Quantum theory of the sticking of an atom on a cold solid: Gettering-theory approach

G. P. Brivio* and T. B. Grimley
Donnan Laboratories, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, United Kingdom
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The sticking of an atom on a cold surface is treated by considering the gettering of a gas in a closed vessel. For a small enough area of getter, the gettering rate is obtained essentially exactly in the quasiparticle approximation, and therefore the key quantity is the imaginary part of the gas-atom self-energy calculated at the initial-state energy. The gettering Hamiltonian has an exact representation in terms of the stuck states and the elastic scattering states, and because of this the gettering T matrix, which determines the gas-atom self-energy, and the rates of sticking and inelastic scattering, can be calculated exactly for nontrivial models. Its calculation when the gas atom loses energy to either the electron system, or the phonon system, is considered in detail.

I. INTRODUCTION

A fundamental process at the gas-solid interface is the sticking of a gas atom on a cold solid, but its theoretical description is not found in standard texts on scattering theory,[1] where it is assumed that the scattering potential is ineffective in the remote past, and in the distant future, because the particle is far from the scatterer in these limits. This is true for a reflected particle, but for a stuck particle the scattering potential is not ineffective in the distant future. On the contrary it is always effective; the elastic part of the atom-solid interaction potential binds the atom to the surface, where it also stays therefore within the range of the inelastic part of the potential. Nevertheless, various authors[2] have used stationary scattering theory to obtain results in the distorted-wave Born approximation (DWBA), and even if these results can be shown to be relevant by considerations based on the time scales of the processes involved,[3] it still seems quite hard to progress to exact results for simple theoretical models. We remark too that, in the DWBA, where the T matrix is calculated with the exact scattering state replaced by an elastic scattering state, some of the problems with using conventional scattering theory to describe sticking, are obscured.

It is not our purpose to address these matters here, but partly because of what has been said above, and partly for other reasons (see below), we shall approach sticking *via* the theory of the "gettering" of a gas. Gettering is the removal of a gas from a closed vessel by adsorbing it on a reactive solid (the getter) placed in the vessel, and it corresponds to a practical arrangement where sticking would be followed by monitoring the falling gas pressure. This has no analogue in a beam scattering approach, since it would require the gas-solid interaction to deplete the incident beam as well as the elastically reflected beam, and this would of course conflict with causality. But the leading term in our formula for the sticking rate [Eqs. (8) and (20) below] is exactly the DWBA rate of conventional scattering theory,[4] although our approach is designed to allow *exact* calculations of the rates of sticking, and inelastic scattering for nontrivial models. Gettering is described theoretically as the decay of a prepared state, and it has a feature which is of crucial importance for practical calculations; for a sufficiently large vessel, the quasiparticle approximation gives the time evolution of the system wave functions essentially exactly.[5]

We shall be concerned in this paper with sticking, and inelastic scattering, at zero surface coverage (there will be only one gas atom in the system), and at zero substrate temperature (the initial state will have the solid in its lowest quantum state). At a finite substrate temperature, the long-time behavior (i.e., for times t which are long compared with the zero-coverage residence time $\tau_{\rm res}$ of the atom on the surface) is that there is no gettering just as there is no sticking on a finite-temperature substrate in a stationary scattering theory approach. However, in gettering theory, we follow the time evolution of the system wave function so that the sticking rate at zero coverage for the physically interesting regime $t \ll \tau_{\rm res}$ is determined. This is what we shall do in this paper; on a zero-temperature solid, $\tau_{\rm res}$ is infinite. We will first (Sec. II) outline the theory of gettering by a zero-temperature solid, using a Hamiltonian $H = H_0 + U + W$, where H_0 is the Hamiltonian for the noninteracting systems, gas atom plus solid, U is the elastic part of the gas-solid interaction potential, and W is the inelastic part. In Sec. III we write down the gettering Hamiltonian, derive the formula for the gas-atom self-energy due to inelastic events, and relate the imaginary part of this self-energy to a T matrix. To obtain a complex self-energy, it is of course necessary for the getter to have a continuum of excitations, and this feature is explicit in our notation. The actual calculation of the T matrix by matrix inversion is considered in Sec. IV for inelastic events due to electron-hole pair generation on the one hand, and phonon generation on the other. At this point an approximation is introduced which means that a strongly inelastic event is not described realistically so that the exact calculation of the T matrix on the energy shell is considered for simple but nontrivial models. Numerical results for the electron-hole pair case will be presented in a separate paper.[6]

