Quantum theory of sticking

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We present an exact solution of a one-dimensional (1D) model: a particle of incident energy E colliding with a target which is a 1D harmonic "solid slab" with N atoms in its ground state; the Hilbert space of the target is restricted to the $(N+1)$ states with zero or one phonon present. For the case of a short-range interaction $V(z)$ between the particle and the surface atom supporting a bound state, an explicit nonperturbative solution of the collision problem is obtained. For finite and large N, there is no true sticking but only so-called Feshbach resonances. A finite sticking coefficient $s(E)$ is obtained by introducing a small phonon decay rate η and letting $N \to \infty$. Our main interest is in the behavior of $s(E)$ as $E \to 0$. For a short-range $V(z)$, we find $s(E) \sim E^{1/2}$, regardless of the strength of the particle-phonon coupling. However, if $V(z)$ has a Coulomb z^{-1} tail, we find $s(E) \to \alpha$, where $0<\alpha<1$. [A fully classical calculation gives $s(E) \to 1$ in both cases.] We conclude that the same threshold laws apply to 3D systems of neutral and charged particles, respectively. In an appendix we elucidate the nature of sticking by the behavior of a wave packet incident on a finite N target.

I. INTRODUCTION

Recent experiments[1,2] on the sticking probability $s(E)$ of particles on surfaces have rekindled interest in its threshold behavior as the incident energy E tends to zero. It is known[3] that in classical mechanics $\lim_{E\to 0} s(E)=1$. A low-energy quantum incident particle, however, because of its wave nature is expected to have a sharply reduced probability density near the reflecting surface where its "effective" wave function is expected to become zero. This effect is named "quantum reflection" in the literature.[4] In the quantum regime, different authors have reached different theoretical conclusions about $s(E)$ near $E=0$.

A general discussion of inelastic particle-surface scattering is due to Cabrera *et al.*,[5] which, however, does not deal explicitly with the threshold behavior of $s(E)$.

The formal theory of $s(E)$ was developed by Brenig[6] who shows that the effects of particle-phonon interactions on the reflection and sticking of the particle can be incorporated in a nonlocal, energy-dependent, complex potential[7] $U_{\text{eff}}(r,r';E)$. Assuming that U_{eff} is short range in r and r' and has a well-defined finite limit as $E \to 0$, he shows that $s(0)=0$. He illustrates this conclusion for two models: one is a reflection from a static potential (no particle-phonon coupling); the other uses a phenomenological resonance.[8]

In a sequel, Böheim *et al.*[9] consider the physically interesting case of a neutral particle where the particle-surface interaction behaves as z^{-3} for large particle-surface separation z. They conclude that $s(0)$ vanishes also in this case. They remark, however, that for this "long-range" potential, $s(E)$ is accurately given by its semiclassical value ($\neq 0$), except for extremely low energies.

Polarization effects associated with virtual phonon excitations and particle continuum states are neglected in Refs. 5 and 9. Knowles and Suhl[10] have shown that surface polarization effects increase $s(E)$ at low energies. As a result of the polarization, the penetration of the particle's effective wave function into the surface region is increased. This effect is in competition with quantum reflection in the determination of $s(E)$ as $E \to 0$.

Martin, Bruinsma, and Platzman[11] calculated $s(E)$ using perturbation theory for the case of a charged particle and concluded (mistakenly) that $s(E) \propto E^{1/4}$ for small E, so that $s(0)=0$. Their subsequent numerical calculations[12] using the time-dependent Hartree approximation indicated to them that $s(0)\neq 0$ if the particle-phonon coupling λ exceeded a critical value λ_c. They concluded that for the case $\lambda > \lambda_c$, polarization effects would dominate the quantum reflection.

In our work we use first a one-dimensional model, exactly solvable for all coupling strengths, and obtain a closed-form expression for $s(E)$; polarization and quantum reflection effects are included and identified. The model consists of a one-dimensional harmonic "solid slab" which interacts with the impinging particle via a potential which supports one bound state (Fig. 1). While true sticking is not possible for a finite solid without dissipation, metastable, resonant many-body states which become longer lived as the thickness of the solid grows are identified as precursors to the adsorbed state. The sticking coefficient $s(E)$ can be found from the limiting behavior of the reflection coefficient as the thickness of the solid tends toward infinity. Adsorption resulting from particle-phonon coupling has some analogy with formation of a "compound nucleus"[13] in nucleon-nucleon collisions. We find that for an interaction potential of finite range or a z^{-3} tail, regardless of its strength, $s(E) \propto E^{1/2}$ for small E. However, for potentials with attractive Coulomb tails, we find, unlike Ref. 11 that, for small E, $s(E) \to \alpha$ where $0<\alpha<1$.

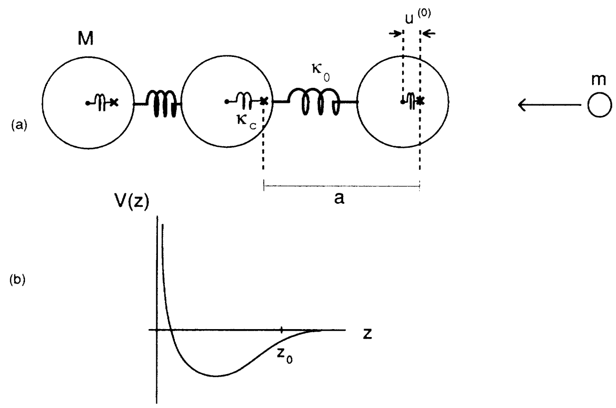

FIG. 1. (a) Schematic view of a particle with mass m impinging upon a one-dimensional solid consisting of atoms with mass M. Lattice atoms are coupled to nearest neighbors and to fixed lattice sites. (b) Particle interacts with the end atom via a finite-range surface potential.

II. THE MODEL

The model is sketched in Fig. 1(a). It has an external particle interacting with a one-dimensional solid slab. All motions are constrained to one dimension. The surface atom and the particle interact by a short-range[14] potential whose generic form is sketched in Fig. 1(b). We take for the Hamiltonian of the system[15]

$$\mathcal{H}=\mathcal{H}_{\rm ph}+\mathcal{H}_p+\mathcal{H}_I \ , \tag{1}$$

where

$$\begin{aligned}\mathcal{H}_{\rm ph}&=\sum_q \hbar\Omega_q a_q^\dagger a_q \ ,\\ \mathcal{H}_p&=\frac{P^2}{2m}+V(z) \ ,\\ \mathcal{H}_I&=u^{(0)}V'(z) \ .\end{aligned} \tag{2}$$

$u^{(0)}$ is the displacement of the surface atom, and $\mathcal{H}_p$ is the Hamiltonian for the particle moving in the static potential $V(z)$. $\mathcal{H}_{\rm ph}$ is the Hamiltonian for the phonons in the solid; $\mathcal{H}_I$ contains the particle-phonon coupling; m is the particle mass; Ω_q is the frequency of the phonon with wave number q; and $a_q^\dagger$ and a_q are phonon creation and annihilation operators, respectively.

The displacement of the surface atom can be expanded in normal modes leading to

$$\mathcal{H}_I=\sum_q u_q(a_q^\dagger+a_q)V'(z) \ , \tag{3}$$

where

$$u_q=\frac{1}{\sqrt{N}}\left[\frac{\hbar}{M\Omega_q}\right]^{1/2}\cos\left[\frac{qa}{2}\right] , \tag{4}$$

N is the number of atoms in the solid, M is the mass of a lattice atom, and a is the equilibrium lattice spacing.[16]

The phonon Hamiltonian describes a chain of N atoms coupled harmonically to their nearest neighbors and to fixed sites as illustrated in Fig. 1. (The coupling to fixed sites is needed in this one-dimensional model to prevent a well-known infrared divergence of $u^{(0)}$ which does not exist in higher dimensions.) The interaction potential V is sufficiently deep so as to support a bound state.

We next restrict the Hilbert space to states with zero or one phonons present.[17] However, we allow an arbitrarily strong particle-lattice interaction. This is in the spirit of the Tamm-Dancoff approximation.[18]

We expand the wave function using zero- and one-phonon eigenstates, ψ_0 and $\{\psi_i\}$,

$$\Psi(z_1,z_2,\ldots,z_N,z)=\phi_0(z)\psi_0(z_1,z_2,\ldots,z_N)+\sum_{i=1}^N\phi_i(z)\psi_i(z_1,z_2,\ldots,z_N) \ , \tag{5}$$

where $(z_1,z_2,\ldots,z_N)$ are the positions of the chain atoms, i labels the modes, and z is the position of the particle. The following coupled system of equations results:

$$\begin{aligned}&(\mathcal{H}_p-E)\phi_0(z)+\sum_{i=1}^N V_{0i}(z)\phi_i(z)=0 \ ,\\ &(\mathcal{H}_p+\hbar\Omega_i-E)\phi_i(z)+V_{i0}(z)\phi_0(z)=0 \ ,\end{aligned} \tag{6}$$

where

$$V_{i0}(z)=V_{0i}(z)=\frac{1}{\sqrt{N}}\left[\frac{\hbar}{M\Omega_i}\right]^{1/2}V'(z)\cos\left[\frac{q_ia}{2}\right] , \tag{7}$$

$\hbar\Omega_i$ is the excitation energy , q_i is the wave number of the ith mode, and E is the total energy of the system. Thus the matrix V_{ij} has the simple form of a bordered matrix.

III. TWO-STATE SYSTEM

In this section we deal with the case $N=1$ where the target is a simple harmonic oscillator and—in our model—the target Hilbert space consists of two states, the oscillator's lowest and first excited state. This case contains many features of the general N-atom chain.

We assume that the energy E of the particle is below the excitation energy $\hbar\Omega$ of the oscillator, and we shall find purely elastic reflection with a sticking resonance which occurs when $E\approx\hbar\Omega-E_b$, where E_b is the (positive) binding energy in the potential $V(z)$.

For this two-state problem, the coupled system of Eq. (6) becomes

$$\left[\frac{d^2}{dz^2}+k^2-U(z)\right]\phi_0(z)=U_{01}(z)\phi_1(z)\ , \qquad (8a)$$

$$\left[\frac{d^2}{dz^2}+k^2-\omega-U(z)\right]\phi_1(z)=U_{01}(z)\phi_0(z)\ , \qquad (8b)$$

where $k^2=(2m/\hbar^2)E$, $\omega=(2m/\hbar^2)\hbar\Omega$, $U(z)=(2m/\hbar^2)V(z)$, and $U_{01}(z)=(2m/\hbar^2)V_{01}(z)$.

Equation (8b) can be solved for ϕ_1 in terms of ϕ_0,

$$\phi_1(z)=\int dz' G_1(z,z')U_{01}(z')\phi_0(z')\ , \qquad (9)$$

where $G_1(z,z')$ is the (real) Green's function which satisfies the differential equation

$$\left[\frac{d^2}{dz^2}+k^2-\omega-U(z)\right]G_1(z,z')=\delta(z-z') \qquad (10)$$

and the conditions that $G_1(-\infty,z')=0$ and $G_1(z,z')\to 0$ as $z\to\infty$. Here and below, spatial integrals run from $-\infty$ to $+\infty$ unless otherwise noted.

