Model for handling the transmission problem in sticking at cold solid surfaces

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The sticking rate is calculated for a simple model Hamiltonian, which assumes a one-dimensional motion of the incident gas atom together with a one- to three-dimensional phonon density of states. The gas-atom–phonon interaction is of short range and treated in a localized basis set. After solving exactly for this short-range interaction the localized wave functions are embedded into the continuum of scattering states. This embedding problem is solved in an approximate way. The calculated sticking coefficient at zero kinetic energy of the incoming particle and zero substrate temperature is unity for a two- and three-dimensional phonon density of states, and finite between zero and one for a one-dimensional phonon density of states. Many phonon events are found to dominate the sticking process.

I. INTRODUCTION

A gas atom incident on a metal surface will exchange energy with the phonons. If the incident gas atom loses enough of its kinetic energy, it remains bound to the metal. The probability that this will happen is called the sticking coefficient. Consider first a simple classical model which was solved twenty years ago.[1] It consists of a one-dimensional chain of metal atoms connected by springs. The incident gas atom interacts with the surface atom via the potential of a truncated harmonic oscillator. If the sticking probability is calculated in this model by solving the classical equations of motion, one finds that there is a critical kinetic energy depending on the mass ratio and the depth of the potential well, below which the particle will stick with certainty, whereas for larger kinetic energies it will be reflected with certainty. More realistic potentials and three-dimensional treatments give analogous results.[2]

The classical mechanical model of Ref. 2 assumes a harmonic substrate at temperature $T_s = 0$ and a head-on collision of the gas atom with a single surface atom, the interaction being a short-range potential. Calculations of the accommodation coefficient within this scheme give good agreement with experimental results. The sticking coefficient at zero kinetic energy has, of course, not been measured yet.

Before turning now to quantum-mechanical calculations it is important to understand the physical reason why in the classical models the gas atom sticks with probability one at low kinetic energies. The collision of the gas atom with the surface atom leads to a local distortion of the lattice, which is transmitted from one metal atom to the neighboring one so that lattice waves are set up which propagate away from the point of impact, thus irreversibly removing kinetic energy from the gas atom.

Figure 1 illustrates how the problem looks from a quantum-mechanical point of view. Indicated here is the distribution of gas atom states in energy space. We have a continuum of scattering states and discrete localized vibrational states with possible resonances in the scattering continuum. The gas-atom–phonon coupling is of short range and will therefore occur from the localized states and the resonances.

The quantum theory, which can be found in the literature, is that developed by Lennard-Jones and his collaborators.[3] This is a one-phonon theory treated in distorted-wave Born approximation (DWBA), which considers only the perturbation of the gas-atom potential by the phonons. The modification of the lattice vibrations is not included in these theories and therefore the physics dominating in the classical models is excluded from the beginning. Hence it should not be surprising that completely different results are obtained. Instead of being unity as in the classical theory, the sticking coefficient is found to tend to zero proportional to the square root of the kinetic energy.[4] The reason for this is that the eigenfunctions of the static potential have to tend to zero at the

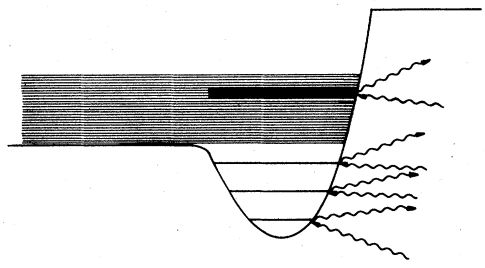

FIG. 1. Spectral resolution of the gas-atom states in a one-dimensional quantum-mechanical model. The coupling to the metal phonons occurs from the localized vibrational states and resonances.

surface so that at long wavelengths they do not have enough amplitude over the adsorption well. This is referred to as the transmission problem, because it means that for low kinetic energy the gas atom is reflected back elastically before it reaches the surface.

This has been realized as a real problem for a long time because, firstly, experimental evidence[5] and physical intuition indicate that gas atoms adsorb entirely on solid surfaces for zero kinetic energy of the incoming particle ($\epsilon_i = 0$) and zero substrate temperature ($T_s = 0$), and secondly, zero substrate temperature and low kinetic energy is just the regime where quantum effects should dominate and the one-phonon approximation is expected to be valid.

One possible explanation has been the demonstration that in DWBA a nonzero sticking coefficient can be obtained at zero kinetic energy for a sufficiently long-range potential.[6] But even then there remains the puzzle that classical mechanical theories with short-range potentials can give a correct description of the experimental accommodation coefficient in the so-called quantum regime,[7] together with the fact that the physics of the classical models has not yet been incorporated into the quantum theories. A paper by Knowles and Suhl[8] tries to attack this point by ascribing an enhanced effective mass to the gas atom near the surface, the enhancement arising from polarization effects similar to those encountered in the polaron problems.[9] The phonons, however, remain unchanged by the interaction with the gas atom[10] and a square-root behavior is still predicted for the sticking coefficient, tending to zero for zero kinetic energy, although the decrease occurs at lower energies than estimated by the DWBA.

The present paper contributes to the problem by examining a model with a short-range potential which has the property that in the limit $\epsilon_i \to 0$ the DWBA gives a zero sticking coefficient, but a better solution including many-body effects yields unit sticking probability. To obtain this result it is essential that the dynamical displacements of the phonons by the incoming gas atom are taken into account.

Throughout this paper it is assumed that the substrate temperature is 0 K; i.e., before the scattering event there is only the zero-point motion of the lattice vibrations. Section II describes the model and demonstrates how the localized gas-atom–phonon interaction can be handled by defining "displaced" phonon modes. The mathematical solution of the transmission problem is presented in Sec. III, whereas the sticking rate and the sticking coefficient are calculated in Secs. IV and V, respectively. A simple numerical example is given in the last section, together with a comparison of the presented many-body calculation to the standard DWBA.