II. GETTERING-THEORY APPROACH

Consider[4-7] a gas atom in a vessel having the shape of a square prism. The solid we are interested in forms one

of the square faces, the other faces are inert, and the length of the prism perpendicular to the square faces is b. At time $t=0$ the system is in an eigenstate $\psi_i(\mathbf{x})$ of the Hamiltonian H_0+U. ψ_i describes the gas atom making elastic collisions with the solid in its lowest quantum state. For $t>0$, the inelastic part of the potential (W) acts to cause the initial state to decay, and other eigenstates of H_0+U to become populated. These "other eigenstates" are the stuck states ψ_s, and the inelastic scattering states ψ_r. If $\psi_i^+(\mathbf{x},t)$ is the exact state at time $t>0$, the probability to observe the initial state at time t is $|\langle\psi_i|\psi_i^+(t)\rangle|^2$ where

$$\langle\psi_i|\psi_i^+(t)\rangle=-\frac{1}{\pi}\int_{-\infty}^{+\infty}d\varepsilon\, e^{-i\varepsilon t/\hbar}\mathrm{Im}\langle i|G^+(\varepsilon)|i\rangle\ . \tag{1}$$

Here G^+ is the Green operator

$$G^+(\varepsilon)=(\varepsilon+i0-H)^{-1} \tag{2}$$

and

$$\langle i|G^+(\varepsilon)|i\rangle=G_i^+=\int d\mathbf{x}_1\int d\mathbf{x}_2\,\psi_i^*(\mathbf{x}_1)G^+(\varepsilon)\psi_i(\mathbf{x}_2)\ . \tag{3}$$

By introducing the (complex) self-energy $q_i(\varepsilon)$ of the initial state

$$q_i(\varepsilon)=\alpha_i(\varepsilon)-i\Gamma_i(\varepsilon)\ , \tag{4}$$

we can write

$$G_i^+(\varepsilon)=[\varepsilon+i0-E_i-q_i(\varepsilon)]^{-1}\ . \tag{5}$$

Consequently, if we evaluate the integral in Eq. (1) in the quasiparticle approximation, we obtain the exponential decay law[1]

$$|\langle\psi_i|\psi_i^+(t)\rangle|^2=\exp[-2\Gamma_i(E_i)t/\hbar]\ . \tag{6}$$

The quasiparticle approximation is valid if

$$|\Gamma_i(E_i)|\ll E_i \tag{7}$$

and it is a basic property of the gettering approach that we can satisfy Eq. (7) simply by making the length b of the vessel containing the gas atom, large enough.[5] The reason for this is that the inelastic processes described by W, which give rise to the self-energy, and cause the decay of the initial state, are localized near the surface of the solid. So by increasing b so as to make the gas atom spend less of its time near the surface, we can make the decay rate as small as we please, i.e., we can make $\Gamma_i(E_i)$ as small as we please. This statement can be verified if necessary when an explicit formula for $q_i(\varepsilon)$ is available (see below).

An extremely important consequence of the validity of the quasiparticle approximation is that Γ_i separates into the sum of sticking, and inelastic scattering contributions, $\Gamma_i^{\mathrm{stick}}$ and Γ_i^{inel}, so we can at once write down the rates of sticking, and inelastic scattering,

$$R_{\mathrm{stick}}=2\Gamma_i^{\mathrm{stick}}(E_i)/\hbar,\quad R_{\mathrm{inel}}=2\Gamma_i^{\mathrm{inel}}(E_i)/\hbar\ . \tag{8}$$

Then the sticking coefficient s follows from the definition[5]

$$s=R_{\mathrm{stick}}/(R_{\mathrm{stick}}+R_{\mathrm{inel}}+\nu_{\mathrm{coll}})\ , \tag{9}$$

where ν_{coll} is the number of collisions per unit time the gas atom makes with the solid. The definition Eq. (9), which is exact, still leads to unitary results when the rates are only calculated approximately.

III. GETTERING HAMILTONIAN AND THE SELF-ENERGY

The Hilbert space of the gettering Hamiltonian is spanned by the eigenstates of H_0+U describing the gas atom either stuck to, or scattering off, the solid in its various quantum states. Thus

$$H=|i\rangle E_i\langle i|+\sum_f|f\rangle E_f\langle f|+W_1+W_2\ , \tag{10}$$

$$W_1=\sum_f(|i\rangle\langle i|W|f\rangle\langle f|+|f\rangle\langle f|W|i\rangle\langle i|)\ , \tag{11}$$

$$W_2=\sum_{f,f'}|f\rangle\langle f|W|f'\rangle\langle f'|\ . \tag{12}$$

Here $|i\rangle$ is the initial state in which the gas atom scatters elastically off the solid in its lowest quantum state, $|f\rangle$ and $|f'\rangle$ are other eigenstates of H_0+U in which the solid is excited, and gas atom is either stuck, or elastically scattered. $W=W_1+W_2$ is the operator for the inelastic processes, and we do not specify either W or U further at this stage so as to keep the theory general enough to include inelastic processes involving either electrons or phonons.