$G_1(z,z')$ can be expanded in eigenfunctions of $[d^2/dz^2-U(z)]$ vanishing at $z=-\infty$,

$$G_1(z,z')=\frac{\Phi_b(z)\Phi_b(z')}{\epsilon_b-\omega+k^2}+\int_0^\infty dk'\frac{\Phi(z,k')\Phi(z',k')}{-\omega+k^2-k'^2}\ , \qquad (11)$$

where $\epsilon_b\equiv 2mE_b/\hbar^2$; the bound-state eigenfunction Φ_b is normalized such that

$$\int dz\, \Phi_b(z)\Phi_b(z)=1\ , \qquad (12)$$

while the continuum eigenfunctions are normalized such that

$$\int dz\, \Phi(z,p)\Phi(z,q)=\delta(p-q)\ . \qquad (13)$$

Since the incident energy is taken to be below the inelastic threshold ($k^2<\omega$), the integrand in Eq. (11) has no singularity, and ϕ_1 is localized, corresponding to a closed channel.

Substituting the above form of the Green's function into the formal solution of ϕ_1 gives

$$\phi_1(z)=\mathcal{A}(k)\Phi_b(z)-\int dz'\int_0^\infty dk'\frac{\Phi(z,k')\Phi(z',k')}{\omega-k^2+k'^2}\times U_{01}(z')\phi_0(z')\ , \qquad (14)$$

where $\mathcal{A}$ is the "bound-state amplitude" linear in ϕ_0 and given by

$$\mathcal{A}(k)=\int dz'\frac{\Phi_b(z')}{\epsilon_b-\omega+k^2}U_{01}(z')\phi_0(z')\ . \qquad (15)$$

Substitution of Eq. (14) into Eq. (8a) gives a linear, homogeneous integro-differential equation for ϕ_0, the elastic channel,

$$\left[\frac{d^2}{dz^2}+k^2-U(z)\right]\phi_0(z)+\int dz' U_{\rm pol}(z,z';k)\phi_0(z') =\mathcal{A}\,U_{01}(z)\Phi_b(z)\ , \qquad (16)$$

where we have introduced a real "polarization potential,"

$$U_{\rm pol}(z,z';k)\equiv\int_0^\infty dk'\frac{U_{01}(z)\Phi(z,k')\Phi(z',k')U_{01}(z')}{\omega-k^2+k'^2}\ , \qquad (17)$$

describing virtual excitations of the particle-phonon system, exclusive of virtual particle binding.

To solve Eq. (16) in terms of the as yet unknown $\mathcal{A}$ and subject to the boundary conditions

$$\phi_0(-\infty)=0 \qquad (18a)$$

$$\phi_0(z)=e^{-ikz}-R(k)e^{ikz},\quad z\to\infty \qquad (18b)$$

we introduce a second complex Green's function $\mathcal{G}(z,z';k)$ which is the solution to

$$\left[\frac{d^2}{dz^2}+k^2-U(z)\right]\mathcal{G}(z,z';k) +\int dz'' U_{\rm pol}(z,z'';k)\mathcal{G}(z'',z';k)=\delta(z-z') \qquad (19)$$

with the boundary conditions

$$\mathcal{G}(-\infty,z';k)=0\ ,\qquad \mathcal{G}(z,z';k)\sim e^{ikz},\quad z\to\infty\ . \qquad (20)$$

Thus

$$\phi_0(z)=-2ie^{i\delta(k)}\chi_0(z;k) +\mathcal{A}\int dz'\mathcal{G}(z,z';k)U_{01}(z')\Phi_b(z')\ . \qquad (21)$$

Here $\chi_0(z;k)$ is the real solution to Eq. (16) with $\mathcal{A}$ set to zero

$$\left[\frac{d^2}{dz^2}+k^2-U(z)\right]\chi_0(z;k) +\int dz' U_{\rm pol}(z,z';k)\chi_0(z';k)=0\ , \qquad (22)$$

which satisfies the boundary conditions that $\chi_0(-\infty;k)=0$ and $\chi_0(z;k)\to\sin(kz+\delta)$ as $z\to\infty$, and the phase shift $\delta(k)$ is due to the two potentials U and $U_{\rm pol}$.

$\mathcal{G}$ can be expressed in terms of χ_0 and a second real solution χ_1 of Eq. (22), which has the asymptotic form $\chi_1(z;k)\to\cos(kz+\delta)$ as $z\to\infty$,

$$\mathcal{G}(z,z';k)=-\frac{1}{k}\begin{cases}\chi_0(z;k)\chi_1(z';k)+i\chi_0(z;k)\chi_0(z';k), & z\le z'\\ \chi_0(z';k)\chi_1(z;k)+i\chi_0(z;k)\chi_0(z';k), & z\ge z'\ .\end{cases} \qquad (23)$$

Substituting Eq. (21) into Eq. (15) gives a closed expression for $\mathcal{A}$,

$$\mathcal{A}(k)=\frac{-2ie^{i\delta(k)}\int dz'\Phi_b(z')U_{01}(z')\chi_0(z';k)}{\epsilon_b-\omega+k^2-\int dz'dz''\Phi_b(z')U_{01}(z')\mathcal{G}(z',z'';k)U_{01}(z'')\Phi_b(z'')} . \tag{24}$$

Using Eq. (23), we separate the denominator of Eq. (24) into its real and imaginary parts and write

$$\mathcal{A}(k)=\frac{-ie^{i\delta(k)}\sqrt{2k\gamma(k)}}{k^2-\omega+\epsilon_b-\Delta\epsilon(k)+i\dfrac{\gamma(k)}{2}} \tag{25}$$

where

$$\Delta\epsilon(k)=\int dz'dz''\Phi_b(z')U_{01}(z')\mathrm{Re}\{\mathcal{G}(z',z'';k)\} \times U_{01}(z'')\Phi_b(z'') \tag{26}$$

and

$$\gamma(k)=\frac{2}{k}\left[\int dz'\Phi_b(z')U_{01}(z')\chi_0(z';k)\right]^2 . \tag{27}$$

When this value of $\mathcal{A}$ is substituted in Eq. (21) and we define $\tilde{\epsilon}(k)\equiv\omega-\epsilon_b+\Delta\epsilon(k)$, we obtain the closed solution for ϕ_0 which has the asymptotic form of Eq. (18b), where

$$R(k)=e^{2i\delta(k)}\left[\frac{k^2-\tilde{\epsilon}(k)-i\dfrac{\gamma(k)}{2}}{k^2-\tilde{\epsilon}(k)+i\dfrac{\gamma(k)}{2}}\right] . \tag{28}$$

We note that $|R(k)|=1$ for all k, reflecting the absence of sticking in this two-state model. For small coupling U_{01} and consequent small γ, the expression for R is characteristic of a resonance at incident energy given by $k_r^2=\omega-\epsilon_b+\Delta\epsilon(k_r)$ and of width $\gamma(k_r)$. The phase of $R(k)$ rapidly passes through 2π. This resonance is between the initial state, with the particle having energy k_r^2 and the target in its ground state, and the final state, with the particle bound and the target in its excited state.[19]

IV. THE $(N+1)$-STATE SYSTEM

For a chain of N atoms, there is a single lattice ground state and N one-phonon states. We rewrite the coupled equations (6) for the $(N+1)$ particle functions $\phi_0,\phi_1,\ldots,\phi_N$ in the form

$$\left[\frac{d^2}{dz^2}+k^2-U(z)\right]\phi_0(z)=\sum_{i=1}^{N}U_{0i}(z)\phi_i(z) , \tag{29a}$$

$$\left[\frac{d^2}{dz^2}+k^2-\omega_i-U(z)\right]\phi_i(z) =U_{0i}(z)\phi_0(z),\quad i=1,2,\ldots,N. \tag{29b}$$

$\omega_i\equiv(2m/\hbar^2)\hbar\Omega_i$, and

$$U_{0i}(z)\equiv\frac{2m}{\hbar^2}V_{0i}(z)=\left[\frac{2m}{NM\omega_i}\right]^{1/2}U'(z)\cos\left[\frac{q_ia}{2}\right] .$$

For $k^2\le\omega_i$, the ith channel is closed. We will again restrict our attention to incident energies below the inelastic threshold so that $k^2-\omega_i$ is negative for all i. The case of k^2 above the inelastic threshold is treated in Appendix C.

Equation (29b) can be formally solved by introducing a Green's function G_i such that

$$\phi_i(z)=\int dz'G_i(z,z')U_{0i}(z')\phi_0(z') , \tag{30}$$

where

$$\left[\frac{d^2}{dz^2}+k^2-\omega_i-U(z)\right]G_i(z,z')=\delta(z-z') \tag{31}$$

and satisfies the appropriate boundary conditions.

The Green's function G_i can be expanded. In analogy with Eqs. (11) and (14), we write

$$G_i(z,z')\equiv\frac{\Phi_b(z)\Phi_b(z')}{\epsilon_b-\omega_i+k^2}+\int_0^\infty dk'\frac{\Phi(z,k')\Phi(z',k')}{k^2-\omega_i-k'^2} \tag{32}$$

and

$$\phi_i(z)=\mathcal{A}_i(k)\Phi_b(z)+\int dz'\int_0^\infty dk'\frac{\Phi(z,k')\Phi(z',k')}{k^2-\omega_i-k'^2} \times U_{0i}(z')\phi_0(z') , \tag{33}$$

where

$$\mathcal{A}_i(k)=\frac{1}{\epsilon_b+k^2-\omega_i}\int dz'\Phi_b(z')U_{0i}(z')\phi_0(z') . \tag{34}$$

A single self-consistent equation for ϕ_0 can be found by substituting Eq. (33) into Eq. (29a),

$$\left[\frac{d^2}{dz^2}+k^2-U(z)\right]\phi_0(z)+\int dz'U_{\mathrm{pol}}(z,z';k)\phi_0(z') =\sum_{i=1}^{N}\mathcal{A}_i(k)U_{0i}(z)\Phi_b(z) , \tag{35}$$

where

$$U_{\mathrm{pol}}(z,z';k)\equiv\int_0^\infty dk'\sum_{i=1}^{N}\frac{U_{0i}(z)\Phi(z,k')\Phi(z',k')U_{0i}(z')}{\omega_i-k^2+k'^2} \tag{36}$$

and $\mathcal{A}_i$ is defined in Eq. (34).

The Green's function $\mathcal{G}(z,z';k)$, which was defined in Eq. (19), can again be used to solve Eq. (35) for ϕ_0,

$$\phi_0(z)=-2ie^{i\delta(k)}\chi_0(z;k) +\int dz'\mathcal{G}(z,z';k)\sum_{i=1}^{N}\mathcal{A}_i(k)U_{0i}(z')\Phi_b(z') \tag{37}$$

in terms of the $\mathcal{A}_i$. The $(N+1)$-state solution is thus a simple generalization of Eq. (21).