II. THE MODEL

The common one-dimensional model with linear coupling to the phonons, which has been used in previous work on sticking,[3,4,6,8] can be written in occupation-number representation if a basis set for the gas atom is introduced:

$$\hat{H} = \sum_{k\ \mathrm{deloc}} \epsilon_k n_k + \sum_{t\ \mathrm{loc}} \epsilon_t n_t + \sum_q \omega_q b_q^\dagger b_q + \sum_{t,t'} \left\langle t \left| \frac{d}{dz} V^0(z) \right| t' \right\rangle c_t^\dagger c_{t'}' \sum_q \frac{b_q^\dagger + b_q}{(2M\omega q)^{1/2}} . \tag{1}$$

The basis set contains localized and nonlocalized functions. $n_k = c_k^\dagger c_k$ is the occupation-number operator for the delocalized scattering states, $c_t^\dagger$ and c_t are the creation and the destruction operators for the gas atom in the localized states, and $b_q^\dagger$ and b_q are those for the phonons. ϵ_k and ϵ_t are the one-particle energies of the states $|k\rangle$ and $|t\rangle$, respectively, the ω_q are the phonon energies, and M is the mass of the metal atoms. $V^0(z)$ is the static gas-atom potential perpendicular to the surface. Only the localized states are coupled directly to the phonons. This is mathematically desirable, but requires a specially constructed basis which does not consist of the eigenstates of the static potential. Formal aspects and mathematical details have been given elsewhere.[11]

This paper examines a simplified version of the Hamiltonian Eq. (1) with only two localized functions in the gas-atom basis set. It probably represents the simplest possible model for sticking. An exact solution is still out of range, but a rather high approximation can easily be obtained. The model Hamiltonian is

$$H = \sum_k \epsilon_k n_k + \epsilon_1 n_1 + H_{\mathrm{loc}} + V_{12} c_1^\dagger c_2 + V_{21} c_2^\dagger c_1 + \sum_k (V_{2k} c_2^\dagger c_k + \mathrm{H.c.}) , \tag{2}$$

$$H_{\mathrm{loc}} = \epsilon_2 n_2 + \sum_q \omega_q b_q^\dagger b_q + n_2 \sum_q \lambda_q (b_q^\dagger + b_q) .$$

The first term describes a continuous set of gas-atom scattering states decaying exponentially at the solid surface. There are two localized states for the gas atom (cf. Fig. 2). One, referred to by the subscript 1, is a localized state with no direct

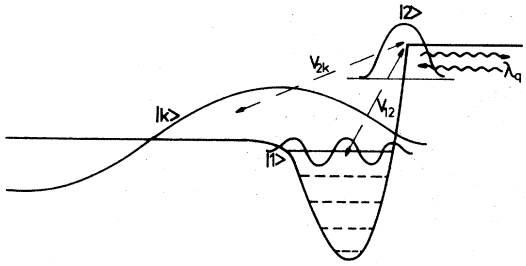

FIG. 2. Illustration of the model Hamiltonian. $|k\rangle$ is a delocalized scattering state, $|1\rangle$ and $|2\rangle$ are localized states with only state $|2\rangle$ coupling to the phonons, V_{2k} is the matrix element describing the embedding of the state $|2\rangle$ into the scattering continuum.

coupling to the phonons; this will accommodate the gas atom in the final stage of the sticking process. The other, labeled by subscript 2 and contained in the operator $H_{\rm loc}$, describing the localized interaction with the phonons, is the only state with direct coupling to the lattice vibrations of the solid. ϵ_2 is greater than zero, hence the spectral resolution of the state $|2\rangle$ in the eigenstates of the static potential is a broad resonance above threshold.

In order to avoid misinterpretation, it is stressed that the model does *not* assume a precursor state or inequivalent adsorption sites for the static potential. The meaning of the state $|2\rangle$ is that it probes the strongly repulsive part of the potential, which leads to strong coupling to the phonons because the gas-atom-phonon coupling constants λ_q are proportional to the gradient of the static potential:

$$\lambda_q = (2NM\omega_q)^{-1/2}\left\langle 2\left|\frac{d}{dz}V^0(z)\right|2\right\rangle . \tag{3}$$

N is the normalization constant. Equation (3) is justifiable for pairwise additive potentials and should be a reasonable order-of-magnitude estimation in general. It will be demonstrated below [Eq. (5)] that $|2\rangle$ develops into a bound state dynamically, i.e., as an intermediate step in the process of sticking. For the gas atom far away from the surface as well as for the gas atom stuck in the state $|1\rangle$, it is just a broad resonance above threshold.

While the model Eq. (2) retains some important properties of the Hamiltonian Eq. (1), it is, of course, not equivalent to it. A numerical example parametrized to describe He scattering from heavy-transition-metal surfaces has demonstrated, however, that a more general Hamiltonian of the form of Eq. (1) can, for the purpose of examining sticking at $\epsilon_i = 0$, be rewritten in the form of Eq. (2).[12] This result depends, of course, on the physical system under investigation. For strongly chemisorbing, heavy atoms or molecules several localized states coupling directly to the phonons will probably have to be included.

A feature of the Hamiltonian Eqs. (1) and (2), which has been criticized in the literature,[13] is the linear coupling to the lattice vibrations. This point requires separate extensive investigations. An examination of a special example showed, however, that the physical phenomenon, which is responsible for sticking coefficient unity at $\epsilon_i = 0$, is existent also if quadratic phonon-coupling terms are included in the Hamiltonian.[12]

In Eq. (2), the states $|1\rangle$ and $|2\rangle$ are assumed to be orthogonal to the $|k\rangle$ states, which is physically wrong. This, however, has no bearing on the result of sticking coefficient one at zero kinetic energy, as will become obvious later (cf. Sec. VI).

