

Quantum diffusion of adatoms on a surface

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We use the small-polaron model to study the mobility for the quantum diffusion of light adatoms on a surface, using a canonical transformation. The Hamiltonian and current operator are separated into two parts. One of them represents quasiparticles with renormalized temperature-dependent effective mass, leading to a band mobility channel while the other contributes to hopping conductivity. The band mobility is studied in this paper with the Mori memory-function projection operator.

The diffusion of light atoms in solids has attracted much theoretical and experimental attention. Recent progress in surface physics has brought the attention to the diffusion of light adatoms on solid surfaces.^{1,2} This problem is of great importance both for technological reasons as well as for the basic underlying physics. A microscopic understanding of surface mobility is crucial for further theoretical progress in such diverse processes as crystal growth, surface reaction, surface phase transition, and catalysis.

For hydrogen atoms diffusing on metallic surfaces such as W(100), a transition from a quantum tunneling regime at low temperatures with weak temperature dependence of diffusion constant to a classical thermal-activation-over-the-barrier motion has clearly been observed.³ The current viewpoint on the low-temperature diffusion of light adatoms is that they proceed via phonon-assisted tunneling.⁴ This problem bears many similarities to that of the electronic polaron mobility.⁵ The difference lies mainly in the extremely narrow bandwidth associated with the relatively large mass of adatoms. In the study of electronic polaron mobility, the memory-function-projection-operator technique has been applied in the past to obtain the resistivity of a two-dimensional electron gas under strong magnetic field⁶ and the transport relaxation time due to interaction with two-dimensional (2D) and 3D LA phonons.⁷ In this paper we show that the same formalism allows us to study the mobility of adatoms on surfaces.

We start with a Fröhlich-like Hamiltonian describing a collection of noninteracting adatoms interacting with lattice vibrations of the substrate:

$$H = \sum_{i,\delta} t_{i,i+\delta} c_{i+\delta}^\dagger c_i + \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}} a_{\mathbf{q}}^\dagger a_{\mathbf{q}} + \sum_{j,\mathbf{q}} c_j^\dagger c_j e^{i\mathbf{q}\cdot\mathbf{R}_j} M_{\mathbf{q}} (a_{\mathbf{q}} + a_{-\mathbf{q}}^\dagger), \quad (1)$$

where t_{ij} is the adatom transfer-matrix element from site

i to site j and c_i (c_i^\dagger) is the destruction (creation) operator for the adatom at site i . The operators $a_{\mathbf{q}}$ and $a_{\mathbf{q}}^\dagger$ refer to phonons of wave vector \mathbf{q} and frequency $\omega_{\mathbf{q}}$ coupled to the adatoms through the potential $M_{\mathbf{q}}$.

We assume that there is one Wannier state per site. This is an assumption valid at temperatures $k_B T \ll \Delta$, where Δ is the diffusion barrier which has the typical magnitude of 1000–2000 K for surface diffusion.³ We also need to decide on an algebra for the Wannier operators. There exists an ambiguity as to what statistic is appropriate for adsorbed atoms such as hydrogen. In this paper we shall assign Fermi statistics. Even for a monolayer of hydrogen adatoms, the Fermi energy is only about 40 K. Thus the experimental situation is usually in the nondegenerate regime. The distribution function for the adatoms then reduces to a Maxwell-Boltzmann form and the fermion or boson character of adatoms becomes irrelevant.

A standard canonical transformation brings the Hamiltonian into the form⁵

$$H = \sum_{i,j} t_{i,i+\delta} c_{i+\delta}^\dagger c_i X_{i+\delta}^\dagger X_i + \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}} a_{\mathbf{q}}^\dagger a_{\mathbf{q}} - \sum_j n_j \Delta, \quad (2)$$

where

$$\Delta = \sum_{\mathbf{q}} \frac{|M_{\mathbf{q}}|^2}{\omega_{\mathbf{q}}} \quad (3)$$

and X_i is defined by

$$X_i = \exp \left[\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{R}_i} \frac{M_{\mathbf{q}}}{\omega_{\mathbf{q}}} (a_{\mathbf{q}} - a_{\mathbf{q}}^\dagger) \right]. \quad (4)$$

