PHYSICAL REVIEW B VOLUME 41, NUMBER 5 15 FEBRUARY 1990-I

Surface adsorption: Quantum reflection versus polaron collapse

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(Received 19 June 1989; revised manuscript received 25 September 1989)

We present a quantum theory for surface adsorption of low-energy charged particles on a dielectric fluid. Quantum effects suppress adsorption (quantum reflection), while polaronic-mass enhancement and coherence loss for the wave function assist it. We provide additional evidence that the sticking coefficient has a singular dependence on the coupling constant which enters the particle-substrate excitation interaction. The system exhibits a transition from perturbative quantum-mechanical regime to a strong-coupling classical regime. We use a time-dependent generalization of the Lee-Low-Pines variational wave function to study the critical regime of intermediate-coupling constants where the transition takes place. The onset of classical adsorption is found to be triggered by the appearance of collapsed bound states on the substrate surface.

I. INTRODUCTION

The behavior of a particle near a solid or liquid surface has been a subject of renewed interest in the last decade.[1] From a number of experiments it has become clear that the results could not be explained by a purely classical description. In particular, for a low-temperature substrate hit by a particle with low incident energy, quantum effects play an important role. Edwards *et al.*[2] found that for ^{4}He atoms impinging on ^{4}He surfaces, so-called quantum reflection (see below) dramatically suppresses the adsorption probability. Neon atoms hitting flat metal surfaces, investigated recently,[3] also show strong quantum effects.

The classical description of surface adsorption was due to Iche and Nozières.[4] They treated the surface interaction by introducing a phenomenological damping term and a noise source in the equation of motion of the particle. At low energies, the incoming particle is then inevitably captured by the surface. Subsequently, much effort was dedicated to provide a microscopic theory for this damping term. Using the work of Brenig,[5] Kumamoto and Silbey[6] showed how a classical equation of motion can be derived from the microscopic Hamiltonian of a particle interacting with a "bath" of surface excitations. In a different context, this was done earlier by Knowles and Suhl.[7] The results obtained by those methods agreed with the theory of Iche and Nozières[4] while giving explicit expressions for the damping term.

The quantum properties of the particle have received much less attention. It is actually here that new phenomena incompatible with classical physics are expected. The first peculiar quantum effect is "quantum reflection," as discussed for instance by Landau:[8] A particle skimming a potential is reflected if the potential undergoes a sudden variation, because of a mismatch between the wavelengths on each side of the potential step. This has an important effect on the adsorption coefficient $\alpha(E)$ (E is the incident-particle energy). Within perturbation theory (distorted-wave Born approximation), $\alpha(E)$ is proportional to the time $\tau(E)$ spent near the surface times the probability $|T(E)|^2$ of reaching the surface. Bethe's law states that $\tau(E)$ is proportional to $E^{-1/2}$, while for a sharp potential step the transmission coefficient $T(E)$ is proportional to $E^{1/2}$. This means that for small E, $\alpha(E)$ is proportional to $E^{1/2}$. Thus, quantum perturbation theory predicts $\alpha(0)=0$, *not* $\alpha(0)=1$ as in classical physics. This suppression of adsorption by quantum reflection was first noted by Lennard-Jones and Devonshire[9] and discussed for the case of hydrogen adsorption by Kagan and Shlyapnikov.[10] A decade ago, Brenig[11] proposed a nonperturbative Green's-function approach and showed that for a closed system with a short-range surface potential, the elastic-reflection coefficient goes to unity in the limit of low incident energy. Unitarity of the S matrix then implies $\alpha(0)=0$ for any value of the coupling constant. Experimentally, however, it is known that for heavy particles even at low energies, the classical result still holds. In a previous paper[12] (hereafter, I), we investigated the fate of quantum reflection within strong-coupling theory, as we increase the coupling constant which enters in the interaction between the particle and the surface excitations. We only allowed for the wave packet to spread in the direction normal to the surface. We discovered that there appears to be a critical value of the coupling constant where quantum reflection is rather suddenly "turned off" and the prediction $\alpha(0)\simeq 1$ of classical physics becomes valid. In this paper, we hope to give some insight on the transition from quantum to classical behavior, explained as a suppression of quantum reflection for sufficiently large coupling constants.

The reduction of the classical adsorption coefficient by quantum reflection is aided by a second quantum effect. If we allow wave-packet spreading in the plane of incidence, we must obey in-plane momentum conservation. If a particle of parallel momentum $\mathbf{P}_{\parallel}$ emits a surface phonon of wave vector $\mathbf{q}$ then $\mathbf{P}_{\parallel}$ is reduced by $\hbar\mathbf{q}$ and the particle energy E by $\hbar\omega_q$, where ω_q is the surface-phonon dispersion relation. At low incoming energies, this greatly reduces the available phase space for phonon emission and absorption. It thus works in the same direction as quantum reflection. In particular, the cutoff for phonon wave vectors is $\mathbf{P}_{\parallel}$ and not the Debye wave vector of the phonons. In a second paper[13] (hereafter, II), we used perturbation theory (weak coupling) and the distorted-wave Born approximation to study this effect. One finds that the adsorption coefficient for a charged particle hitting a dielectric fluid depends on E as $(E/E_R)^{1/4}$, where E_R is a typical bound-state energy. This result is due to a combination of quantum reflection and momentum conservation. As perturbation theory predicts that $\alpha(0)=0$ to all orders, the fact that $\alpha(0)$ is finite for large coupling constants suggests that there is a critical coupling constant below which $\alpha(0)$ is zero and above which it is finite.

The third striking feature is polaronic "self-trapping."[14] A particle trapped in a bound state on a translationally invariant surface shares many features with electrons in polar crystals.[15] Similar to real polarons, a surface polaron[16] can either be an extended plane wave ("large polaron") or can create a localized dimple on the surface ("small polaron"). As one varies the coupling constant, one encounters large polarons for small coupling constants and vice versa. We showed in a third paper[17] (hereafter, III) that the normal component of the surface-polaron wave function collapses before the in-plane component. The collapse of the polaron wave function is a purely static effect. However, it should also affect the transport properties. In the small-polaron limit, the in-plane effective mass is considerably larger than in the large-polaron limit. If the normal component of the wave function has collapsed, deep bound states appear close to the surface with enhanced effective coupling constants to the surface modes. This dramatic reorganization of the bound-state wave function occurs in the same ranges of coupling strengths where in I we discovered the onset of "classical" adsorption. This suggests that polaronic mass enhancement could be an important mechanism for the supression of quantum reflection.

A fundamental problem for the interaction of a particle with an adsorptive substrate is that in general we are neither in the strong- nor in the weak-coupling limit. More precisely, far from the surface we are always in the weak-coupling regime, while close to the surface we may or may not be in the strong-coupling regime. We thus expect that as the particle approaches the surface it can evolve from an extended wave packet (far from the surface) to a "collapsed" surface state. The collapse would be brought about by a combination of mass enhancement and the destruction of phase coherence through inelastic scattering.

This observation raises considerable doubts on the validity of the strong-coupling theory of I: If a particle undergoes quantum reflection before it ever enters the strong-coupling regime close to the surface, $\alpha(0)$ could indeed be zero for *all* coupling constants, as perturbation theory claims. A proper definition of the sticking coefficient is thus needed. In the context of perturbation theory, the definition of α provides no difficulties: the Fermi "golden rule" explicitly connects initial and finite states for an open, infinite system. However, in a numerical calculation, or in an experimental setup, we are constrained to measure α over a finite time, thus introducing some ambiguity in the result. The maximum time T_M for the measurement is limited by the characteristic size L of the system and the classical particle velocity v_{cl} ($T_M \simeq L/v_{\mathrm{cl}}$). Also, when dealing with a *closed* system, the energy absorbed by the surface excitations after collision may be restored to the particle after a long time, say $\tau(L)$. Obviously, the adsorption measurement must be terminated in a time smaller than both T_M and $\tau(L)$. As we are to compare our theoretical predictions with experimental results, we shall elaborate more on this subject when dealing with the strong-coupling regime, where we must rely on numerical calculations.

To investigate the possibility that $\alpha(0)=0$, we will present in this paper a calculation of the sticking coefficient in the weak- to intermediate-coupling regime. We will assume that the wave function is extended along the plane of the surface. In the strong-coupling theory [time-dependent Hartree (TDH) approximation], the wave function was assumed to be collapsed in the plane. The outline is as follows. In Sec. II, we discuss the Hamiltonian and show how to derive the TDH approximation of Kumamoto and Silbey, as well as the classical limit of Knowles and Suhl. In Sec. III, we present our formalism for the intermediate-coupling regime which conserves momentum. It is based on a time-dependent Lee-Low-Pines (LLP) variational wave function. In Sec. IV, we discuss a mean-field method to solve the variational equation. In Sec. V, we define α, present our numerical solutions, and compare the results with TDH. We conclude in Sec. VI.