Substituting Eq. (37) into the definition of $\mathcal{A}_i$ given in

Eq. (34) yields the following coupled equations for the $\mathcal{A}_i$:

$$\sum_{j=1}^{N} [(\epsilon_b-\omega_i+k^2)\delta_{ij}-W_{ij}]\mathcal{A}_j=P_i, \tag{38}$$

here

$$W_{ij}=\frac{1}{N}W(k)\frac{\cos\left[\frac{q_i a}{2}\right]}{\sqrt{\omega_i}}\frac{\cos\left[\frac{q_j a}{2}\right]}{\sqrt{\omega_j}}, \tag{39}$$

where

$$W(k)=2\left[\frac{m}{M}\right]\int dz'dz''\Phi_b(z')U'(z')\mathcal{G}(z',z'';k)\times U'(z'')\Phi_b(z'') \tag{40}$$

and

$$P_i=-2ie^{i\delta(k)}\int dz'\Phi_b(z')U_{0i}(z')\chi_0(z';k)=\frac{1}{N}P(k)\frac{\cos\left[\frac{q_i a}{2}\right]}{\sqrt{\omega_i}}, \tag{41}$$

where

$$P(k)=-2ie^{i\delta(k)}\sqrt{2m/M}\int dz'\Phi_b(z')U'(z')\chi_0(z';k). \tag{42}$$

The matrix equation for the channel amplitudes can be solved by noting that W_{ij} has a product form. Thus Eq. (38) can be rewritten in the form

$$(\epsilon_b-\omega_i+k^2)\mathcal{A}_i=\frac{\cos\left[\frac{q_i a}{2}\right]}{\sqrt{\omega_i}}\left[\frac{1}{N}\right]W(k)\times\sum_{j=1}^{N}\frac{\cos\left[\frac{q_j a}{2}\right]}{\sqrt{\omega_j}}\mathcal{A}_j+\frac{\cos\left[\frac{q_i a}{2}\right]}{\sqrt{N\omega_i}}P(k). \tag{43}$$

After multiplying Eq. (43) by $\sqrt{\omega_i}/\cos(q_i a/2)$, it should be noted that the right-hand side is now independent of i. Hence $\mathcal{A}_i(k)$ has the form

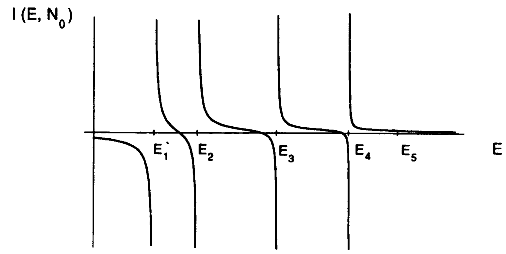

FIG. 2. Sketch of $I(E,N)$ for $N=5$. [The last singularity at $E=E_5$ is suppressed by the factor $\cos(q_i a/2)$ in Eq. (7), corresponding to the reduction of particle coupling to phonons near the zone edge.]

$$\mathcal{A}_i(k)=\frac{B(k)\cos\left[\frac{q_i a}{2}\right]}{(k^2+\epsilon_b-\omega_i)\sqrt{\omega_i}}. \tag{44}$$

$B(k)$ can be determined by substitution of Eq. (44) into Eq. (43), yielding

$$B(k)=\frac{P(k)}{\sqrt{N}[1-W(k)I(k,N)]}, \tag{45}$$

where $W(k)$ is given by Eq. (40) and

$$I(k,N)\equiv\left[\frac{1}{N}\right]\sum_{i=1}^{N}\frac{\cos^2\left[\frac{q_i a}{2}\right]}{(k^2+\epsilon_b-\omega_i)\omega_i}. \tag{46}$$

$I(k,N)$ is a nearly periodic function of k^2 with slowly varying period and alternating poles and zeros along the real axis for any finite N (see Fig. 2).

Equation (44) now gives the explicit expression for the channel amplitudes

$$\mathcal{A}_i(k)=\left[\frac{\cos\left[\frac{q_i a}{2}\right]}{(k^2+\epsilon_b-\omega_i)\sqrt{\omega_i}}\right]\left[\frac{\sqrt{1/N}P(k)}{1-W(k)I(k,N)}\right]. \tag{47}$$

As in the two-channel case, the asymptotic form of ϕ_0 from Eq. (37) gives an expression for the reflection coefficient R

$$R(k,N)=e^{2i\delta(k)}\left[1-\frac{4i}{k}\left[\frac{m}{M}\right]\frac{I(k,N)}{1-W(k)I(k,N)}\left[\int dz'\Phi_b(z')U'(z')\chi_0(z';k)\right]^2\right]=e^{2i\delta(k)}\left[\frac{1-W^*(k)I(k,N)}{1-W(k)I(k,N)}\right]=e^{2i[\delta(k)+\bar{\delta}(k)]}, \tag{48}$$

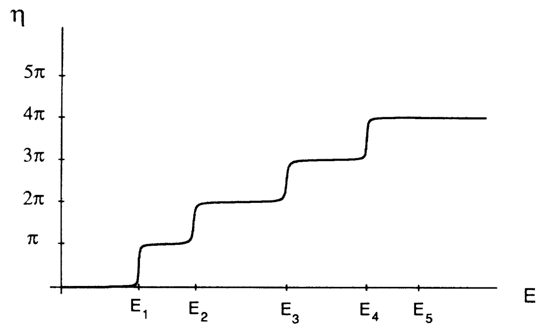

FIG. 3. Sketch of $\eta(E)$ for $N=5$.

where

$$\tilde{\delta}(k)=\tan^{-1}\left[\frac{I(k,N)\mathrm{Im}W(k)}{1-\mathrm{Re}W(k)I(k,N)}\right]. \tag{49}$$

Again the elastic reflection coefficient has a magnitude of unity for finite N, and thus $s(E)\equiv 0$. The typical behavior of $\tilde{\delta}$ is given in Fig. 3. The implications of this rapid variation of $\tilde{\delta}$ with k for the reflection of a wave packet (showing "Poincaré cycles") are developed in Appendix E.

V. STICKING IN CONTINUUM LIMIT

Real phonons have a finite lifetime (e.g., due to anharmonic coupling) which adds a small, negative imaginary part, independent of N, to the phonon excitation energies,

$$\omega_j \to \omega_j - i\eta , \tag{50}$$

where η^{-1} represents the lifetime of the phonon.[20] With the addition of this small imaginary part, the poles of $I(k,N)$ are pushed off the real k axis by small but N-independent distances.

As N becomes large, the discrete lattice modes become increasingly dense. When their spacing becomes small compared to η, the summation in the definition of $I(k,N)$ can be replaced by a Riemann integral

$$\begin{aligned}\mathcal{I}(k)&=\lim_{N\to\infty} I(k,N)\\ &=\int_{\omega_c}^{\omega_m} d\omega \frac{\rho(\omega)\cos^2\left[\dfrac{q(\omega)a}{2}\right]}{(k^2+\epsilon_b-\omega+i\eta)\omega} ,\end{aligned} \tag{51}$$

where $\rho(\omega)$ is the density of vibrational states per atom.[21]

The dispersion for the solid, schematically shown in Fig. 1, is of the form

$$\omega(q)=\left[\omega_D^2\sin^2\left[\frac{qa}{2}\right]+\omega_c^2\right]^{1/2} , \tag{52}$$

where $\omega_D=4m/\hbar\sqrt{\kappa_0/M}$ and $\omega_c=2m/\hbar\sqrt{\kappa_c/M}$. The density of vibrational states per atom is then

$$\begin{aligned}\rho(\omega)&=\frac{dn}{dq}\left[\frac{d\omega}{dq}\right]^{-1}\\ &=\frac{2}{\pi}\frac{\omega}{[(\omega^2-\omega_c^2)(\omega_m^2-\omega^2)]^{1/2}} ,\end{aligned} \tag{53}$$

where $\omega_m=(\omega_D^2+\omega_c^2)^{1/2}$ and n is the number of modes per atom.

There is a simple pole in the integrand of Eq. (51) just above the real ω axis. The integration can be performed by using the integration contour illustrated in Fig. 4. The contribution of the integral in the vicinity of the pole gives a negative imaginary part,

$$\begin{aligned}\mathcal{I}(k)=&\frac{2}{\pi}\frac{1}{\omega_m^2-\omega_c^2}\\ &\times \mathbf{P}\int_{\omega_c}^{\omega_m} d\omega \frac{1}{(k^2+\epsilon_b-\omega)}\left[\frac{\omega_m^2-\omega^2}{\omega^2-\omega_c^2}\right]^{1/2}\\ &-i\frac{2}{(\omega_m^2-\omega_c^2)}\left[\frac{\omega_m^2-(k^2+\epsilon_b)^2}{(k^2+\epsilon_b)^2-\omega_c^2}\right]^{1/2} .\end{aligned} \tag{54}$$

P denotes the principal part.[22]

Since $\mathcal{I}(k)$ now has a finite imaginary part, the magnitude of the reflection coefficient differs from unity even for energies below the inelastic threshold. We identify the deviation of $|R|^2$ from unity as the sticking coefficient. Thus the sticking coefficient is given by

$$\begin{aligned}s(k)&=1-\lim_{N\to\infty}|R(k,N)|^2\\ &=1-\left|e^{2i\delta(k)}\left[\frac{1-W^*(k)\mathcal{I}(k)}{1-W(k)\mathcal{I}(k)}\right]\right|^2\\ &=\frac{4\,\mathrm{Im}W(k)\mathrm{Im}\mathcal{I}(k)}{1-2\,\mathrm{Re}[W(k)\mathcal{I}(k)]+|W(k)|^2|\mathcal{I}(k)|^2} .\end{aligned} \tag{55}$$

In the limit of low energy ($k\to 0$), χ_0 and χ_1 can be expressed in the form

$$\begin{aligned}&\chi_0(z;k)=kg_0(z), \quad k\to 0\\ &\chi_1(z;k)=g_1(z), \quad k\to 0\end{aligned} \tag{56}$$

where g_0 and g_1 are independent of k. From Eq. (40), in the low-energy limit W is given by

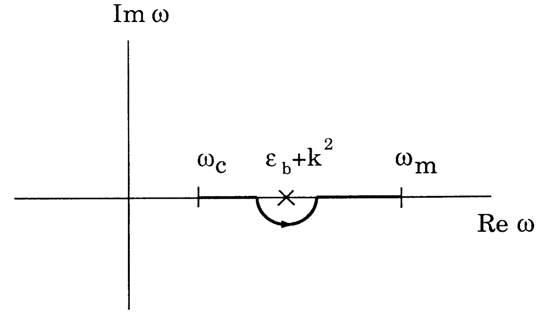

FIG. 4. Integration contour in the complex ω plane for evaluating $\mathcal{I}$.

$$\mathrm{Re}W(k)=-w_0 \;,$$
$$\mathrm{Im}W(k)=-k\gamma_0^2 \;, \tag{57}$$

where

$$w_0=2\left[\frac{m}{M}\right]\int dz'dz''\Phi_b(z')U'(z')g(z',z'')\times U'(z'')\Phi_b(z'') \;, \tag{57'}$$

$$g(z,z')=\begin{cases} g_0(z)g_1(z'), & z\le z' \\ g_0(z')g_1(z), & z\ge z' \end{cases} \tag{58}$$

and

$$\gamma_0^2=2\left[\frac{m}{M}\right]\left[\int dz'\Phi_b(z')U'(z')g_0(z')\right]^2 . \tag{59}$$

$\mathcal{J}$ approaches a constant as $k\to 0$; namely,

$$\mathcal{J}_0=\frac{2}{\pi}\frac{1}{\omega_m^2-\omega_c^2}\mathrm{P}\int_{\omega_c}^{\omega_m}d\omega\frac{1}{(\epsilon_b-\omega+i\eta)}\left[\frac{\omega_m^2-\omega^2}{\omega^2-\omega_c^2}\right]^{1/2} -i\frac{2}{\omega_m^2-\omega_c^2}\left[\frac{\omega_m^2-\epsilon_b^2}{\epsilon_b^2-\omega_c^2}\right]^{1/2} \equiv \mathcal{J}_1-i\mathcal{J}_2 \;. \tag{60}$$

Substituting Eqs. (57) and (60) into the expression for s in Eq. (55) gives

$$s(k)=k\left[\frac{4\gamma_0^2\mathcal{J}_2}{(1+\omega_0\mathcal{J}_1)^2+w_0^2\mathcal{J}_2^2}\right] . \tag{61}$$

We see that $s(E)\sim E^{1/2}$, regardless of the strength of the particle-phonon coupling. We shall now verify that for weak coupling, Eq. (61) reduces to the result obtained in the distorted-wave Born approximation (DWBA). The *exact* transition rate $\mathcal{R}$ from the elastic channel to the bound state is given by

$$\mathcal{R}=\frac{2\pi}{\hbar}\int_{\omega_c}^{\omega_m}d\omega\, N\rho(\omega)|\langle\phi_0|V_\omega|\Phi_b\rangle|^2\frac{2m}{\hbar^2}\delta(\omega-\epsilon_b-k^2) =\frac{2\hbar}{M}|\langle\phi_0|U'|\Phi_b\rangle|^2|\mathrm{Im}\mathcal{J}(k)| \;, \tag{62}$$

where V_ω is given by the continuum form of Eq. (7)

$$V_\omega(z)=\frac{1}{\sqrt{N}}\left[\frac{2m}{M\omega}\right]^{1/2}V'(z)\cos\left[\frac{q(\omega)a}{2}\right] \tag{63}$$

and ρ is the density of states per atom.

