Dissipative Effects on Quantum Sticking

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Using variational mean-field theory, many-body dissipative effects on the threshold law for quantum sticking and reflection of neutral and charged particles are examined. For the case of an Ohmic bosonic bath, we study the effects of the infrared divergence on the probability of sticking and obtain a nonperturbative expression for the sticking rate. We find that for weak dissipative coupling α, the low-energy threshold laws for quantum sticking are modified by an infrared singularity in the bath. The sticking probability for a neutral particle with incident energy $E \to 0$ behaves asymptotically as $s \sim E^{(1+\alpha)/2(1-\alpha)}$; for a charged particle, we obtain $s \sim E^{\alpha/2(1-\alpha)}$. Thus, ''quantum mirrors''—surfaces that become perfectly reflective to particles with incident energies asymptotically approaching zero—can also exist for charged particles. We provide a numerical example of the effects for electrons sticking to porous silicon via the emission of a Rayleigh phonon.

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Since the very early years of quantum theory, theorists have considered the interaction of low-energy atoms and molecules with surfaces [1]. In comparison to a classical particle, a quantum particle at low energy was predicted to have a reduced probability to adsorb to surfaces. The reason is despite the long-range attractive van der Waals interaction between a neutral particle and surface, at sufficiently low energies, quantum particles have little probability of coming near the surface [2].

This effect is named ''quantum reflection,'' and it is a simple result of the wavelike nature of low-energy particles moving in a finite-range attractive potential. This reduction in the particle's probability density near the surface leads to a reduction in the transition probability of the particle to a state bound to the surface. In one of the earliest applications of quantum perturbation theory, Lennard-Jones and Devonshire concluded that the probability of a neutral particle with energy E sticking to the surface should vanish as $\sqrt{E}$ as $E \to 0$.

In contrast, charged particles do not experience the effects of quantum reflection. Far from the surface, charged particles interact with the surface through a Coulomb potential generated by the image charge. Because of the slow spatial variation of the Coulomb potential, incident particles behave semiclassically. As a result, Clougherty and Kohn [2] found that the sticking probability should tend to a nonvanishing constant as $E \to 0$.

Without a mechanism for the incident particle to transfer energy to the target, a particle cannot adsorb to the surface; however, previous theoretical studies have concluded that the *detailed* form of the dynamical particle-surface interaction responsible for energy transfer is inessential to the sticking threshold law [3–5]. This seemingly universal scaling law for neutral particles was shown to hold even within a nonperturbative model that includes arbitrarily strong quantum fluctuations of the surface [2,6]. The model considered, however, was regularized with the use of a low-frequency cutoff. Thus the effects of an infrared divergence involving low-frequency excitations were not included in the analysis.

In the 1980s, experiments went to sub–millidegrees Kelvin temperatures to look for this threshold law scaling in a variety of physical systems without success [7]. Theorists [8] realized that the experiments suffered from unwanted interactions from a substrate supporting the target of a superfluid helium film. By increasing the thickness of the film, the next generation of experiments [9] produced data consistent with the $\sqrt{E}$ law, and the controversy subsided.

In recent years, with dramatic advances in producing and manipulating ultracold atoms, there is renewed interest in interactions between low-energy atoms and surfaces. New technologies have been proposed that rely on the quantum dynamics of ultracold atoms near surfaces; microfabricated devices called ''atom chips'' would store and manipulate cold atoms near surfaces for quantum information processing and precision metrology [10]. Our understanding of device performance will depend in part on our understanding of ultracold atom-surface interactions. Experiment is now in a position to test detailed theoretical predictions on the behavior of low-energy sticking and scattering from surfaces.

In this Letter, we consider a standard physisorption model nonperturbatively and we focus on the effects of low-frequency excitations on quantum reflection and sticking. Our primary interest is in exploring theoretically how the threshold laws might be modified by many-body effects. We follow the mean-field variational method introduced by Silbey and Harris in their analysis of the quantum dynamics of the spin-boson model [11]. Using this method we analyze the effects of the infrared divergence on the sticking process. Our analysis reveals two distinct scaling regimes in the parameter space in analogy with localized and delocalized phases in the spin-boson model. In the delocalized regime, an infrared divergence in the bath is cut off by an energy scale that depends on the incident energy of the particle E. As a consequence, we find that both the threshold laws for neutral and charged particles are modified by the dissipative coupling strength α. As a result of the low-frequency fluctuations, the threshold law for neutral particles is no longer universal, and the threshold law for charged particles no longer precludes perfect reflection at ultralow energies.

