Long Jumps in Surface Diffusion: A Microscopic Derivation of the Jump Frequencies

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Starting from a microscopic Hamiltonian for a particle on the corrugated surface of a solid we derive the master equation for phonon-mediated hopping and friction using the Wannier representation. For a sinusoidal corrugation (in addition to a Morse surface potential) we investigate the role of interband transitions and numerically calculate transition probabilities. We find that long hops beyond nearest neighbor sites are significant, particularly for weakly coupled systems. [S0031-9007(97)05244-7]

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Diffusion of particles on solid surfaces is most often controlled by a hopping mechanism by which the particle resides in well-defined adsorption wells for times much longer than it takes to jump into neighboring sites [1]. This idea goes back at least to Chudley and Elliott [2] who developed a lattice gas model for diffusion by discrete jumps. They suggested that in liquids jumps are not only to nearest neighbor sites but that jumps into more distant sites must also be considered. Recent advances in quasielastic helium scattering on surfaces [3–7] and in field ion microscopy [8] have given ample evidence that on surfaces diffusion of adsorbed particles is not restricted to jumps between nearest neighbor adsorption sites but that for weakly coupled adsorbates jumps to second and even third neighbor sites are non-negligible. This does not come as a total surprise because molecular dynamics simulations—which one may view as numerical experiments—have shown this repeatedly [9–15].

Apart from classical molecular dynamics simulations almost all theoretical approaches to surface diffusion, and also the analysis of experimental data [16], are based on the master equation for a kinetic lattice gas model with *ad hoc* hopping probabilities, and consequent simplifications to the Langevin, Kramers, or Fokker-Planck equations. Several, more or less identical, calculations of the (phonon-mediated) friction coefficient have been published based on a correlation function approach within classical statistical mechanics both for the motion perpendicular [17–19] and parallel to the surface [18–20] (with the exception of Refs. [21–23] where the friction coefficient for the perpendicular motion is derived quantum mechanically together with the Fokker-Planck and Kramers equations). It has also been discussed recently that jump probabilities on surfaces (and as a result friction) are not only due to the coupling of the adsorbate to the phonons of the substrate but also to the electronic degrees of freedom [15,20,24].

In this paper we will sketch a microscopic derivation of the master equation, and thus of a kinetic lattice gas model, for surface diffusion. It is based on a quantum mechanical treatment of the coupled solid-gas system which has been used before to derive the kinetic equations for adsorption and desorption [21–23]. To study surface diffusion we will use the Wannier representation of the wave functions for a periodic system that provide the natural framework for the localization of the particles at lattice sites. This approach has several advantages: (i) Being quantum mechanical, no assumptions need to be made concerning the mass of the diffusing particles and the coupling to the substrate; (ii) we will get explicit expressions of the jump frequencies in terms of microscopic parameters of the coupled adsorbate-substrate system. Numerical results will be presented for one-dimensional motion.

We begin by considering a single particle of mass m on the surface of a solid (lateral interactions at nonzero coverages will be considered in the full account of this work). Its Hamiltonian can be written

$$H_g = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \mathbf{r}^2} + V_s(z,\mathbf{R})\,. \tag{1}$$

Here $\mathbf{r} = (z,\mathbf{R})$ with the z axis perpendicular to the surface and $\mathbf{R}$ a two-dimensional vector in the surface. We assume that the surface potential has translational symmetry along the surface, i.e., $V_s(z,\mathbf{R}+\mathbf{R}_\mathbf{l}) = V_s(z,\mathbf{R})$, where $\mathbf{R}_\mathbf{l} = l_1\mathbf{a}_1 + l_2\mathbf{a}_2$ with l_1 and l_2 integers and $\mathbf{a}_1$ and $\mathbf{a}_2$ lattice vectors in two dimensions spanning a surface unit cell.

