

**Critical-like behavior in quantum adsorption**

Th. Martin and R. Bruinsma

*Collège de France, 11 Place Marcelin-Berthelot, 75321 Paris CÉDEX 05, France  
and Department of Physics-Solid State Science Center, University of California, Los Angeles, California 90024*

P. M. Platzman

*AT&T Bell Laboratories, Murray Hill, New Jersey 07974*

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The sticking coefficient  $\alpha(E)$  describes the probability that an incoming charged particle with a low-energy  $E$  will stick to the surface of a dielectric fluid. The quantum-mechanical prediction  $\lim_{E \rightarrow 0} \alpha(E) = 0$  is found to hold to all orders in  $\lambda$ , the coupling to surface excitations. When  $\lambda$  exceeds a critical value  $\lambda_c$ , inelastic scattering destroys quantum interference and  $\lim_{E \rightarrow 0} \alpha(E) \neq 0$ . For larger  $\lambda$  a classical description is valid. Near  $\lambda_c$  we find features reminiscent of critical phenomena in systems with continuous phase transitions.

A particle hitting the surface of a solid or a liquid may be either scattered back or adsorbed by the surface. Both processes are relevant to many applications. Surface scattering is a powerful tool for elucidating surface structures, while adsorption is important for coating purposes. Although the two processes are obviously related, their respective descriptions have developed along very different lines.

Scattering probabilities can be computed using the distorted-wave Born approximation<sup>1</sup> (DWBA). For a low-incident energy  $E$ , the de Broglie wavelength of the particle becomes comparable to the characteristic size of the surface potential well  $V$  so that the wave function is severely deformed. Since the wavelengths inside and outside the well differ considerably for  $E \ll V$ , the "impedance mismatch" at the threshold of the well prevents the particle from reaching the surface [see Fig. 1(a)], an interference effect better known as quantum reflection.<sup>2</sup>

Consequently, if one tries to compute the adsorption probability  $\alpha$  ("sticking coefficient") due to the creation of surface or bulk excitations near  $z=0$ , one finds that  $\lim_{E \rightarrow 0} \alpha(E) = 0$ .

On the other hand, the description of particle adsorption by surfaces, which is based on classical mechanics, disagrees with this result. In this description the incident particle is a classical point particle, while the surface excitations are treated quantum mechanically. The incoming particle acts as a drive on the surface modes and loses energy. It is found that  $\lim_{E \rightarrow 0} \alpha(E) = 1$ , both for energy adsorption by surface phonons<sup>3</sup> as well as by electron-hole pairs.<sup>4</sup> Thus, there is no low-energy adiabatic regime. The simplest way to treat this effect is to include the surface excitations as giving rise to a frictional drag on the classical particle.<sup>5</sup> A low-energy incoming particle is inevitably captured [see Fig. 1(b)].

The "quantum" and "classical" descriptions of surface scattering are thus in contradiction at low energies.<sup>6</sup> Which description is valid will depend on to what degree inelastic scattering destroys phase coherence and suppresses quantum interference. To investigate the range of validity of these two pictures, we consider a case where the surface is smooth and the Hamiltonian well understood:<sup>7</sup> a charged particle of mass  $M$  impinging on a zero-temperature dielectric fluid of density  $S$ , surface tension  $\sigma$ , and dielectric constant  $\epsilon$ . The Hamiltonian is

$$H = \frac{P^2}{2M} + V(z) + \sum_q \frac{Q_q}{(S)^{1/2}} V_q'(z) (a_q + a_q^\dagger) e^{iq \cdot R} + \sum_q \hbar \omega_q a_q^\dagger a_q, \tag{1}$$

with

$$V(z) = \begin{cases} -\Lambda_0/z, & z > z_0, \\ -\Lambda_0/z_0, & 0 < z < z_0, \\ \infty, & z < 0, \end{cases} \tag{2}$$

