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Sticking Coefficient of Atoms on Solid Surfaces at Low Temperatures

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It is shown that because of a polarization effect the sticking coefficient of atoms on surfaces remains finite down to much lower temperatures than has hitherto been supposed on the basis of the Born approximation to the sticking process.

This Letter addresses a long-standing puzzle in the interpretation of data on the sticking coefficient, or sticking probability, of atoms on solid surfaces at low temperatures (T). Computer calculations based on classical lattice dynamics[1] predict, and experimental results indicate, coefficients approaching unity as $T\to 0$. However, a quantum mechanical calculation, based on the distorted-wave Born approximation (DWBA) to the capture process,[2] gives a coefficient which tends to zero as $T\to 0$. A similar situation occurs in the case of the of the thermal accommodation coefficient (α) as pointed out by Goodman, whose classical theory[3,4] is in accord with the experimental fact that $\alpha\to 1$ as $T\to 0$, while the quantum theory based on DWBA[5] predicts $\alpha\to 0$ as $T\to 0$. The smallness of these coefficients in quantum theory may be traced to the prevalent use of *rigid* adsorption wells for the adatom-surface interaction. The adatom wave function goes to zero on the barrier side of the adsorption well and, at long wavelengths, cannot build up appreciable amplitude in or near the well. The matrix elements entering the DWBA are confined to this region and are thus very small for low incident energies. The point of this Letter is that the usual distorted wave does not sufficiently account for the nonstatic nature of the actual well. It is necessary to take into account nonperturbatively the polarization response of the surface to the adatom. We have accounted for a large part of this response by constructing polaron-type variational states, using the Tomonaga approximation of uncorrelated virtual phonons.[6] Within such a set of basis states, the adatom becomes a quasiparticle of greatly enhanced effective mass (m^*) presumably due to the large inertia of the accompanying lattice distortion. The reason for the failure of the DWBA and for the success of a classical or semiclassical calculation is thus clear. As shown below, m^* is position dependent, being large and sensibly constant over the well and decreasing rapidly to the bare mass (m) outside. The wave function in the well still begins at zero on the barrier side but rises with a slope m^*/m times greater.[7] An increase in the density of low-energy resonance levels by $(m^*/m)^{1/2}$ also increases penetration.

Our approach begins with the commonly used quasi-one-dimensional[8] Hamiltonian for the adatom-surface system:

$$H=\frac{P^2}{2m}+V(z)+\sum_q \hbar\omega_q a_q^\dagger a_q+\sum_q \gamma_q(a_q+a_q^\dagger)V'(z), \tag{1}$$

where V is the interaction potential between the adatom and a surface atom; a_q and $a_q^\dagger$ are the annihi-

lation and creation operators for a phonon of frequency ω_q; $\gamma_q = (\hbar/2MN\omega_q)^{1/2}$, M is the mass of a host atom, m is the mass of the adatom, N is the number of atoms in the solid, and $V'(z) = dV/dz$. No qualitative modification of these results comes from retaining in H the V'' terms discussed by Caroli, Roulet, and Saint-James.[9]

As suitable basis states of (1) consider the states

$$|\psi\rangle = \varphi(z)e^{iS(z)}|\mathrm{vac}\rangle,$$

where

$$iS = \sum_q [s_q(z)a_q - s_q^*(z)a_q^\dagger]$$

and $|\mathrm{vac}\rangle$ is the phonon vacuum. These states make $\langle\psi|H|\psi\rangle$ stationary if s_q and φ satisfy

$$\frac{\hbar^2}{2m}s_q'' + \frac{\hbar^2}{2m}\left(\frac{2\varphi^{*\prime}}{\varphi^*} + \mathfrak{S}\right)s_q' - \left[\hbar\omega_q + \frac{\hbar^2}{4m}\left(\frac{\varphi^{*\prime}}{\varphi^*} - \frac{\varphi'}{\varphi}\right)\mathfrak{S} + \frac{\hbar^2}{4m}\mathfrak{S}'\right]s_q = \gamma_q V', \tag{2}$$

and

$$\left(\frac{P^2}{2m} + \tilde{V}\right)\varphi = E\varphi, \tag{3}$$

where

$$\mathfrak{S} = \sum_q (s_q^{*\prime}s_q - s_q^* s_q'),$$

and

$$\tilde{V} = V + \sum_q \left[\gamma_q V'(s_q + s_q^*) + \hbar\omega_q|s_q|^2 + \frac{\hbar^2}{2m}|s_q'|^2\right] - \frac{\hbar^2}{8m}\mathfrak{S}^2.$$