Translational symmetry implies that we can write the surface potential as

$$V_s(z,\mathbf{R}) = V_0(z) + \sum_{\mathbf{m}\neq 0} V_\mathbf{m}(z)\exp(i\mathbf{K}_\mathbf{m}\cdot\mathbf{R})\,. \tag{2}$$

The first term is the surface potential of a flat surface and the sum extends over all the Fourier components describing the surface corrugation where $\mathbf{K}_\mathbf{m} = 2\pi(m_1\mathbf{b}_1 + m_2\mathbf{b}_2)$ with m_1 and m_2 integers and $\mathbf{b}_i$ reciprocal lattice vectors such that $\mathbf{a}_i\cdot\mathbf{b}_j = \delta_{ij}$. The z dependence of the higher Fourier components, $V_\mathbf{m}(z)$, introduces some coupling between the eigenstates of $V_0(z)$ (bound states and continuum) and of the Bloch states in the periodic potential along

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the surface. Because of the extended (and periodic) nature of the Bloch states they are not well suited to study localized hopping on the surface. We therefore switch to Wannier functions, constructed from the Bloch functions via a two-dimensional Fourier transform [25]. These functions are orthogonal in the band index and also on different lattice sites, but are not eigenfunctions of the (static) single particle Hamiltonian (1). They are centered around a particular unit cell of the surface with their localization within that cell being the highest for the lowest energy band and becoming progressively more delocalized for higher bands. Because Bloch functions can be multiplied by a phase factor that is an arbitrary function of the wave vector, this phase factor makes the Wannier functions nonunique and can be used to control their localization. This, of course, does not affect jump frequencies, friction, and diffusion coefficients but can be used advantageously in the numerical calculations.

Expanding the particle field operators in terms of Wannier functions we introduce creation and annihilation operators, e.g., $\beta_\nu^\dagger(\mathbf{R}_\mathbf{l}, t)$ creates a particle in band ν at site $\mathbf{R}_\mathbf{l}$ and time t. In terms of these operators the various contributions to the Hamiltonian read

$$H = \sum_{\nu,\mathbf{R}_\mathbf{l},\mathbf{R}'_\mathbf{l}} E_\nu(\mathbf{R}_\mathbf{l} - \mathbf{R}'_\mathbf{l})\beta_\nu^\dagger(\mathbf{R}'_\mathbf{l}, t)\beta_\nu(\mathbf{R}_\mathbf{l}, t) + \sum_J \hbar\omega_J b_J^\dagger b_J + \sum_{\nu,\mathbf{R}_\mathbf{l},\nu',\mathbf{R}'_\mathbf{l},J} \tilde{X}(\nu, \mathbf{R}_\mathbf{l}; \nu', \mathbf{R}'_\mathbf{l}; J)\beta_{\nu'}^\dagger(\mathbf{R}'_\mathbf{l}, t) \times [b_J^\dagger(t) + b_J(t)]\beta_\nu(\mathbf{R}_\mathbf{l}, t), \tag{3}$$

where the energies are given in terms of the Bloch eigenvalues $E_\nu(\mathbf{R}_\mathbf{l} - \mathbf{R}'_\mathbf{l}) = \sum_\mathbf{K} E_{\nu,\mathbf{K}} e^{-i\mathbf{K}\cdot(\mathbf{R}_\mathbf{l} - \mathbf{R}'_\mathbf{l})}$. The substrate degrees of freedom are excited by the operators $b_J^\dagger$ and can be elastic, magnetic, or electronic in origin. In this Letter we will consider only coupling to the phonon bath of the substrate in which case the matrix elements $\tilde{X}$ involve the derivative of the surface potential, taken between Wannier states and can be expressed in terms of matrix elements between Bloch states.

The master equation for phonon-mediated adsorption and desorption has been derived elsewhere [21–23] and we follow the same procedure here to include the motion parallel to the surface. We solve Heisenberg's equation of motion for the creation and annihilation operators of Wannier states to second order in the phonon coupling and get for the occupation probabilities $f_\nu(\mathbf{R}_\mathbf{l}, t) = \langle \beta_\nu^\dagger(\mathbf{R}_\mathbf{l}, t)\beta_\nu(\mathbf{R}_\mathbf{l}, t)\rangle$,