$S$  is the surface area,  $Q_q = (\hbar q / 2\rho\omega_q)^{1/2}$ , and  $\Lambda_0 = e^2(\epsilon - 1)/4(\epsilon + 1)$ . The cutoff  $z_0$  is of the order of the interatomic spacing of the fluid.<sup>7</sup> For distances  $z < z_0$  the im-

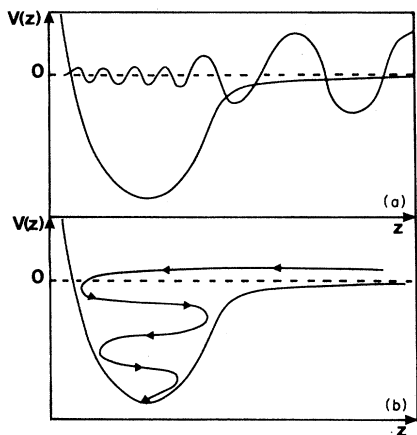


FIG. 1. (a) Amplitude reduction of an incoming low-energy plane wave in a potential well due to quantum reflection at the threshold of the well. (b) Adsorption of a low-energy particle in the classical limit.

age potential is invalid. For  $z < 0$ , a particle would be inside the fluid. The repulsive barrier it needs to overcome was taken here to be infinite. The range of the interaction between particle and capillary waves is determined by

$$V_q'(z) = \Lambda_0/z^2 - (\Lambda_0/z)qK_1(qz), \quad (3)$$

where  $K_1$  is the modified Bessel function of the first kind. Equation (3) is valid only for  $z > z_0$ . For a thick helium film, the quantized capillary waves ("ripples") have a dispersion

$$\omega_q = (\sigma/\rho)^{1/2}q^{3/2}, \quad (4)$$

$$W = \frac{2\pi}{\hbar} \sum_F \left| \langle F | H_{\text{int}} | I \rangle + P \int \frac{\langle F | H_{\text{int}} | \nu \rangle \langle \nu | H_{\text{int}} | I \rangle}{E_I - E_\nu} d\nu + \dots \right|^2 \delta(E_F - E_I). \quad (5)$$

If we keep only the first term (Fermi's golden rule), then for  $E \ll E_R$ ,

$$\alpha(E) \sim (E/E_R)^{1/4}, \quad (6)$$

so  $\alpha(0) = 0$  for the Coulomb potential. For a potential well of finite range<sup>9</sup>  $\alpha(E) \sim E^{1/2}$ .

Higher-order terms involve multiripplon emission, self-energy, and vertex corrections. We computed<sup>9</sup>  $\alpha$  up to third order in  $H_{\text{int}}$  and found  $\alpha(0) = 0$ . In fact, every term in the perturbation series [Eq. (5)] contains one factor  $\langle \nu | H_{\text{int}} | I \rangle$  which vanishes as  $E \rightarrow 0$  because  $I$  is a scattering state. The density of states at  $E = 0$  is smooth for Coulomb potentials so the integration over the intermediate states  $|\nu\rangle$  does not lead to any logarithmic divergences for  $E_I \rightarrow 0$ , while for  $E_\nu \rightarrow 0$ , the intermediate states again contain quantum-reflection terms proportional to  $(E_\nu/E_R)^{1/4}$ . Hence, we conclude that  $\alpha(0) = 0$  term by term in the perturbation theory.

The coupling parameter  $\lambda$  of the perturbation series is found by noting that  $H_{\text{int}} = (\partial V/\partial z)u(\mathbf{R}_\parallel)$ , with  $u(\mathbf{R}_\parallel)$  the height deformation of the surface at  $\mathbf{R}_\parallel$ , and  $\mathbf{R}_\parallel$  the in-plane coordinate. Comparing this with  $V(z)$  suggests

$$\lambda = \langle u^2 \rangle^{1/2}/a_B, \quad (7)$$

which is (almost) correct.<sup>9</sup> As long as the perturbation series converges, i.e., for small  $\lambda$ , we expect Eq. (6) to be valid.