We now calculate the self-energy q_i of the initial state by writing the expression defining the Green function in the representation afforded by the basis states $|i\rangle$ and $\{|f\rangle\}$;

$$\begin{bmatrix}\varepsilon-E_i & -\underline{W}_{\mathrm{if}}\\ -\underline{W}_{fi} & \underline{1}\varepsilon-\underline{H}_f\end{bmatrix}\begin{bmatrix}G_i & \underline{G}_{\mathrm{if}}\\ \underline{G}_{\mathrm{if}} & \underline{G}_f\end{bmatrix}=\begin{bmatrix}1 & \underline{0}\\ \underline{0} & \underline{1}\end{bmatrix}\ . \tag{13}$$

Here $\underline{H}_f$ has diagonal elements E_f, and nondiagonal elements $\langle f|W|f'\rangle$, $\underline{W}_{\mathrm{if}}$ is a row matrix with elements $\langle i|W|f\rangle$, and $\underline{W}_{fi}$ is a column matrix with elements $\langle f|W|i\rangle$. From Eq. (13) we find

$$G_i=(\varepsilon-E_i-q_i)^{-1} \tag{14}$$

with

$$q_i(\varepsilon)=\underline{W}_{if}(\underline{1}\varepsilon-\underline{H}_f)^{-1}\underline{W}_{fi}\ . \tag{15}$$

If we separate $\underline{1}\varepsilon-\underline{H}_f$ into the diagonal matrix $\underline{G}_f^0$ with diagonal elements $\varepsilon-E_f$, and the remainder $\underline{W}_f$ say with zeros on the diagonal, then

$$(\underline{1}\varepsilon-\underline{H}_f)^{-1}=\underline{G}_f^0(\underline{1}-\underline{W}_f\underline{G}_f^0)^{-1}\ . \tag{16}$$

Consequently, Eq. (15) becomes

$$q_i=\underline{W}_{\mathrm{if}}\underline{G}_f^0\underline{T}_{fi}\ , \tag{17}$$

where

$$\underline{T}_{fi}=(\underline{1}-\underline{W}_f\underline{G}_f^0)^{-1}\underline{W}_{fi}=\underline{W}_{fi}+\underline{W}_f\underline{G}_f^0\underline{T}_{fi}\ . \tag{18}$$

Equation (18) defines the gettering T matrix (a column

matrix) whose elements $\langle f \mid T \mid i \rangle$ will determine the rates of the inelastic processes causing the decay of the initial state.

According to Eqs. (4)—(9) we need $\Gamma_i = -\mathrm{Im}q_i$ on the energy shell where $\varepsilon = E_i$, and although both $\underline{W}_{\mathrm{if}}$ and $\underline{T}_{fi}$ appear in Eq. (17), the imaginary part of $q_i(\varepsilon)$ can be written in terms of $\underline{T}_{fi}$ alone.[8] We can assume without loss of generality that $\underline{W}_{\mathrm{if}}$ is real so that from Eq. (17), and its Hermitian conjugate

$$q_i(\varepsilon) - q_i^*(\varepsilon) = 2i\ \mathrm{Im}q_i(\varepsilon) = \underline{W}_{\mathrm{if}}\underline{G}_f^0\underline{T}_{fi} - \underline{T}_{\mathrm{if}}^*\underline{G}_f^{0*}\underline{W}_{fi} \ . \tag{19}$$

Using Eq. (18) for $\underline{W}_{fi}$, and taking $\underline{W}_{\mathrm{if}}$ from the Hermitian conjugate of Eq. (18), we obtain

$$2i\ \mathrm{Im}q_i = \underline{T}_{\mathrm{if}}^*(\underline{G}_f^0 - \underline{G}_f^{0*})\underline{T}_{fi} = -2\pi i \sum_f \mid \langle f \mid T \mid i \rangle \mid^2 \delta(\varepsilon - E_f) \ .$$

Consequently,

$$\Gamma_i(E_i) = -\mathrm{Im}q_i(E_i) = \pi \sum_f \mid \langle f \mid T \mid i \rangle \mid^2 \delta(E_i - E_f) \ . \tag{20}$$

Equations (6), (7), (9), (18), and (20) are the basic equations of the gettering theory approach to sticking, and inelastic scattering. Since the sum of f in Eq. (20) goes over stuck states s, and inelastic scattering states r, we verify the statement made at the end of Sec. II that Γ_i is the sum of sticking, and inelastic scattering contributions.