II. MODEL HAMILTONIAN AND TDH EFFECTIVE HAMILTONIAN

The Hamiltonian of the coupled particle–surface-phonon system is

$$H=H_0+H_{\mathrm{ph}}+H_{\mathrm{int}} , \tag{1}$$

where

$$H_0=-\frac{\hbar^2\nabla^2}{2m}+V_0(z) \tag{2a}$$

$$H_{\mathrm{ph}}=\sum_{\mathbf{q}} \hbar\omega_q a_{\mathbf{q}}^{\dagger}a_{\mathbf{q}} \tag{2b}$$

$$H_{\mathrm{int}}=\sum_{\mathbf{q}} V_q(z)(a_{\mathbf{q}}e^{i\mathbf{q}\cdot\mathbf{r}_{\parallel}}+\mathrm{c.c.}) . \tag{2c}$$

In the above formulas, $V_0(z)$ and $V_q(z)$ are, respectively, the elastic and inelastic surface potentials. Furthermore, ω_q is the frequency of a surface excitation with a wave-vector $\mathbf{q}$, $\mathbf{r}_{\parallel}$ is the particle position along the surface, while z is the distance perpendicular to the surface. Finally, m is the mass of the particle. Derivations of H for various special cases are discussed in Refs. 7, 10, 13, and 18.

The connection with the existing semiclassical Hartree theory is established by reducing the many-body Hamiltonian to a self-consistent single-particle Hamiltonian (TDH approximation[6]). This approximation is valid in the strong-coupling limit, where the particle wave packet is of a narrow extent and where the kinetic energy of the particle is large compared to the average vibrational energy of the surface modes. A Born-Oppenheimer approximation is justified in that limit where one writes the wave-function $|\psi\rangle$ as a product of a particle wave function and a phonon wave function:

$$|\psi(\mathbf{r},t)\rangle = g(\mathbf{r}_{\parallel},z,t)|\phi_{\mathrm{ph}}(t)\rangle \ . \tag{3}$$

The spatial degrees of freedom appear only in the particle wave function $g(\mathbf{r}_{\parallel},z,t)$.

To simplify the problem, we only consider normal incidence and we assume that $g(\mathbf{r}_{\parallel},z,t)=\delta(\mathbf{r}_{\parallel})g(z,t)$, neglecting the spreading of the wave packet in the direction parallel to the surface. The problem is then reduced to the motion of a one-dimensional wave packet along the direction normal to the surface.

The wave-function $|\psi\rangle$ is determined variationally (see Sec. III), which leads to the following two coupled equations for g and $|\phi_{\mathrm{ph}}\rangle$:

$$i\hbar\frac{\partial}{\partial t}g = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}+V_0(z)+\langle\phi_{\mathrm{ph}}|H_{\mathrm{int}}|\phi_{\mathrm{ph}}\rangle_t\right]g \ , \tag{4a}$$

$$i\hbar\frac{\partial}{\partial t}|\phi_{\mathrm{ph}}\rangle = \left[\sum_{\mathbf{q}}\hbar\omega_q a_{\mathbf{q}}^{\dagger}a_{\mathbf{q}}+\langle g|H_{\mathrm{int}}|g\rangle_t\right]|\phi_{\mathrm{ph}}\rangle \ . \tag{4b}$$

The particle acts as an external tine-dependent drive on the surface phonons and vice versa.

The effectiive-phonon Hamiltonian in Eq. (4b) is quadratic in the creation-annihilation operators $a_{\mathbf{q}}^{\dagger}$ and $a_{\mathbf{q}}$. It can therefore be diagonalized, and the expectation value of H_{int} in Eq. (4a) can be evaluated. The resulting self-consistent particle Hamiltonian reads

$$\begin{aligned} H_{\mathrm{TDH}} = &-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}+V_0(z) \\ &-\frac{2}{\hbar}\sum_{\mathbf{q}}V_q(z)\int_{-\infty}^{t}dt'\langle g|V_q|g\rangle_{t'} \\ &\times\sin[\omega_q(t-t')] \ . \end{aligned} \tag{5}$$

The third term in the Hamiltonian depends on the past history of the wave function (i.e., the process is non-Markovian). The time kernel is a function of the surface-phonon-dispersion relation. The nonlocality in time is due to the emission of a surface phonon at time t' and its subsequent absorption at a later time t.

The wave-function g must still be determined self-consistently. Numerical solutions were discussed in I (see also Fig. 6). H_{TDH} still contains the competition between quantum reflection, which suppresses adsorption, and inelastic scattering, which is necessary for the energy transfer and which also suppresses quantum reflection through destruction of wave-function coherence. However, since it does not include the in-plane component of the wave function, it cannot describe the polaronic mass enhancement near the surface. Obviously, it also violates momentum conservation along the surface. The TDH approximation is, as mentioned, only valid for well-localized wave functions. However, both in the weak-coupling limit, and far from the surface, wave functions are extended. In particular, TDH cannot reproduce lowest-order perturbation theory. If the incoming energy is nearly degenerate with the energy of an excited state of the particle-surface system, we can have resonant-energy transfer, an effect which is easily demonstrated by perturbation theory but which is absent in the TDH method. We also note that a strong-coupling theory such as TDH can only be valid close to the surface. Even if strong coupling is valid on impact, it is certainly invalid if the wave packet is far from the surface.

The classical limit is derived from TDH by going one step further and also neglecting wave-packet spreading in the direction normal to the surface. One thus replaces $\langle g|V_q|g\rangle_{t'}$ by $V_q(z_{\mathrm{cl}}(t'))$, where $z_{\mathrm{cl}}(t')$ is the average (or classical) position of the particle at time t'. The resulting Hamiltonian describes a classical particle governed by the following equation of motion:

$$\begin{aligned} m\frac{\partial^2}{\partial t^2}z_{\mathrm{cl}}(t) = &-\frac{\partial V_0(z_{\mathrm{cl}}(t))}{\partial z} \\ &+\frac{2}{\hbar}\sum_{\mathbf{q}}\frac{\partial V_q(z_{\mathrm{cl}}(t))}{\partial z} \\ &\times\int_{-\infty}^{t}dt'\,V_q(z_{\mathrm{cl}}(t')) \\ &\times\sin[\omega_q(t-t')] \ . \end{aligned} \tag{6}$$

By expanding the memory kernel around $t'=t$, one finds a frictional force $\gamma(dz_{\mathrm{cl}}/dt)$ on the right-hand side of Eq. (6), with

$$\gamma(t)=\frac{2}{\hbar}\int_0^{\infty}d\tau\,\tau\sum_{\mathbf{q}}\left[\frac{\partial Vq(z_{\mathrm{cl}}(t))}{\partial z}\right]^2\sin(\omega_q\tau) \ , \tag{7}$$

the friction coefficient. If $\gamma(t)$ is finite, we recover the classical description of Iche and Nozières (at zero temperature), so that the adsorption coefficient at low incident energies equals unity. Whether the integral in Eq. (7) converges depends on the small-q limit of the phonon density of states. We shall assume a finite γ (so-called Ohmic damping).

III. MOMENTUM-CONSERVING FORMALISM

The most interesting aspect of the surface-adsorption problem is the crossover from quantum to classical physics, a regime where both perturbation theory and the strong-coupling TDH method are expected to fail. In this section, we will discuss how one can deal with the intermediate-coupling regime. The method we propose is a time-dependent extension of our previous work on the static surface polaron, which in turn finds it roots in the Lee-Low-Pines[15] (LLP) variational method.

In the weak-to intermediate-coupling regime, the wave function of the whole system is extended in the direction parallel to the surface. It is then natural to look for eigenstates of the total parallel momentum. Let $\mathbf{P}$ be the total momentum of the combined particle-phonon system. It follows that $\mathbf{p}=\mathbf{P}-\sum_{\mathbf{q}}\hbar q\, a_{\mathbf{q}}^{\dagger}a_{\mathbf{q}}$ is the particle momentum. The first step in the LLP method is to go to the rest frame of the particle in order to eliminate the $\mathbf{r}_{\parallel}$ dependence of the wave function. This means that we perform the unitary transformation

$$|\psi\rangle=S|\phi(z,t)\rangle\ , \tag{8}$$

with

$$S=\exp\left[-\frac{i}{\hbar}\left[\mathbf{P}-\sum_{\mathbf{q}}\hbar\mathbf{q}\, a_{\mathbf{q}}^{\dagger}a_{\mathbf{q}}\right]\mathbf{r}_{\parallel}\right]\ . \tag{9}$$

Here, $|\phi(z,t)\rangle$ is a particle-phonon many-body wave function which depends only on the normal coordinate z and the time t. The second step is to use the LLP ansatz for the dependence of $|\phi(z,t)\rangle$ on the phonon coordinates:

$$|\phi(z,t)\rangle=Ug(z,t)|0\rangle\ , \tag{10}$$

where U is again a unitary transformation:

$$U=\exp\left[\sum_{\mathbf{q}}f_{\mathbf{q}}^{*}(z,t)a_{\mathbf{q}}-f_{\mathbf{q}}(z,t)a_{\mathbf{q}}^{\dagger}\right]\ . \tag{11}$$

In this expression, g represents the particle wave function and $f_{\mathbf{q}}$ is the amplitude of the phonon mode with wave vector $\mathbf{q}$. In III, we showed that for a surface-adsorbed polaron, this ansatz is valid in a number of limiting cases, provided that the wave function is extended along the surface.