Equation (2) is reminiscent of a Hamiltonian which has been investigated by Hewson and Newns[14] in a different context, namely, the image force in chemisorption theory. The method of solution presented here is quite different, however. Defining displaced phonon operators β_q by

$$\beta_q = b_q + \lambda_q/\omega_q , \tag{4}$$

allows us to write $H_{\rm loc}$ in the form

$$H_{\rm loc} = \epsilon_2 n_2 + \sum_q \omega_q \beta_q^\dagger \beta_q + \sum_q [\,|\lambda_q|^2/\omega_q (1-2n_2)] + \sum_q (\lambda_q n_2 - \lambda_q)(\beta_q^\dagger + \beta_q) . \tag{5}$$

The displaced and undisplaced phonon wave functions and their overlap, which play a dominating role in the present theory, are illustrated in Fig. 3. The potential energy curve defining the phonon with wave vector q is displaced if the gas atom

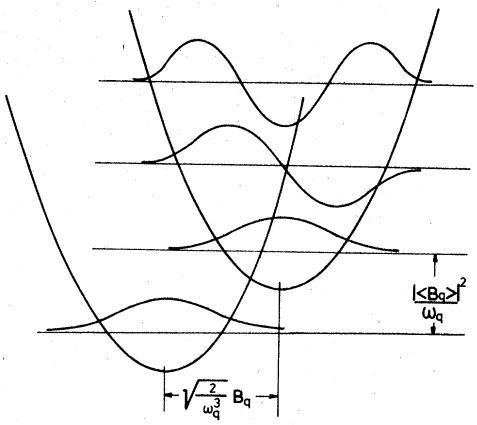

FIG. 3. Displaced and undisplaced phonon wave functions and their overlap, the quantum-mechanical analog to the local distortion of the lattice by the incident gas atom.

hops from a delocalized scattering state into the localized state $|2\rangle$. This is the quantum-mechanical analog to the local distortion of the lattice by the incoming gas atom which is so important in the classical mechanical theories. The effect of displacing the phonons is contained in the third and fourth terms of Eq. (5). The third term might be described as the "phonon image" term. It implies a decrease of the self-energy of the gas atom and a constant shift of the potential and is formally similar to the attractive potential felt by an electron in front of a metal surface. The physical meaning of the fourth term is that the phonons get displaced if the gas atom hops into the state $|2\rangle$, and that the phonons transform back into the undisplaced ones whenever the gas atom leaves the state $|2\rangle$. This term is conveniently handled in a many-body basis, where it can be absorbed into hopping terms between many-body states.

III. THE COUPLING TO THE SCATTERING CONTINUUM

In this section the Hamiltonian Eq. (2) will first be cast in the form

$$H = H_{\rm loc} + \sum_n (H_n + V_{\rm hop}^{(n)}) \,. \tag{6}$$

$H_{\rm loc}$ is diagonalized by the canonical transformation Eq. (4). The eigenfunctions of $H_{\rm loc}$ are given by the set $\{|2\rangle|nd\rangle\}$, where $|nd\rangle$ indicates a product state of displaced phonons. The eigenfunctions of

$$\sum_k \epsilon_k n_k + \epsilon_1 n_1 + \sum_q \omega_q b_q^\dagger b_q$$

are given by the set $\{|1\rangle|n\rangle\}\cup\{|k\rangle|n\rangle\}$, where $|n\rangle$ is a product state of undisplaced phonons.

If the Hamiltonian matrix is set up in the many-body basis constructed above, it would have the structure of Eq. (6). It can be written in an occupation-number representation by introducing the following annihilation operators:

$$\begin{aligned} &A_{1n}|1\rangle|n\rangle = |0\rangle \,, \\ &A_{kn}|k\rangle|n\rangle = |0\rangle \,, \\ &A_{2n}|2\rangle|nd\rangle = |0\rangle \,. \end{aligned} \tag{7}$$

$|0\rangle$ is the vacuum state of the total Hamiltonian. It describes the zero-point motion of the phonons without a gas atom present. The operators satisfy the canonical commutation relations

$$[A_{in}, A_{jm}] = \delta_{ij}\,\delta_{nm} \,, \tag{8}$$

because the gas atom states are assumed to be orthogonal:

$$\langle 2|1\rangle = \langle 2|k\rangle = \langle 1|k\rangle = 0, \quad \langle k|k'\rangle = \delta_{kk'} \,.$$

H_n and $V_{\rm hop}^{(n)}$ are then given by

$$H_n = (\epsilon_1 + E_n) A_{1n}^\dagger A_{1n} + \sum_k (\epsilon_k + E_n) A_{kn}^\dagger A_{kn} \,, \tag{9}$$

$$\begin{aligned} V_{\rm hop}^{(n)} = &\sum_{k,m} (V_{2k} \langle md|n\rangle A_{2m}^\dagger A_{kn} + \text{H.c.}) \\ &+ \sum_m (V_{21} \langle md|n\rangle A_{2m}^\dagger A_{1n} + \text{H.c.}) \,. \end{aligned} \tag{10}$$

The form of $V_{\rm hop}^{(n)}$ arises, because

$$\langle md|\langle 2|V_{2k} c_2^\dagger c_k|k\rangle|n\rangle = V_{2k}\langle md|n\rangle \,. \tag{11}$$

E_n is the energy of the phonon states. In the many-body basis $H_{\rm loc}$ has the form

$$\begin{aligned} H_{\rm loc} = &\sum_n \left(\epsilon_2 - 2\sum_q |\lambda_q|^2/\omega_q + E_n\right) A_{2n}^\dagger A_{2n} \\ &+ \sum_q |\lambda|^2/\omega_q \,. \end{aligned} \tag{12}$$

H_n and $H_{\rm loc}$ are diagonal in the created many-body basis. The difficulty in solving the problem lies in the interaction terms $V_{\rm hop}^{(n)}$, which describe hopping between many-body states with displaced and undisplaced phonons. They contain now the dynamical deformation of the phonons, which is induced if the gas atom penetrates into the surface region (here, into the state $|2\rangle$).

Diagonalizing the Hamiltonian matrix constructed above, would yield an exact solution, which is formally analogous to the method of configuration interaction (CI) used in quantum chemistry. As is generally the case, one cannot do a full CI calculation, but must be contented with a limited CI scheme. This is achieved by restricting the basis to those many-body states which are expected to be most important for the wave function one wants to know. With out notation, such an approximation is obtained if we couple $H_{\rm loc}$ only to H_0. This defines an approximate Hamiltonian $\bar{H}$,

$$\bar{H} = H_{\rm loc} + H_0 + V_{\rm hop}^{(0)} \,, \tag{13}$$

whose exact diagonalization constitutes the limited CI calculation.