$$\frac{d}{dt} f_\nu(\mathbf{R}_\mathbf{l}, t) = \sum_{\nu',\mathbf{R}'_\mathbf{l}} [W(\nu, \mathbf{R}_\mathbf{l}; \nu', \mathbf{R}'_\mathbf{l}) f_{\nu'}(\mathbf{R}'_\mathbf{l}, t) - W(\nu', \mathbf{R}'_\mathbf{l}; \nu, \mathbf{R}_\mathbf{l}) f_\nu(\mathbf{R}_\mathbf{l}, t)], \tag{4}$$

where the transition probabilities (per unit time) are given by

$$W(\nu', \mathbf{R}'_\mathbf{l}; \nu, \mathbf{R}_\mathbf{l}) = \frac{2\pi}{\hbar} \sum_J |\tilde{X}(\nu, \mathbf{R}_\mathbf{l}; \nu', \mathbf{R}'_\mathbf{l}; J)|^2 \times \{n^{(ph)}(\omega_J)\delta[E_{\nu'}(0) - E_\nu(0) - \hbar\omega_J] + [n^{(ph)}(\omega_J) + 1]\delta[E_\nu(0) - E_{\nu'}(0) - \hbar\omega_J]\}. \tag{5}$$

In deriving the above master equation, we neglected off-diagonal contributions of the kind $\langle \beta_\nu^\dagger(\mathbf{R}', t)\beta_\nu(\mathbf{R}, t)\rangle$ since such contributions decrease exponentially with $|\mathbf{R}'_\mathbf{l} - \mathbf{R}_\mathbf{l}|$. This master equation describes the phonon-mediated transitions between the states of the static Hamiltonian. If, for the sake of a qualitative discussion, we neglect the z dependence in the higher Fourier components, $V_\mathbf{m}(z)$, of the surface potential, then adsorption and desorption are controlled mainly by the transitions in $V_0(z)$ with a cascade of transitions between the bound states predating the final desorption transition into the continuum [23]. If the lowest two eigenstates of $V_0(z)$ are further separated than the height of the surface corrugation then diffusion along the surface is decoupled from the motion perpendicular to it. This is most likely the case for the light noble gases and for closed shell molecules such as N_2 that are physisorbed. However, for heavier particles (and, in particular, those that are chemisorbed) the bound state levels in $V_0(z)$ become close (and a continuum in the classical limit) and the surface corrugation becomes large so that one expects significant coupling between the motion parallel and perpendicular to the surface.

To confine the processes in (4) to surface diffusion only we must restrict the eigenstates to the bound states of the system and consider only transitions between them. A further simplification results if the coupling to the substrate is sufficiently strong so that the adsorbate remains in local equilibrium [23]. We then write $f_\nu(\mathbf{R}_\mathbf{l}, t) = f(\mathbf{R}_\mathbf{l}, t)e^{-E_\nu/k_BT} / \sum_{\nu'} e^{-E_{\nu'}/k_BT}$ and sum the master equation over all states to get

$$\frac{d}{dt} f(\mathbf{R}_\mathbf{l}, t) = \sum_{\mathbf{R}'_\mathbf{l}} [W(\mathbf{R}_\mathbf{l}, \mathbf{R}'_\mathbf{l}) f(\mathbf{R}'_\mathbf{l}, t) - W(\mathbf{R}'_\mathbf{l}, \mathbf{R}_\mathbf{l}) f(\mathbf{R}_\mathbf{l}, t)], \tag{6}$$

where

$$W(\mathbf{R}'_\mathbf{l}, \mathbf{R}_\mathbf{l}) = \sum_{\nu,\nu'} W(\nu', \mathbf{R}'_l; \nu, \mathbf{R}_l) e^{-\beta E_\nu} \Big/ \sum_{\nu''} e^{-\beta E_{\nu''}}. \tag{7}$$

These probabilities do not only describe transitions between nearest neighbor sites but also longer ranged jumps.

Restricted to nearest neighbor jumps this is the master equation for a symmetrical (asymmetrical) one-step process in the absence (presence) of an external field and can be solved by well-known methods [26].

