom adsorbed on a face centered cubic (fcc) (001) surface. We consider here different temperatures and the diffusion constant D is found to follow an Arrhenius curve. Quite similar results for D are obtained if one uses the absolute rate theory for the escape rate together with the assumption of single uncorrelated jumps. The static potential is treated properly by including the local distortion of the lattice around the adatom and by taking into account the thermal fluctuations of the substrate atoms. The distortion of the lattice has a significant effect on D , particularly at low temperatures. With all the various physical effects included the calculated values for the diffusion constant and for the velocity correlation function are found to be consistent with available molecular dynamics data on the same system.

I. INTRODUCTION

Results of a detailed theoretical analysis of the motion of an atom adsorbed on a solid surface were reported recently in a series of papers.¹⁻⁴ In the first paper, referred to as I, the basic theory was presented and it can be viewed as a generalization of the Fokker-Planck equation with the friction coefficient replaced by a certain memory function. The latter contains the full dynamics of the substrate as well as the motion of the adsorbed atom, and it was calculated within the framework of nonlinear mode-coupling approximations.⁵

In the previous papers we were mainly concerned with the above memory function. We made comparisons between some different approximations, implying various degrees of sophistication, and we considered situations where the characteristic time scale for the adatom was varied relative to that of the dynamics of the substrate. However, we kept the temperature at a constant, and nonzero value, and we ignored purposely the local relaxation of the lattice around the adatom.

This paper is the last in the series and here we consider different temperatures and are concerned with how the diffusion constant and the velocity correlation function of the adatom vary. The adatom experiences a static periodic potential when moving along the solid surface and the corrugation determines a certain activation energy for the diffusion process. Here we study the effect of the local relaxation of the lattice⁶ on this static potential and we find that it changes the value of the activation energy significantly. The lattice relaxation also influences the coupling function, which enters in the memory function, and this is also included in the present calculations. Otherwise, everything is done as before and we refer in particular to paper I for more details. With all the various physical effects included in the calculations the theory gives qualitative agreement with available molecular dynamics data on the same system.^{7,8}

The results we present here refer to the same situation as consider in paper I, where the adatom is identical with the substrate atoms. The interaction between every pair of atoms is a Lennard-Jones 6-12 potential and the adatom is moving

on a fcc (001) surface. We found before^{1,3} that the ordinary Fokker-Planck equation with a position dependent friction coefficient is appropriate in this case. This may be somewhat surprising in light of the fact that the adatom is identical with the substrate atoms. However, the adatom has less number of nearest neighbors and its distance to the nearest neighbor is slightly larger than for the substrate atoms. This makes the adatom move on a slower time scale than the substrate atoms and we found this to be enough to make the Fokker-Planck approximation (FPA)¹ valid. Especially, the diffusive motion is very well described by FPA. This approximation is used here and it reduces the computational work considerably.

The most relevant parts of the calculational procedure is described in Sec. II and the numerical results are given in Sec. III. We finish by making some general remarks and stating the main conclusions in Sec. IV.

II. CALCULATIONAL PROCEDURE

The Fokker-Planck equation for the relevant phase-space correlation function is¹

$$\left[\frac{\partial}{\partial t} + \frac{\mathbf{p}_1 \cdot \nabla_{\mathbf{r}_1}}{m} + \mathbf{F}^{\text{ad}}(\mathbf{r}_1) \cdot \nabla_{\mathbf{p}_1} \right] C^s(11't) \quad (1)$$

$$= \nabla_{\mathbf{p}_1} \cdot \boldsymbol{\eta}(\mathbf{r}_1) \cdot [\mathbf{p}_1 + m k_B T \nabla_{\mathbf{p}_1}] C^s(11't),$$

where "1" stands for the phase-space point $(\mathbf{r}_1, \mathbf{p}_1)$ of the adatom. The static force \mathbf{F}^{ad} is equal to

$$\mathbf{F}^{\text{ad}}(\mathbf{r}) = - \left\langle \sum_{\mathbf{r}'} \nabla_{\mathbf{r}} v(\mathbf{r} - \mathbf{R}_{\mathbf{r}'}) \right\rangle_{\mathbf{r}}, \quad (2)$$

with $\langle \dots \rangle_{\mathbf{r}}$ denoting an average over the degrees of freedom of the substrate, keeping the adatom fix at position \mathbf{r} . In paper I the following expression for the position dependent friction tensor:

$$\eta^{\alpha\beta'}(\mathbf{r}_1) = \frac{1}{m k_B T} \sum_{11'} \sum_{\alpha\alpha'} v_{\text{eff}}^{\alpha\beta}(\mathbf{r}_1 - \mathbf{R}_1^0) \times \int_0^\infty dt \langle u_i^\alpha(t) u_{i'}^{\alpha'} \rangle v_{\text{eff}}^{\alpha'\beta'}(\mathbf{r}_1 - \mathbf{R}_1^0) \quad (3)$$

was derived together with an effective coupling term

$$v_{\text{eff}}^{\alpha\beta}(\mathbf{r} - \mathbf{R}_l^0) = \int d\bar{\mathbf{r}} \nabla_{\bar{\mathbf{r}}}^{\alpha} \nabla_{\bar{\mathbf{r}}}^{\beta} v(\mathbf{r} - \mathbf{R}_l^0 - \bar{\mathbf{r}}) w_l(\bar{\mathbf{r}}), \quad (4)$$

where the Debye–Waller factor

$$w_l(\mathbf{r}) = (8\pi^3 U_{\parallel}^2 U_{\perp}^2)^{-1/2} \exp\left[-\frac{1}{2}\left(\frac{x^2 + y^2}{U_{\parallel}} + \frac{z^2}{U_{\perp}}\right)\right] \quad (5)$$

has been introduced. The positions of the U substrate atoms are denoted by $\mathbf{R}_l(t) = \mathbf{R}_l^0 + \mathbf{u}_l(t)$, and U_{\parallel} and U_{\perp} are the mean square displacements parallel and perpendicular to the surface, respectively. In Eq. (3) we have only included coupling to single phonon processes. By retaining higher order terms in the expansion of the density of the surrounding medium (cf. paper I) multiphonon effects can be included, but at least at low temperatures these can be neglected in the present context.

The lattice is distorted locally around the adatom. This implies that the equilibrium positions of the substrate atoms are displaced and the atoms vibrate then collectively around the new equilibrium positions. We always expand in the lattice displacements $\mathbf{u}_l(t)$ from the perturbed equilibrium positions \mathbf{R}_l^0 and one should keep in mind that these depend on the position of the adatom \mathbf{R}^a , $\mathbf{R}_l^0 = \mathbf{R}_l^0(\mathbf{R}^a)$. To simplify the calculations we will here assume the harmonic approximation for the substrate lattice. Adopting this approximation the collective vibrational motion of the substrate atoms is not changed by the local distortion of the lattice, and the displacements of the equilibrium positions are given by

$$\mathbf{R}_l^{\alpha} = \bar{\mathbf{R}}_l^{\alpha} + \frac{1}{k_B T} \sum_{l'} \sum_{\alpha'} \langle u_l^{\alpha} u_{l'}^{\alpha'} \rangle F_{l'}^{\alpha'}. \quad (6)$$

Here $\bar{\mathbf{R}}_l^0$ are the equilibrium positions of the undistorted lattice and F_l^{α} is the force acting on the l th substrate atom in the α direction. This force is determined self-consistently according to $\mathbf{F}_l = -\nabla v(\mathbf{R}_l^0 - \mathbf{R}^a)$,⁹ and the response function $\langle u_l^{\alpha} u_{l'}^{\alpha'} \rangle / k_B T$ should be evaluated for the undistorted lattice. We notice that the displacements of the equilibrium positions are temperature independent, since $\langle u_l^{\alpha} u_{l'}^{\alpha'} \rangle$ is proportional to T . Equation (2) can now be simplified to

$$\mathbf{F}^{\text{ad}}(\mathbf{r}) = - \sum_l \int d\bar{\mathbf{r}} \nabla v(\mathbf{r} - \mathbf{R}_l^0 - \bar{\mathbf{r}}) w_l(\bar{\mathbf{r}}), \quad (7)$$

where the Debye–Waller factor w_l contains the thermal fluctuations of the undistorted lattice. The corresponding potential, the free energy, is then obtained from the definition $\mathbf{F}^{\text{ad}}(\mathbf{r}) = -\nabla V^{\text{ad}}(\mathbf{r})$ and we call it the adiabatic potential.