Computing $f_{\mathbf{q}}$ and g is in general a daunting problem. For static problems, they are determined by minimizing the total energy. For dynamical problems, we will use the following variational principle. We introduce the functional

$$F[f_{\mathbf{q}},f_{\mathbf{q}}^{*},g,g^{*}]=\int_{-\infty}^{+\infty}dt\left[\langle\psi|H|\psi\rangle-i\hbar\left\langle\psi\left|\frac{\partial}{\partial t}\right|\psi\right\rangle\right]\ . \tag{12}$$

The variational principle is $\delta F=0$. When $|\psi\rangle$ is an exact solution of Schrödinger's equation, one can immediately check that

$$\frac{\partial F}{\partial\langle\psi|}-\partial_t\frac{\partial F}{\partial(\partial_t\langle\psi|)}=H|\psi\rangle-i\hbar\frac{\partial}{\partial t}|\psi\rangle=0 \tag{13a}$$

and

$$\frac{\partial F}{\partial|\psi\rangle}-\partial_t\frac{\partial F}{\partial(\partial_t|\psi\rangle)}=\langle\psi|H-i\hbar\frac{\partial}{\partial t}\langle\psi|=0\ . \tag{13b}$$

We are thus guaranteed that the exact solution obeys $\delta F=0$. The TDH equations can also be derived from this variational principle using the Born-Oppenheimer approximation as a variational ansatz.[19] In the Appendix, we discuss why this variational principle is an improvement on the conventional pseudoquantization of the Hamilton-Jacobi equations.[20] This is discussed in further detail in Ref. 21.

The calculation of the functional is tedious straightforward. To simplify further expressions, we introduce the two quantities

$$\eta(z,t)=\sum_{\mathbf{q}}\frac{\hbar\mathbf{q}\cdot\mathbf{P}}{P^2}|f_{\mathbf{q}}(z,t)|^2 \tag{14a}$$

and

$$\delta(z,t)=\frac{1}{2}\sum_{\mathbf{q}}\left[f_{\mathbf{q}}^{*}\frac{\partial}{\partial z}f_{\mathbf{q}}-f_{\mathbf{q}}\frac{\partial}{\partial z}f_{\mathbf{q}}^{*}\right] \tag{14b}$$

Here, η represents the fraction of the total parallel momentum which is absorbed by the vibrations of the surface, and δ has the form of a superposition of quantum-mechanical fluxes.

The functional can now be written as

$$\begin{aligned}F=\int_{-\infty}^{+\infty}dt\int_{0}^{\infty}dz\Bigg[&\frac{P^2}{2m}(1-\eta)^2|g|^2+\frac{\hbar^2}{2m}\left|\left[\frac{1}{i}\frac{\partial}{\partial z}-i\delta\right]g\right|^2\\&+\left\{V_0+\sum_{\mathbf{q}}\left[\frac{\hbar^2}{2m}\left|\frac{\partial}{\partial z}f_{\mathbf{q}}\right|^2+\left[\hbar\omega_q+\frac{\hbar^2q^2}{2m}\right]|f_{\mathbf{q}}|^2+V_q(f_{\mathbf{q}}+f_{\mathbf{q}}^{*})\right]\right\}|g|^2\\&-i\hbar g^{*}\frac{\partial}{\partial t}g-\frac{i\hbar}{2}|g|^2\sum_{\mathbf{q}}\left[f_{\mathbf{q}}^{*}\frac{\partial}{\partial t}f_{\mathbf{q}}-f_{\mathbf{q}}\frac{\partial}{\partial t}f_{\mathbf{q}}^{*}\right]\Bigg]\end{aligned} \tag{15}$$

Minimizing F with respect to g and the amplitudes $f_{\mathbf{q}}$ yields the following system of coupled equations:

$$\begin{aligned}\Bigg\{&\frac{P^2}{2m}(1-\eta)^2+\frac{\hbar^2}{2m}\left[\frac{1}{i}\frac{\partial}{\partial z}-i\delta\right]^2+V_0+\sum_{\mathbf{q}}\left[\frac{\hbar^2}{2m}\left|\frac{\partial}{\partial z}f_{\mathbf{q}}\right|^2+\left[\frac{\hbar^2q^2}{2m}+\hbar\omega_q\right]|f_{\mathbf{q}}|^2+V_q(f_{\mathbf{q}}+f_{\mathbf{q}}^{*})\right]\\&-\frac{i\hbar}{2}\sum_{\mathbf{q}}\left[f_{\mathbf{q}}^{*}\frac{\partial}{\partial t}f_{\mathbf{q}}-f_{\mathbf{q}}\frac{\partial}{\partial t}f_{\mathbf{q}}^{*}\right]\Bigg\}g=i\hbar\frac{\partial}{\partial t}g\ ,\end{aligned} \tag{16a}$$

$$-\frac{\partial}{\partial z}|g|^2\frac{\partial}{\partial z}f_{\mathbf{q}}+\left[-g^*\frac{\partial}{\partial z}g+g\frac{\partial}{\partial z}g^*-2\delta|g|^2\right]\frac{\partial}{\partial z}f_{\mathbf{q}}$$
$$+\left[q^2+\frac{2m}{\hbar}\omega_q-\frac{2\mathbf{q}\cdot\mathbf{P}}{\hbar}(1-\eta)\right]f_{\mathbf{q}}|g|^2+\frac{2m}{\hbar^2}V_q|g|^2=i\frac{2m}{\hbar}|g|^2\frac{\partial}{\partial t}f_{\mathbf{q}}\ . \tag{16b}$$

Equation (16a) is a time-dependent Schrödinger equation for the particle wave function. It contains a variety of terms: the elastic potential V_0, and the time-dependent terms involving $\eta(z,t)$, $\delta(z,t)$, and $f_{\mathbf{q}}(z,t)$, which can change the energy of the particle. In particular, note the term $-i\delta$. It has the form of a time-dependent scalar potential. The physical meaning of δ is clarified when multiplying Eq. (16b) by g^* and subtracting the complex conjugate. This yields the conservation law

$$\frac{\partial}{\partial z}i\frac{\hbar}{2m}\left[g^*\frac{\partial}{\partial z}g-g\frac{\partial}{\partial z}g^*+2\delta|g|^2\right]=\frac{\partial}{\partial t}|g|^2\ . \tag{17}$$

There are thus two contributions to the probability flux in the z direction: the usual particle current, and the "phonon current" $\delta|g|^2$.

An important check on the validity of our variational ansatz is to see whether it reproduces time-dependent perturbation theory in the weak-coupling limit and thus properly includes momentum conservation and resonant energy transfer. For simplicity, we set the elastic potential to zero, so that the eigenstates of the noninteracting system are plane waves. The initial state is assumed to contain no phonons, so that $|\psi_0\rangle=g_0(z,t)|0\rangle$, with

$$g_0(z,t)=\exp\left[-ikz-\frac{i}{\hbar}\left[\frac{\hbar^2k^2}{2m}+\frac{P^2}{2m}\right]t\right]\ , \tag{18}$$

and $f_{\mathbf{q}}=0$ at $t=t_0$. If we allow a small coupling to be present, then the correction to $f_{\mathbf{q}}$ will be of the order V_q [see Eq. (16b)]. On the other hand, the correction to g in Eq. (16a) will be of the order $(V_q)^2$ since all effective potentials are quadratic in $f_{\mathbf{q}}$ and V_q. We can neglect the latter to lowest order. The resulting equation of motion for the phonon modes now reads

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}f_{\mathbf{q}}-i\frac{\hbar^2k}{2m}\frac{\partial}{\partial z}f_{\mathbf{q}}+\left[\frac{\hbar^2q^2}{2m}+\hbar\omega_q-\frac{\hbar\mathbf{q}\cdot\mathbf{P}}{m}\right]f_{\mathbf{q}}+V_q=i\hbar\frac{\partial}{\partial t}f_{\mathbf{q}}\ . \tag{19}$$

This equation can be solved via a Fourier transform:

$$f_{\mathbf{q}}(z,t)=-\frac{i}{\hbar}\int_0^{t-t_0}d\tau\exp\left[-\frac{i}{\hbar}\left[\hbar\omega_q+\frac{(\mathbf{P}-\hbar\mathbf{q})^2}{2m}-\frac{P^2}{2m}\right]\tau\right]$$
$$\times\int_0^{\infty}dz'\,V_q(z')\frac{1}{i^{1/2}}\left[\frac{m\pi}{2\hbar\tau}\right]^{1/2}\exp\left[i\frac{m(z-z')^2}{2\hbar\tau}+ik(z-z')+\frac{i}{\hbar}\frac{\hbar^2k^2}{2m}\tau\right]\ . \tag{20}$$