Using the basis set $|\Psi\rangle$ for H amounts to using the basis set $\varphi(z)|\mathrm{vac}\rangle$ for $\tilde{H} = e^{-iS}He^{iS}$. $\tilde{H}$ contains two kinds of terms linear in a_q and $a_q^\dagger$: terms proportional to V'' which are discarded, and terms proportional to momentum p. These latter terms may be eliminated by a canonical transformation:

$$T = \sum_q [(\sigma_q, p)_+ a_q + (\sigma_q^*, p)_+ a_q^\dagger]$$

with $(A, B)_+ = AB + BA$,

$$\sigma_q = s_q'/[2m\omega_q(1+\Gamma)],$$

where

$$\Gamma = (2\hbar/m)\sum_q |s_q'|^2/\omega_q.$$

Then the transformed Hamiltonian takes the form

$$\tilde{\tilde{H}} = e^{-iT}\tilde{H}e^{iT} = \frac{1}{2m^*}p^2 - \frac{i\hbar}{2}\frac{\partial}{\partial z}\left(\frac{1}{m^*}\right)p + \mathfrak{V}, \tag{4}$$

where

$$m^* = m(1+\Gamma), \quad \mathfrak{V} = \tilde{V} + V_1 + V_2,$$

with V_1 a term linear in a_q and $a_q^\dagger$ but essentially proportional to V'', and V_2 consisting of multiphonon terms. This effective potential will be discussed in a forthcoming paper, including a damping effect due to V_1. It is easily verified that in the usual polaron case of a homogeneous medium,[10] the above yields the results of Lee, Low, and Pines[6] exactly. For motion parallel to the surface, there is also a mass enhancement but it is much smaller due to the translational symmetry.

To evaluate the quasiparticle mass m^* in an actual surface situation an important point must be noted. For a static potential high enough to give total reflection, the most obvious choice for the particle wave function φ would have nodes. But, in the presence of coupling to phonons, the probability for a particle to be at z with either 0, 1, 2, etc., phonons in the field can never be zero. This feature is

possessed by polaron-type solutions which are superpositions of incident and reflected basis states, $\varphi_- e^{iS_-}|\text{vac}\rangle + R\varphi_+ e^{iS_+}|\text{vac}\rangle$, rather than $(\varphi_- + R\varphi_+)e^{iS}|\text{vac}\rangle$. For example, in the standard case of the static Morse potential, the positive-energy solutions are Whittaker functions which can be written as sums of confluent hypergeometric functions $M_\pm(z)$ having $e^{\pm ikz}$ asymptotic forms ($z \to \infty$). Our corresponding polaron-type solution would be $\tilde{M}_- e^{iS_-}|\text{vac}\rangle + R\tilde{M}_+ e^{iS_+}|\text{vac}\rangle$, where $\tilde{M}_\pm$ are self-consistent versions of $M_\pm$. Because the phases of the two terms differ, this wave function possesses no nodes. This is an essential feature of a "squashy" as distinct from a static potential.

We have considered two model potentials which may be solved analytically. One is a simple barrier: $V(z<0) = V_0$, $V(z>0) = 0$, with $V_0 \gg \hbar\omega_D$, the maximum phonon energy. For low incident energy,

$$\Gamma(z>0) = \frac{9mV_0}{4m\hbar\omega_D}\left\{\left(\frac{z_0}{z}\right)^4 - \exp\left(\frac{-2z}{z_0}\right)\left[\left(\frac{z_0}{z}\right)^4 + 2\left(\frac{z_0}{z}\right)^3 + 2\left(\frac{z_0}{z}\right)^2 + \left(\frac{4z_0}{3z}\right)\right]\right\},$$

$$\Gamma(z<0) = \frac{6m}{M}\left\{-\left(\frac{z_1}{z}\right) + \exp\left(\frac{z}{z_1}\right)\left[\left(\frac{z_1}{z}\right)^3 - \left(\frac{z_1}{z}\right)^2 + \left(\frac{z_1}{2z}\right)\right]\right\},$$

where $z_0 = (\hbar/2m\omega_D)^{1/2}$ and $z_1 = (V_0/2m\omega_D^2)^{1/2}$. The other model is a barrier plus well, as shown in Fig. 1, along with its $\Gamma(z)$ function for low incident energy and V_0, $V_1 \gg \hbar\omega_D$. The enhancement outside declines as in the first case, but over the well it is constant and has the following range of values depending on well width a. For $e^{i\bar{k}a} = 1$, where $\bar{k} = (2mV_1)^{1/2}\hbar$,

$$\Gamma_{\text{well}} = (3mV_0^2/M\hbar^2\omega_D^2)(1 + 4V_0/V_1),$$

and for $e^{i\bar{k}a} = i$,

$$\Gamma_{\text{well}} = 3mV_0V_1/M\hbar^2\omega_D^2;$$

other widths give results intermediate to these.

