Theory of Surface Diffusion: Crossover from Classical to Quantum Regime

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A theory is developed for adatom diffusion on surfaces, employing the memory function formalism. The diffusion constant is expressed in terms of static correlation functions which are computed via Monte Carlo path integrations. Our theory is valid at all temperatures in the high friction limit and indicates a sharp crossover from the classical Arrhenius regime at high temperatures to the quantum tunneling regime at low temperatures. Comparisons with experimental data are presented for the H/Ni(100) system.

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The diffusion of light atoms adsorbed on a crystal surface has been of experimental and theoretical interest over the recent years [1–8]. A unique feature that has been observed for H/Ni systems [4] is the existence of a sharp crossover from the classical thermal activated behavior to the quantum tunneling regime as the temperature is lowered. When the temperature is high compared with the adatom parallel vibrational energy quantum (but still low compared with the energy barrier), diffusion proceeds mainly through thermally activated jumps between adsorption sites, and the temperature dependence obeys the well known Arrhenius form. As the temperature is lowered, there is a sharp crossover to a temperature independent diffusion regime where the mobility of the adatom is presumably dominated by tunneling through the barrier. Very recently a theoretical study [8] of the H/Ni(100) system based on the quantum transition state theory produced the experimentally observed sharp crossover behavior but the predicted crossover temperature and quantum diffusion constant are far away from the measured data. In this Letter, we present an alternative theory of adatom diffusion based on the project operator formalism [9]. We model the system as an adatom moving in a periodic adsorption potential, coupled to the substrate vibrational excitations. The coupling results in frictional damping and random forces acting on the adatom. The frictional damping destroys the phase coherence of the adatom wave functions even at low temperatures and therefore the quantum diffusion proceeds by incoherent sequence of tunneling through adsorption potential barriers. Our approach is based on an inverse friction expansion of the velocity and density autocorrelation functions as detailed in our previous studies of classical diffusion [10]. In this work, we will examine only the leading term in this expansion which is valid in the high friction limit. Our results are valid for all the different temperature regimes. When applied to H/Ni(100), the crossover behavior and the values of the crossover temperature and the quantum diffusion constant predicted by our theory agree well with the experimental data by Lin and Gomer [4].

The Hamiltonian for our system is chosen as

$$H = \frac{p^2}{2m} + V(R) + \sum_{\lambda} \mathbf{M}(R,\lambda) \cdot \mathbf{u}_{\lambda} + H_{\mathrm{ph}}. \tag{1}$$

Here m, R, and p are respectively, the mass, displacement vector, and momentum of the adatom. $V(R)$ is the periodic adsorption potential. $\mathbf{u}_\lambda$ is the eigenvector for the λth eigenmode of the substrate vibrational excitations characterized by the harmonic Hamiltonian H_{ph} [11] and $\mathbf{M}(R,\lambda)$ is the coupling coefficient. The scattering of substrate phonons results in an effective friction which plays a central role in the diffusion process and destroys the phase coherence of the adatom wave functions at low temperatures.

We have already studied the adatom diffusion in the classical region in detail using the projection operator formalism [10]. Below, we briefly outline the formalism with appropriate adaptations so that the theory is extended to be valid also in the quantum regime. A set of variables complete in the subspace of adatom dynamics is defined as

$$\begin{aligned} A_0(K) &= e^{i(K+q)\cdot R}, \\ A_1(K) &= (1 - P_0)\left(\frac{p}{2m}\, e^{i(K+q)\cdot R} + e^{i(K+q)\cdot R}\, \frac{p}{2m}\right), \\ &\cdots \\ A_{n+1}(K) &= \left(1 - \sum_{m=0}^{n} P_m\right) \dot{A}_n(K), \\ &\cdots \end{aligned} \tag{2}$$

Here K represents the complete set of reciprocal lattice vector and q a fixed wave vector in the first Brillouin zone. $\dot{A} = \frac{i}{\hbar} LA \equiv \frac{i}{\hbar}[H,A]$. P_n is the projection operator onto vector A_n and χ_{nn} is the norm matrix of A_n, $(A_n(K), A_{n'}(K)) = \delta_{nn'}\chi_{nn}(K,K')$. The scalar product of two arbitrary vectors A and B is defined as the quantum statistical average

$$(A,B) = \frac{1}{\beta Z} \int_0^\beta d\lambda\, \mathrm{Tr}[e^{-\beta H} A^\dagger(\lambda) B] \tag{3}$$

with $Z = \mathrm{Tr}e^{-\beta H}$ the partition function and $\beta = 1/kT$ the inverse temperature. $A(\lambda) = e^{\lambda H} A e^{-\lambda H}$ is the operator in the Heisenberg representation with imaginary time $\hbar\lambda$. The scalar product defined in Eq. (3) correctly reduces back to its classical counterpart at high temperatures.