The many-body wave function can then be written as

$$|\psi\rangle=g_0|0\rangle+g_0f_{\mathbf{q}}a_{\mathbf{q}}^{\dagger}|0\rangle+O(V_q)^2\ . \tag{21}$$

The overlap of $|\psi\rangle$ with an eigenstate $|k',\mathbf{P}'\rangle$ of the noninteracting system is then

$$\langle k',\mathbf{P}'|\psi\rangle=-\frac{i}{\hbar}\int dz\exp\left[\frac{i}{\hbar}\left[\frac{\hbar^2k'^2}{2m}-\frac{\hbar^2k^2}{2m}+\frac{P'^2}{2m}-\frac{P^2}{2m}\right](t-t_0)+i(k-k')z\right]f_{\mathbf{q}}(z,t)$$
$$=-\frac{i}{\hbar}\exp(-i\omega_qt)\int_{t_0}^{t}dt'\langle k',\mathbf{P}'|V_q|k,\mathbf{P}\rangle\ . \tag{22}$$

Equations (21) and (22) reproduce lowest-order perturbation theory (Born approximation), which of course satisfies inplane momentum conservation. The present variational calculation thus takes into account quantum fluctuations, and it at least treats one-phonon interaction processes corectly, while the TDH method fails to do so.

For normal incidence, the equations of motion simplify because of isotropy in the plane parallel to the surface. Since we do not allow any motion along the surface, the global system is in a zero parallel-momentum eigenstate, so $\mathbf{P}=0$. For a given wavelength, all phonon amplitudes must be equal, regardless of their direction. By rotational invariance η is zero. Integrating the current equation over position, we can eliminate $\delta(z,t)$ from Eq. (16b):

$$-\frac{\hbar^2}{2m}\frac{\partial}{\partial z}|g|^2\frac{\partial}{\partial z}f_q+i\hbar\left[\frac{\partial}{\partial z}f_q\right]\frac{\partial}{\partial t}\int_0^z dz'|g|^2 + \left[\frac{\hbar^2 q^2}{2m}+\hbar\omega_q\right]|g|^2 f_q+V_q|g|^2=i\hbar|g|^2\frac{\partial}{\partial t}f_q \ . \tag{23}$$

The average of f_q is found by integrating this equation over position. Defining

$$\langle f_q\rangle \equiv \int_0^\infty dz|g|^2 f_q \ , \tag{24}$$

we find

$$\left[\frac{\hbar^2 q^2}{2m}+\hbar\omega_q\right]\langle f_q\rangle+\langle V_q\rangle=i\hbar\frac{\partial}{\partial t}\langle f_q\rangle \ . \tag{25}$$

The above equation is a time-dependent generalization of the Lee-Low-Pines equation for the phonon amplitude of a bulk polaron.[15] It can be solved as an initial value problem with the solution

$$\langle f_q\rangle_t=\langle f_q\rangle_0\exp\left[-\frac{i}{\hbar}\left[\frac{\hbar^2 q^2}{2m}+\hbar\omega_q\right](t-t_0)\right] -\frac{i}{\hbar}\int_{t_0}^t dt'\exp\left[-\frac{i}{\hbar}\left[\frac{\hbar^2 q^2}{2m}+\hbar\omega_q\right](t-t')\right] \times\langle V_q\rangle_{t'} \ . \tag{26}$$

Thus, the modulus of the average phonon amplitude progressively differs from its initial value as the overlap between the particle wave packet and the inelastic potential builds up. In particular, even if initially no phonons were present ($\langle f_q\rangle_0=0$), they will be generated once $\langle V_q\rangle_t$ becomes appreciable.

IV. MEAN-FIELD THEORY

We shall only treat Eqs. (16a) and (16b) in the mean-field approximation. This means that we will neglect the spatial variations of f_q around its average $\langle f_q\rangle$. Replacing f_q by its expectation value Eq. (26) and inserting in Eq. (16b) leads to the following effective Hamiltonian for g:

$$H_{\mathrm{MF}}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}+V_0 -\frac{2}{\hbar}\sum_q V_q\int_{t_0}^t dt'\langle V_q\rangle_{t'} \times\sin\left[\left[\frac{\hbar q^2}{2m}+\omega_q\right](t-t')\right] \ . \tag{27}$$

This mean-field Hamiltonian closely resembles H_{TDH} except for the fact that we replaced $\hbar\omega_q$ by $\hbar^2 q^2/2m+\hbar\omega_q$. Note that $\hbar^2 q^2/2m$ is the *particle* energy evaluated at a *phonon* wave vector. If the particle is sufficiently heavy, then $\hbar^2 q^2/2m \ll \hbar\omega_q$, and we recover H_{TDH}. However, for most practical circumstances the opposite is true. For instance, for electrons impinging on a ^{4}He surface, the above inequality could only be valid for unrealistically large wavelengths. The effect of the new term is to reduce the memory time of the kernel from ω_q^{-1} to $2m/\hbar q^2$. As we shall see, this will suppress the effects of dissipation.

How good is mean-field theory? For the statics, we showed earlier that if $\lambda\equiv[(dV_q/dz)/V_q]^{-1}$ is the characteristic length scale of the inelastic potential, then mean-field theory is valid for $q\gg\lambda^{-1}$, i.e., for smooth potentials.

Turning to dynamics, the fluctuations of f_q satisfy the following equation:

$$\hbar\frac{\partial}{\partial t}[\langle f_q^2\rangle-\langle f_q\rangle^2]=2\,\mathrm{Im}[\langle V_q f_q\rangle-\langle V_q\rangle\langle f_q\rangle] \ . \tag{28}$$

It follows from Eq. (23) that if $V_q(z)$ is smooth compared to $|g|^2$, to lowest order we can neglect the first two terms of the left-hand side of this equation. The corresponding solution is time independent:

$$f_q(z,t)\simeq\frac{V_q(z)}{\hbar^2 q^2/2m+\hbar\omega_q} \ . \tag{29}$$

Since f_q is real, it follows from Eq. (27) that $\langle f_q^2\rangle-\langle f_q\rangle^2$ is also time independent. The error we make in neglecting the fluctuations does not grow as a function of time. In particular, if $f_q=0$ at $t=-\infty$, then $\langle f_q^2\rangle=\langle f_q\rangle^2$ at later times. We conclude that the validity condition for mean-field theory is the same as that for the statics, i.e., we are restricted to smooth potentials.

To explore the impact of the replacement of $\hbar\omega_q$ by $\hbar\omega_q+(\hbar^2 q^2/2m)$ in the memory kernel, we go to the classical limit. We follow the method of Knowles and Suhl[7] to derive the corresponding classical equation of motion. In the memory term of Eq. (27), we expand the potential as

$$V_q(z_{\mathrm{cl}}(t'))\simeq V_q(z_{\mathrm{cl}}(t))+\left[(t'-t)\frac{dz_{\mathrm{cl}}(t)}{dt}+\tfrac{1}{2}(t'-t)^2\frac{d^2z_{\mathrm{cl}}(t)}{dt^2}\right]\frac{\partial}{\partial z(t)}V_q(z_{\mathrm{cl}}(t)) \tag{30}$$

and calculate the first three moments, introducing a small imaginary frequency to perform the time integrals. This procedure is justified by noting that phonons do not have infinite lifetimes. Phonon decay is modeled by just such an imaginary frequency. For a state which is extended (MF) along the surface, the renormalized potential V_{MF}, the friction coefficient γ_{MF} and the effective mass m^*_{MF} are

$$V_{\mathrm{MF}}=V_0\left[1+\int_0^{q_D}dq\frac{Sq}{2\pi[\hbar\omega_q+(\hbar^2q^2/2m)]}\frac{V_q^2(z_{\mathrm{cl}})}{V_0(z_{\mathrm{cl}})}\right], \tag{31a}$$

$$\gamma_{\mathrm{MF}}=\lim_{q\to 0}\left[\frac{\pi}{2}\frac{\rho_{\mathrm{ph}}(\hbar\omega_q)}{[\omega_q+(\hbar q^2/2m)]}\left[\frac{\partial V_q(z_{\mathrm{cl}})}{\partial z}\right]^2\right], \tag{31b}$$

$$m^*_{\mathrm{MF}}=m\left[1+\frac{1}{m}\int_0^{q_D}dq\frac{Sq}{\hbar\pi}\left[\frac{\partial V_q(z_{\mathrm{cl}})}{\partial z}\right]^2\frac{1}{[\omega_q+(\hbar q^2/2m)]^3}\right], \tag{31c}$$

where ρ_{ph} is the phonon density of states, and S is the surface area. Using the fact that V_q is proportional to $S^{-1/2}$, we note that none of these quantities depend on the size of the system. Their values should be compared to those obtained using the equation of motion in the TDH case of Kumamoto and Silbey:[6]

$$V_{\mathrm{TDH}}=V_0\left[1+\int_0^{q_D}dq\frac{Sq}{2\pi\hbar\omega_q}\frac{V_q^2(z_{\mathrm{cl}})}{V_0(z_{\mathrm{cl}})}\right], \tag{32a}$$

$$\gamma_{\mathrm{TDH}}=\lim_{q\to 0}\left[\frac{\pi}{2}\frac{\rho_{\mathrm{ph}}(\hbar\omega_q)}{\omega_q}\left[\frac{\partial V_q(z_{\mathrm{cl}})}{\partial z}\right]^2\right], \tag{32b}$$

$$m^*_{\mathrm{TDH}}=m\left[1+\frac{1}{m}\int_0^{q_D}dq\frac{Sq}{\hbar\pi}\left[\frac{\partial V_q(z_{\mathrm{cl}})}{\partial z}\right]^2\frac{1}{\omega_q^3}\right]. \tag{32c}$$