Elsewhere [21–23], it has been shown how to extract analytical forms for the friction coefficient (for the motion perpendicular to the surface) in terms of the microscopic parameters of the coupled adsorbate substrate system, and we will do the same for the motion parallel to the surface in a longer paper. Here we will report only some results on the jump frequencies for single and multiple site hops. To get some explicit results we take for the corrugated potential a simple cosine form, namely, $V_{\|}(\mathbf{R}) = V_L(z)\cos(2\pi x/a) + V_L(z)\cos(2\pi y/b)$. Here, a and b stand for the lattice parameters in the x and y directions, respectively. If $\sigma_{\|}^2 = 2ma^2V_L/\hbar^2 \gg 1$, such a potential has narrow atomiclike bands well below the potential barrier, which widen for energies around the top of the barrier and become free electronlike much above it [25,27]. Hopping involves foremost the transitions between the two bands around the top of the barrier. Assuming that the occupations of the lowest levels are kept in thermal equilibrium by fast transitions we can concentrate on the above two bands. In this Letter we deal with only light physisorbed particles with diffusion barriers so small that a two-band approximation can be employed. In one dimension we then get for the energy spectrum [28] $E^{\pm}(K) = (1/2) * (\varepsilon_1 + \varepsilon_2 \pm \sqrt{(\varepsilon_1 - \varepsilon_2)^2 + V_L^2})$ where $\varepsilon_1 = \hbar^2K^2/2m$ and $\varepsilon_2 = \hbar^2(K - K_0)^2/2m$. If, for simplicity in this Letter, we take the corrugation of the surface potential to be independent of z, then the whole surface potential is separable and there are two bands for the motion parallel to the surface for each (bound state) eigenstate perpendicular to the surface. We then get a set of two coupled master equations with intraband and interband transition probabilities. In the case where the transverse motion to the surface is negligible (when the particle performs a very large number of hops before desorption can occur), only interband transitions contribute. For a semi-infinite continuum, these are given by

$$W(R_l - R_l') = \frac{3\sigma_{\|}^2}{16\pi}\frac{m}{M_s}\left(\frac{\omega_0}{\omega_D}\right)^3 \omega_0 \Gamma(\Delta, R_l - R_l') \times \frac{1}{e^{\Delta/k_BT} - 1}\,\frac{1}{e^{-\Delta/k_BT} + 1}, \tag{8}$$

where $\Delta = \mathcal{N}^{-1}\sum_K[E^+(K) - E^-(K)]$, $\mathcal{N}$ being the total number of sites on the solid surface. Here $\omega_0^2 = 4\pi^2V_L/ma^2$ is the vibrational frequency at the bottom of the corrugated surface potential, and ω_D is an average Debye energy of the solid substrate. Moreover

$$\begin{aligned}\Gamma(\Delta, R_l - R_l') = {} & \frac{\Delta}{V_L}\sum_{\sigma=L,T,T'}\frac{\omega_D^3}{\omega_D^3(\sigma)}\int_0^{\pi} d\theta \int_0^{2\pi} d\theta \sin\theta (e_x^{(\sigma)})^2 \\ & \times \Bigg| \sum_{K=0,2\pi/\mathcal{N}a,\ldots}\frac{1}{N_K}\Bigg\{\sum_{p=\pm}\frac{p[A_K - A_{K+2p\pi/a-\Delta\cos\phi\sin\theta/\hbar c_\sigma}]}{N_{K+2p\pi/a-\Delta\cos\phi\sin\theta/\hbar c_\sigma}} \\ & \qquad + A_K\left[\frac{A_{K-\Delta\cos\phi\sin\theta/\hbar c_\sigma}}{N_{K-\Delta\cos\phi\sin\theta/\hbar c_\sigma}} - \frac{A_{K+4\pi/a-\Delta\cos\phi\sin\theta/\hbar c_\sigma}}{N_{K+4\pi/a-\Delta\cos\phi\sin\theta/\hbar c_\sigma}}\right] \\ & \qquad - \frac{1}{N_{K-4\pi/a-\Delta\cos\phi\sin\theta/\hbar c_\sigma}} + \frac{1}{N_{K-\Delta\cos\phi\sin\theta/\hbar c_\sigma}}\Bigg\} e^{iK(R_l - R_l')}\Bigg|^2 \end{aligned} \tag{9}$$

is a dimensionless quantity with $N_K = \sqrt{1 + A_K^2}$

$$A_K = \sigma_{\|}^{-2}[(Ka)^2 - (Ka - 2\pi)^2] - \sqrt{[(Ka)^2 - (Ka - 2\pi)^2]^2 + \sigma_{\|}^4}, \tag{10}$$

and $e_x^{(L)} = \sin\theta\cos\phi$, $e_x^{(T)} = -\cos\theta\cos\phi$, $e_x^{(T')} = -\sin\phi$ are the x components of the polarization vector.