We take a standard model that is commonly used to describe physisorption where the adatom moves in a static potential and exchanges energy with a bath of oscillators. In the second quantized form, it becomes

$$H = H_p + H_b + H_c, \tag{1}$$

where

$$H_p = Ec_k^\dagger c_k - E_b b^\dagger b, \tag{2}$$

$$H_b = \sum_q \omega_q a_q^\dagger a_q, \tag{3}$$

$$\begin{aligned} H_c = &-(c_k^\dagger b + b^\dagger c_k) g_1 \sum_q \sigma(\omega_q)(a_q + a_q^\dagger) \\ &- c_k^\dagger c_k g_2 \sum_q \sigma(\omega_q)(a_q + a_q^\dagger) \\ &- b^\dagger b g_3 \sum_q \sigma(\omega_q)(a_q + a_q^\dagger) \end{aligned} \tag{4}$$

$c_k^\dagger$ (c_k) creates (annihilates) a particle in the entrance channel $|k\rangle$ with energy E; $b^\dagger$ (b) creates (annihilates) a particle in the bound state $|b\rangle$ with energy $-E_b$. $a_q^\dagger$ (a_q) creates (annihilates) a boson in the target bath with energy ω_q. (We use natural units throughout where $\hbar = 1$.) H_c is a general dynamical particle-surface interaction where g_1, g_2, and g_3 are model coupling constants, obtainable from the specific particle-excitation mechanism. The form of $\sigma(\omega_q)$ also depends on the specific particle-excitation coupling. These quantities are made explicit in the Supplemental Material [12] using the coupling to Rayleigh phonons as an example.

The g_2 term gives the strength of the coupling of the particle in the continuum to the bath, while g_3 gives the strength of the coupling of the bound particle to the bath. g_1 gives the strength of bath-assisted particle transitions between the continuum state and the bound state. The coupling constants g_2 and g_3 are analogous to those found in polaron models, and these terms give rise to self-energy corrections from the coupling to surface excitations.

There is ample evidence that such interactions are present in physisorption systems. A hydrogen atom bound to the surface of a liquid helium film has been seen experimentally to locally deform the surface [13], increasing the adatom binding energy and creating a type of surface polaron.

We work in the regime where $E \ll E_b$. We neglect the probability of "prompt" inelastic scattering, where bosons are created and the particle escapes to infinity with degraded energy, as the phase space available for these processes vanishes as $E \to 0$. Thus only the incoming and bound channels are retained for the particle.

We consider a model with Ohmic dissipative spectral density. Physically this can be realized with a dynamical particle-surface interaction resulting from surface displacements of an elastically isotropic target. (Brivio [14] showed this in a semiclassical model for the case of interactions with bulk phonons. We have found that an Ohmic spectral density also results for interactions with either Rayleigh phonons or "mixed mode" phonons [15]. We note that the particle-ripplon interaction [16], appropriate for the case of hydrogen sticking to superfluid helium films, gives a super-Ohmic spectral density. Hence, the $\sqrt{E}$ law would remain unchanged in this case by the nonperturbative effects considered here.) The spectral density function that characterizes the coupling to the excitation bath is given by

$$J(\omega) \equiv \sum_q g_3^2 \sigma^2(\omega_q) \delta(\omega - \omega_q) = \alpha\omega, \tag{5}$$

where α, the dissipative coupling strength, is a frequency-independent constant.

This model differs in an important way from the model of Ref. [2] where low-frequency modes were cut off to prevent an infrared divergence in the rms displacement of the surface atom in a 1D chain. In this model, low-frequency modes are included, and their effects on quantum reflection and sticking are the focus of this study.

We start with the variational approach used by Silbey and Harris [11] for the Ohmic spin-boson model. A generalized unitary transformation $U = e^S$ is first performed on the Hamiltonian H, with

$$S = b^\dagger b x \tag{6}$$

and

$$x = \sum_q \frac{f_q}{\omega_q}(a_q - a_q^\dagger). \tag{7}$$

The variational parameters to be determined are denoted by f_q. The unitary transformation displaces the oscillators to new equilibrium positions in the presence of the particle bound to the surface and leaves the oscillators unshifted when the particle is in the continuum state.