Comparing first the mass renormalization for the MF and TDH limits, we note that m^*_{MF} is always less than m^*_{TDH}. In particular, the reduction of the mass enhancement for the former case is large if the bare mass m is small. For a dispersion $\omega_q=cq$, with c the velocity of sound, the small-q limit in the integral of Eq. (31c) is dominated by ω_q, while the large-q limit is dominated by $\hbar q^2/2m$. The "crossover" is located around $q^*\simeq mc/\hbar$. For an electron $(q^*)^{-1}\simeq 1000$ Å and for a proton $q^*\simeq 1$ Å. In the former case, the suppression of the mass renormalization by momentum conservation is clearly significant and TDH is a poor approximation. In the latter case, $m^*_{\mathrm{TDH}}\simeq m^*_{\mathrm{MF}}$ and TDH should be reasonable. The friction coefficients γ_{MF} and γ_{TDH} are exactly the same for phonon dispersions which satisfy $\omega_q=q^\zeta$ with $\zeta<2$ at small wave vectors. This is the case for both bulk and surface phonons. This indicates that momentum conservation will have a greater impact on the mass (and the potential) renormalization than on the friction coefficient.

V. NUMERICAL SOLUTION

We first define the adsorption coefficient. Let $L_\parallel$ $(L_\perp)$ be the typical size of the system in the direction parallel (perpendicular) to the surface, ξ the range of the surface potential (the Bohr radius in our case), and T the surface temperature. The particle is thus astrained to move in a box of dimension $L_\parallel^2 L_\perp$, one side of which is the adsorbing surface. During an inelastic collision, phonons are emitted, and then absorbed back after a characteristic time $\tau(L_\parallel)$. However, $\tau(L_\parallel)\to\infty$ when $L_\parallel\to\infty$ (the surface then acts as a reservoir, as in an open system, where irreversible processes are allowed). If we denote by $|\Psi_L(\{n_q,T\},\mathbf{r},t)\rangle$ the many-body wave function of the coupled electron-phonon system, we can introduce the quantity

$$|g_L^2(z,t)|\equiv\langle\Psi_L|\Psi_L\rangle_z\ , \tag{33}$$

where the subscript z indicates that the spatial integration over z has been omitted. We define a time-dependent adsorption coefficient as

$$\alpha(E,t)=\lim_{L_\parallel,L_\perp\to\infty}\ \lim_{T\to 0}\int_0^{L^*}dz\,|g_L^2(z,t)|\ , \tag{34}$$

with $\xi \ll L^* \ll L_\perp$, and with L^* the distance over which the adsorption coefficient is measured (measurement length). The measurement time t must be chosen with care. First, we must demand that $t\gg L^*/v_{\mathrm{cl}}$, with $v_{\mathrm{cl}}\equiv(2E/m)^{1/2}$ the classical velocity of the particle outside the surface region. This assures us that the center of mass of the recoiling wave packet is located outside the measurement length L^* for α. To avoid reflection on the wall opposite to the surface, we also demand $t\ll L_\perp/v_{\mathrm{cl}}$. Finally, to avoid "phonon return," we impose $t\ll\tau(L_\parallel)$. Since we have already taken the limit $L_\parallel\to\infty$, the last of these constraints is automatically satisfied. We set the surface temperature $T=0$ to avoid reevaporation. Our definition of the energy-dependent sticking coefficient $\alpha(E)$ is then

$$\alpha(E)=\lim_{t\to\infty}\alpha(E,t)\ . \tag{35}$$

The ordering of the limits in t and $L_\parallel$ is crucial if we want physically meaningful answers.

We now wish to follow the evolution of a wave packet incident on the surface as it interacts with the surface excitations. For the Hamiltonian, we will either use H_{TDH} [Eq. (5)] or H_{MF} [Eq. (27)]. Neither is rigorous, but they describe the limiting behavior with the wave packet either extended or localized in the direction parallel to the surface, and those two limits can be expected to act as bounds on $\alpha(E)$.

Both Hamiltonians depend on the behavior of the wave packet at all previous times through the memory kernel. We will start with an initial wave packet far away from the surface, where the inelastic interaction can be neglected, and allow it to move towards the surface, using the integration scheme of Goldberg *et al.*[22] As it approaches the surface, we calculate the kernel step by step. For a given time step, we first compute the time integral of the kernel and then update the particle wave function.

The physical system on which we concentrate will be the same as discussed in papers I–III: charged particles (electrons) incident on the surface of liquid ^{4}He. The elastic potential is the screened static image charge potential:

$$V_0(z)=\begin{cases}-\dfrac{\Lambda_0}{z}, & z_c \le z\\ -\dfrac{\Lambda_0}{z_c}, & 0\le z\le z_c\\ +\infty, & z<0\,,\end{cases}\tag{36}$$

where $\Lambda_0=e^2(\epsilon-1)/4(\epsilon+1)$ and ϵ is the dielectric constant of liquid ^{4}He. The cutoff z_c is the distance from the surface where the image potential approximation breaks down. The infinite potential barrier prohibits the electron from entering the bulk, which is true for small incident energies. The inelastic potential is taken to be

$$V_q(z)=\left[\frac{\hbar q}{2\rho\omega_q S}\right]^{1/2}\Lambda_0^2\begin{cases}\dfrac{1}{z^2}, & z_c\le z\\ \dfrac{1}{z_c^2}, & 0\le z<z_c\,,\end{cases}\tag{37}$$

where ρ is the ^{4}He density, σ the surface tension, $\omega_q=(\sigma/\rho)^{1/2}q^{3/2}$ is the dispersion relation for Rayleigh waves on a thick helium film, and S is the surface area. This inelastic model potential overestimates the contribution from low-energy excitations.[17] The actual inelastic potential for ^{4}He phonons vanishes for $qz \ll 1$. This could potentially affect the long-time behavior of the memory kernel. However, the surface excitations which are relevant for the adsorption process have wave vectors of order q^*, with $\omega_{q^*}\tau\simeq 1$, where τ is the characteristic time for the collision process. For incident energies of order 1 K or larger, τ is of order 10^{-10} s or shorter. The relevant phonon wavelength $\lambda^*\simeq\tau^{2/3}(\sigma/\rho)^{1/3}$ which is of order 10^{-7} cm or shorter. Since typical values of z for the wave packet during the collision are in excess of 100 Å (see Fig. 1), we are in the regime $qz \gg 1$.

We can perform the sums over the phonon modes in the memory kernels. We write the two inelastic potential in the form

$$V_{\text{in}}(z)=-\frac{\Lambda_0^2}{3\pi\sigma z^2}\int_{t_0}^{t}dt'\langle\frac{1}{z^2}\rangle_{t'}K(t-t')\,,\tag{38}$$

with K equal to either one of the following:

$$K_{\text{TDH}}(t)=\frac{1-\cos(\omega_D t)}{t}\,,\tag{39a}$$

$$K_{\text{MF}}(t)=\left[\frac{\sigma}{\rho}\right]^{1/2}\int_0^{q_D}dq\,q^{1/2}\sin\left[\left[\frac{\hbar q^2}{2m}+\omega_q\right]t\right]\,.\tag{39b}$$

Here, ω_D (q_D) is the Debye frequency (wave number) of the surface phonons. The Debye frequency for ^{4}He surface phonons is not known. We will assume it to be of order 10^{11} s^{-1}.

Comparing the two kernels, one can make a qualitative comparison: the "extended" kernel oscillates far more rapidly than the TDH kernel, due to the presence of the free-electron dispersion. Consequently, only short-term memory is expected in the momentum-conserving formalism. We recall that for extended wave packets, less energy will be exchanged with the phonons during a collision on the surface because momentum-conservation requirements reduce the number of phonons that can be emitted.