To deal with the strong-coupling limit  $\lambda \gg 1$ . We note

$$H_{\text{TDH}} = -\frac{\hbar^2}{2M}\nabla^2 + V(z) - \frac{2}{\hbar S} \sum_q V_q'(z) Q_q^2 \int_{-\infty}^t dt' \langle \phi | V_q' | \phi \rangle_t \sin \omega_q(t-t'). \quad (10)$$

Since our wave function is assumed to be well localized, we set  $e^{i\mathbf{q}\cdot\mathbf{R}_\parallel} = 1$ , i.e., we neglect spreading parallel to the surface on length scales of order of the ripplon wavelength.

If, following KS, we also neglect spreading of  $\phi$  along the  $z$  direction, we recover an equation of motion for the classical coordinate  $z_{\text{cl}}(t)$

$$M \ddot{z}_{\text{cl}} = -V'(z_{\text{cl}}) + \frac{2}{\hbar S} \sum_q [V_q''(z_{\text{cl}})] Q_q^2 \int_{-\infty}^t dt' V_q'[z_{\text{cl}}(t')] \sin \omega_q(t-t'). \quad (11)$$

This is a well-known equation, shown by Knowles and Suhl<sup>11</sup> to be the classical limit of the adsorption problem. The memory kernel in Eq. (11) leads to frictional loss and  $\alpha(0) = 1$ , as expected.

neglecting gravitational effects.

We start by computing  $\alpha(0)$  perturbatively in  $H_{\text{int}}$ , the particle-ripplon term in Eq. (1). In the absence of coupling, the bound-state spectrum is hydrogenic with a characteristic Rydberg energy  $E_R = M\Lambda_0^2/2\hbar^2$  and a Bohr "radius"  $a_B = \hbar^2/M\Lambda_0$ . For  $z \sim a_B$ , the incoming and outgoing scattering states have their amplitudes reduced by a factor  $(E/E_R)^{1/4}$  with respect to their amplitude at  $z = \infty$ . The transition probability  $W$  for an incoming wave  $|I\rangle$  with energy  $E_I$  to be trapped and turned into one of the bound states  $|F\rangle$  is<sup>8</sup>

that our Hamiltonian is of the form of the polaron problem. In the strong-coupling limit, the wave function of a polaron is of a narrow extent and the energy scale of the particle due to zero-point motion is high compared to the energy scale of the phonon degrees of freedom. This justifies a Born-Oppenheimer approximation for the many-body wave function  $\Psi$ . In our case

$$\Psi = \psi\phi(\mathbf{R}, t), \quad (8)$$

where  $\psi$  and  $\phi$  are, respectively, the ripplon and particle wave functions. The optimal choice for those functions can then be determined variationally, and is found to correspond to the time-dependent Hartree (TDH) approximation. This method was introduced by Kumamoto and Silbey (KS) in surface scattering,<sup>10</sup> but was used previously in nuclear and molecular physics. One obtains two coupled equations for  $\psi$  and  $\phi$ :

$$i\hbar \frac{\partial \phi}{\partial t} = \left[ -\frac{\hbar^2 \nabla^2}{2M} + V(z) \right] \phi + \langle \psi | H_{\text{int}} | \psi \rangle_t \phi, \quad (9a)$$

$$i\hbar \frac{\partial \psi}{\partial t} = \sum_q \hbar \omega_q a_q^\dagger a_q \psi + \langle \phi | H_{\text{int}} | \phi \rangle_t \psi, \quad (9b)$$

where the subscript  $t$  indicates the time dependence of the matrix elements. Since Eq. (9b) represents a set of driven harmonic oscillators, it can be solved exactly. Inserting the result in Eq. (9a) gives a self-consistent particle Hamiltonian for  $\phi$