Within the DWBA the transition rate is found by substituting the approximate distorted wave $\Phi(z;k)$, the elastic scattering state in the presence of only the static potential $U(z)$, for the true elastic wave function $\phi_0(z;k)$

$$\mathcal{R}_{\mathrm{DWBA}}=\frac{2\hbar}{M}|\langle\Phi|U'|\Phi_b\rangle|^2|\mathrm{Im}\mathcal{J}(k)| \;. \tag{64}$$

The sticking probability is the transition rate per incoming particle flux. The incoming flux $\mathcal{F}$ is found from the asymptotic behavior of the distorted wave Φ

$$\Phi(z;k)\to\frac{1}{2i}\sqrt{2/\pi}(e^{i(kz+\delta_0)}-e^{-i(kz+\delta_0)}) \;, \tag{65}$$

where δ_0 is the phase shift from the potential $V(z)$. Thus

$$\mathcal{F}=\frac{\hbar k}{2\pi m} \;. \tag{66}$$

The sticking coefficient s in the DWBA is then

$$s(k)=\frac{4\pi}{k}\left[\frac{m}{M}\right]|\langle\Phi|U'|\Phi_b\rangle|^2|\mathrm{Im}\mathcal{J}(k)| \;. \tag{67}$$

For small k, the distorted wave $\Phi(z;k)$ has the form

$$\Phi(z;k)=kg_2(z), \quad k\to 0 \;. \tag{68}$$

Substitution of Eq. (68) into Eq. (67) yields

$$s(k)=k\left[\frac{4\pi m}{M}\right]\mathcal{J}_2\left|\int dz'\Phi_b(z')U'(z')g_2(z')\right|^2 , \quad k\to 0 \tag{69}$$

which is identical with the weak-coupling limit of Eq. (61).

So far we have limited the discussion to a single bound state. When there are several bound states, N_b, the total sticking coefficient in the DWBA is, of course, the sum of contributions from each bound state,

$$s(k)=\sum_{n=1}^{N_b}s_n(k) \;. \tag{70}$$

The generalization of our one-phonon model, which is not limited to weak interactions, leads—instead of the single equation [Eq. (45)] for $B(k)$—to N_b coupled linear equations for N_b coefficients, $B_n(k)$, of the form

$$\sum_{n'=1}^{N_b}M_{nn'}(k)B_{n'}(k)=Q_n(k) \;. \tag{71}$$

VI. LONG-RANGE PARTICLE-TARGET INTERACTIONS

So far we have considered sticking of one-dimensional (1D) particles interacting with the surface atoms of the target by a "short-range" potential which supports a single bound state. The real situation for three-dimensional (3D) systems is quite different. To first order in the displacements of the target atoms l, the interaction potential can be written in the form

$$U(\mathbf{r})+\sum_l \mathbf{u}_l\cdot\mathbf{w}_l(\mathbf{r}) \;. \tag{72}$$

Where $\mathbf{r}$ and $\mathbf{u}_l$ are, respectively, the position of the particle and the displacement of the target atom l; $U(\mathbf{r})$ is the particle's interaction with the target atoms in their equilibrium positions; and the next term describes its interactions with the lattice vibrations.

If the particle is neutral, $U(\mathbf{r})$ has the form

$$U(\mathbf{r})=-\frac{C_3}{z^3}+U^{(s)}(\mathbf{r}) \;, \tag{73}$$

where the first term is a van der Waals type polarization potential[23] and $U^{(s)}$ is relatively short range, i.e., decreasing more rapidly than z^{-3}; if the particle is charged, $U(\mathbf{r})$ has the form

$$U(\mathbf{r})=-\frac{C_1}{z}+U^{(s)}(\mathbf{r}) \ , \tag{74}$$

where the first term is the image potential and again the second term is relatively short range.

The coefficients $w_l(\mathbf{r})$ have various forms of asymptotic behavior, depending on whether the particle is charged or neutral and whether the target is ionic or not. But for purposes of calculating matrix elements between the eigenstates of the uncoupled Hamiltonians of the particle [including $U(\mathbf{r})$] and of the lattice vibrations, the $w_l(\mathbf{r})$ are in all cases effectively short range.

In view of the foregoing, we now consider in some detail the unperturbed 1D particle wave functions in the potential $U(z)$ in the two cases. In the first case,

$$U(z)=U^{(s)}(z)-\frac{C_3}{z^3} \ , \tag{75}$$

where $U^{(s)}$ is short range. Depending on the strength of the attractive part of this potential, it may support 0, 1, 2, or a larger but finite number of bound states. Traditional effective range theory[24] for low-energy scattering states $[k\cot\delta(k)=-1/a_s+\frac{1}{2}r_0k^2+\cdots]$ does not hold, and so in this sense z^{-3} is *not* a short-range potential. However, as far as quantum reflection is concerned, this potential does behave like a short-range potential such as a square well. The relevant ratio is

$$Q(k)\equiv\frac{|\psi_k(z^*)|^2}{|\psi_k(\infty)|^2} \ , \tag{76}$$

near $k=0$, where z^* is any *fixed* point near the surface. For both the square well and the potential (75), one obtains

$$Q(k)\rightarrow \text{const}\times k^2, \quad k\rightarrow 0 \tag{77}$$

where the constant [of dimension (length)^2] depends on the particulars of the potential.[25] Thus the 1D case of a z^{-3} tail is covered by our earlier calculation and leads to $s(E)\sim E^{1/2}$. We have convinced ourselves that this behavior also persists for physical 3D systems, with any number of surface-bound states provided only that the incident particle is neutral. The details are tedious and are not presented here.

The second case, corresponding to a *charged* incident particle,

$$U(z)=U^{(s)}(z)-\frac{C_1}{z} \tag{78}$$

is radically different from the previously considered cases. First of all this Coulombic potential, as is well known, supports an infinite number of bound states. Second, as we shall see, the low-energy behavior of $Q(k)$ is different,

$$Q(k)=\text{const}\times k, \quad k\rightarrow 0 \tag{79}$$

where the constant [of dimension (length)] again depends on the particulars of the potential. This leads to a *finite* sticking coefficient at $E=0$,

$$s(E)\sim E^0 \ . \tag{80}$$

The essential features of sticking in a Coulomb potential appear already in the DWBA. In the DWBA, the sticking coefficient associated with the nth bound state is given by

$$s_n(k)=\frac{4\pi}{\hbar^2k}|\langle k|V'|n\rangle|^2 \times\int_{\Omega_c}^{\Omega_m}d\Omega\,\rho(\Omega)\frac{\hbar}{M\Omega}\cos^2\left[\frac{q(\Omega)a}{2}\right] \times\delta(E(k)+E_{b,n}-h\Omega) \ , \tag{81}$$

where k and n denote, respectively, the continuum and bound-state wave functions satisfying the normalization conditions Eqs. (13) and (12).

Clearly the integral in Eq. (82) goes to a finite limit $\mathcal{Z}$ as $k\rightarrow 0$. The k dependence of the matrix element $\langle k|V'|n\rangle$ can be determined by realizing that in the case of a potential with a Coulombic tail, the WKB approximation is valid for the continuum wave functions $\Phi(z,k)$ beyond a minimum z $(z\geq z^{**})$ (see Appendix F). The inner portion of $\Phi(z,k)$ is obtained by solving the Schrödinger equation for $k=0$ with the boundary condition $\Phi(-\infty,0)=0$ and determining the amplitude by matching at z^{**} to the outside WKB solution. The result for small k is that for any fixed z

$$\Phi(z,k)=k^{1/2}h(z), \quad k\rightarrow 0 \tag{82}$$

where $h(z)$ is independent of k. Therefore, by Eq. (81),

$$\lim_{k\rightarrow 0}s_n(k)=\frac{4\pi}{\hbar^2}\left|\int_0^\infty dz\,h(z)V'(z)\Phi_{b,n}(z)\right|^2\mathcal{Z}\sim E^0 \tag{83}$$

for $\hbar\Omega_c\leq E_{b,n}\leq\hbar\Omega_m$.

In our model the infrared phonon cutoff artificially eliminates the sticking contribution from bound states which are close to the continuum edge. However, for real surfaces without an infrared phonon cutoff where there are nonzero contributions to the total sticking from high-lying bound states, we must concern ourselves with the convergence of the infinite summation of the terms from Eq. (83). The amplitude of high-lying bound states near the surface behaves as $n^{-3/2}$ as for pure Coulomb wave functions. Thus the square of the matrix elements decrease as n^{-3}, ensuring convergence of the summation. In fact, most sticking will be in the lowest bound state. Again, we have convinced ourselves that the threshold behavior Eq. (80) of $s(E)$ applies equally to sticking of charged particles on 3D surfaces.

VII. CONCLUDING REMARKS

The sticking on $T=0$ surfaces of low-energy incident particles is a challenging problem, both experimentally and theoretically. The main experimental problem is that to measure the *threshold* behavior of the sticking coefficient $s(E)$, one needs to work at extremely low temperatures and energies, much lower than one would at first expect.[9,2,26] However, suitable particle beams are becoming available[2] and one may expect valuable new data in the next few years.

The theoretical challenge is immediately signaled by the "paradox" that in a classical treatment of the particle-target system $\lim_{E\to 0} s(E)=1$, while quantum mechanically in perturbation theory $\lim_{E\to 0} s(E)=0$ for neutral particles and α (where $0<\alpha<1$) for charged particles. (The latter result is pointed out in this paper.) A second paradox is the fact that one can easily show that true quantum sticking is impossible on a finite target, i.e., $s(E)\equiv 0$, so that one needs to carefully examine the effects of increasing target dimensions and of thermal coupling of the target to a heat bath (at $T=0$). Finally there are very interesting temperature effects, to which we plan to return in a subsequent paper.

There are important analogies to the famous problem of compound nucleus formation. But there is an essential difference: the number of atoms N of the target is larger than any other parameter of the system, i.e., the target is effectively semi-infinite.