We separate the interaction term of the Hamiltonian into two parts:

$$H_0 = \sum_{i,\delta} t_{i,i+\delta} c_{i+\delta}^\dagger c_i \langle X_{i+\delta}^\dagger X_i \rangle = \sum_{i,\delta} \tilde{t}_{i,i+\delta} c_{i+\delta}^\dagger c_i, \quad (5)$$

and

$$H_1 = \sum_{i,\delta} t_{i,i+\delta} c_{i+\delta}^\dagger c_i [X_{i+\delta}^\dagger X_i - \langle X_{i+\delta}^\dagger X_i \rangle], \quad (6)$$

where $\langle \dots \rangle$ refers to thermodynamic average. The current can be separated in a similar way into J_0 and J_1 :

$$J_0 = \frac{i}{\hbar} \sum_{i,\delta} t_{i,i+\delta} \delta c_{i+\delta}^\dagger c_i \langle X_{i+\delta}^\dagger X_i \rangle, \quad (7)$$

$$J_1 = \frac{i}{\hbar} \sum_{i,\delta} t_{i,i+\delta} \delta c_{i+\delta}^\dagger c_i (X_{i+\delta}^\dagger X_i - \langle X_{i+\delta}^\dagger X_i \rangle). \quad (8)$$

Fourier transforming into the \mathbf{k} space, we have

$$H_0 = \sum_{\mathbf{k}} \tilde{\epsilon}_{\mathbf{k}} c_{\mathbf{k}}^\dagger c_{\mathbf{k}}, \quad (9)$$

$$H_1 = \sum_{\mathbf{k},\mathbf{q}} [F(\mathbf{k},\mathbf{q}) - \tilde{\epsilon}_{\mathbf{k}} \delta_{\mathbf{q},0}] c_{\mathbf{k}+\mathbf{q}}^\dagger c_{\mathbf{k}}, \quad (10)$$

where

$$F(\mathbf{k},\mathbf{q}) = \frac{1}{N} \sum_{i,\delta} t_{i,i+\delta} e^{-i\mathbf{q}\cdot\mathbf{R}_i} e^{-i(\mathbf{k}+\mathbf{q})\cdot\delta} X_{i+\delta}^\dagger X_i \quad (11)$$

and

$$\langle F(\mathbf{k},\mathbf{q}) \rangle = \delta_{\mathbf{q},0} \tilde{\epsilon}_{\mathbf{k}}. \quad (12)$$

In Eq. (9) we have introduced the renormalized energy

$$\tilde{\epsilon}_{\mathbf{k}} = \sum_{\delta} e^{-i\mathbf{k}\cdot\delta} t_{i,i+\delta} \langle X_{i+\delta}^\dagger X_i \rangle = \sum_{\delta} e^{-i\mathbf{k}\cdot\delta} \tilde{t}_{i,i+\delta}, \quad (13)$$

where

$$\tilde{t}_{i,i+\delta} = t_{i,i+\delta} \exp \left[- \sum_{\mathbf{q}} \left[\frac{|M_{\mathbf{q}}|}{\omega_{\mathbf{q}}} \right]^2 [1 - \cos(\mathbf{q}\cdot\delta)] (2\langle n_{\mathbf{q}} \rangle + 1) \right]. \quad (14)$$

We observe, from Eqs. (5)–(13), that now $c_{\mathbf{k}}$ and $c_{\mathbf{k}}^\dagger$ represent noninteracting quasiparticles with renormalized energy $\tilde{\epsilon}_{\mathbf{k}}$. The current operator terms are then expressed as

$$J_0 = - \frac{1}{\hbar} \sum_{\mathbf{k}} \frac{\partial \tilde{\epsilon}_{\mathbf{k}}}{\partial \mathbf{k}} c_{\mathbf{k}}^\dagger c_{\mathbf{k}}, \quad (15)$$

$$J_1 = - \frac{1}{\hbar} \sum_{\mathbf{k},\mathbf{q}} \left[\frac{\partial}{\partial \mathbf{k}} [F(\mathbf{k},\mathbf{q}) - \delta_{\mathbf{q},0} \tilde{\epsilon}_{\mathbf{k}}] \right] c_{\mathbf{k}+\mathbf{q}}^\dagger c_{\mathbf{k}}. \quad (16)$$

The above formulas are general and valid for arbitrary lattice structure. We now specialize to the case of a square lattice. In this case the mobility is just a scalar. The frequency-dependent mobility can be expressed in terms of the current-current correlation function,⁶

$$\mu(z) = \beta C(z), \quad (17)$$

where

$$C(z) = \langle J_x(t) | J_x(0) \rangle_z \quad (18)$$

while the diffusion constant is just $D = \lim_{z \rightarrow 0} [C(z)/N]$ for a noninteracting system.