Equations (6) and (7) were used in the numerical evaluation of $V^{\text{ad}}(\mathbf{r})$ and in the summation in Eq. (7) we included all substrate atoms within a distance of roughly 2.5σ from the adatom, where σ enters in the Lennard-Jones potential. It corresponds to including 73 substrate atoms from the three uppermost layers, and this was found to give sufficient accuracy. We here improve upon the previous calculations where only a few substrate atoms in the uppermost layer were included. The fcc (001) surface forms a quadratic lattice with the lattice distance a being equal to the nearest neighbor distance. For this we have used the value a

$= 1.105\sigma$ for all temperatures and thereby neglected the thermal expansion of the lattice. The relaxation of the layers normal to the surface has been accounted for according to the results in Ref. 10 (Fig. 2). This defines the positions of the undistorted lattice $\bar{\mathbf{R}}_l^0$.

The local distortion of the lattice depends on the static response function in Eq. (6). We have used molecular dynamics data (MD) from Ref. 10 (Fig. 4) for the diagonal elements $\langle u_l^{\alpha} u_l^{\alpha} \rangle / k_B T$, which are most important in determining the adiabatic potential. In order to estimate the off-diagonal elements ($l \neq l'$) we first calculated the ratios $\langle u_l^{\alpha} u_{l'}^{\alpha'} \rangle / \langle u_l^{\alpha} u_l^{\alpha} \rangle$ from the Debye model in the bulk and we then used the same ratios in determining $\langle u_l^{\alpha} u_{l'}^{\alpha'} \rangle$ from the MD values of $\langle u_l^{\alpha} u_l^{\alpha} \rangle$. In the summation in Eq. (6) we included all nearest and next nearest substrate atoms. The adiabatic force is then determined from Eq. (7), using the same MD values as above for the mean square displacements entering in Eq. (5).

The friction coefficient has been calculated correspondingly by taking into account the distorted lattice and by including the interaction with the same number of substrate atoms. Besides $\langle u_l^{\alpha} u_{l'}^{\alpha'} \rangle$ one needs the time-integrated value of the displacement correlation function, given by the zero frequency limit of the phonon spectrum. This has been derived from the phonon modes presented in Ref. 2. These modes are based on a continuum model of the substrate and they give an accurate description of the low frequency part of the true spectrum.

III. NUMERICAL RESULTS

We now turn to the presentation of the result from our numerical calculations. All quantities with a superscript star are in conventional reduced units,⁸ which are expressed in terms of ϵ , σ , and m , where ϵ and σ are the parameters entering in the Lennard-Jones potential and m is the mass of the atoms.

A. The adiabatic potential

Following paper I we restrict the adatom to move along a certain trajectory corresponding to a minimum energy path. The location of this trajectory is temperature dependent due to the thermal fluctuations of the substrate atoms. At higher temperatures the adatom moves slightly further away from the surface. The binding energy for the adatom increases when the lattice is allowed to relax.⁶ This increase differs at the center and bridge positions and the activation energy, $\Delta V^{\text{ad}} \equiv V^{\text{ad}}(0) - V^{\text{ad}}(a/2)$, therefore changes. The change is small compared to the binding energy, but it is significant when compared with the temperature. Also the curvature of the potential is modified. The characteristic vibrational frequency at the bottom of the potential well, ω_a , is reduced from 7.67 to 5.98 in reduced units for $T^* = 0.30$, when the lattice is allowed to relax around the adatom. The distortion of the lattice is quite small. The maximum displacement is for $T^* = 0.30$ equal to 0.044 and 0.034 in reduced units for the adatom at the center and bridge positions, respectively, and is in both cases directed towards the adatom.

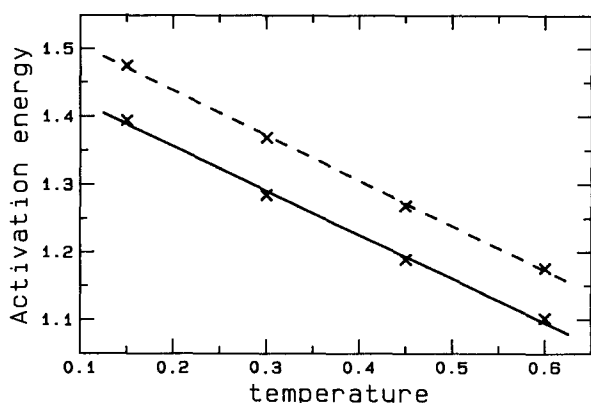


FIG. 1. The temperature dependence of the activation energy for the diffusion process in reduced units with a locally distorted (solid curve) and an undistorted (dashed curve) lattice.