The transformed Hamiltonian $\tilde{H}$ is given by

$$\tilde{H} = e^S H e^{-S} \tag{8}$$

$$= \tilde{H}_p + \tilde{H}_b + \tilde{H}_c \tag{9}$$

where

$$\tilde{H}_p = E c_k^\dagger c_k - \tilde{E}_b b^\dagger b, \tag{10}$$

$$\tilde{H}_c = -c_k^\dagger b \sum_q g_{1q}(a_q + a_q^\dagger)e^{-x} - b^\dagger c_k e^x \sum_q g_{1q}(a_q + a_q^\dagger) - c_k^\dagger c_k \sum_q g_{2q}(a_q + a_q^\dagger) - b^\dagger b \sum_q (g_{3q} - f_q)(a_q + a_q^\dagger), \tag{11}$$

$$\tilde{H}_b = H_b, \tag{12}$$

$$\tilde{E}_b = E_b + \sum_q \frac{2 f_q g_{3q} - f_q^2}{\omega_q}, \tag{13}$$

and where $g_{iq} \equiv g_i \sigma(\omega_q)$. We define a mean transitional matrix element Δ

$$\Delta \equiv \left\langle e^x \sum_q g_{1q}(a_q + a_q^\dagger)\right\rangle, \tag{14}$$

where $\langle \cdots \rangle$ denotes the expectation over the bath modes.

The Hamiltonian is then separated into the following form:

$$\tilde{H} = H_0 + V, \tag{15}$$

where V is chosen such that $\langle V \rangle = 0$. Hence, we obtain

$$H_0 = E c_k^\dagger c_k - \tilde{E}_b b^\dagger b - \Delta^* c_k^\dagger b - \Delta b^\dagger c_k + \sum_q \omega_q a_q^\dagger a_q, \tag{16}$$

$$V = -c_k^\dagger b \left(\sum_q g_{1q}(a_q + a_q^\dagger)e^{-x} - \Delta^* \right) - b^\dagger c_k \left(e^x \sum_q g_{1q}(a_q + a_q^\dagger) - \Delta \right) - c_k^\dagger c_k \sum_q g_{2q}(a_q + a_q^\dagger) - b^\dagger b \sum_q (g_{3q} - f_q)(a_q + a_q^\dagger). \tag{17}$$

We calculate the ground state energy of H_0 in terms of the variational parameters $\{f_q\}$ and minimize to obtain the following condition:

$$f_q \left(1 + \frac{\epsilon + 2\Delta^2 \omega_q^{-1}}{\sqrt{\epsilon^2 + 4\Delta^2}} \right) = g_{3q} \left(1 + \frac{\epsilon}{\sqrt{\epsilon^2 + 4\Delta^2}} \right) + \frac{2\Delta \sqrt{u} g_{1q}}{\sqrt{\epsilon^2 + 4\Delta^2}}, \tag{18}$$

which is an implicit equation for f_q. For convenience, in the above we have defined

$$\epsilon = E + \tilde{E}_b = E + E_b + \sum_q \frac{2 f_q g_{3q} - f_q^2}{\omega_q} \tag{19}$$

and

$$\Delta = \sqrt{u}\,\Omega_1, \tag{20}$$

$$u \equiv e^{-\sum_q f_q^2/\omega_q^2}, \tag{21}$$

$$\Omega_1 \equiv \sum_q \frac{g_{1q} f_q}{\omega_q}. \tag{22}$$

Under the condition $\Delta \ll \epsilon$, Eq. (18) can be simplified to

$$f_q = \frac{g_{3q}}{1 + \frac{z}{\omega_q}}, \tag{23}$$

where

$$z \equiv \frac{\Delta^2}{\epsilon}. \tag{24}$$

We find the following, valid for $z \ll \omega_c$,

$$u \approx (ez/\omega_c)^\alpha, \tag{25}$$

$$\Omega_1 \approx g_1 \alpha \omega_c / g_3, \tag{26}$$

$$\epsilon \approx E + E_b + \alpha \omega_c. \tag{27}$$

The closed-form expression for z is thus obtained

$$z \approx K \left(\frac{eK}{\omega_c} \right)^{\alpha/1-\alpha}, \tag{28}$$

where

$$K \approx \frac{(g_1 g_3 \rho \omega_c)^2}{E + E_b + g_3^2 \rho \omega_c} \tag{29}$$

and $\rho = \alpha / g_3^2$.