The contribution due to the term J_1 has been treated perturbatively by Mahan⁵ in the context of electronic transport leading to the hopping channel, which is important only at high temperatures. At low temperature, however, the “band-conduction” channel which comes out from the contribution of J_0 is dominant. Here we study the band conduction in detail using the memory-function–projection-operator method. Then $C(z)$ becomes^{6,7}

$$C(z) = \frac{i\beta^{-1}\chi}{z + M(z)}, \quad (19)$$

where $\chi = N/m^*$, m^* being the effective mass $m^* = \partial^2 \tilde{\epsilon}_{\mathbf{k}} / \partial k_x^2 |_{k=0}$. The diffusion constant then takes the familiar form $D = kT/m^*\eta$, where $\eta = (-i)M(0)$ is the microscopic friction. In transport theory, η is just the inverse of the transport relaxation time, i.e., $\eta = \tau^{-1}$. As can be seen from Eqs. (13) and (14), m^* is now temperature dependent through the temperature dependence of the hopping matrix elements $\tilde{t}_{i,i+\delta}$. The bandwidth narrows and m^* increases as temperature is increased. $M(z)$ in (19) is the memory function calculated through the force-force propagator:

$$\Pi(\tau) = - \langle \mathcal{T}_\tau [j_x^{0\dagger}(\tau) j_x^0(0)] \rangle, \quad (20)$$

where $\dot{J} = -i[J, H]$. Then,

$$M(z) = \frac{1}{z\chi} [\Pi(z) - \Pi(0)]. \quad (21)$$

Since

$$j_x^0 = j_x^{00} + j_x^{01} = -i[J_x^0, H_0] - i[J_x^0, H_1] \quad (22)$$

and $j_x^{00} = 0$, then

$$\Pi(\tau) = - \langle \mathcal{T}_\tau [j_x^{01\dagger}(\tau) j_x^{01}(0)] \rangle. \quad (23)$$

In order to obtain the propagator above we used the conventional decoupling

$$\langle \mathcal{T}_\tau [F^\dagger(\mathbf{k},\mathbf{q},\tau) F(\mathbf{k}',\mathbf{q}',0) c_{\mathbf{k}}^\dagger(\tau) c_{\mathbf{k}+\mathbf{q}}(\tau) c_{\mathbf{k}'+\mathbf{q}'}^\dagger c_{\mathbf{k}'}] \rangle \simeq \langle \mathcal{T}_\tau [F^\dagger(\mathbf{k},\mathbf{q},\tau) F(\mathbf{k}',\mathbf{q}',0)] \rangle \langle \mathcal{T}_\tau [c_{\mathbf{k}}^\dagger(\tau) c_{\mathbf{k}+\mathbf{q}}(\tau) c_{\mathbf{k}'+\mathbf{q}'}^\dagger c_{\mathbf{k}'}] \rangle. \quad (24)$$

Fourier transforming Eq. (23) and performing Matsubara's frequency summation we obtain in the lowest order of perturbation

$$\begin{aligned} \Pi(i\omega) = & \frac{-2}{\hbar^2} \sum_{\mathbf{k}, \mathbf{q}} \left[\frac{\partial \bar{\epsilon}_{\mathbf{k}+\mathbf{q}}}{\partial(\mathbf{k}+\mathbf{q})} - \frac{\partial \bar{\epsilon}_{\mathbf{k}}}{\partial \mathbf{k}} \right]_x^2 \\ & \times \frac{1}{\beta} \sum_{ip} \frac{f(\bar{\epsilon}_{\mathbf{k}}) - f(\bar{\epsilon}_{\mathbf{k}+\mathbf{q}})}{i\omega - ip + \bar{\epsilon}_{\mathbf{k}} - \bar{\epsilon}_{\mathbf{k}+\mathbf{q}}} D(\mathbf{k}, \mathbf{q}, ip), \end{aligned} \quad (25)$$

where

$$D(\mathbf{k}, \mathbf{q}; \tau) = -\langle T_\tau [F^\dagger(\mathbf{k}, \mathbf{q}, \tau) F(\mathbf{k}, \mathbf{q}, 0)] \rangle \quad (26)$$

and $f(\bar{\epsilon}_{\mathbf{k}})$ is the Fermi-Dirac distribution function and $\beta \equiv (k_B T)^{-1}$.