The structure of the Hamiltonian $\bar{H}$ is illustrated in Fig. 4. In contrast to Fig. 1, where the energy resolution of one-particle (gas atom) states was given, Fig. 4 represents in the upper two rows schematically the energetic distribution of many-body states, the eigenstates of H_0 and $H_{\rm loc}$. The density of states is indicated by the energy separation of neighboring energy levels. The third row

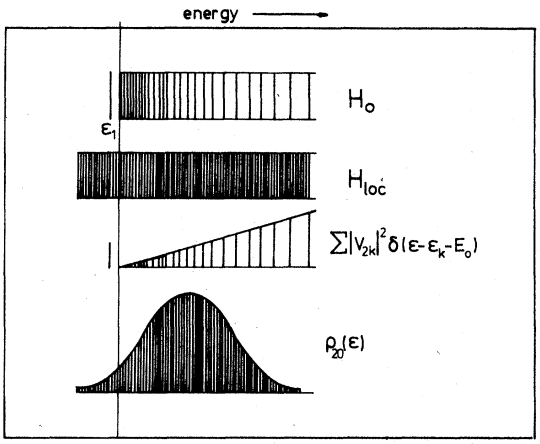

FIG. 4. Level scheme, spectra resolution of the coupling to the k states, and spectral resolution $\rho_{20}(\epsilon)$ of the state $|2\rangle|0\rangle$ in the local Hamiltonian (schematic).

gives the spectral resolution of the term $V^{(0)}_{\text{hop}}$ *in the scattering continuum*, which is taken to be

$$\sum_k |V_{2k}|^2\delta(\epsilon-\epsilon_k-E_0)=|V|^2(\epsilon-E_0)^{1/2}\,. \tag{14}$$

It is exactly this form of the hopping between the localized and the scattering states which leads to the transmission problem. The fourth row represents the spectral resolution of the state $|2\rangle|0\rangle$ in the eigenstates of the local Hamiltonian H_{loc}:

$$\rho_{20}(\epsilon)=\sum_n |\langle 0|nd\rangle|^2\,\delta(\epsilon-E_n)\,. \tag{15}$$

(The vertical height of the lines in the lower two rows indicates the size of $|V_{2k}|^2$ and $|\langle 0|nd\rangle|^2$, respectively.) Because the interaction between the scattering continuum and H_{loc} occurs only via the state $|2\rangle|0\rangle$, $(\sum_k |V_{2k}|^2)\,\rho_{20}(\epsilon)$ is the spectral resolution of $V^{(0)}_{\text{hop}}$ *in the local Hamiltonian* H_{loc}.

It is now apparent that we have two interacting continua (those of H_0 and H_{loc}), where every energy level of one continuum couples to every energy level of the other. The wave functions of two degenerate energy levels get mixed with coefficients of the order of 1 for arbitrarily small interaction between them. If the phonon coupling in the localized state $|2\rangle$ is strong enough so that the lower edge of $\rho_{20}(\epsilon)$ is below zero, i.e.,

$$\epsilon_2-\sum_q |\lambda_q|^2/\omega_q+E_0<0, \tag{16}$$

then the scattering state at $\epsilon_i=0$ has an eigenstate of H_{loc} degenerate with it. In this case, a gas atom incident in the scattering state at $\epsilon_i=0$ will be transmitted with high probability into the localized state $|2\rangle$. In fact, Eq. (16) will turn out to be a sufficient criterion for sticking coefficient unity at $\epsilon_i=0$.

Of course, in the case of two interacting continua, the expression "degenerate levels" has no precise meaning. One has, instead, to talk about the average energetic distance of the nearest eigenstate of H_{loc} from a scattering state at $\epsilon_i=0$, which is given by the reciprocal density of the eigenstates of H_{loc}. Hence we would have a transmission coefficient of order 1, if

$$|V_{2k}|^2\rho_{\text{loc}}(\epsilon)\rho_{20}(\epsilon)$$

is of the order of 1 or larger.

In order to justify mathematically the qualitative discussion above, one has to evaluate the coefficient of the state $|2\rangle|nd\rangle$ in the eigenstate $|k0+\rangle$ of the total Hamiltonian H, i.e., the quantity $\langle nd|\langle 2|k0+\rangle$. From the Lippmann-Schwinger equation

$$|k0+\rangle=|k0\rangle+GV^{(0)}_{\text{hop}}|\,k0\rangle\,, \tag{17}$$

one obtains with the help of Eq. (10),

$$\langle nd|\,k0+\rangle=V_{2k}\,\langle nd|\,G|\,0\rangle\,. \tag{18}$$

Here and in the following, an abbreviated notation is used for convenience:

$$|nd\rangle\equiv|2\rangle|nd\rangle,\quad |0\rangle\equiv|2\rangle|0\rangle,\quad |k0\rangle\equiv|k\rangle|\,0\rangle\,.$$

In order to evaluate the matrix element $\langle nd|\,G\,|0\rangle$ of the Green operator, we use Dyson's equation in the two forms:

$$G=G^0+GV^{(0)}_{\text{hop}}\,G^0\,, \tag{19}$$

$$G=G^0+G^0V^{(0)}_{\text{hop}}\,G\,. \tag{20}$$

Using Eq. (19) one has

$$\langle nd|\,G|0\rangle=\langle nd|\,0\rangle\,G^0_{nd}+\sum_l\langle nd|\,G|\,l0\rangle\,V_{l_2}G^0_2\,, \tag{21}$$

where

$$G^0_2=\sum_m |\langle 0|md\rangle|^2\,G^0_{md}\,. \tag{22}$$

From Eq. (20) one obtains

$$\langle nd|\,G\,|\,l0\rangle=G^0_{nd}\langle nd|\,0\rangle\sum_k V_{2k}\langle k0|\,G|\,l0\rangle \tag{23}$$

and

$$\langle k0|\,G|\,l0\rangle=G^0_k\,\delta_{kl}+G^0_k\,V_{k2}\sum_m\langle 0|md\rangle\langle md|\,G|\,l0\rangle. \tag{24}$$