In this paper we have aimed at clarifying the nature of the threshold sticking both analytically and conceptually by means of an exactly solvable one-dimensional model, shown in Fig. 1. The essential approximation is the truncation of the Hilbert space, admitting only states with zero phonons or with one phonon in any one of the target normal modes. There is no limitation on the strength of the particle-phonon coupling. We believe that for $T=0$, our model contains all the essential elements of physical sticking of particles on surfaces.

For a finite number of target atoms N we find no true sticking but only very particular dense resonances, whose spacing and widths both scale as N^{-1}. Their physical meaning becomes clear in the time domain when one considers the evolution of an incident particle wave packet (see Appendix E). One finds a finite probability for prompt particle reflection, which, as $N\to\infty$, becomes $[1-s(E)]$. This is followed by finite particle ejection probabilities at times $\sim n\tau_P$ ($n=1,2,\dots$), where τ_P—a kind of Poincaré recursion time—is the time it takes for a phonon, originally created on first impact, to traverse the sample once to the back and once again from the back to the front, when it can eject the temporarily trapped particle with a certain probability, or be reflected back once more. $\tau_P=2L/v_g$, where L is the target thickness and v_g the phonon group velocity. $n=2,3,\dots$ corresponds to multiple double traversals of the sample followed by particle ejections. As N and $L\to\infty$, the sum of these more and more delayed ejection probabilities become the sticking probability $s(E)$.

In relating quantum sticking to classical sticking we want to point out *two* quite distinct quantum effects.

(1) A Debye-Waller-type effect. In quantum mechanics there is a *finite* probability (even as $N\to\infty$) that *no* lattice vibrations are excited and hence the particle is reflected. Thus under all circumstances $s(E)<1$. By contrast, classically, in the case of an attractive particle-target interaction, a *finite* amount of impact energy is delivered to the target, even when $E\to 0$, because of the particle's acceleration by the interaction potential. When $N\to\infty$, some of this energy disappears to $z=-\infty$. Thus for E sufficiently small, $E<E_{\min}$, the particle cannot escape and $s(E)=1$.

(2) Quantum reflection. We consider first the particle striking a rigid target in the classical regime. The particle coming in with a *low* velocity, $-v_\infty$, spends a time of the order $t_{\rm res}\sim 2z_0/\bar v$ in the interaction region, where z_0 is the range of interaction and $\bar v$ is a mean speed in the interaction region. As $v_\infty\to 0$, $\bar v$ approaches a finite limit and the ratio of the time spent by the particle in the interaction region to the time spent in a spatial interval z_0 outside the interaction region is

$$\frac{P_i}{P_\infty}\equiv\frac{t_{\rm res}}{\left[\dfrac{z_0}{v_\infty}\right]}\sim\left[\frac{E}{\bar E}\right]^{1/2}, \tag{84}$$

where $\bar E\sim\frac{1}{2}m\bar v^{\,2}$ is a typical kinetic energy in the interaction region, when $v_\infty\to 0$.

Now we consider the problem quantum mechanically for small incident energy. In the *rigid* target potential, assumed sufficiently short range, the particle is described by a standing wave $\Phi(z,k)$, with the properties

$$\begin{aligned}&\Phi(z,k)=\mathcal{N}\sqrt{2/\pi}\,\sin(kz+\delta')\ ,\quad z\to\infty\ .\\&\Phi(z,k)\sim\mathcal{N}(kz_0)f(z),\quad z\to 0\end{aligned}\tag{85}$$

where $\mathcal{N}$ is an (irrelevant) normalization factor, δ' is a phase shift, and $f(z)$ becomes independent of k for small k and is of order 1. (This is well known from so-called effective range theory[27] and can easily be checked for a square-well interaction potential backed by an infinite wall.) Thus the ratio of the probability of finding the particle in the interaction region to the probability of finding it in an asymptotic interval of length z_0 is

$$\frac{P_i}{P_\infty}\approx\frac{\int_0^{z_0}[(kz_0)f(z)]^2dz}{z_0}\approx k^2z_0^2\approx\frac{2mz_0^2}{\hbar^2}E\ . \tag{86}$$

Note the power of E^1 compared to the classical result $E^{1/2}$: as $E\to 0$ the quantum particle spends less time in the interaction region than the classical particle, by a power $E^{1/2}$. This is the so-called quantum reflection. We can also note that for unit incident current, the probability of a quantum particle being in the interaction region is $\sim E^{1/2}$. This is the physical origin of the sticking threshold behavior, $s(E)\sim E^{1/2}$.

In the foregoing, we have assumed a "sufficiently short range" interaction potential. Suppose now that asymptotically the interaction potential $U(z)\sim -C_1/z$. Then one finds that for *all* $E\to 0$, there is a point $z_0\sim 1/C_1$, beyond which the essential characteristics of the wave functions are correctly given by the WKB solutions,

$$\Psi_{\rm WKB}=\frac{1}{k^{1/2}(z)}\exp\left[\pm i\int_{z_0}^{z}k(z')dz'\right],\quad z\ge z_0 \tag{87}$$

where

$$\frac{\hbar^2}{2m}k^2(z)=E-\frac{C_1}{z} \ . \tag{88}$$

Thus

$$\frac{|\Psi(z_0)|^2}{|\Psi(\infty)|^2}\sim\frac{k}{k(z_0)} \ . \tag{89}$$

For small k, one matches to zero-energy solutions for $z<z_0$ and finds

$$\frac{P_i}{P_\infty}\sim\left[\frac{E}{\bar{E}}\right]^{1/2} \tag{90}$$

as in the classical case. However, due to the Debye-Waller factor, the sticking coefficient[28] for $E\to 0$ is not 1 but α, where $0<\alpha<1$.

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APPENDIX A: CONSERVATION OF CURRENT

We shall now explicitly verify total particle current conservation for a finite "solid," in which there is no true sticking but only sticking resonances. In the case of a potential with a finite range z_0 where $U(z)=0$ for $z\geq z_0$, the wave function in the elastic channel has the asymptotic form given by Eq. (18b). The net particle current density in this channel is found from the expression

$$j_0=\frac{\hbar}{m}\mathrm{Im}\left[\phi_0^*(z)\frac{d}{dz}\phi_0(z)\right]\Bigg|_{z=z_0} , \tag{A1}$$

where z_0 is in the asymptotic region. Substituting Eq. (18b) into Eq. (A1), we find that the particle current density in the elastic channel is

$$j_0=-\frac{\hbar k}{m}(1-|R|^2) \ . \tag{A2}$$

The net current density for the ith channel can be found similarly from

$$j_i=\frac{\hbar}{m}\mathrm{Im}\left[\phi_i^*(z)\frac{d}{dz}\phi_i(z)\right]\Bigg|_{z=z_0} . \tag{A3}$$

j_i vanishes for closed channels and may be nonzero for open ones.

We shall now verify that the sum of the net current densities over all channels is zero. Multiplying Eq. (29b) through by $\phi_i^*(z)$ and integrating from $z=-\infty$ to z_0, we obtain

$$\begin{aligned}\int_{-\infty}^{z_0}dz\,\phi_i^*(z)\frac{d^2}{dz^2}\phi_i(z)=&-(k^2-\omega_i)\int_{-\infty}^{z_0}dz|\phi_i(z)|^2\\&+\int_{-\infty}^{z_0}dz\,U(z)|\phi_i(z)|^2\\&+\int_{-\infty}^{z_0}dz\,\phi_i^*(z)U_{0i}(z)\phi_0(z) \ .\end{aligned} \tag{A4}$$

The right-hand side can be simplified by an integration by parts

$$\begin{aligned}\int_{-\infty}^{z_0}dz\,\phi_i^*(z)\frac{d^2}{dz^2}\phi_i(z)=&\phi_i^*(z_0)\frac{d}{dz}\phi_i(z_0)\\&-\int_{-\infty}^{z_0}dz\left|\frac{d}{dz}\phi_i(z)\right|^2\end{aligned} \tag{A5}$$

since $\phi_i(-\infty)=0$. Taking the imaginary part of Eq. (A4) and multiplying through by $\hbar/m$, we obtain an expression for the net current density in each inelastic channel, namely

$$j_i=\frac{\hbar}{m}\mathrm{Im}\left[\int_{-\infty}^{z_0}dz\,\phi_i^*(z)U_{0i}(z)\phi_0(z)\right] \ . \tag{A6}$$

The summation of net current densities over all inelastic channels is

$$\sum_{i=1}^{N}j_i=\frac{\hbar}{m}\mathrm{Im}\left[\int_{-\infty}^{z_0}dz\,\phi_0(z)\sum_{i=1}^{N}\phi_i^*(z)U_{0i}(z)\right] \ . \tag{A7}$$

From the complex conjugate of Eq. (29a),

$$\sum_{i=1}^{N}\phi_i^*(z)U_{0i}(z)=\frac{d^2}{dz^2}\phi_0^*(z)+k^2\phi_0^*(z)-U(z)\phi_0^*(z) \ . \tag{A8}$$

Combining Eq. (A7) with Eq. (A8) and integrating by parts gives the desired result that

$$\sum_{i=0}^{N}j_i=0 \ . \tag{A9}$$

APPENDIX B: INELASTIC AND ADSORPTION CURRENT DENSITIES

From the effective single-particle equation for the elastic channel given in Eq. (35), the total inelastic current can be written in terms of U_{pol}. We multiply Eq. (35) through by $\phi_0^*(z)$, and we integrate over z from $z=-\infty$ to z_0, giving

$$\begin{aligned}\int_{-\infty}^{z_0}dz\,\phi_0^*(z)\frac{d^2}{dz^2}\phi_0(z)=&-k^2\int_{-\infty}^{z_0}dz|\phi_0(z)|^2+\int_{-\infty}^{z_0}dz\,U(z)|\phi_0(z)|^2-\int_{-\infty}^{\infty}dz'\int_{-\infty}^{z_0}dz\,\phi_0^*(z)U_{\mathrm{pol}}(z,z')\phi_0(z')\\&+\sum_{i=1}^{N}\int_{-\infty}^{z_0}dz\,\mathcal{A}_iU_{0i}(z)\phi_0^*(z)\Phi_b(z) \ .\end{aligned} \tag{B1}$$

If we perform an integration by parts of the right-hand side and take the imaginary part, we identify the right-hand side as being proportional to j_0, since $\phi_0(-\infty)=0$. By conservation of current density, $j_0=-\sum_{i=1}^{N} j_i$. Hence,

$$\sum_{i=1}^{N} j_i=\frac{\hbar}{m}\int_{-\infty}^{\infty} dz'\int_{-\infty}^{z_0} dz\, \mathrm{Im}[\phi_0^*(z)U_{\mathrm{pol}}(z,z')\phi_0(z')]-\frac{\hbar}{m}\mathrm{Im}\sum_{i=1}^{N}\int_{-\infty}^{z_0} dz\,\mathcal{A}_i U_{0i}(z)\phi_0^*(z)\Phi_b(z) . \quad \text{(B2)}$$

Since U and U' are zero for $z \ge z_0$, we can extend the integration range to infinity. Equation (B2) can thus be rewritten as

$$\sum_{i=1}^{N} j_i = j_{\mathrm{inel}}+j_a , \quad \text{(B3)}$$

where

$$j_{\mathrm{inel}} \equiv \frac{\hbar}{m}\sum_{k^2>\omega_i}\int_0^{\infty} dk'\,\mathrm{Im}\left[\frac{1}{k'^2-k^2+\omega_i-i\eta_1}\right] \times \left|\int_{-\infty}^{\infty} dz\,\phi_0(z;k)U_{0i}(z)\Phi(z,k')\right|^2 \quad \text{(B4)}$$

and

$$j_a \equiv \frac{\hbar}{m}\sum_{k^2\le\omega_i}\mathrm{Im}\left[\frac{1}{k^2-\omega_i+\epsilon_b}\right] \times \left|\int_{-\infty}^{\infty} dz\,\phi_0(z)U_{0i}(z)\Phi_b(z)\right|^2 . \quad \text{(B5)}$$

j_a is zero for finite N as the bracketed term in Eq. (B5) is purely real. However, in the continuum limit, Eq. (B5) is replaced by

$$j_a=-\frac{2\hbar}{M}\int_{\omega_c}^{\omega_m} d\omega\,\mathrm{Im}\left[\frac{\rho(\omega)\cos^2\left[\frac{q(\omega)a}{2}\right]}{(k^2+\epsilon_b-\omega+i\eta_2)\omega}\right] \times \left|\int_{-\infty}^{\infty} dz\,\phi_0(z)U'(z)\Phi_b(z)\right|^2$$

$$=\frac{2\hbar}{M}|\langle\phi_0|U'|\Phi_b\rangle|^2|\mathrm{Im}\mathcal{I}(k)| , \quad \text{(B6)}$$

where the insertion of η_2 follows from the arguments preceding Eq. (51) and is used in the sense that $\eta_2\to 0$. We now recognize that j_a is equal in magnitude to the transition rate $\mathcal{R}$ to the bound state Φ_b resulting from Eq. (62). Thus j_a in Eq. (B6) is interpreted as the adsorption current density resulting from transitions to the bound state, while j_{inel} is interpreted as the inelastic current density.