A classical version of this effect can be obtained from the equations of motion of a_q and z based on (1). Solving the coupled equations in the manner of, for example, Kartheuser[11] gives a generalized Langevin equation:

$$m\ddot{z} = -V'(z) + V''(z)\int V'(z(t-\tau))\kappa(\tau)d\tau,$$

where

$$\kappa(\tau) = (1/MN)\textstyle\sum_q \sin\omega_q\tau/\omega_q.$$

For small $\dot{z}$ and $\ddot{z}$, keeping only the lowest three moments of $\kappa(\tau)$ gives

$$m^*\ddot{z} = -\tilde{V}'_{\text{class}} - \eta\dot{z},$$

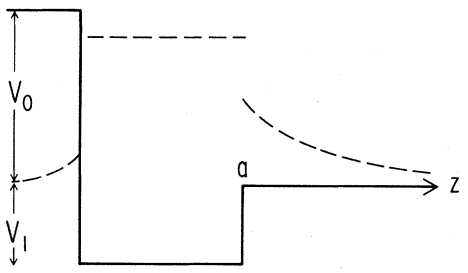

FIG. 1. The model potential (solid line) used in calculating the mass enhancement function $\Gamma(z)$ (dashed line).

where

$$\tilde{V}'_{\text{class}} = V'(1 - 3V''/M\omega_D^2),$$

$$\eta = 3\pi(V'')^2/2M\omega_D^3, \quad m^* = m(1 + \Gamma_{\text{class}}),$$

and

$$\Gamma_{\text{class}} = (V'')^2(mMN)^{-1}\textstyle\sum_q \omega_q^{-4}.$$

η is the classical friction that in a quantum calculation must be obtained from the V_1 part of $\mathcal{V}$ in (4). Observe that Γ_{class}, essentially the second moment of $\kappa(\tau)$, is divergent (for acoustic phonons) and thus invalidates a description local in time. Γ_{class} is also the value that one would calculate above if one were to neglect terms of order $\hbar^2$ in (2). These terms are of quantum origin and tend to permit a description local in time [as would a classical theory with phonons of finite lifetime, for which all moments of $\kappa(\tau)$ are finite].

We believe that the heavy mass for the quasiparticle as calculated above for the positive-energy states does not preclude its behaving with its ordinary mass in collective modes like phonons, where the particle is bound in periodic motion. States of the form $\varphi e^{iS}|\text{vac}\rangle$ cannot be expected to approximate the bound states. An exact calculation for a quadratic interaction potential yields a mode (discrete if m is small, resonant if m is large) with an increased frequency (corresponding to a diminished mass). A similarly exact calculation for the inverted quadratic potential yields an instability with a decreased growth constant (increased effective mass). The expression for the mass increase in the latter case is approximately the same as that obtained from the variational procedure.

We conclude by noting that granted a quasiclassical motion of the adatom, the low-T experi-

mental results can be fitted excellently by solving

$$m^*\ddot{z} = -V'(z) - \eta\dot{z},$$

with $V(z<0) = \frac{1}{2}K(z+a)^2 - \frac{1}{2}Ka^2$, $V(z>0) = 0$, and noting the lowest velocity of incidence which permits escape after one passage. The resulting sticking coefficient takes the universal form

$$s = \mathrm{erf}(T_c/T)^{1/2},$$

where

$$T_c = 2\pi a^2 \eta K^{1/2}/k_B m^{1/2},$$

and k_B is Boltzmann's constant, and erf is the error function. The model gives results that simulate closely the computer results utilized by Goodman in proposing a formula for $\alpha(T)$.[12]

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Low-Temperature Thermal Conductivity of Amorphous Germanium

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The thermal conductivtiy k of a-Ge films has been measured between 0.4 and 10 K. The temperature dependence of k shows that heat conduction by phonons is limited by some intrinsic scattering mechanism in addition to boundary scattering. Evidence is presented that these scatterers are localized low-energy excitations which are common in glasses.

The thermal properties of amorphous dielectrics show a distinct temperature dependence below 1 K. As discovered by Zeller and Pohl,[1] the specific heat varies as $C \sim T$ and the thermal conductivity k is roughly proportional to T^2, whereas in crystalline dielectrics both quantities vary as T^3. From these anomalies in the thermal —and similar ones in the acoustic[2]—properties, one infers the existence of localized low-energy excitations (LEE) from which phonons are scattered. However, the microscopic nature of these excitations is far from being understood. Among the phenomenological models proposed, the "tunneling model"[3,4] has proved to be the most successful. This model implies tunneling of atoms (or groups of atoms) between nearly degenerate equilibrium positions. For this model, an "open structure" (e.g., a wide range of bond angles) seems to be required, as found in glasses, polymers, or amorphous Se.

In contrast, amorphous germanium (a-Ge) was not expected to show such low-temperature anomalies since its structure is rather closed.[4] Experimental support for this assumption comes from specific heat measurements on a-Ge above 2 K, which yielded an enhanced T^3 term as compared to crystalline Ge, but did not give evidence for a linear term.[5] Thus, the question whether LEE do or do not exist in a-Ge appears to be of great importance with respect to the physical na-