The dynamic correlation functions $S_{nn}(K, K', t) = (A_n(K, t), A_n(K'))$ carry the full information about adatom diffusion. In particular, the density correlation functions $S(q, \omega) = \int dt e^{i\omega t} S_{00}(K = 0, K' = 0, t)$ possesses a diffusive pole in the hydrodynamic regime, i.e., $S(q, \omega) \sim (\omega - iDq^2)^{-1}$ in the $(q, \omega) \rightarrow 0$ limit. Hence the diffusion constant D can be extracted from the analytical behavior of the correlation functions.

At this point, we can follow our previous development of the formalism [11] to show that in the high friction limit, D is given by the inverse of the memory function formed from the autocorrelation of random force from scattering off the substrate excitations, i.e.,

$$\begin{aligned} D^{-1} &= \Sigma_{11}(K = 0, K' = 0, \omega = 0) \\ &= \int dt \left\{ \chi_{11}^{-1} (\hat{L} A_1, e^{i\hat{L}t} \hat{L} A_1) \chi_{11}^{-1} \right\}_{K=0, K'=0} . \end{aligned} \tag{4}$$

Here $\hat{L}$ is the Liouville operator in the Hilbert space orthogonal to the adatom dynamics subspace. In the initial value approximation, the memory function can be expressed as

$$\Sigma_{11}(t) = \eta(t) \frac{kT}{m} \chi_{11}^{-1} \chi_{00} \chi_{11}^{-1} \tag{5}$$

with the friction $\eta(t)$ resulting from the adatom's scattering off the substrate excitations, given by the expression

$$\eta(t) = \frac{1}{mkT} \sum_{\lambda} |\nabla M(R, \lambda)|^2 (u_\lambda^*(t), u_\lambda). \tag{6}$$

At this point, we see from Eqs. (4)–(6) that the evaluation of the diffusion constant reduces to the evaluation of the static correlation functions χ_{11} and χ_{00} (which are matrices in the indices K, K') as well as the $\omega = 0$ component of the friction $\eta \equiv \int_0^\infty \eta(t)\, dt$. A first principle calculation of these quantities require the input of the adsorption potential and the adatom coupling to the substrate excitations $M(R, \lambda)$, and the substrate vibrational spectrum corresponding to H_{ph} in the Hamiltonian described in Eq. (1). In the absence of detailed knowledge of these quantities for most adsorption systems, we will adopt an empirical approach to determine the adsorption potential and the friction η as detailed below.

The matrices χ_{00} and χ_{11} appearing in the expression for Σ_{11} are just the static density and momentum density correlation functions. They can be conveniently expressed in terms of path integrals as

$$\begin{aligned} &\chi_{00}(K, K') \\ &= \frac{1}{Z} \int dx \int [dR(\lambda)] \left[\frac{1}{\beta} \int d\lambda e^{-iKx(\lambda)} \right. \\ &\qquad \left. \times \exp\left(- \int_0^\beta d\lambda \mathcal{L}[R(\lambda)] \right) \right] e^{iK'x}, \end{aligned} \tag{7}$$

$$\chi_{11}(K, K') = \frac{1}{m\beta} \int dx e^{-i(K-K')x} p(x), \tag{8}$$

$$p(x) = \frac{1}{Z} \int [dR(\lambda)] \exp\left(- \int_0^\beta d\lambda \mathcal{L}[R(\lambda)] \right). \tag{9}$$

In the above equations, $\int [dR(\lambda)]$ stands for the imaginary time path integrations [12]. Each path $R(\lambda)$ starts and ends at x, i.e., $R(0) = R(\beta) = x$. All the x integrations are defined within one lattice period from 0 to d. The partition function Z is just the normalization factor for the density function $\rho(x)$. $\mathcal{L}[R(\lambda)]$ is the Lagrangian corresponding to the Hamiltonian in Eq. (1). We note that the major dynamical effects of the coupling of adatom to phonons has already been included in the friction term $\eta(t)$. In the evaluation of the static correlations we shall neglect the explicit coupling to the phonons in the Lagrangian except that the bare potential $V(R)$ is replaced by $V_a(R)$ including adiabatic relaxation effects.