Depending on the value of α, there are two solutions to the variational parameters f_q. We see from Eq. (28) that as $\alpha \to 1$, $z \to 0$. Thus,

$$f_q \approx \begin{cases} g_{3q}, & \alpha \geq 1, \\ \frac{g_{3q}}{1+\frac{z}{\omega_q}}, & \alpha < 1. \end{cases} \tag{30}$$

In the regime where $\alpha < 1$, we see that the parameter f_q for excitations whose frequency $\omega_q \ll z$ vanishes as $\omega_q \to 0$. It is this weakening of the coupling to nonadiabatic excitations that allows us to extract a finite mean transitional matrix element. In the process, the sticking rate is altered from the perturbative result.

We can now show that the condition $\Delta \ll \epsilon$ is satisfied so that our variational solution is self-consistent. According to Eq. (24), $\Delta/\epsilon = \sqrt{z/\epsilon}$. For $\alpha \geq 1$, $z = 0$, so $\Delta = 0$ and $\Delta \ll \epsilon$ holds true. For $\alpha < 1$, $z \sim g_1^{2/1-\alpha}$.

The coupling constant g_1 has a dependence on the initial energy of the particle E. This can be seen from the transition matrix element

$$g_{1q} = -\langle b, 1_q | H_c | k, 0 \rangle. \tag{31}$$

The amplitude of the initial state in the vicinity of the surface is suppressed by quantum reflection. It is a simple consequence of wave mechanics [2] that in the low-energy regime, $g_{1q} \sim \sqrt{E}$ as $E \to 0$ for a neutral particle. For a charged particle, the coupling constant behaves as $g_{1q} \sim E^{1/4}$ as $E \to 0$, as it is not subject to the effects of quantum reflection. Thus in either case, the mean-field amplitude Δ becomes arbitrarily small as E tends to zero, while ϵ approaches a nonzero value. Consequently, the conditions for our variational solution are always satisfied for sufficiently cold particles.

For $\Delta \ll \epsilon$, the rate of incoming atoms sticking to the surface can be calculated using Fermi's golden rule [17]:

$$R = 2\pi \sum_q |\langle b, 1_q | \tilde{H}_c | k, 0 \rangle|^2 \delta(-\tilde{E}_b - E + \omega_q), \tag{32}$$

where $|1_q\rangle$ denotes a state of one excitation with wave vector q.

After calculating the relevant matrix elements, we find the leading order of the rate R in the incident energy E to be

$$R = 2\pi \left(\frac{z}{\omega_c}\right)^\alpha e^\alpha g_1^2 \rho E_b \left(\frac{E_b}{E_b + \alpha \omega_c}\right), \tag{33}$$

where z given in Eq. (28) is a constant with a power dependence on g_1.

We compare this rate to that obtained by Fermi's golden rule on the untransformed Hamiltonian

$$\begin{aligned} R &= 2\pi \sum_q |\langle b, 1_q | H_c | k, 0 \rangle|^2 \delta(-E_b - E + \omega_q) \\ &= 2\pi g_1^2 \rho E_b. \end{aligned} \tag{34}$$

The matrix elements of transformed Hamiltonian $\tilde{H}_c$ are reduced by a Franck-Condon factor which gives the nonperturbative rate with an additional dependence on z.

The coupling constant g_1 can be expressed in terms of a matrix element of the unperturbed states using Eq. (31). We take H_c to have the general form in coordinate space [18]

$$H_c = -\sum_{q,\nu} \frac{\partial V_0(x)}{\partial x} u_{q,\nu,x}, \tag{35}$$

where the normal surface displacement $u_{q,\nu,x} = U_{q,\nu,x}(a_q + a_q^\dagger)$ with branch index ν and phonon wave vector q, while $V_0(x)$ is the static surface potential.

The coupling constant g_1 is given by

$$g_1 = \left\langle k \left| \frac{\partial V_0(x)}{\partial x} \right| b \right\rangle = \int_0^\infty \phi_k^*(x) \frac{\partial V_0(x)}{\partial x} \phi_b(x) dx. \tag{36}$$

(We have assumed the case of normal incidence; however, results for the more general case follow from decomposing the wave vector into normal and transverse components [16].)

The continuum wave functions have the asymptotic form for a neutral particle

$$\phi_k(x) \overset{k \to 0}{\sim} k h_1(x) \tag{37}$$

and for a charged particle [2]

$$\phi_k(x) \overset{k \to 0}{\sim} \sqrt{k} h_2(x), \tag{38}$$

where $k = \sqrt{2mE}$ and $h_i(x)$ are functions, independent of E.