The activation energy ΔV^{ad} as function of temperature is shown in Fig. 1 both with a distorted (solid curve) and an undistorted (dashed curve) lattice. It is found to depend linearly on the temperature and the local distortion of the lattice reduces its value by about 6%. We cannot directly compare this with the results obtained by Flahive and Graham,⁶ due to their use of a Morse potential for the pair interaction. They also considered only the change for $T = 0$ and they obtained reductions of about 10%–15%. At lower temperatures the adatom will be closer to the surface and one cannot exclude the possibility that the distortion is substantially larger for $T = 0$. We have tried to check this in our calculations but we did not obtain convergence for the relaxed positions \mathbf{R}_i^0 , especially with the adatom located at the bridge position. This may be due to the use of the harmonic approximation for the lattice.

B. The friction coefficient

The friction tensor is calculated along the trajectory and as in the previous papers we have used the xx component, $\eta^{xx}(\mathbf{r})$, in the calculations. The different components differ considerably and we have found that $\eta^{zz}(\mathbf{r})$ is substantially larger than $\eta^{xx}(\mathbf{r})$, especially for the bridge position. This implies that the motion perpendicular to the surface is more strongly damped (cf. Ref. 11). In a proper three-dimensional treatment all components of the friction tensor $\eta^{\beta\beta'}(\mathbf{r})$, including the off-diagonal terms ($\beta \neq \beta'$), would influence the motion. However, we believe that the η^{xx} component calculated along the trajectory represents a proper, or at least reasonable, averaging over the friction along the true paths. The agreement with the MD results for the velocity correlation function (see Fig. 4) supports this assumption.

The friction tensor is also changed when one takes into account the local distortion of the lattice. The average value of $\eta^{xx}(\mathbf{r})$ is reduced from 1.85 to 1.67 in reduced units for $T^* = 0.30$, and the position dependence is similar in shape in both cases.

C. The diffusion constant

The diffusion constant D is determined from the low frequency limit of the frequency spectrum of the velocity

correlation function.¹ The calculations have been done at four different temperatures and D is found to follow an Arrhenius curve over the whole considered temperature range. This is seen in Fig. 2 where also results from MD simulations on exactly the same system by Mruzik and Pound⁷ (triangles) and by McDowell and Doll⁸ (squares) are shown. The differences between these two simulations are large and our results are located essentially in between.

In the same figure (circles) we also show the results obtained by using the absolute rate theory (ART) for the escape rate¹² and by assuming uncorrelated jumps with the jump distance being equal to the lattice spacing a . One should keep in mind that these values are independent of the friction coefficient. The agreement with the calculated values is very close, especially at lower temperatures. The reason is that the position dependence of the friction coefficient is very well adapted for the assumption behind ART,¹ giving a considerably larger friction when the adatom is at its potential minimum compared with the value at the top of the potential barrier. The small value at the bridge position is due to the fact that the directions of the fluctuating forces on the adatom are mainly perpendicular to the diffusion path at that position. It seems plausible that these arguments for the validity of ART also would apply for impurity diffusion in bulk.¹³ At higher temperatures the mean velocity of an escaping adatom increases and the magnitude of the friction coefficient is found to be slightly smaller. These two facts imply that the probability for the adatom to move several lattice distances before being stopped increases and it is reflected in a deviation of the diffusion constant from the ART result at higher temperatures.

Fitting our calculated values to the Arrhenius curve $D = D_0 \exp(-E_0/k_B T)$ gives $D_0^* = 2.76$ and $E_0^* = 1.54$, and the value for E_0^* is consistent with the value obtained for $\Delta V^{\text{ad}}(T)$, when extrapolating to zero temperature, $\Delta V^{\text{ad}}(T = 0) = 1.57$. We notice that the ART result does not follow exactly an Arrhenius curve due to the tempera-

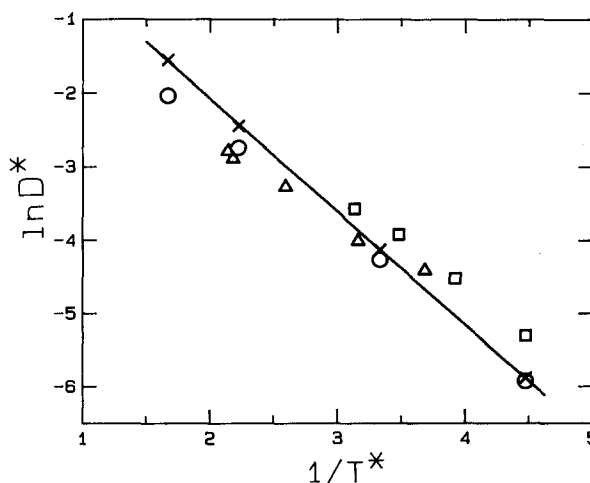


FIG. 2. The diffusion constant for various temperatures in reduced units. The different symbols correspond to calculated values (crosses), MD values from Ref. 7 (triangles), and from Ref. 8 (squares), and values determined from the absolute rate theory (open circles). The solid curve is fitted to the calculated values.