With Eqs. (4), (5), (7), and (8), the diffusion constant can be expressed in terms of path integrals as

$$\begin{aligned} D^{-1} &= \frac{m\eta}{d^2} \frac{1}{Z} \int dx \frac{1}{\rho(x)} \int [dR(\lambda)] \\ &\quad \times \left[\int d\lambda \frac{1}{\rho[R(\lambda)]} \exp\left(- \int_0^\beta d\lambda \mathcal{L}[R(\lambda)] \right) \right]. \end{aligned} \tag{10}$$

We first examine this expression in the high temperature ($\beta \rightarrow 0$) classical regime. In this case, the contributions to the path integral are dominated by a single path $R(\lambda) = x$. Then from Eqs. (9) and (10) it is easy to see that one recovers the classical results [10] for the density function

$$\rho(x) \simeq \frac{1}{Z} e^{-\beta V_a(x)}, \tag{11}$$

and the diffusion constant

$$D = \frac{kT}{m\eta} \frac{d^2}{\int dx e^{-\beta V_a(x)} \int dx e^{\beta V_a(x)}} . \tag{12}$$

The diffusion constant here has an Arrhenius form for temperatures much lower than the diffusion barrier and goes over to the correct free particle behavior $D = \frac{kT}{m\eta}$ at temperatures much higher than the barrier.

For lower temperatures, quantum effects start to manifest themselves. To compute the density function $\rho(x)$ and the diffusion constant D in this regime, we need to evaluate the full path integrations in Eqs. (9) and (10). This can be achieved numerically for general values of temperatures. We have employed the modified Fourier transform path-integral Monte Carlo method proposed by Doll *et al.* [13]. Our simulations were performed with the explicit inclusion of the first 16 Fourier components of the path $R(\lambda)$ and a partial average over the remaining fast components. This yields accurate results for the path integrals in the entire temperature range (70–700 K) we studied.

We now discuss the application of the theory to the H/Ni(100) system. We have evaluated the path integrations for two model adsorption potentials as shown in Fig. 1. The first one is just a simple cosine potential, $V_a^I(R) = v_0[1 - \cos(2\pi R/d)]$, whereas the second one has a flatter barrier of the form

$$V_a^{II}(R) = v_0\left(1.325 - 0.947\cos\frac{2\pi R}{d} - 0.379\cos\frac{4\pi R}{d}\right). \tag{13}$$

Both potentials have barrier equal to $2v_0$ and a period $d = 2.49$ Å. However, the second one is closer to the adsorption potential determined by the embedded atom method [8]. The value of v_0 is chosen such that in the classical Arrhenius regime, the activation energy E_d agrees with the experimental value (3.2 kcal/mol) of Lin and Gomer [4] which is consistent with experimental data by others [2,3]. This results in the value of $v_0 =$ 80 meV for the choice V_a^I and $v_0 = 81$ meV for the choice V_a^{II}. We note that the theoretical value of $E_d =$ 140 meV (3.2 kcal/mol) in the Arrhenius regime is not equal to the classical barrier $2v_0$. This indicates a sizable correction from the zero point motion even in the "classical regime." The difference between $2v_0$ and E_d is 20 meV for V_a^I and 22 meV for V_a^{II} which is comparable with the zero point energy $\hbar\Omega/2$ ($\hbar\Omega/2 = 22$ meV for V_a^I and $\hbar\Omega/2 = 34$ meV for V_a^{II}, respectively). In Fig. 2, we show the temperature dependence of the diffusion constant. Our results clearly show a crossover from the Arrhenius form to the quantum tunneling regime where the diffusion constant remains constant as the temperature is further lower. The crossover is more gradual for the simple cosine potential where the deviation from Arrhenius form begins at around 200 K and D approaches a constant only for $T < 100$ K. For the potential V_a^{II} with a flatter barrier, the crossover is very sharp and occurs in the narrow temperature range $100\text{ K} < T < 140$ K. The abruptness of the crossover and the crossover temperature for this choice of the adsorption potential are in excellent agreement with the experimental observation of Lin and Gomer [4] for the adsorption system H/Ni(100). The overall magnitude or the scale of the diffusion constant is determined by the choice of the friction parameter. At the moment, there are considerable discrepancies among the different experimental groups regarding the value of the prefactor for the diffusion constant in the classical regime. Accordingly, we estimate that the value of the friction η could range between $1 \lesssim \eta/\Omega \lesssim 600$. This is consistent with the high friction approximation in our theoretical approach. An empirical estimate of η of course includes the contribution from coupling to substrate vibrational excitations [cf. Eq. (6)] as well as that from coupling to electronic excitations.