Since we are interested in the quantum regime, we impose incident electron energies which are much smaller than the Rydberg [$(m\Lambda_0^2/\hbar^2)$, of order 10 K for electrons]. For the TDH Hamiltonian, this allows us to choose a typical time step of the order $dt=10^{-12}$ s. However, the maximum frequency entering in K_{MF} is several orders of magnitude larger ($\simeq 10^{15}$ s^{-1}) than the Debye frequency, and we cannot reduce the time step to include those frequencies (for numerical reasons). We thus separate the integral in Eq. (39b) in two parts:

$$K_{\text{MF}}(t)=\frac{1}{2}\left[\frac{\sigma}{\rho}\right]^{1/2}\left[\frac{2m}{\hbar}\right]^{3/4}\left[\int_0^{\omega_D}d\omega\frac{1}{\omega^{1/4}}\sin(\omega t)+\int_{\omega_D}^{\hbar q_D^2/2m}d\omega\frac{1}{\omega^{1/4}}\sin(\omega t)\right]\,.\tag{40}$$

In these expressions, we have neglected the phonon-dispersion relation when compared to the free-particle dispersion. The second contribution is sharply peaked near $t=0$ and represents the short-term memory of the system. When inserted in the effective potential (38), it plays the role of a δ function which is centered at a time t' close to t. The effective inelastic potential is then

$$V_{\text{MF}}=-\frac{\Lambda_0^2}{4\pi(\sigma/\rho)^{1/2}z^2}\left[\frac{2m}{\hbar}\right]^{3/4}\left[\int_{t_0}^{t}dt'\left\langle\frac{1}{z^2}\right\rangle_{t'}\int_0^{\omega_D}d\omega\frac{1}{\omega^{1/4}}\sin[\omega(t-t')]+\left\langle\frac{1}{z^2}\right\rangle_t\frac{4}{\omega_D^{1/4}}\right]\,.\tag{41}$$

We first begin without any inelastic interaction, and follow the evolution of the wave packet, which starts far away (10^4 Å) from the surface (see Fig. 1). The initial state is a Gaussian wave packet of average energy 0.2 K. The particle energy is chosen to be several orders of magnitude smaller than the Rydberg energy. As the wave packet enters the well of the elastic potential (left-hand side of the figure), the large momentum contributions can

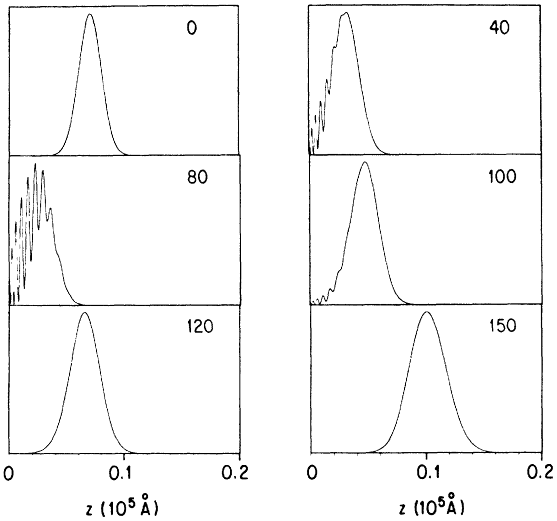

FIG. 1. Density probability of a wave packet initially 10^4 Å away from the surface in the absence of coupling with the surface. The surface is on the left-hand side of the picture. The time in picoseconds is displayed in the upper-right corner of the pictures. The ordinate scale is normalized to the maximum of the wave packet.

penetrate the well and bounce off the hard wall at $z=0$, while the low-energy contributions suffer quantum reflection. The oscillations of the probability density seen during the collision are interference effects between the incoming and outgoing part of the wave packet.[13]

With the same initial conditions, we now turn on the interaction. The dimensionless coupling constant $\lambda=\langle u^2\rangle^{1/2}/a_B$, where $\langle u^2\rangle^{1/2}$ is the root-mean-square amplitude of the zero-point motion on the surface and a_B is the bound-state "radius" for an electron on ^{4}He ($a_B \simeq 60$ Å; $\langle u^2\rangle^{1/2}\simeq 1$ Å).

After a collision, the wave packet in general has broken into two distinctive parts. One part stays close to the surface while the remainder moves out to infinity. To monitor adsorption, we compute the sticking coefficient and the quantity

$$E(t)=\begin{cases}\langle g|H_{\mathrm{MF}}|g\rangle, & \text{extended}\\ \langle g|H_{\mathrm{TDH}}|g\rangle, & \text{localized}\ .\end{cases} \tag{42}$$

We will treat $E(t)-E(-\infty)$ as a measure of the energy transfer between the particle and the ripplons.

We start with the TDH Hamiltonian.

For $\lambda \ll 1$, we note little adsorption. The evolution of the wave packet is similar to Fig. 1. The physical value of λ for electrons is in this range ($\lambda\simeq 0.02$).

For $\lambda=1.8$ [Fig. 2(a)], a small fraction of the wave function gets trapped. The distinction between trapped and reflected parts, however, is not very clear. The characteristic length scale of the trapped wave function (last frame) is of the order of several Bohr radii, so that the effective potential is presumably not yet strongly affected. Given the extent of the trapped wave function, it is obviously not in the ground state of the elastic potential. The particle energy is plotted as a function of time in Fig. 3. The particle hits the surface after 80 ps, after which it looses its energy in a time scale of order 20 ps. The velocity v of a classical particle would be roughly 10 Å/ps, so the collision time is of order a_B/v. There is a small recoil effect with the surface returning some of the energy dissipated by the particle. The relaxation of the trapped wave function to the ground state is apparently slow since $E(t)$ does not apparently change after the collision.

For $\lambda=2.7$, there has been a qualitative change. To a great extent, the wave packet got trapped. The trapped wave function has collapsed onto the substrate. In III, we showed that with increasing λ there is a collapse of the normal part of the wave function. Evidently, the rapid increase of $\alpha(0)$ around $\lambda=2$ is triggered by this collapse. To put it in picturesque language, it seems as if the

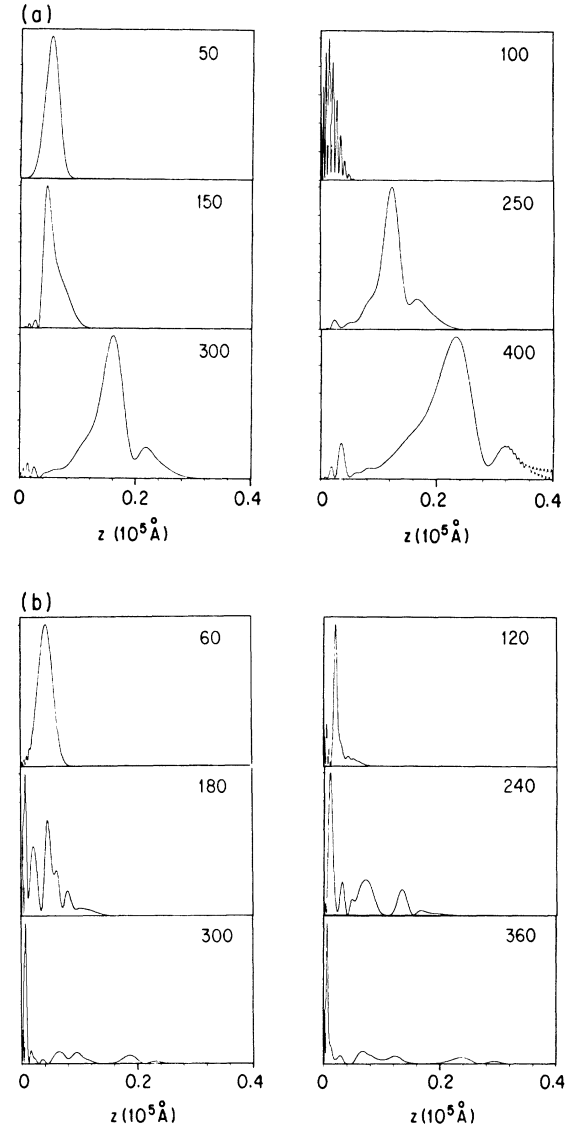

FIG. 2. (a) With the same initial condition, the particle interacts with the surface exitations via the mean-field Hamiltonian H_{TDH}. The state is localized in the plane of the surface, and the coupling constant is $\lambda=1.8$. (b) Same as Fig. 2(a) with a coupling constant $\lambda=2.7$.