We now allow the wave function  $\phi(z)$  to spread along the  $z$  direction and solve numerically the corresponding nonlinear Schrödinger equation [Eq. (9a)] with  $H_{\text{TDPH}}$  as Hamiltonian.<sup>12</sup> Thus, we fully include quantum reflection, while treating electron-rippion coupling through the mean-field approximation [Eq. (8)]. For an electron normally incident on a  $^4\text{He}$  surface, we deliberately vary the surface tension away from its physical value in order to change the coupling strength  $\lambda$  without changing  $V(z)$ . We take as our initial wave function an incoming Gaussian wave packet of average energy  $E=0.1$  K, 8000 Å away from the surface ( $a_B \approx 50$  Å). We choose the energy range  $E \ll E_R$  ( $E_R \approx 10$  K) in order to observe quantum-interference effects. The results are shown in Fig. 2. For large  $\lambda$ , we find  $\alpha(0) \approx 1$ , and the wave function is highly localized near the surface. As we reduce  $\lambda$ ,  $\alpha(0)$  drops and develops a nonmonotonic dependence on  $\lambda$  in the  $\lambda \approx 1-10$  range. The reflected wave packet is delocalized and has a broad energy spectrum which extends down to  $E=0$ . Because of finite-size effects, it is difficult to establish the precise value of  $\alpha$  in this range. For  $\lambda < 1$ ,  $\alpha(0)$  goes to zero and the wave function is indistinguishable from a Coulomb scattering state.

The essential point is that for  $\lambda \gg 1$  quantum reflection does *not* completely suppress  $\alpha(0)$ , contrary to the predictions of perturbation theory. We have checked this result for different values of  $E$  as well. This indicates that, as a function of  $\lambda$ ,  $\alpha(0)$  has a nonanalyticity around  $\lambda=1$ , although an  $\exp(-1/\lambda)$  dependence would also be possible. The suppression of quantum-interference effects by inelastic scattering could proceed through a phase transition, as in the case of level splitting in a double-well potential coupled to an "Ohmic" bath.<sup>13</sup> This possibility is reinforced by the observation of low-frequency "noise" in the wave function for  $\lambda \sim 1-10$ . However, our numerical accuracy is insufficient to check whether indeed we have true critical slowing down.

Experimental realization of the transition region should be quite readily achieved. If we take the real value of  $\sigma$

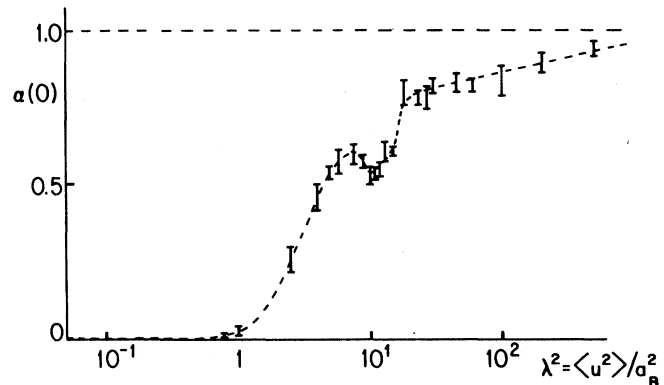


FIG. 2. Sticking coefficient  $\alpha(0)$  vs coupling strength  $\lambda$  for an incoming electron of momentum  $k = 2 \times 10^5$  cm $^{-1}$ . (The broken line is a guide to eye.)

for  $^4\text{He}$ , then  $\lambda^2 \sim 10^{-3}$ , and so electrons are well into the weak-coupling regime. However, the crossover to the strong-coupling regime could be seen either by decreasing the width of the  $^4\text{He}$  layer<sup>14</sup> or by increasing the mass of the incident particle. At low energies, we find no adsorption for a proton, but an  $\text{F}^-$  ion has a sticking coefficient  $\alpha(0) = 0.54$ . We have also repeated the above calculation for the scattering of  $^4\text{He}$  atoms from  $^4\text{He}$  surfaces, and found  $\alpha(0) \approx 0.5$ . Thus, both  $^4\text{He}$  and  $\text{F}^-$  would be in the intermediate to strong-coupling regime.

In summary, we find that for the case of adsorption of low-energy charged particles by dielectric fields, neither perturbation theory nor the classical approximation are valid over a large range of coupling constants. Low-energy adsorption involves a complex interplay between quantum interference and dissipation which is not well described by either of the two standard pictures.

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