ture dependence in the prefactor.¹² At low temperatures the slope is given by $\Delta V^{\text{ad}}(T=0)$ and the prefactor becomes proportional to the vibrational frequency ω_a times a factor containing the temperature dependent part of ΔV^{ad} . At higher temperatures the anharmonicity of the static potential becomes important and the prefactor is reduced compared with the low temperature value. It is quite surprising that our calculated values, based on a more correct description of the dynamics, is found to follow more closely the simple Arrhenius law.

Due to the exponential dependence the diffusion constant is sensitive to the magnitude of the activation energy. The improvement made here by including a larger number of interacting substrate atom is found to be significant. Considering an unrelaxed lattice we obtained here $D^* = 0.014$ and $\Delta V^{\text{ad}*} = 1.37$ for $T^* = 0.30$ and this should be compared with the values $D^* = 0.029$ and $\Delta V^{\text{ad}*} = 1.13$ in paper I. When we in the present calculations allow for lattice relaxation around the adatom we get $D^* = 0.016$ and $\Delta V^{\text{ad}*} = 1.29$.

The diffusion constant can for comparatively low temperatures be extracted from the field ion microscope experiments.¹⁴ Due to the uncertainties in the form and magnitude of the basic interaction potentials a quantitative comparison with the experimental values would, however, be more a test of the potentials than of the theory and we have therefore not made use of these values.

D. The velocity correlation function

The details of the motion is rather well revealed in the frequency spectrum of the velocity correlation function $\phi(t)$. At low temperatures the adatom is mainly localized around one of the potential minima and oscillates around it. This shows up as a pronounced resonance peak. At higher temperatures the adatom is moving fairly often above the maxima of the potential and one finds, in addition, a diffusive peak. This is clearly seen in Fig. 3, where the frequency spectrum $\phi(\omega)$ is shown for $T^* = 0.30, 0.45$, and 0.60 .

In molecular dynamic calculations (MD) one obtains

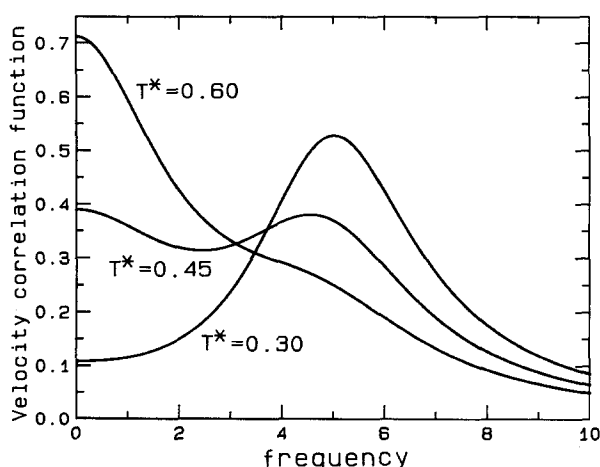


FIG. 3. The frequency spectrum of the velocity correlation function at three different temperatures in reduced units.

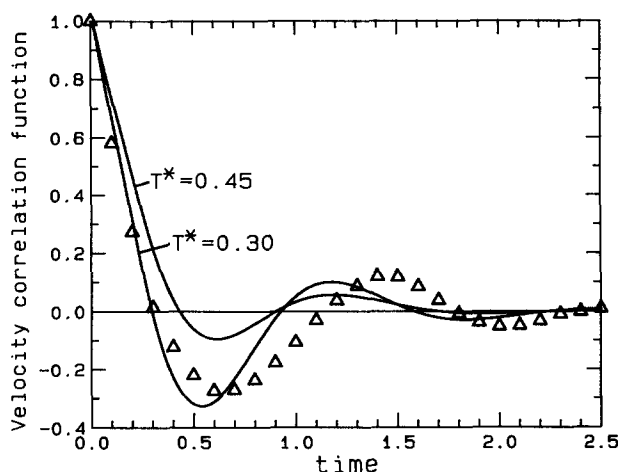


FIG. 4. The time dependence of the velocity correlation function at two different temperatures (solid curves) in reduced units. The triangles show the corresponding MD values for $T^* = 0.30$ given in Ref. 7.