The probability of sticking to the surface s is the sticking rate per surface area per unit incoming particle flux. Hence, $s(E) = \sqrt{\frac{2\pi^2 m}{E}} R$. From Eq. (33) we conclude that with $\alpha < 1$ for a neutral particle,

$$s(E) \sim C_1 E^{(1+\alpha)/2(1-\alpha)}, \qquad E \to 0 \tag{39}$$

and for a charged particle,

$$s(E) \sim C_2 E^{\alpha/2(1-\alpha)}, \qquad E \to 0 \tag{40}$$

where C_i are energy-independent constants. It is apparent from the nonanalyticity in α (signaling a quantum critical point at $\alpha = 1$) that the probability obtained goes beyond any finite-order perturbation theory in g_3.

We now provide a numerical calculation of the low-energy sticking probability of electrons to porous silicon via the emission of a Rayleigh phonon to illustrate our new threshold law. Porous silicon has a low static dielectric constant that varies with porosity and a low shear modulus, conditions that we predict will lead to measurable experimental effects in the one-phonon regime.

A comparative plot of the sticking probability is given in Fig. 1. The rate of sticking was calculated using Eq. (33). Using a cut-off image potential, we find a binding energy on highly porous silicon of $E_b = 7.8$ meV, a dissipative coupling $\alpha = 0.008$, and $g_3 = 1.3$ meV Å^{-1}. Further computational details are given in the Supplemental Material [12].

The sticking probability is reduced and the slope of the energy-dependent sticking probability has increased in comparison to the threshold law based on perturbation theory. We can quantify the size of the predicted effect on sticking: the relative error of omitting the effect of the infrared singularity is 13.6% over the incident energies considered in Fig. 1. The relative error will grow further at lower incident energies. The relative error made in the

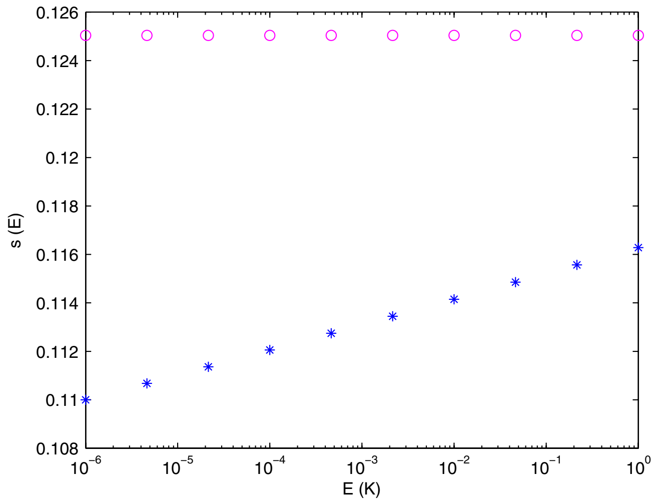

FIG. 1 (color online). The sticking probability of an electron of energy E to the surface of porous silicon by the emission of a Rayleigh phonon. The perturbative result using Fermi's golden rule is given by (red) circles, while the variational mean-field result is given by (blue) stars. The variational mean-field method gives a new threshold law for quantum sticking. We take a porosity $P = 92.9\%$, giving a dielectric constant $\kappa = 1.2$. The shear modulus of $G = 230$ MPa and Poisson's ratio $\sigma = 0.03$ are calculated using Ref. [20].

exponent of the scaling law by omitting the effect of the infrared singularity is 100%.

In summary, we have considered the effects of the infrared singularity resulting from interaction with an Ohmic bath on surface sticking. We calculated using a variational mean-field method the sticking rate as a function of the incident energy in the low-energy asymptotic regime. We have shown that for an Ohmic excitation bath the threshold rate for neutral particles decreases more rapidly with decreasing energy E, in comparison with the perturbative rate. We predict new threshold laws for surface sticking, where the energy dependence varies with the dissipative coupling α.

The new threshold laws are beyond simple perturbation theory where only first-order transitions are considered or the Fock space of the excitations is truncated. The new threshold laws are a result of a bosonic orthogonality catastrophe [19]; the ground states of the bath with different particle states are orthogonal. The sticking transition amplitude acquires a Franck-Condon factor whose infrared singularity is cut off by z. As with the x-ray absorption edge [19], a new power law results at threshold. The low-frequency fluctuations alter the power law to a bath-dependent, nonuniversal exponent.

For the case of charged particles, we find that dissipative coupling causes the sticking probability to vanish as $E \to 0$, in contrast to the perturbative result [2]. Thus, "quantum mirrors"—surfaces that become perfectly reflective to particles with incident energies asymptotically approaching zero—can also exist for charged particles.

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