APPENDIX C: INCLUSION OF INELASTIC PROCESSES

We can generalize the $(N+1)$-state solution to situations where the incident energy is above the inelastic threshold ($k^2>\omega_c$). The formal expression for the open inelastic channel wave functions is identical to that found in Eq. (29); however, the Green's function for open inelastic channels differs from that found for the closed channels in Eq. (32). The boundary condition of asymptotically outgoing waves for the open inelastic channels is satisfied by the addition of an infinitesimal positive imaginary part $i\eta_1$ ($\eta_1\to 0$). The Green's function is thus written generally

$$G_i(z,z')=\frac{\Phi_b(z)\Phi_b(z')}{\epsilon_b-\omega_i+k^2}+\int_0^{\infty} dk'\frac{\Phi(z,k')\Phi(z',k')}{k^2-\omega_i-k'^2+i\eta_1} . \quad \text{(C1)}$$

The solution now proceeds exactly as in the case below inelastic threshold. A single equation of the entrance channel wave function is found to be of the same form as Eq. (35), where U_{pol} is given by

$$U_{\mathrm{pol}}(z,z';k)=U_{\mathrm{pol}}^0(z,z';k)+U_{\mathrm{pol}}^c(z,z';k) , \quad \text{(C2)}$$

$$U_{\mathrm{pol}}^0(z,z';k)=\int_0^{\infty} dk'\sum_{k^2>\omega_i}\frac{U_{0i}(z)\Phi(z,k')\Phi(z',k')U_{0i}(z')}{k'^2-k^2+\omega_i-i\eta_1} , \quad \text{(C3)}$$

$$U_{\mathrm{pol}}^c(z,z';k)=\int_0^{\infty} dk'\sum_{k^2\le\omega_i}\frac{U_{0i}(z)\Phi(z,k')\Phi(z',k')U_{0i}(z')}{k'^2-k^2+\omega_i} . \quad \text{(C4)}$$

The channel amplitudes are defined by

$$\mathcal{A}_i=\frac{1}{\epsilon_b+k^2-\omega_i}\int dz'\Phi_b(z')U_{0i}(z')\phi_0(z') . \quad \text{(C5)}$$

U_{pol} is an "optical potential"[29] which now has an imaginary part.

The single-particle equation (35) and appropriate boundary conditions can be replaced by the integral equation

$$\phi_0(z)=f(k,z)-S_0(k)f(-k,z)+\int dz'\mathcal{G}(z,z';k)\sum_{i=1}^{N}\mathcal{A}_i U_{0i}(z')\Phi_b(z') . \quad \text{(C6)}$$

$\mathcal{G}$ is the Green's function satisfying

$$\left[\frac{d^2}{dz^2}+k^2-U(z)\right]\mathcal{G}(z,z';k)+\int dz''U_{\mathrm{pol}}(z,z'';k)\mathcal{G}(z'',z';k)=\delta(z-z') \quad \text{(C7)}$$

with the boundary conditions that $\mathcal{G}(-\infty,z')=0$ and $\mathcal{G}$ is asymptotically outgoing only. $f(\pm k,z)$ are Jost functions[30] which are linearly independent solutions of Eq. (22)

$$\left[\frac{d^2}{dz^2}+k^2-U(z)\right]f(\pm k,z) + \int dz' U_{\rm pol}(z,z';k)f(\pm k,z')=0 \ , \qquad \text{(C8)}$$

subject to the asymptotic conditions that $f(\pm k,z)\rightarrow e^{\mp ikz}$ as $z\rightarrow\infty$.

The Green's function $\mathcal{G}$ can also be written in terms of Jost functions

$$\mathcal{G}(z,z';k)=\frac{1}{2ik}\begin{cases} f(-k,z)f(k,z')-S_0(k)f(-k,z)f(-k,z'), & z\geq z' \\ f(-k,z')f(k,z)-S_0(k)f(-k,z)f(-k,z'), & z\leq z' \end{cases} \qquad \text{(C9)}$$

where S_0 is defined

$$S_0(k)=\lim_{z\rightarrow 0}\frac{f(k,z)}{f(-k,z)} \ . \qquad \text{(C10)}$$

The asymptotic form of $\phi_0(z)$ is

$$\phi_0(z)\rightarrow e^{-ikz}-\mathrm{R}e^{ikz} \ , \qquad \text{(C11)}$$

where, by Eq. (C6), R is given by

$$R=S_0-\frac{1}{2ik}\sum_{i=1}^{N}\mathcal{A}_i\int dz'\Phi_b(z')U_{0i}(z')[f(k,z')-S_0f(-k,z')] \ . \qquad \text{(C12)}$$

Substituting the expression of ϕ_0 in Eq. (C6) into Eq. (C5) gives a matrix equation for $\mathcal{A}$ of the same form as Eq. (38), where P is now

$$P(k)=\sqrt{2m/M}\int dz'\Phi_b(z')U'(z')[f(k,z')-S_0f(-k,z')] \ . \qquad \text{(C13)}$$

The solution of this matrix equation is given in Eq. (47). Substituting this result into Eq. (C12) yields a simple expression for the reflection coefficient R,

$$R(k)=S_0\left[\frac{1-J(k)I(k,N)}{1-W(k)I(k,N)}\right] , \qquad \text{(C14)}$$

where

$$J(k)=2\left[\frac{m}{M}\right]\left[\int dz'dz''\Phi_b(z')U'(z')h(z',z'';k)U'(z'')\Phi_b(z'')\right] , \qquad \text{(C15)}$$

and

$$h(z,z';k)=-\frac{1}{2ik}\begin{cases} f(k,z)f(-k,z')-S_0^{-1}(k)f(k,z)f(k,z'), & z\geq z' \\ f(k,z')f(-k,z)-S_0^{-1}(k)f(k,z)f(k,z'), & z\leq z' \ . \end{cases} \qquad \text{(C16)}$$

For a finite N, and below threshold ($k^2<\omega_c$), both factors in Eq. (C14) have magnitude unity, leading to complete elastic reflection. Above threshold ($k^2>\omega_c$), we shall show that the first factor $|S_0|$ becomes less than unity due to inelastic scattering and the second factor also is no longer of unit magnitude as the numerator differs from the complex conjugate of the denominator.

We define the combination $\chi(z,k)$

$$\chi(z;k)\equiv f(k,z)-S_0f(-k,z) \qquad \text{(C17)}$$

which occurs in Eq. (C12) for R and

$$\chi_h(z,k)\equiv -2i\sqrt{\pi/2}e^{i\delta_0}\Phi(z,k) \ . \qquad \text{(C18)}$$

This $\chi(z,k)$ satisfies the boundary conditions

$$\begin{aligned} &\chi(-\infty,k)=0 \ , \\ &\chi(z,k)=e^{-ikz}-S_0e^{ikz}, \quad z\rightarrow\infty \ . \end{aligned} \qquad \text{(C19)}$$

χ also satisfies Eq. (C8) which can be placed in Lippmann-Schwinger form

$$\chi(z,k)=\chi_h(z,k)+\int dz'dz''G_0(z,z';k)U_{\rm pol}(z',z'';k)\chi(z'',k) \ , \qquad \text{(C20)}$$

where

$$G_0(z,z';k)=\frac{\Phi_b(z)\Phi_b(z')}{k^2+\epsilon_b}+\int_0^\infty dk'\frac{\Phi(z,k')\Phi(z',k')}{k^2-k'^2+i\eta_1}\ . \tag{C21}$$

Equation (C20) requires that S_0 satisfy the self-consistent relation

$$S_0=e^{2i\delta_0}\left[1+\frac{1}{k}\sqrt{\pi/2}e^{-i\delta_0}\int dz'dz''\Phi(z',k)U_{\text{pol}}(z',z'';k)[f(k,z'')-S_0f(-k,z'')]\right], \tag{C22}$$

where δ_0 is the phase shift associated with U, and the following asymptotic form of G_0 was used:

$$G_0(z,z')=-\frac{1}{k}\sqrt{\pi/2}e^{i\delta_0}\Phi(z',k)e^{ikz},\quad z\to\infty\ . \tag{C23}$$

This results in

$$S_0=e^{2i\delta_0}\left[\frac{1+\frac{1}{k}\sqrt{\pi/2}e^{-i\delta_0}\int dz'dz''\Phi(z',k)U_{\text{pol}}(z',z'';k)f(k,z'')}{1+\frac{1}{k}\sqrt{\pi/2}e^{i\delta_0}\int dz'dz''\Phi(z',k)U_{\text{pol}}(z',z'';k)f(-k,z'')}\right]. \tag{C24}$$

Below threshold ($k^2<\omega_c$), U_{pol} is a *real* potential, and from Eq. (C8) we see that $f^*(k,z)=f(-k,z)$ for real k. The numerator of the bracketed term in Eq. (C24) is the complex conjugate of the denominator so that $|S_0|=1$. From Eqs. (23) and (C16), $h(z,z')=\mathcal{G}^*(z,z')$; and from Eqs. (40) and (C15), $W^*(k)=J(k)$. Hence the second factor in Eq. (C14) also has magnitude unity. Thus $|R|^2=1$.

Above the inelastic threshold ($k^2>\omega_c$), because of the imaginary part of U_{pol}, we can see from Eq. (C24) that the denominator is no longer the complex conjugate of the numerator, so that $|S_0|\neq 1$. Furthermore, since $\text{Im}U_{\text{pol}}>0$ [Eq. (C3)], describing loss of particles from the elastic channel, $|S_0|<1$. Also in this case, from Eqs. (23) and (C16), $h(z,z')\neq\mathcal{G}^*(z,z')$ so that from Eqs. (40) and (C15), $W^*(k)\neq J(k)$. Thus the previous argument for $k^2<\omega_c$, leading to complete elastic scattering ($|R|=1$), no longer applies. In fact, we know from unitarity that when there is inelastic scattering, $|R|<1$.