Multiplying Eq. (24) by V_{2k}, summing over all k,

and inserting into Eq. (23) yield

$$\langle nd|G|l0\rangle = G^0_{nd}\langle nd|0\rangle \times \left(V_{2l}\, G^0_l + q_2 \sum_m \langle 0|md\rangle\langle md|G|l0\rangle\right), \tag{25}$$

where we have defined an "embedding function"

$$q_2(\epsilon) = \sum_k \frac{|V_{2k}|^2}{\epsilon - \epsilon_k - E_0}\ . \tag{26}$$

After multiplying Eq. (25) by $\langle 0|nd\rangle$ and summing over all $|nd\rangle$, one arrives at

$$\sum_n \langle 0|nd\rangle\langle nd|G|l0\rangle = \frac{G^0_2 V_{2l}\, G^0_l}{1 - G^0_2 q_2}\ . \tag{27}$$

Putting this expression back into Eq. (25) gives the desired formula for $\langle nd|G|l0\rangle$, which after substituting into Eq. (21) yields the final result:

$$\langle nd|G|0\rangle = \langle nd|0\rangle\, G^0_{nd}(1 - G^0_2 q_2)^{-1}\ . \tag{28}$$

$G^0_{nd}(\epsilon)$ has a pole at $\epsilon = \epsilon_2 - \sum_q |\lambda_q|^2/\omega_q + E_n$. If $|2\rangle|nd\rangle$ is degenerate with the scattering state $|k\rangle|0\rangle$, $G^0_{nd}(\epsilon)$ will compensate the factor $V_{2k}\langle nd|0\rangle$ occurring in the formula Eq. (18). For large energetic separation of $|2\rangle|nd\rangle$ and $|k\rangle|0\rangle$ and small $q_2(\epsilon)$, Eq. (18) is equivalent to the perturbation expression for the coefficient.

IV. THE STICKING RATE

For the sticking rate the golden rule might be used with the initial state taken as an exact eigenstate of the total Hamiltonian H. The sticking inducing potential is $\lambda_q b^\dagger_q n_2$. The rate is then

$$R(q) = 2\pi|\lambda_q|^2 \sum_f |\langle f-|\, b^\dagger_q n_2\,|i+\rangle|^2 \delta(\epsilon_f - \epsilon_i - E_0)\ . \tag{29}$$

If the occupation-number operator n_2 is written in Dirac notation,

$$n_2 = \sum_n |2\rangle|nd\rangle\langle nd|\langle 2|\ , \tag{30}$$

one has instead

$$R(q) = 2\pi|\lambda_q|^2 \sum_f \left|\sum_n \langle f-|\, b^\dagger_q |nd\rangle\langle nd|\, i+\rangle\right|^2 \delta(\epsilon_f - \epsilon_i - E_0)\ . \tag{31}$$

The final state $|f-\rangle = |\hat{f}-\rangle|n_q\rangle$ is an eigenstate of $H - \lambda_q n_2(b_q + b^\dagger_q)$, corresponding to a gas atom bound to the surface with locally displaced phonons, except for the emitting phonon mode, which is undisplaced. If the exact final state is approximated by the corresponding eigenstate of H_0 with again the emitting mode undisplaced, $|f-\rangle \approx |\hat{f}d\rangle|n_q\rangle$, one has

$$R(q) = 2\pi|\lambda_q|^2 n_q |\langle n_q - 1|n_q d\rangle|^2 \sum_f |\langle fd|\, i+\rangle|^2 \delta(\epsilon_f - \epsilon_i - E_0)\ . \tag{32}$$

Here, of course, $|\hat{f}d\rangle|n_q\rangle$ is energetically degenerate with $|i+\rangle$, which fixes n_q. It is important to realize that this approximate rate deviates from the exact rate by a factor of order 1, the square of the coefficient of the state $|fd\rangle$ in the exact *final* state. The phonon overlap factor for $(\lambda_q/\omega_q) \ll 1$ is given by

$$\langle n_q - 1|n_q\, d\rangle = (n_q/2)^{1/2}(\lambda_q/\omega_q)\ . \tag{33}$$

The qualitative picture which emerges for the sticking process at low kinetic energies is obviously the following: The incoming gas atom is trapped with high probability in the eigenstate $|2\rangle|nd\rangle$ of $H_{\rm loc}$, which is degenerate with the scattering state describing the incident particle. Then there is emission of n_q phonons with wave vector q, because the displaced phonons have a finite overlap with the unperturbed phonons of the clean metal; i.e., the strain caused by the colliding particle is released in waves of vibrating metal atoms. It follows from Eqs. (32) and (33) that many-phonon transitions dominate over one or few-phonon transitions. Instead of having just one emitting phonon mode, we could use in Eq. (29) a final state with several emitting phonon modes with the sticking inducing potential then being

$$\sum_{i=1}^{N} \lambda_{qi}\, b^\dagger_{qi} n_2\ .$$

In order to proceed with our analysis, we now have to insert Eqs. (18) and (28) for $\langle fd|\, i+\rangle$. Squaring yields

$$|\langle fd|i+\rangle|^2 = |V_{2i}|^2 |\langle fd|\, 0\rangle|^2 |\, G^0_{fd}\,|^2 |1 - G^0_2 q_2|^{-2}\ . \tag{34}$$

Substituting in Eq. (32) gives

$$R(q)=\pi(|\lambda_q|^4/\omega_q^2)m_q^2|V_{2i}|^2\rho_{\rm loc}(\epsilon_f)|\langle fd|0\rangle|^2 \times|G^0_{fd}|^2|1-G^0_2q_2|^{-2}\,. \tag{35}$$

The total sticking rate is, of course, obtained by summing over all possible many-mode transitions.