For low temperature, $k_BT \ll \Delta$, the transition probabilities (8) are of Arrhenius form for a thermally activated process, but non-Arrhenius behavior sets in as the temperature is raised. The dependence of the jump frequencies on the mass ratio, on the Debye frequency $\omega_D(\sigma) = (\frac{6\pi^2\rho_0}{M_s})^{1/3}c_\sigma$, and on the vibrational frequency in the surface potential is analogous to that of the friction coefficient for the motion perpendicular to the surface [21–23]. σ refers to the (surface) phonon mode corresponding to the velocity c_σ, and M_s is the mass of the unit cell of the solid. The (additional) function $\Gamma(\Delta, R_l - R_l')$ incorporates the coupling to the phonon bath. Γ also contains all the information about the energy transfer between the adsorbed particle and the substrate degrees of freedom. The earlier estimates of parallel friction [18–20] essentially assign a constant to this function. Γ also controls the jump length in diffusion with the relative weight of jumps into first or further neighbor sites being controlled by $\sigma_{\|}^2$. For light physisorbed particles $\sigma_{\|}^2$ is of the order of 10–100, a range for which the two-band approximation for the cosine potential is acceptable. For the complete characterization of the system we introduce a second dimensionless parameter, $\alpha = \hbar/mac$, where c is an average phonon velocity.

Numerical values for the relative jump frequencies (with respect to the jumps to nearest neighbor sites) are shown

TABLE I. Numerical values for relative jump frequencies.

$\sigma_\parallel^2 \to$ $\alpha \to$	1 0.1	10 0.1	50 0.	50 0.01	50 0.001	4000 0.03	MD
0 → 1	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.000
0 → 2	0.6899	0.0870	0.1333	0.0406	0.0388	0.250	0.381
0 → 3	0.4615	0.0178	0.0552	0.0077	0.0068	0.11	0.191
0 → 4	0.2820	0.0014	0.0302	0.0023	0.0018	0.062	0.062
0 → 5	0.1582	0.0003	0.0191	0.0009	0.0006	0.040	0.046

in Table I for several situations. It is clear that the smaller the $\sigma_\parallel^2$ the more likely are longer jumps, the reason being that then the coupling to the phonon bath via the derivative of the surface potential becomes weaker and friction is less efficient. We point out that the friction coefficient can be obtained from the jump frequencies as their second moments. As a function of α the jump frequencies first increase reaching a maximum and then decrease. We found numerically that for large α the jump frequencies decay like a Lorentzian over a considerable distance range. For very large distances they must eventually decay faster to guarantee a finite diffusion coefficient. Indeed, for small α a faster decay than Lorentzian is observed even for the smallest jump distances. For the last two columns in Table I we have chosen parameters such that the jump distribution obtained by Ellis and Toennies [15] [through molecular dynamics (MD) simulations for Na/Cu] is reproduced.

In this paper we have derived the master equation for adsorption/desorption and diffusion and calculated from first principles the frequencies of long jumps. We confirm that jumps to further than first neighbors are unavoidable, particularly in weakly coupled systems. What remains to be done is (i) to improve the treatment of the surface potential beyond a two-band approximation including the coupling between the motion parallel and perpendicular to the surface, (ii) to include lateral interactions in the adsorbate and study finite coverage effects. Both problems find natural solutions in the Wannier function representation. (iii) It is straightforward to derive a Kramers equation from the master equation and to get microscopic expressions for friction and diffusion coefficients. (iv) The Wannier representation is also a natural framework to deal with the interface between incommensurate lattices.

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