For finite N, $R(k)$ is a rapidly varying, real, nearly periodic function of k,[2] with slowly varying period due to the singularities of $I(k,N)$ [Eq. (46)]. No real adsorption is possible. When we introduce a finite but small phonon lifetime and pass to the continuum limit, $N\to\infty$, $\mathcal{J}(k)$ becomes a smooth but complex function of k, reflecting adsorption processes.

APPENDIX D: STICKING IN THE PRESENCE OF OTHER INELASTIC PROCESSES

The asymptotic form of the open-channel wave functions is given by

$$\phi_n(z)\to\sqrt{k/k_n}S_{0n}e^{ik_nz},\quad z\to\infty \tag{D1}$$

where $k_n^2=k^2-\omega_n$. This will serve as the definition of S_{0n}. Using the exact expressions for the open-channel wave functions, the asymptotic limits can be taken and the elements of the S matrix can be identified.

The asymptotic form of the Green's function for the nth channel can be obtained from Eq. (C1). Since Φ_b decays as $\exp(-\sqrt{\epsilon_b}z)$, the first term can be neglected asymptotically, leaving

$$G_n(z,z')\to\int_0^\infty dk'\frac{\Phi(z,k')\Phi(z',k')}{k_n^2-k'^2+i\eta}\ . \tag{D2}$$

The eigenfunctions $\Phi(z,k)$ are real for real k, behaving as $\Phi(z,k)\to\sqrt{2/\pi}\sin(kz+\delta_0)$ as $z\to\infty$. We can rewrite Φ as a sum of two linearly dependent eigenfunctions $H^{(\pm)}(z,k)$,

$$\left[\frac{d^2}{dz^2}+k^2-U(z)\right]H^{(\pm)}(z,k)=0\ , \tag{D3}$$

which behaves asymptotically as $H^{(\pm)}(z,k)\to\sqrt{2/\pi}e^{\pm i(kz+\delta_0)}$, as $z\to\infty$. Hence

$$\Phi(z,k)=\frac{1}{2i}[H^{(+)}(z,k)-H^{(-)}(z,k)]\ . \tag{D4}$$

The asymptotic form of G_n can be expressed in terms of $H^{(\pm)}$

$$G_n(z,z')\to-\tfrac{1}{8}\int_{-\infty}^{\infty}dk'\frac{H^{(+)}(z,k')H^{(+)}(z',k')-H^{(-)}(z,k')H^{(+)}(z',k')}{k_n^2-k'^2+i\eta}$$
$$-\tfrac{1}{8}\int_{-\infty}^{\infty}dk'\frac{-H^{(+)}(z,k')H^{(-)}(z',k')+H^{(-)}(z,k')H^{(-)}(z',k')}{k_n^2-k'^2+i\eta}\ . \tag{D5}$$

The above integration can be performed in the complex plane using contour integration. Thus,

$$G_n(z,z')\to\frac{\pi i}{8k_n}\{H^{(+)}(z,k_n)[H^{(+)}(z',k_n)-H^{(-)}(z',k_n)]+H^{(-)}(z,-k_n)[H^{(-)}(z',-k_n)-H^{(+)}(z',-k_n)]\}$$
$$\to-\sqrt{\pi/2}\frac{1}{k_n}e^{i\delta_0}e^{ik_nz}\Phi(z',k_n)\ . \tag{D6}$$

We see that G_n is asymptotically outgoing.

Substituting the above form for G_n into Eq. (30) yields the asymptotic form for the open-channel wave functions

$$\phi_n(z)\to-\frac{1}{k_n}\sqrt{\pi/2}e^{i\delta_0}\langle\Phi_{k_n}|U_{0n}|\phi_0\rangle e^{ik_nz},\ z\to\infty\ . \tag{D7}$$

A comparison of this asymptotic expression with Eq. (D1) gives an expression for the S-matrix elements for open channels

$$S_{0n}=\sqrt{\pi/2}\frac{1}{\sqrt{kk_n}}\langle\Phi_{k_n}|U_{0n}|\phi_0\rangle e^{i\delta_0}\ . \tag{D8}$$

We will define $\tilde{r}$ such that

$$\tilde{r}=\sum_{n=1}^{N_0}|S_{0n}|^2\ , \tag{D9}$$

where N_0 is the number of open channels. With the above form for S_{0n}, we find that

$$\begin{aligned}\tilde{r}_N&=\sum_{n=1}^{N_0}\frac{\pi}{2k_n}\frac{1}{k}|\langle\Phi_{k_n}|U_{0n}|\phi_0\rangle|^2\\&=-\frac{1}{k}\sum_{n=1}^{N_0}\int_0^\infty dk'\,\mathrm{Im}\left[\frac{1}{k_n^2-k'^2+i\eta}\right]\\&\qquad\times|\langle\Phi_{k_n}|U_{0n}|\phi_0\rangle|^2\\&=\frac{|j_{\rm inel}|}{\dfrac{\hbar k}{m}}\ ,\end{aligned} \tag{D10}$$

where $\langle z|\Phi_{k_n}\rangle$ denotes $\Phi(z,k_n)$; $\tilde{r}$ is the total probability of inelastic scattering. Additionally it is seen from Eqs. (B6) and (62) that

$$s=\lim_{N\to\infty}\frac{|j_a|}{\hbar k/m} \tag{D11}$$

and thus in the continuum limit

$$r+\tilde{r}+s=1\ , \tag{D12}$$

where $r=|R|^2$ is the elastic reflection coefficient.

Combining Eqs. (B6) and (D11) we derive an expression for s for $k^2>\omega_c$,

$$s(k)=\frac{2m}{M}|\langle\phi_0|U'|\Phi_b\rangle|^2|\mathrm{Im}\mathcal{J}(k)|\ . \tag{D13}$$

From Eq. (C6) we see that ϕ_0 can be written as

$$\begin{aligned}\phi_0(z;k)=\chi(z;k)+\frac{2m}{M}\frac{I(k,N)}{1-W(k)I(k,N)}\langle\Phi_b|U'|\chi\rangle\\\times\int_{-\infty}^{\infty}dz'\mathcal{G}(z,z';k)U'(z')\Phi_b(z')\ .\end{aligned} \tag{D14}$$

Using Eqs. (D14) and (C13), the matrix element $|\langle\phi_0|U'|\Phi_b\rangle|^2$ can be simplified to

$$|\langle\phi_0|U'|\Phi_b\rangle|^2=\frac{M}{2m}\frac{1}{k}\frac{|P(k)|^2}{|1-W(k)\mathcal{J}(k)|^2}\ . \tag{D15}$$

Substituting Eq. (D15) into Eq. (D13) yields

$$s(k)=\frac{1}{k}\frac{|P(k)|^2|\mathrm{Im}\mathcal{J}(k)|}{|1-W(k)\mathcal{J}(k)|^2}\ . \tag{D16}$$

For $k^2<\omega_c$, the above result reduces to Eq. (55).

APPENDIX E: TIME ANALYSIS OF A SCATTERED WAVE PACKET

In this appendix we consider how the rapid variation of R with k for finite N affects an incident wave packet. This incident wave packet is written in the standard way as a superposition of plane waves,

$$\phi_-(z,t)=\int d\epsilon\ A(\epsilon)e^{-i(\sqrt{\epsilon}z+\epsilon t)}\ , \tag{E1}$$

where we take $A(\epsilon)$ to be a broad envelope function peaked at ϵ_0 with a width of $\Delta\epsilon_0$. [Energy is scaled as before with $\epsilon\equiv(2m/\hbar^2)E$, and time is scaled as $t\equiv(\hbar/2m)T$, where T is time.]

The reflected wave is given by

$$\phi_+(z,t)=\int d\epsilon\ A(\epsilon)R(\epsilon)e^{i(\sqrt{\epsilon}z-\epsilon t)}\ , \tag{E2}$$

where $R(\epsilon)$ is the reflection coefficient whose exact form is given in Eq. (48).

We choose $\Delta\epsilon_0\ll\epsilon_0,\Delta$, where Δ is the width of the phonon spectrum; but also $\Delta\epsilon_0\gg\Delta/N$, the spacing of phonon modes at $\omega=\epsilon_0+\epsilon_b$. We can rewrite the Eq. (E2) as the sum of two terms

$$\phi_+(z,t)=\phi_1(z,t)+\phi_2(z,t), \tag{E3}$$

where

$$\phi_1(z,t)=\int d\epsilon\ A(\epsilon)e^{2i\delta(\epsilon)}e^{i(\sqrt{\epsilon}z-\epsilon t)}\ , \tag{E4}$$

$$\phi_2(z,t)=\int d\epsilon\ A(\epsilon)e^{2i\delta(\epsilon)}\tilde{R}(\epsilon)e^{i(\sqrt{\epsilon}z-\epsilon t)}\ , \tag{E5}$$

and

$$\tilde{R}(\epsilon)=\frac{2iI(\epsilon,N)\mathrm{Im}W(\epsilon)}{1-W(\epsilon)I(\epsilon,N)}\ . \tag{E6}$$

The width $\Delta\epsilon_0$ of the envelope is taken to be sufficiently narrow such that $\delta(\epsilon)$ ($\sim\sqrt{\epsilon}$ for small ϵ) changes little over $\Delta\epsilon_0$. In this case, $\delta(\epsilon)$ may be approximated as $\delta(\epsilon_0)$, and Eq. (E4) becomes

$$\phi_1(z,t)=\int d\epsilon\ \tilde{A}(\epsilon)e^{i(\sqrt{\epsilon}z-\epsilon t)}\ , \tag{E7}$$

where

$$\tilde{A}(\epsilon)\equiv A(\epsilon)e^{2i\delta(\epsilon_0)}\ . \tag{E8}$$

ϕ_2 differs from ϕ_1 by the additional factor in the integrand of $\tilde{R}(\epsilon)$, which for large N is a rapidly oscillating, nearly periodic function of ϵ. $\tilde{R}(\epsilon)$ depends upon two functions: $W(\epsilon)$ and $I(\epsilon,N)$. Since $\delta(\epsilon)$ changes little over $\Delta\epsilon_0$, $W(\epsilon)$, defined in Eq. (40), is also approximately constant over the interval $\Delta\epsilon_0$,

$$\begin{aligned} W(\epsilon) &\approx W(\epsilon_0) \\ &\equiv W_1 - iW_2 , \end{aligned} \tag{E9}$$

where W_1 and W_2 are real.

$I(\epsilon,N)$ [Eq. (46)], however, is responsible for the rapid oscillations in $\tilde{R}(\epsilon)$, due to the poles at $\epsilon=\omega_i-\epsilon_b$.

We can separate I into a term with simple poles in ϵ, and a smooth function of ϵ,

$$I(\epsilon,N)=I_1(\epsilon,N)+I_2(\epsilon,N) , \tag{E10}$$

where

$$I_1(\epsilon,N)\equiv\frac{1}{N}\frac{\cos^2\left[\dfrac{q(\epsilon+\epsilon_b)a}{2}\right]}{(\epsilon+\epsilon_b)}\sum_{n=1}^{N}\frac{1}{\epsilon+\epsilon_b-\omega_n} \tag{E11}$$

and

$$I_2(\epsilon,N)\equiv\frac{1}{N}\sum_{n=1}^{N}\left[\frac{\cos^2\left[\dfrac{q_n a}{2}\right]}{\omega_n}-\frac{\cos^2\left[\dfrac{q(\epsilon+\epsilon_b)a}{2}\right]}{\epsilon+\epsilon_b}\right]\frac{1}{\epsilon+\epsilon_b-\omega_n} . \tag{E12}$$

Over the narrow energy interval $\Delta\epsilon_0$ of the wave packet, I_1 can be simplified to

$$I_1(\epsilon,N)\approx\frac{1}{N}\frac{\cos^2\left[\dfrac{q(\epsilon_0+\epsilon_b)a}{2}\right]}{(\epsilon_0+\epsilon_b)}\sum_{n=1}^{N}\frac{1}{\epsilon+\epsilon_b-\omega_n} . \tag{E13}$$

The smooth function $I_2(\epsilon,N)$ tends to a well-defined limit, $I_2(\epsilon)$, as $N\to\infty$.