Then, after a lengthy calculation, we obtain for the friction the following expression:

$$\eta = (-i)M(0) = \frac{2\beta}{\chi m^2} \sum_q |M_q|^2 q^2 \frac{e^{\beta\omega_q}}{(e^{\beta\omega_q} - 1)^2} \tilde{S}_2(q, \omega_q), \quad (27)$$

where $\tilde{S}_2(q, \omega_q)$ is the imaginary part of the dynamic structure factor of the noninteracting-quasiparticle system:

$$\tilde{S}_2(q, \omega) = 2\pi \sum_{\mathbf{k}} \delta(\bar{\epsilon}_{\mathbf{k}} - \bar{\epsilon}_{\mathbf{k}+\mathbf{q}} + \omega) [f(\bar{\epsilon}_{\mathbf{k}}) - f(\bar{\epsilon}_{\mathbf{k}+\mathbf{q}})]. \quad (28)$$

We treat the interaction potential $M(q)$ in the deformation-potential approximation and consider the interaction of the adatom with longitudinal surface phonons. First we consider the interaction with a low-frequency branch of surface phonon with dispersion relation $\omega_q = c_s q$.

A realistic limit for studying surface diffusion is the regime $E_F \ll k_B T \ll k_B \theta_D$, which is the case for finite H concentration near room temperature. In that range we can take the Maxwell-Boltzmann distribution for $f(\epsilon)$ instead of the Fermi-Dirac one. Then, the imaginary part of the dynamic structure factor becomes

$$\begin{aligned} \tilde{S}_2(q, \omega) = & \frac{n}{\hbar} \left[\frac{\beta \pi m^*}{2} \right]^{1/2} \frac{1}{q} \{ \exp[-\beta(\bar{\epsilon}_q - \omega)^2 / 4\bar{\epsilon}_q] \\ & - \exp[-\beta(\bar{\epsilon}_q + \omega)^2 / 4\bar{\epsilon}_q] \}, \end{aligned} \quad (29)$$

where $\bar{\epsilon}_q = \hbar^2 q^2 / 2m^*$. Bringing this result into Eq. (25), we obtain

$$\eta = \frac{12\Xi_d^2 \sqrt{2}}{\hbar^3 \sqrt{\pi} N' m_i m^2 c_s^5} m^{*3/2} (k_B T)^{5/2} \exp \left[-\frac{m^* c_s^2}{2k_B T} \right]. \quad (30)$$

In the above equation we have substituted the expression of $|M(q)|^2$ by

$$|M(q)|^2 = \frac{\hbar q^2 \Xi_d^2}{2m_i N' \omega_q A}, \quad (31)$$

where A is the area of the sample, Ξ_d is the deformation constant, m_i is the lattice ion mass, N' is the number of cells per unit area, and n is the number of adatoms per unit area.

Next, we consider the interaction with a high-frequency branch of surface phonon with nonzero frequency at $q=0$. We now assume the dispersion relation has the form $\omega_q = \omega_0 + cq^2$. The finite frequency ω_0 at $q=0$ comes from the influence of the underlying substrate. Again, we consider the regime $E_f \ll k_B T \ll k_B \theta_D$. Then from (27) and (28), we obtain the following expression for the friction:

$$\begin{aligned} \eta \simeq & \frac{12\Xi_d^2 m^{*4}}{m^2 N' m_i \hbar^4 \omega_0} (k_B T) \\ & \times \exp(-cm^* \omega_0 / k_B T) \exp(-3\beta \hbar \omega_0 / 4), \end{aligned} \quad (32)$$

where we have assumed $m^*/c\hbar \ll 1$. The interesting feature here is that for a substrate undergoing either an intrinsic or an adsorbate-induced structural transition such as H/W(110),⁸ the phonon frequency ω_0 can have a strong temperature dependence near the transition region due to the soft mode effect. In this case, the friction η and hence the diffusion constant would have anomalous temperature dependence near the transition region.