V. THE STICKING COEFFICIENT

The common definition of the sticking coefficient is (with F_0 and $F_{\rm refl}$ the incident and reflected fluxes):

$$S=\frac{F_0-F_{\rm refl}}{F_0}=\frac{F_{\rm stick}}{F_0}\,, \tag{36}$$

with the following standard normalization for the incident flux[4]:

$$F_0=k_i/(mL)\,. \tag{37}$$

Here k_i is the momentum of the incoming particle. This means that the exact initial-state wave function is not normalized to unity over a volume L. According to Schiff[15] the interpretation is "that we choose a large enough number of systems each described by ψ_{i+} that are identical and independent." The number of systems is

$$c_{i+}=\int_L dr\,|\psi_{i+}(r)|^2\,, \tag{38}$$

which can be larger or smaller than unity. However, most treatments on collision theory start from a Hilbert space with a scalar product, which normalizes the wave functions to unity. Therefore, the expression

$$R_{\rm stick}=2\pi\sum_f|\langle f|V_{\rm stick}|i+\rangle|^2\delta(E_i-E_f)\,,$$

gives the flux for one gas atom contained in the many-body state ψ_{i+}, which in this paper is called "rate." Of course, $R_{\rm stick}$ contains the rate of the outgoing phonons. One then has

$$F_{\rm stick}=c_{i+}R_{\rm stick}\,. \tag{39}$$

Under steady-state conditions—which can be assumed, because there is no desorption at $T_s=0$—the incoming flux equals the outgoing flux:

$$F_0=F_{\rm refl}+F_{\rm stick}=c_{i+}(R_{\rm refl}+R_{\rm stick})\,. \tag{40}$$

Equations (37), (40), and (41) yield

$$S=\frac{F_{\rm stick}}{F_0}=\frac{c_{i+}R_{\rm stick}}{F_0}=\frac{R_{\rm stick}}{R_{\rm refl}+R_{\rm stick}}\,. \tag{41}$$

The reflection rate $R_{\rm refl}$ includes elastic and inelastic transitions. For substrate temperature $T_s=0$ and zero kinetic energy of the incoming particle there is, however, no inelastic reflection, because in this limit it would require energy transfer from the metal to the gas atom and there are no phonons available to supply it. Hence, only elastic reflection is possible and the rate for it is in the limit $\epsilon_i\to 0$ equal to the rate of reflection from an infinite rigid potential step, which is

$$R_{\rm refl}(\epsilon_k=0)=k/(2mL)\,. \tag{42}$$

Here m is the mass of the gas atom and L is the normalization length for the scattering states. It is sufficient to use the one-mode sticking rate, because including many-mode sticking can only increase the sticking coefficient:

$$s(\epsilon_i=0,\ T_s=0)=\sum_q R(q)\Big/\Big(\sum_q R(q)+R_{\rm refl}(\epsilon_k=0)\Big)\,. \tag{43}$$

The next thing needed is an estimate of $R(q)$. Because G^0_{fd} has a pole at $\epsilon=E_0$, one can, with the prescription

$$\lim_{\eta\to 0}(\epsilon+i\eta-E_0)^{-1}=\mathcal{P}(\epsilon-E_0)^{-1}-i\pi\delta(\epsilon-E_0)\,,$$

write

$$|G^0_{fd}(\epsilon=E_0)|^2=\pi^2\rho^2_{\rm loc}(\epsilon=E_0)\,.$$

This yields

$$R(q)=\pi^3n_q^2(|\lambda_q|^4/\omega_q^2)\rho_{\rm loc}(\epsilon=E_0)Q(k)\,, \tag{44}$$

where the k dependence of this rate is contained in the quantity

$$Q(k)=\frac{1}{\pi}\,{\rm Im}G^0_2|1-G^0_2q_2|^{-2}|V_{2k}|^2\rho_{\rm loc}\,. \tag{45}$$

$Q(k)$ is a dimensionless number, which is characteristic for the interaction of the state $|k\rangle|0\rangle$ with the displaced phonon states of $H_{\rm loc}$. For strong interaction $Q(k)$ gives the number of eigenstates of $H_{\rm loc}$ coupling to the scattering state $|k\rangle|0\rangle$.

Approximating $\rho_{\rm loc}(\epsilon)$ by the phonon density of states reduces the rate. Now, the models found in the literature[3,4,6,8] consider a one-dimensional motion of the gas atom, but a three-dimensional phonon density of states. For an n-dimensional solid with characteristic phonon frequency ω_D and normalization length L, the phonon density of states is of order L^n/ω_D. According to Eq. (14), $|V_{2k}|^2$ in the limit $k\to 0$ is of order

$$|V_{2k}|^2=|W|^2k^2/(mL)=2|W|^2\epsilon_k L^{-1}\,.$$

Here W is a number characteristic of the shape

and depth of the adsorption well. W can also account for different normalization lengths for the solid and the gas phase. Q is then for an n-dimensional phonon density of states given by

$$Q(k) = L^{n-1} \rho_{20} 2|W|^2 \epsilon_k / \omega_D .$$

The kinetic energy ϵ_k becomes in the limit $k \to 0$ small, of order $O(L^{-2})$. The symbol $O(\cdots)$ is here and in the following used to denote an order of magnitude estimate. Depending on the dimensionality of the phonon spectrum, one obtains the following estimates for Q:

$$Q(k=0) = \begin{cases} O(1) \text{ for } n=3 \\ O(L^{-1}) \text{ for } n=2 \\ O(L^{-2}) \text{ for } n=1 . \end{cases} \tag{46}$$

The rate of elastic reflection is given by Eq. (42) and becomes of order $O(L^{-2})$ in the limit $k \to 0$. The explicit appearance of the inverse powers of the normalization length in the order of magnitude estimates means that the corresponding rate tends to zero when the transition to the continuum is performed. The sticking coefficient at zero kinetic energy is now obtained by inserting the estimates of Eq. (46) in the formula Eq. (43). In the three-dimensional case the sticking rate remains finite at $k=0$ and therefore the sticking coefficients is clearly unity. For $n=2$ the sticking rate tends to zero more slowly, being of order $O(L^{-1})$ as $L \to \infty$, than the elastic rate, which is of order $O(L^{-2})$. Therefore, in this case one also has sticking coefficient unity. For $n=1$ elastic and inelastic rates tend to zero equally fast as $L \to \infty$ and, therefore, a finite sticking coefficient is expected between zero and unity.