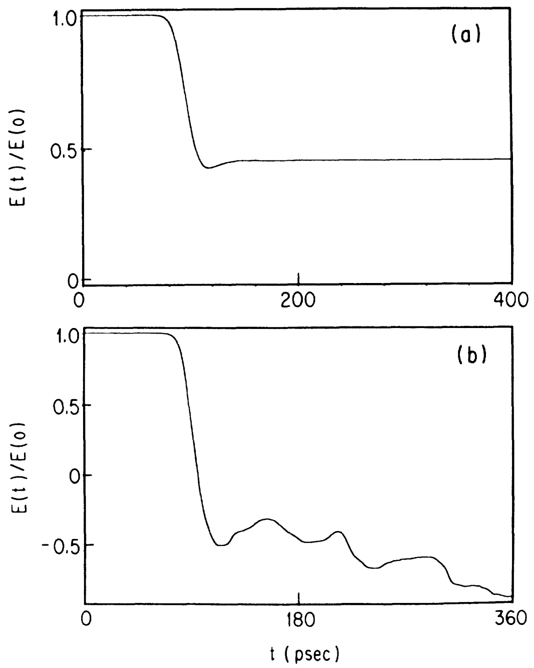

FIG. 3. Particle energy as a function of time for a localized state in the case of (a) $\lambda=1.8$, (b) $\lambda=2.7$. (The energy is normalized to the initial energy of the particle.)

strong inelastic scattering for small z "sucks in" the wave function towards $z=0$ and overcomes quantum reflection. In Fig. 3(b), we show the energy loss. The erratic behavior of $E(t)$ after the collision is probably a combination of the "ringing" of the surface and transition between bound states.

Next, we go to the extended case (MF). The required coupling constants for adsorption are considerably larger. In Fig. 4(a), we show $\lambda=17$. Most of the wave packet still manages to escape, but a small part has broken off and may be trapped. There is a strong recoil effect which returns about $\frac{1}{3}$ of the initially adsorbed energy. For $\lambda=20$ [Fig. 4(b)], the sticking coefficient has increased considerably and, as for the TDH case, collapsed bound states now appear. The escaped fraction of the wave function has initially a narrow extent ($150<t<250$ ps) and then rapidly disperses ($250<t<300$ ps). This is an interesting demonstration of the strong–weak-coupling crossover as we move away from the surface. Close to the surface, inelastic scattering and mass enhancement lead to highly localized wave functions. As the wave packet moves into the weak-coupling regime, Heisenberg's uncertainty principle forces a rapid dispersion. The particle energy behaves again erratically. There is no well-defined time of impact and there is a continuous loss of energy [see Fig. 5(b)].

We can now plot the sticking coefficient $\alpha(0)$ as a function of the coupling constant for the two cases (see Fig. 6). The transition from weak to strong coupling is rather abrupt, especially in the extended case: as the coupling constant is increased by a factor of 2, we go all the way from weak to strong adsorption. For H_{TDH} the transition occurs in the region $1\leq\lambda\leq5$. As expected, the sticking coefficient of TDH is always larger than that of the extended case. The basic results are first, that in either case, for sufficiently large values of the coupling strength, the particle wave function loses its coherence and starts behaving like a classical object, and secondly, that momentum conservation reduces the adsorption coefficient. it does however change the qualitative dependence of the adsorption coefficient on λ.

VI. SUMMARY AND CONCLUSION

In the Introduction, we raised two questions: first, are the results of TDH trustworthy, and is $\alpha(0)$ indeed singular? Second, what is the relation between static polaron collapse and nonzero $\alpha(0)$?

We have found that for a Lee-Low-Pines variational

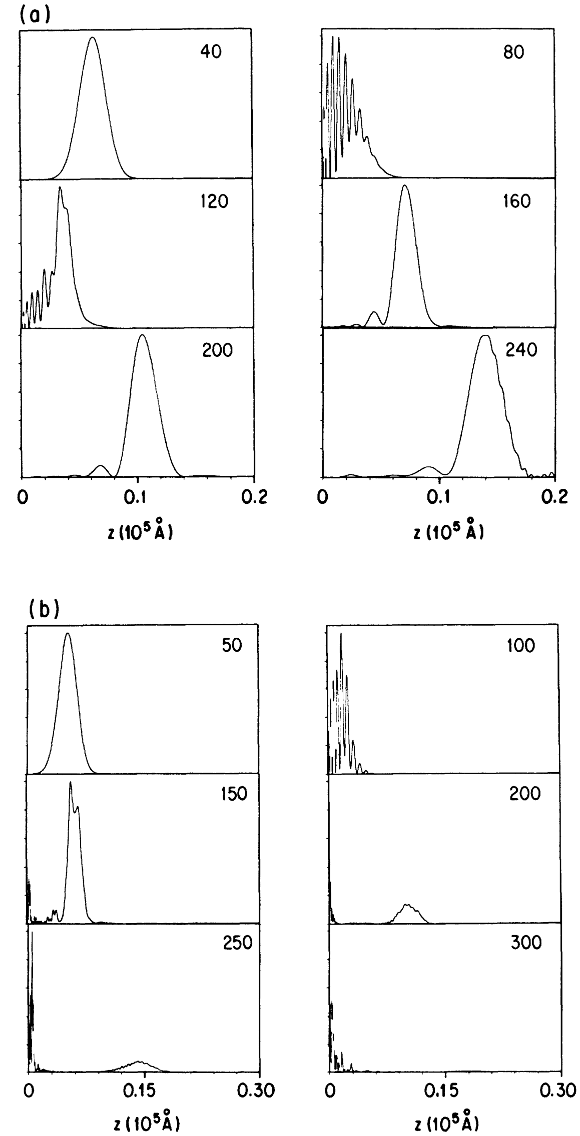

FIG. 4. (a) With the initial conditions of Fig. 1, the particle interacts with the surface phonons via H_{KS} in the momentum-conserving formalism. The coupling constant is $\lambda=17$. (b) Same as Fig. 4(a), with a coupling constant $\lambda=20$.

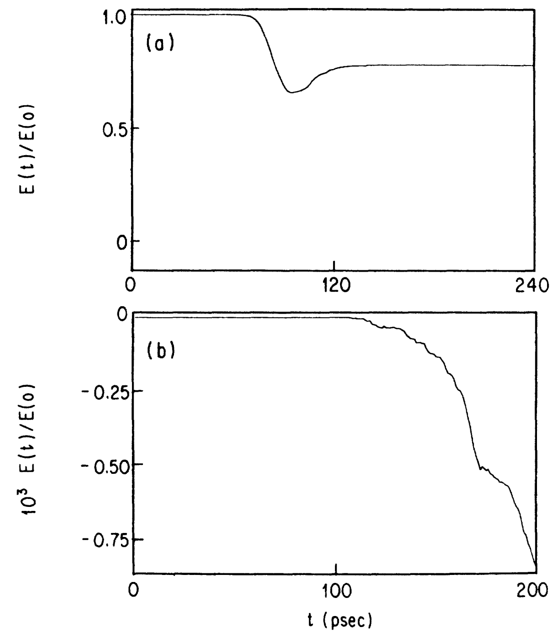

FIG. 5. Particle energy as a function of time in the momentum-conserving formalism, in the case of (a) $\lambda=17$, (b) $\lambda=20$.

wave function—which is valid for weak- to intermediate-coupling constants—we recover results which are qualitatively similar to TDH *if* we use a mean-field approximation. This provides additional evidence for singular dependence of $\alpha(0)$ on the coupling constant λ. In the "critical" region, there is a very rapid transition from quantum to classical physics. The main question concerning this conclusion is the validity of the mean-field approximation for the variational equations. The mean-field approximation should be valid for potentials $V_q(z)$ whose characteristic length scale is large compared to the particle wavelength. This, however, means that quantum reflection is weak in the validity range of mean-field theory. We cannot rule out the possibility that at very low energies, mean-field theory breaks down and $\alpha(0)$ would go to zero. Thus, although we have provided additional evidence for it, we did not prove the singular dependence of $\alpha(0)$ on the coupling constant.

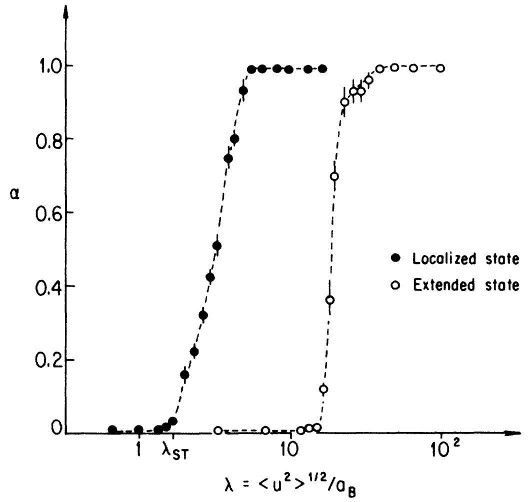

FIG. 6. Adsorption probability as a function of the coupling constant for the localized and extended cases. The value λ_{ST} is the coupling constant at which strong renormalization of the elastic potential is expected for the ground state of the static extended system. The curves are a guide to the eye.