For the sake of completeness, we consider here also the extreme low temperature and high concentration limit such that $k_B T \ll E_F$. This case is somewhat unrealistic in view of our negligence of H-H interaction and uncertainty in the statistics of the adsorbate as mentioned earlier. Here we consider only the interaction with the low-frequency-branch surface phonon, since the contribution of the high-frequency-branch in this limit is negligible. In this case the friction turns out to be

$$\eta \simeq \frac{E_F^{-1/2} \Xi_d^2 \sqrt{2}}{8\pi^2 \hbar^5 m^2 m_i c_s^5 n N'} (k_B \theta_D)^4 m^{*5/2} \left[\frac{T}{\theta_D} \right]^4 J_4 \left[\frac{\theta_D}{T} \right], \quad (33)$$

where $J_n(x)$ is the Debye integral

$$J_n(y) = \int_0^y dx x^n \frac{e^x}{(e^x - 1)^2}. \quad (34)$$

For $n=4$ we have

$$\lim_{y \rightarrow \infty} J_4(y) = \frac{4\pi^4}{15}. \quad (35)$$

So, we obtain a result similar to the two-dimensional electron gas interacting with 2D longitudinal acoustic phonons.⁷ We note, however, that this result, unlike the other limit $E_f \ll k_B T \ll \hbar \omega_D$ is dependent upon the assumption of Fermi statistics for the adatom. It is unclear at the moment whether this is an appropriate description for the H adatoms.

Finally we estimate the magnitude of the diffusion constant evaluated above. For this purpose, we concentrate only on expression (32) for η since it is the most appropriate one for making contact with experiment. The value of the parameters appearing in (32) are chosen as

$\omega_0 = 10^{13} \text{ sec}^{-1}$, $T = 100 \text{ K}$, $N' = a^{-2}$ with $a = 3 \text{ \AA}$, $m_i = 184m_p$ (where m_p is the proton mass). The deformation potential Ξd is taken from bulk studies⁹ to be between 1 and 10 eV. The band mass m^* for the H adatom is estimated by calculating the tunneling probability between neighboring sites using the empirically observed diffusion barrier of approximately 0.2 eV.¹⁰ This yields a value for m^*/m between 5 and 10. This choice of parameters yields a value for the diffusion constant between 10^{-11} and $10^{-14} \text{ cm}^2/\text{sec}$ at the temperature 100 K. This covers nicely the range of observed values of the diffusion constant at this temperature for systems such as H/W(110).³ We must note, however, that at lower temperatures the phonon contribution to the friction would be negligible compared with that due to impurity scattering, leading to a temperature-independent diffusion con-

stant.

In conclusion, we have studied the band mobility of a hydrogen atom interacting with longitudinal surface phonon of the substrate. The temperature dependence of the mobility comes both from the phonon occupation factor and the renormalization of the effective band mass of the adatom. We also predict that near a surface structural phase transition the friction, and hence the diffusion constant of the adatom, can acquire an anomalous temperature dependence.

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¹*Hydrogen in Metals. I—Basic Properties*, Vol. 28 of *Topics in Applied Physics*, edited by G. Alefeld and J. Völkl (Springer, Berlin, 1978).

²*Hydrogen in Metals. II—Applications Oriented Properties*, Vol. 29 of *Applied Physics* edited by G. Alefeld and J. Völkl (Springer, Berlin, 1978).

³R. DiFoggio and R. Gomer, *Phys. Rev. Lett.* **44**, 258 (1980); *Phys. Rev. B* **25**, 3490 (1982).

⁴M. D. Miller, *Surf. Sci.* **127**, 383 (1983); C. Aslangul, N. Potier, and D. Saint James, *Phys. Lett.* **111A**, 175 (1985).

⁵G. D. Mahan, *Many-Particle Physics* (Plenum, New York, 1981).

⁶S. C. Ying and I. C. da Cunha Lima, *J. Phys. (Paris) Colloq.* **45**, C5-91 (1984); I. C. da Cunha Lima and S. C. Ying, *J. Phys. C* **18**, 2887 (1985).

⁷C. E. Leal, I. C. da Cunha Lima, A. Troper, and S. Das Sarma, *Phys. Rev. B* **35**, 4095 (1986).

⁸J. W. Chung, S. C. Ying, and P. J. Estrup, *Phys. Rev. Lett.* **56**, 749 (1987).

⁹F. Kawaji, *J. Phys. Soc. Jpn.* **27**, 906 (1969); J. P. Kothaus, *Surf. Sci.* **58**, 199 (1976).

¹⁰E. Seebauer, A. C. F. Kong, and L. D. Schmidt, *J. Chem. Phys.* **88**, 6597 (1988).