VI. DISCUSSION AND CONCLUSIONS

The first remarkable point to observe is that the result of sticking coefficient unity does not depend in any sensitive way on the model parameters. The necessary and sufficient condition is given by Eq. (16), which means that the gas-atom–phonon interaction has to be strong enough to pull an additional state, the state $|2\rangle$, below the vacuum level. Because the only criterion depends solely on the gas-atom–phonon coupling strength, various mathematical properties of the model Hamiltonian, as e.g., the orthogonality of the gas-atom basis states, cannot affect the conclusion that sticking occurs with unit probability at $\epsilon_i = 0$.

To see how easily the condition Eq. (16) can be met, let us investigate a weakly interacting system. The static potential seen by the gas atom is chosen to be a Morse potential, as has been done in the related earlier DWBA calculations[4,16]

$$V^0(z) = \begin{cases} D(e^{2az} - 2e^{az}) & \text{for } z < 1/a , \\ D(e^2 - 2e) & \text{for } z > 1/a . \end{cases} \tag{47}$$

$z > 1/a$ means penetration of the gas atom into the solid. The potential has to be truncated at some point because an infinitely increasing static potential implies an infinitely increasing gas-atom–phonon interaction upon penetration, which is unphysical. The potential is truncated shortly above the vacuum level. Up to this energy the Morse potential can be expected to give a rather reasonable description. A rough parametrization for scattering of a light gas atom with a mass corresponding to He or D_2 from a tungsten surface is given by (all units a.u.)

$$D = 10^{-3}, \quad a = 0.8, \quad m = 10^4, \quad M = 3 \times 10^5 .$$

The detailed form of the spectral resolution of the phonon coupling is not important. Whatever the energy distribution looks like, if

$$\lambda_a = \left(\sum_q |\lambda_q|^2 \right)^{1/2} \tag{48}$$

is in the correct range, there will be sticking at $\epsilon_i = 0$. Therefore, for mathematical simplicity, consider an example where the phonon coupling has a resonance in the interaction strength at some phonon energy ω_a with width Γ:

$$\sum_q |\lambda_q|^2 \delta(\omega - \omega_q) = \frac{|\lambda_a|^2}{\pi} \frac{\Gamma}{(\omega - \omega_a)^2 + \Gamma^2} . \tag{49}$$

One reason for choosing this special form is that $\rho_{1oc}(\epsilon)$ can easily be calculated and has the shape given in Fig. 4.

The model is not completely defined before we have specified the shape and position of the localized wave function $|2\rangle$. According to Eq. (3) this will fix, together with Eq. (49), the gas-atom-phonon coupling constants λ_q. The wave function $|2\rangle$ must not be chosen arbitrarily; it is determined by the potential Eq. (48), as has been demonstrated in Ref. 12. The way to calculate it is to do a variational calculation, which minimizes the ground-state energy of H_{1oc}. We do this here in a simple way by making the ansatz

$$\langle z|2\rangle = \langle z|\alpha, z_0\rangle = (\alpha/\sqrt{\pi})^{1/2} \exp[-(\alpha^2/2)(z - z_0)^2] . \tag{50}$$

The exponent $-\frac{1}{2}\alpha^2$ and the position z_0 of the Gaussian are the variational parameters. The

quantity we minimize is the gas atom energy, including the effective phonon-image potential

$$\langle \alpha, z_0 | \Delta/(2m) + V^0(z) - \frac{d}{dz} V^0(z)/(2M\omega_a^2) | \alpha, z_0 \rangle = \min. \quad (51)$$

With $\omega_a = 10^{-4}$ a.u., a local minimum shows up for the values $\alpha = 5$ a.u. and $z_0 = 1$ a.u. Through Eqs. (3), (48), and the expression

$$\epsilon_2 = \langle 2 | \Delta/(2m) + V^0(z) | 2 \rangle , \quad (52)$$

this fixes the values for ϵ_2 and λ_a: $\epsilon_2 = 1.2 \times 10^{-3}$ a.u., $\lambda_a = 5.5 \times 10^{-4}$ a.u. The phonon-image potential is then $2|\lambda_a|^2/\omega_a = 3 \times 10^{-3}$ a.u., and the criterion Eq. (16) is fulfilled.

For the resonance coupling given by Eq. (49), the rate can be written in the form

$$\sum_q R(q) = -\frac{\pi^2}{\omega_D} \left(\frac{|\lambda_a|^4}{\omega_a^2} \right) n_a^2 |V_{2i}|^2 \rho_{1oc}(\epsilon = E_0) \times |1 - G_2^0 q_2|^{-2} \operatorname{Im} G_2^0 . \quad (53)$$

Assuming $|W|^2 = 10^{-7}$ a.u., the sticking rate is 2×10^{-5} a.u., which means that an infinitely slow gas atom near the tungsten surface will stick within 10^{-12} sec emitting a bunch of 18 phonons. This time is valid for a three-dimensional phonon density of states. Even with a one-dimensional gas atom motion, a three-dimensional phonon density of states appears physically more reasonable than two or one-dimensional densities, because restricting the metal atoms to move only perpendicular to the surface will for a three-dimensional solid give a three-dimensional phonon density of states.

After being trapped in the ground state of H_{1oc}, the gas atom can relax into the state $|1\rangle$ with rate

$$R_{1\to 2} = 2\pi |\langle 0 | 0d \rangle|^2 |\lambda_a|^2 |\langle 1 - | 2 \rangle|^2 / \omega_D . \quad (54)$$

With $|\langle 0 | 0d \rangle|^2 = \exp[-\lambda_a^2/(4\omega_a^2)] = 3.5 \times 10^{-4}$, this takes about 10^{-10} sec to happen. This transition is, of course, independent of the dimensionality of the phonons.