These findings obviously are in strong disagreement with Brenig's (rigorous) result $\alpha(0)=0$. There are a number of possible origins for the discrepancy. First of all, it could be argued that Brenig's result is valid only for a closed and globally coherent system, while we assumed an open system. For a closed system, irreversible processes, such as adsorption, are strictly speaking not possible. In the derivation of our effective "single-particle" Hamiltonian, we implicitly included a small but finite lifetime for the phonons. However, if this were the cause of the problem, $\alpha(E)$ would have been zero also for finite incident energies in Brenig's proof, which was not the case.

A second possibility is that Brenig implicitly assumed that perturbation theory is *convergent*. We previously also found that $\alpha(0)=0$ term by term in perturbation theory. However, this need not be valid anymore if the perturbation series does not converge.

Finally, Brenig could be right after all. Our results are numerical, and we cannot exactly go to $E=0$, since the De Broglie wavelength would exceed the sample size. Nevertheless, if this was the answer, we would expect a strong dependence on E in the adsorption coefficient $\alpha(E)$. In particular, the onset of nonzero $\alpha(E)$ should have shifted to larger λ values on reducing E. We did not observe this, although of course we cannot rule out a strong E dependence in $\alpha(E)$ for extremely low E. Even if this were the case, we would still expect our results for α to remain valid experimentally, since the asymptotic regime $E\rightarrow 0$ would require unrealistically low energies. The puzzle still remains to be solved.

On the second question, we have shown that the transition in the adsorptive behavior both for the LLP and TDH variational wave functions occurs very close to the critical coupling constants for which collapsed bound states appear close to the surface. In III, we found that for the present model problem, the ground-state wave function of a surface polaron collapses around $\lambda=2$. This is close to the value of λ where $\alpha(0)$ becomes noticeably different from zero in TDH, but somewhat less than the LLP value ($\lambda\simeq 20$). However, the numerical solution for LLP still showed that for $\lambda\leq 17$, the trapped part of the wave function is extended in the normal direction and collapsed for $\lambda\geq 17$. This demonstrates clearly that the onset of adsorption is indeed triggered by the appearance of collapsed surface bound states. Obviously, the effective coupling to the surface excitations is much larger for the collapsed states so that the result is intuitively reasonable. The finiteness of $\alpha(0)$ thus appears *not* to be due to wave-function coherence by inelastic scattering (and suppression of quantum reflection), but rather to polaronic mass enhancement in the *normal* direction close to the surface. This leaves us with the possibility that if we go to much lower energies for large λ, we could still recover $\alpha(0)=0$.

The problem of energy transfer between a particle and an adsorptive substrate is remarkably subtle—even for the simplest possible model problem discussed here. The heart of the problem lies in the manner in which quantum mechanics is suppressed as we couple a particle to a "heat bath" such as phonons or electron-hole pairs. Loss of wave-function coherence, polaronic mass enhancement, and potential renormalization all lead to substantial changes in the wave function. Loss of coherence and mass enhancement both aid adsorption. For our problem, mass enhancement and potential renormalization have obscured a possible loss of coherence.

For quantum tunneling problems the same questions have arisen. At least for the case of escape from a metastable well, a coherent description has emerged. As surface adsorption and quantum-reflection problems have to deal with a continuum of scattering states, we are faced here with a considerable challenge.

Experimental tests of the predicted critical dependence of $\alpha(0)$ on λ seem quite possible. Electrons reflecting off ^{4}He are, as mentioned, always in the weak-coupling regime. Hydrogen atoms have λ values around 10–20 in the critical regime. The question of whether $\alpha(0)=0$ or not for hydrogen atoms is of considerable importance for achieving Bose condensation for spin-polarized hydrogen.

The most useful experiment would be one where λ could be varied. One possibility would be the adsorption of charged particles on Si surfaces, while one varies the dielectric constant through doping.

Finally, we limited ourselves to a zero-temperature calculation. Finite-temperature effects are likely to change the dependence of $\alpha(0)$ on λ. For low incident energies, we expect the adsorption probability to have a finite (nonzero) value, even in the weak-coupling regime. The transition from weak to strong adsorption is also expected to be less abrupt, as renormalization effects are damped by thermal motion (see I). An extension of the present formalism to include finite-temperature effects is possible but goes beyond the scope of this paper.

ACKNOWLEDGMENTS

We would like to thank Professor K. Lindenberg for useful discussions concerning the variational method. This work was supported by National Science Foundation Grant No. DMR-86-03217.

APPENDIX

In this section, we point out the differences between the extremum principle and the Hamilton-Jacobi equations for variational wave functions which were proposed by Davidov.[20] We then explain why our method yields better results.

The particle-phonon Hamiltonian we are concerned with is similar to the one used by Davydov[20] to describe the propagation of excitons in one-dimensional molecular crystals. The exciton position amplitude at site n, corresponds to our particle wave function at position z. The quantization of the molecular displacements leads to a phonon representation. Davidov used the single-phonon approximation to model the wave function of the global system, which corresponds to our LLP ansatz.

To obtain the evolution equation of the wave-function parameters, Davydov proceeded as follows: in the classical regime, one can write exact Hamilton-Jacobi equations for the displacements of the molecular chain and their associated canonical conjugates. To quantize this system, Davydov replaced the classical variables in the Hamilton-Jacobi equations by the expectation values of their quantum-mechanical analogs. This approximation is certainly justified for systems which are close to the classical regime, such as DNA molecules. However, as we will see at the end of this section, it does not yield the correct equations for the quantum-mechanical evolution.

In our system, the "intuitive" Hamilton-Jacobi equation can be written as

$$i\hbar\frac{\partial}{\partial t}(f|g|^2)=\frac{\delta\langle H\rangle_\psi}{\delta f^*} . \tag{A1}$$

The equation of motion obtained from $\delta F=0$ differs from the above equation. The functional was defined as

$$F=\int_{t_i}^{t_f}dt\,L , \tag{A2}$$

where we introduce the Lagrangian

$$L=\int_0^\infty dx\,\mathcal{L} , \tag{A3}$$

and the Lagrangian density $\mathcal{L}$ is defined as

$$\mathcal{L}=\psi^*H\psi-i\hbar\psi^*\frac{\partial}{\partial t}\psi . \tag{A4}$$

This Lagrangian is a functional of the quantities $f_{\mathbf{q}},f_{\mathbf{q}}^*,g,g^*$ and their time derivatives. To obtain the equations of motion, we can proceed as in Sec. III, or, alternatively, we can write the Hamilton's principle associated with the above extremum principle. Here, we take the latter point of view. The canonical conjugate $\pi_{\mathbf{q}}$ of $f_{\mathbf{q}}^*$ is by definition

$$\pi_{\mathbf{q}}=\frac{\delta L}{\delta(\partial_t f_{\mathbf{q}}^*)}=i\hbar|g|^2f_{\mathbf{q}} . \tag{A5}$$

The Hamiltonian density $\mathcal{H}$ associated to the Lagrangian density $\mathcal{L}$ is then defined by the expression

$$\begin{aligned}\mathcal{H}&=\sum_{\mathbf{q}}\pi_{\mathbf{q}}\frac{\partial f_{\mathbf{q}}^*}{\partial t}-\mathcal{L}\\&=-\psi^*H\psi-\frac{i\hbar}{2}\sum_{\mathbf{q}}|f_{\mathbf{q}}|^2\frac{\partial|g|^2}{\partial t} ,\end{aligned} \tag{A6}$$

so that the "true" Hamilton-Jacobi equation takes the form

$$\frac{\delta}{\delta f_{\mathbf{q}}^*}\left[\langle H\rangle_\psi+\frac{i\hbar}{2}\sum_{\mathbf{q}}\int_0^\infty dz|f_{\mathbf{q}}|^2\frac{\partial|g|^2}{\partial t}\right]=i\hbar\frac{\partial}{\partial t}(f_{\mathbf{q}}|g|^2) . \tag{A7}$$

This equation corresponds exactly to the equation of motion (15b) of Sec. IV. However, it is easy to see that it differs from Eq. (A1). To see why Eq. (A7) should be used instead of Eq. (A1), we go to the exact solution: if the wave-function ansatz described by Eqs. (7)–(10) represents an exact solution of the time-dependent Schrödinger equation associated to the particle-phonon Hamiltonian (1), then it certainly extremizes the functional F. This is demonstrated in the derivation of Eqs. (12a) and (12b). Assuming that the exact solution is of the variational form prescribed, Eq. (A7) is obeyed while Eq. (A1) is not.

The conclusion we have drawn here is in agreement with the work of Brown *et al.*[23] on the applicability of Hamiltons equations in quantum dissipative systems. Nevertheless, when the system behaves classically, the particle wave function is well localized so that we can forget about the spatial dependence of the phonon amplitudes. In this situation, the Hamilton-Jacobi equation (A1) coincides with the extremal principle (A7). The views we have expressed here are also confirmed in a series of recent publications[21] on the evolution of Davidov solitons.

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