Now we consider polaronic effects which have not been included in this work explicitly other than the implicit renormalization of the adsorption potential. It could lead

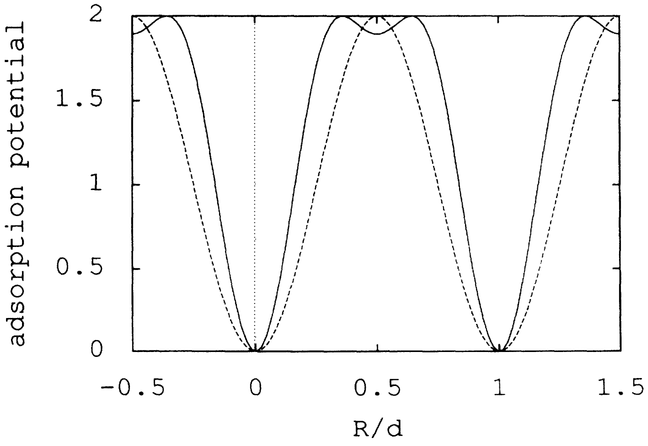

FIG. 1. Model adsorption potential $V_a(R)$. The solid line is for the model potential in Eq. (13) and the dashed for the cosine potential.

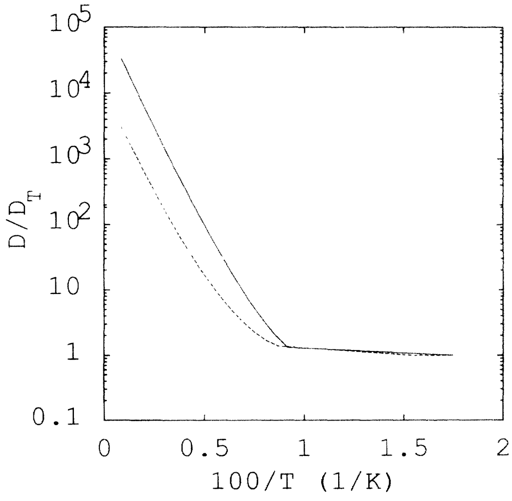

FIG. 2. Diffusion constant D/D_T of H on Ni(100). D_T is the constant value of diffusion at low temperatures. The solid line is for adsorption potential in Eq. (13) and the dashed line for the cosine potential.

to substantial renormalization of the mass of the adatom which could then account for the very weak isotope effects observed for H/Ni(100). The conventional small polaron theory would also predict an activation energy even in the tunneling regime due to lattice relaxation effects in the tunneling process. However, this activated tunneling regime only occurs for $kT > \frac{1}{2}\hbar\omega_D$ with ω_D being the Debye temperature of the substrate ($\hbar\omega_D \sim 300$ K for Ni) [14,15]. The observed quantum tunneling regime lies in a temperature region too low for this to occur. Indeed, even though the lack of isotope effects suggests a strong adatom phonon coupling for this system, the temperature dependence of the observed diffusion constant in the quantum tunneling regime is consistent with zero activation energy [4]. We are now pursuing the generalization of the present work including the coupling to phonons explicitly in the evaluation of the static correlation functions χ_{00} and χ_{11}.

In summary, we have presented a microscopic theory for the diffusion of an adatom on a crystal surface. The results are valid for all temperatures in the high friction limit. In the high temperature regime, the diffusion is found to conform to a thermal activated Arrhenius form, but substantial corrections to the barrier from zero point motion can occur. The diffusion constant crosses over rather sharply to a constant quantum tunneling limit as the temperature is decreased below a crossover temperature determined by the parallel vibrational energy quantum. When applied to H/Ni(100), the theoretical results for the diffusion constant are in excellent agreement with the experimental data.

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