The dependence of the sticking coefficient on the mass of the gas atom is contained in the exponent α of the Gaussian wave function $|\alpha, z_0\rangle$. A heavier particle can better localize near the point of greatest ascent of the static potential and this therefore, leads to a larger λ_a. In the heavy-mass limit ($m \to \infty$) more and more bound states are pulled into the phonon-image potential well and sticking becomes certain. In the zero-mass limit ($m \to 0$) the sticking rate at $\epsilon_i = 0$ tends to zero, because eventually the image potential can no longer support any bound state. Analogous considerations are valid for the dependence on the characteristic phonon frequency, because $\omega_a \to 0$ implies $\lambda_a \to \infty$, and $\omega_a \to \infty$ implies $\lambda_a \to 0$.

It might be illuminating to discuss more approximate methods of solving the proposed model. For comparison with the development in Sec. III, we give in Fig. 5 the spectral resolution of approximate eigenstates of H_0 and H_{1oc} as they are obtained if a standard DWBA calculation is done for the Hamiltonian $\bar{H}$ of Eq. (13). DWBA means here that the wave functions to be inserted into the golden rule are calculated *without* the gas-atom–phonon coupling; i.e., they are product states of gas-atom functions and phonon states. Because H_0 is diagonal from the beginning, the first and third rows of Fig. 5 look the same as those of Fig. 4. The approximate eigenstates of H_{1oc} to be used in the DWBA are products of the state $|2\rangle$ times phonon distributions describing various excitations of undisplaced phonons. Hence the spectral resolution of H_{1oc} as given by the second row of Fig. 5 now has its lower edge at the energy $\epsilon_2 + E_0$ far above threshold with a continuum of excited, undisplaced phonons on top. The spectral resolution of the state $|2\rangle|0\rangle$ is therefore a δ function at the energy $\epsilon_2 + E_0$. It is obvious that the scattering channel, which in the exact solution of $\bar{H}$ leads to sticking coefficient unity at $\epsilon_i = 0$, is closed in the DWBA, because energy cannot be conserved. But even if the approximate ground state of H_{1oc} would be pulled below the vacuum level by including the phonon-image correction only in the self-energy of the gas atom, there would still be no sticking into $|2\rangle|0\rangle$ at $\epsilon_i = 0$, because the phonon parts of degenerate states of H_0 and H_{1oc} are orthogonal. It is only after one has included the modification of the lattice vibrations by the gas atom that this

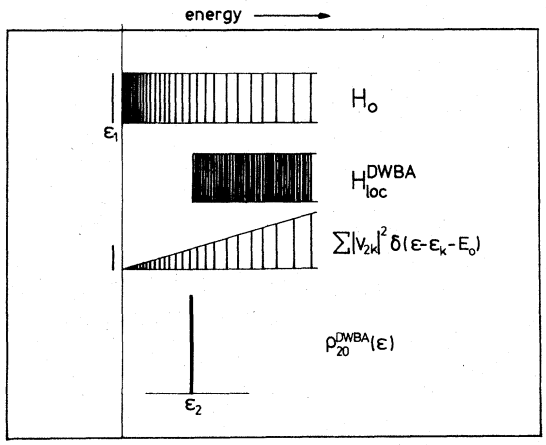

FIG. 5. Same as Fig. 4 for a DWBA calculation.

orthogonality is removed and sticking at $\epsilon_i = 0$ becomes possible.

The sticking channel that is open in the DWBA is transition into the state $|1\rangle$. The rate for this is

$$R_{\text{stick}}(k \to 1) = 2\pi |\langle 1 - |2\rangle|^2 |V_{2i}|^2 |G_2(\epsilon_i + E_0)|^2 \times \sum_q |\lambda_q|^2 / \omega_D . \quad (55)$$

The rate is proportional to k^2/m and hence tends to zero for zero kinetic energy of the gas atom due to the transmission problem as discussed in the Introduction.

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[1]N. Cabrera, Faraday Discuss. Chem. Soc. 28, 16 (1959); R. W. Zwanzig, J. Chem. Phys. 32, 1173 (1960); B. McCarrol and G. Ehrlich, J. Chem. Phys. 38, 523 (1963).
[2]F. O. Goodman and H. Y. Wachman, J. Chem. Phys. 46, 2376 (1967).
[3]See Refs. 126–166 in F. O. Goodman, Prog. Surf. Sci., 5, Pt. 3, 261 (1974).
[4]F. O. Goodman, Surf. Sci. 24, 667 (1971).
[5]L. B. Thomas, *Rarefied Gas Dynamics*, Suppl. 4 (Academic, New York, 1967), Vol. 1, p. 155.
[6]F. O. Goodman, Surface Sci. 27, 157 (1971); J. Chem. Phys. 55, 5742 (1971); N. Garcia and J. Ibanez, J. Chem. Phys. 64, 4803 (1976); F. O. Goodman and N. Garcia, Phys. Rev. B 20, 813 (1979).
[7]F. O. Goodman, Prog. Surf. Sci., 5, 261 (1974).
[8]T. R. Knowles and H. Suhl, Phys. Rev. Lett. 39, 1417 (1977).
[9]T. D. Lee, F. E. Low, and D. Pines, Phys. Rev. 90, 297 (1953).
[10]See also the erratum to Ref. 8 in Phys. Rev. Lett. 40, 911 (1978).
[11]G. Doyen and T. B. Grimley, Surf. Sci. 91, 51 (1980).
[12]G. Doyen, Surf. Sci. 89, 238 (1979).
[13]C. Caroli, B. Roulet, and D. Saint-James, Phys. Rev. B 18, 545 (1978); see also Ref. 1.
[14]A. C. Hewson and D. M. Newns, Jpn. J. Appl. Phys. Suppl. 2, Pt. 2, 121 (1974).
[15]L. I. Schiff, *Quantum Mechanics* (McGraw-Hill, New York, 1968), p. 102.
[16]F. O. Goodman and J. D. Gillerlein, J. Chem. Phys. 57, 3645 (1972).