$\phi(t)$ directly and comparing our results with such data would give a sensitive test on the validity of the theory. Unfortunately, the statistical uncertainties in the available MD results⁷ are too large to make a quantitative comparison meaningful. The uncertainties are clearly seen in the unphysical oscillations in $\phi(t)$ at large times, $t^* > 4$ (see Fig. 17 in Ref. 7). Nevertheless, we show in Fig. 4 the MD results (triangles) for $T^* = 0.30$ together with our calculated values (solid curves) for $T^* = 0.30$ and $T^* = 0.45$. The qualitative agreement indicates that the damping is rather well described by our model. It demonstrates that the theory gives a quite reasonable description of the dynamics, but more accurate computer data are needed in order to justify a more quantitative comparison. At higher temperature multiphonon processes can become important. These effects are neglected here, but one should keep in mind that the vibrational frequency for the adatom is about one-third of the Debye frequency for the substrate lattice.

IV. CONCLUDING REMARKS

This paper completes a theoretical investigation of the motion of an atom adsorbed on a solid surface, where one of the main aims has been to clarify the validity of some commonly used models for such a process. Here, we have studied the temperature dependence and also the importance of including the local distortion of the lattice around the adatom.

The diffusion constant is found to follow closely an Arrhenius curve over the temperature range we have considered, $0.2 < T^* < 0.6$. Our values for the diffusion constant are consistent with available MD data,^{7,8} but more accurate MD results are needed for a detailed quantitative comparison. It is also found that the absolute rate theory (ART) for the escape rate together with the assumption of single uncorrelated jumps gives good agreement for low temperatures but too low values for higher temperature. The discrepancies for higher temperatures indicate the existence of correlated jumps. It seems plausible that the arguments for the validity of ART in our case also would apply for the diffusion in bulk. This would support the classic theory of impurity diffusion

proposed by Vineyard¹³ and refined by several others.¹⁵

The local distortion of the lattice influences the value of the activation energy as well as the coupling to the fluctuations in the medium and through this the friction coefficient. We found a 6% decrease of the activation energy and the characteristic vibrational frequency at the bottom of the potential well is reduced by 10%–25%, depending on the temperature. The larger value refers to the lower temperature limit. The distortion of the lattice has therefore a significant effect on the diffusion constant, particularly at low temperatures and mainly due to the change of the activation energy. Concerning the friction coefficient, its position dependence is essentially unchanged and we find a quantitative change, which however is of only minor importance.

The velocity correlation function $\phi(t)$ is sensitive to the value of the friction coefficient. The fact that our results are in reasonable agreement with available MD data,⁷ shows that our treatment of the fluctuations in the medium is appropriate. Again, more accurate MD results are required in order to make a detailed quantitative comparison meaningful.

Here like in our earlier papers we have restricted the adatom to move along a one-dimensional trajectory corresponding to a minimum energy path. Besides the fact that strong tendency of one-dimensional diffusion is observed on certain surfaces, we have other justifications for our assumption. If the adatom makes uncorrelated jumps to only nearest sites, the primary events would be essentially a one-directional motion. This is particularly true at low temperatures, when the adatom is located in spatial regions with low potential energy. When we begin to have correlated jumps over several lattice spacings, it seems obvious that these jumps are mainly along the same direction due to the inertia of the adatom,¹¹ again implying a one-directional motion. It should also be stated clearly, that the choice of the trajectory is crucial. The potential barrier and position dependent friction coefficient, calculated along the trajectory, should represent a proper averaging over the true paths. In the present situation it seems quite appropriate to evaluate these along a minimum energy path. The qualitative agreement with the MD results supports this conclusion.

Another justification is that the comparisons we have

made between some different models and the conclusions we have drawn from this, would most likely not change in any significant way, if we did the full two- or even three-dimensional calculation for the motion of the adatom. The restriction to one dimension was done in order to reduce the computational work. With the experience we have gained through these calculations it seems now feasible to extend them to at least a proper two-dimensional treatment. This would be desirable but it is at the same time somewhat premature, considering the lack of relevant data to compare with.

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