For ϵ in the interval $\Delta\epsilon_0$, the sum in Eq. (E13) can be written as

$$\begin{aligned} S(\epsilon,N) &\equiv \frac{1}{N}\sum_{n=1}^{N}\frac{1}{\epsilon+\epsilon_b-\omega_n} \\ &= S_1(\epsilon,N)+S_2(\epsilon,N) , \end{aligned} \tag{E14}$$

where

$$S_1(\epsilon,N)\equiv\frac{1}{N}\sum_{n=n_0-\bar{n}}^{n_0+\bar{n}}\frac{1}{\epsilon+\epsilon_b-\omega_n} \tag{E15}$$

and

$$\begin{aligned} S_2(\epsilon,N) \equiv{} & \frac{1}{N}\sum_{n=1}^{n_0-\bar{n}}\frac{1}{\epsilon+\epsilon_b-\omega_n} \\ & +\frac{1}{N}\sum_{n=n_0+\bar{n}}^{N}\frac{1}{\epsilon+\epsilon_b-\omega_n} , \end{aligned} \tag{E16}$$

where n_0 labels the frequency, ω_{n_0}, nearest to $\epsilon_0+\epsilon_b$, and $\bar{n}$ is chosen such that $\omega_{n_0+\bar{n}}-\omega_{n_0-\bar{n}}\gg\Delta\epsilon_0$, the width of the wave packet and $\Delta\epsilon_0\ll\omega_m-\omega_c$, the width of the phonon spectrum. The choice of $\bar{n}=N[\Delta\epsilon_0/(\omega_m-\omega_c)]^{1/2}$ satisfies these conditions.

Since the sum in Eq. (E15) is limited to a small fraction of the width of the phonon spectrum, we can write

$$\begin{aligned} S_1(\epsilon,N) &= \frac{1}{N}\sum_{n=n_0-\bar{n}}^{n_0+\bar{n}}\frac{1}{\epsilon+\epsilon_b-\left[\omega_{n_0}+(n-n_0)\dfrac{\Delta}{N}\right]} \\ &= \frac{1}{N}\sum_{n'=-\bar{n}}^{\bar{n}}\frac{1}{\epsilon+\epsilon_b-\left[\omega_{n_0}+n'\dfrac{\Delta}{N}\right]} \\ &= \frac{1}{N}\sum_{n'=\infty}^{\infty}\frac{1}{\epsilon+\epsilon_b-\left[\omega_{n_0}+n'\dfrac{\Delta}{N}\right]} \\ &= \frac{\pi}{\Delta}\cot\left[\frac{N\pi(\epsilon+\epsilon_b-\omega_{n_0})}{\Delta}\right] , \end{aligned} \tag{E17}$$

where

$$\frac{\Delta}{N}=v_g\frac{2M}{\hbar}\frac{\pi}{Na} \tag{E18}$$

and v_g is the phonon group velocity[31] at ω_{n_0}.

For ϵ limited to $\Delta\epsilon_0$, the summand in Eq. (16) is a smooth function of ω_n; furthermore, the excluded interval is symmetric about $n=n_0$ for $\epsilon=\epsilon_0$, and the ϵ dependence of S_2 is negligible in $\Delta\epsilon_0$. Thus we can write

$$\begin{aligned} S_2(\epsilon,N) &\approx S_2(\epsilon_0,N) \\ &\approx \mathrm{P}\int_{\omega_c}^{\omega_m}d\omega\,\rho(\omega)\frac{1}{\epsilon_0+\epsilon_b-\omega} , \end{aligned} \tag{E19}$$

where $\rho(\omega)$ is the phonon density of states per atom [Eq. (53)].

We call

$$q(\epsilon+\epsilon_b)\approx q(\epsilon_0+\epsilon_b)\approx q(\omega_{n_0})\equiv q_0 . \tag{E20}$$

Then we can write $I(\epsilon,N)$ in the compact form

$$I(\epsilon,N)=I_0\cot\left[\frac{N\pi(\epsilon+\epsilon_b-\omega_{n_0})}{\Delta}\right]+C , \tag{E21}$$

where

$$I_0 \equiv \frac{\pi \cos^2\left(\frac{q_0 a}{2}\right)}{\omega_{n_0}\Delta} \tag{E22}$$

and

$$C \equiv \frac{1}{N}\sum_{n=1}^{N}\left[\frac{\cos^2\left(\frac{q_n a}{2}\right)}{\omega_n} - \frac{\cos^2\left(\frac{q(\epsilon_0+\epsilon_b)a}{2}\right)}{\epsilon_0+\epsilon_b}\right] \times \frac{1}{\epsilon_0+\epsilon_b-\omega_n} + \frac{\cos^2\left(\frac{q_0 a}{2}\right)}{\omega_{n_0}} \mathrm{P}\int_{\omega_c}^{\omega_m} d\omega\, \rho(\omega)\frac{1}{\omega_{n_0}-\omega} . \tag{E23}$$

With the above form for $I(\epsilon,N)$ and Eq. (E9), $\tilde{R}(\epsilon)$ is a periodic function of ϵ over the interval $\Delta\epsilon_0$. We Fourier analyze $\tilde{R}$

$$\tilde{R}(\tau)=\int_{-\infty}^{\infty} d\epsilon\, \tilde{R}(\epsilon)e^{-i\epsilon\tau} . \tag{E24}$$

$\tilde{R}(\epsilon)$ has N poles in the complex ϵ plane. The poles are determined by the equation

$$\epsilon+\epsilon_b-\omega_{n_0}=\frac{\Delta}{N\pi}\tan^{-1}\left[\frac{W_0 I_0}{1-W_0 C}\right] . \tag{E25}$$

We then write them in the form

$$\epsilon_n=\bar{\epsilon}+\frac{1}{N}\left[n\Delta-i\frac{\Gamma}{2}\right] . \tag{E26}$$

The integral of Eq. (E24) can be done by contour integration, giving

$$\tilde{R}(\tau)=\begin{cases} -\dfrac{4\pi i I_0}{(1-W_0C)^2}\exp\left[-\dfrac{\Gamma}{2N}\tau\right]e^{-i\bar{\epsilon}\tau}\exp\left[-i\dfrac{\tau\Delta(N+1)}{2N}\right]\displaystyle\sum_{n=-\infty}^{\infty}\delta_N\left[\tau-n\frac{2\pi N}{\Delta}\right], & \tau>0 \\ 0, \quad \tau<0 \end{cases} \tag{E27}$$

where

$$\sum_{n=-\infty}^{\infty}\delta_N\left[\tau-n\frac{2\pi N}{\Delta}\right]\equiv\frac{\Delta}{2\pi N}\left[\frac{\sin\frac{\tau\Delta}{2}}{\sin\frac{\tau\Delta}{2N}}\right] \tag{E28}$$

and approaches a train of normalized δ functions,

$$\sum_{n=-\infty}^{\infty}\delta\left[\tau-n\frac{2\pi N}{\Delta}\right] \quad \text{as } N\to\infty .$$

ϕ_2 can be subsequently rewritten

$$\phi_2(z,t)=-\frac{4W_2I_0}{(1-W_0C)^2}\int_0^{\infty}d\epsilon\, \tilde{A}(\epsilon)e^{i(\sqrt{\epsilon}z-\epsilon t)} -\frac{4W_2I_0}{(1-W_0C)^2}\sum_{n=1}^{\infty}e^{in\pi[(N/\Delta)\bar{\epsilon}-(N+1)]}e^{-n\pi(\Gamma/\Delta)}\int_0^{\infty}d\epsilon\, \tilde{A}(\epsilon)e^{i[\sqrt{\epsilon}z-\epsilon(t-\tau_P)]} . \tag{E29}$$

The time dependence of ϕ_2 is seen in Eq. (E29). ϕ_2 is an infinite sum of wave packets; each successive wave packet is delayed by a time τ_P (a "Poincaré recursion time") corresponding to the time it takes a phonon to travel the length of the chain and return, with velocity v_g,

$$\tau_P=\frac{2Na}{v_g} . \tag{E30}$$

The amplitude of the nth delayed wave packet is diminished by a factor $e^{-n\pi(\Gamma/\Delta)}$.

APPENDIX F: WKB ANALYSIS OF LONG-RANGE INTERACTIONS

The difference between the z^{-3} and z^{-1} cases can be understood from consideration of the WKB approximation for large z. WKB's validity condition is

$$\left|\frac{dk(z)}{dz}\right| \ll k^2(z) , \tag{F1}$$

where

$$k^2(z)\equiv k^2+U(z)=k^2+\frac{C_\beta}{z^\beta}, \quad \beta=1 \text{ or } 3 . \tag{F2}$$

This leads to

$$\frac{\beta C_\beta}{2z^{\beta+1}\left[k^2+\frac{C_\beta}{z^\beta}\right]^{3/2}} \ll 1 . \tag{F3}$$

Clearly, for fixed k this will be satisfied for sufficiently large z. To find out where the inequality breaks down, replace it by an equality and solve for $z = z^*(k)$ for small k.

This gives, for $\beta=1$

$$\frac{C_1}{2[z^*(k)]^2\left[k^2+\frac{C_1}{z^*}\right]^{3/2}}=1\ , \tag{F4}$$

so that

$$z^*(0)=\frac{1}{4C_1}$$

and

$$z^*(k)<z^*(0)\ . \tag{F5}$$

Thus the WKB approximation is valid for *all* k for $z>z^{**}$, where z^{**} is a k-independent value much greater than $z^*(0)$. The low-energy wave functions can then be obtained by matching the WKB solution for $z \geq z^{**}$ to the $k=0$ exact solution for $z \leq z^{**}$. This leads to the result of Eq. (82). The validity of the *semiclassical* WKB solution for $z \geq z^{**}$ for all k, no matter how small, corresponds to the absence of quantum reflection beyond z^{**}.

On the other hand, for $\beta=3$, the condition (F4) is replaced by

$$\frac{3C_3}{2[z^*(k)]^4\left[k^2+\frac{C_3}{[z^*(k)]^3}\right]^{3/2}}=1\ , \tag{F6}$$

giving

$$z^*(k)=\left[\frac{3C_3}{2}\right]^{1/4}k^{-3/4}\ . \tag{F7}$$

Therefore, as $k\to 0$, $z^*(k)\to\infty$, and quantum reflection takes place at $+\infty$. (A little reflection shows that for a square well, quantum reflection occurs for $z^{**}\sim\gamma k^{-1}$ with $\gamma \ll 1$.) It is easily verified that for long-range potentials of the form $U^{(s)}(z)-C_\beta/z^\beta$, quantum reflection occurs[32] as soon as $\beta>2$.

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[21]In the context of a time-dependent approach, it is conventional to add a small imaginary part to the energy, leading to retarded Green's functions.

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