In the next section, we will consider the calculation of the gettering T matrix in the approximation in which intermediate interactions with energy nonconserving states are neglected. In this case Eq. (18) for $T_{fi}(E_i)$ reads

$$\underline{T}_{fi}(E_i) = \underline{W}_{fi} - i\pi \underline{W}_f \underline{\delta}(E_i - E_f)\underline{T}_{fi}(E_i) \ , \tag{21}$$

where $\underline{\delta}(E_i - E_f)$ is a diagonal matrix with diagonal elements $\delta(E_i - E_f)$, and Eq. (17) for $q_i(E_i)$ reads

$$q_i(E_i) = -i\pi \underline{W}_{\mathrm{if}} \underline{\delta}(E_i - E_f)\underline{T}_{fi}(E_i) \ . \tag{22}$$

To conclude this section, we emphasize that the gettering T matrix defined by Eq. (18) is not the T matrix of scattering theory. The scattering-theory T matrix is the *square matrix* $\underline{W} + \underline{W}\ \underline{G}\ \underline{W}$, and its fi-block has the extra term $\underline{W}_{fi}\underline{G}_{\mathrm{if}}\underline{W}_{fi}$ over $\underline{T}_{fi}$ defined by Eq. (18). It is easy to prove that, for the Hamiltonian of Eqs. (10)—(12), the matrix elements of this transition operator between states $\mid f \rangle$ and $\mid i \rangle$ are zero on the energy shell. This simply corresponds to the fact that, when the gettering collision is over ($t \to +\infty$), the wave function describing the system has no projection on the initial state. The scattering-theory T matrix, and to a lesser extent the S matrix,[5] are therefore trivial quantities in gettering.

IV. THE CALCULATION OF $\underline{T}_{fi}(E_i)$

The T matrix which determines the decay of the initial state according to Eqs. (6) and (20) is calculated from Eq. (21). Evidently a matrix inversion is involved, and because of the δ-function matrix in Eq. (21) we will develop this equation further so that the actual calculation $\underline{T}_{fi}(E_i)$ becomes transparent in simple but nontrivial cases. But there are serious difficulties still to be overcome before the gettering T matrix can be calculated exactly for a fully realistic specification of the inelastic processes.

There are two important mechanisms for energy loss leading to sticking in gas-solid collisions; loss to electrons,[7,9] and loss to phonons.[10] We consider the electron loss mechanism first. It is important for a light reactive atom on a heavy metal.

The exact situation where multiexcitation final states would be populated is very complicated, but the model of the electronic structure we shall deal with has a simplifying feature (below) which rules out multiexcitation final states. Accordingly, attention will be confined here to the case where: (i) the electronic structure is described with sufficient accuracy by single Slater determinants, (ii) low-lying excited state electronically adiabatic potential-energy surfaces have the same shape as the ground-state surface, being merely shifted vertically by the excitation energy, (iii) the operator W_2 in the Hamiltonian (10) is diagonal in the number of electron-hole pairs in the set $\{ \mid f \rangle \}$.

Only low-lying excited states are specified in (ii) because only low-energy electron-hole pairs are created in sticking (see below). Consequently, a system whose prominent adsorbate-induced electronic structure consists of a very sharp resonance very close to the Fermi level (within say 25 meV for a gas at room temperature), is excluded. Because of (ii) the elastic gas metal potential is independent of the existence or otherwise of a low-energy electronic excitation.[4,7] (i) means that the matrix elements of the operator W for inelastic processes has a tridiagonal block structure; states with ν electron-hole pairs ($\nu \geq 1$) are connected to states with $\nu \pm 1$. Correspondingly, there is a hierarchy of coupled matrix equations relating the block of $\underline{T}_{fi}$ for ν electron-hole pairs in the states $\mid f \rangle$, to the blocks with $\nu \pm 1$. A practical scheme for dealing exactly with this hierarchy does not exist. One can of course terminate the hierarchy at some small value of ν, and then solve the resulting truncated system, and as a first step in this direction, we will terminate the hierarchy at $\nu = 1$. This is what the assumption (iii) does; it makes $\underline{W}_f$ diagonal in the number of electron-hole pairs. We note that W_1 in the Hamiltonian (10) is not affected, but because W_2 is approximated, strongly inelastic events will not be described realistically. This limitation should not be forgotten. It is however important to remember that the entities we shall be dealing with are electron-hole pairs in the coupled system, and a state of the coupled system with one electron-hole pair requires states of the uncoupled system with arbitrary numbers of electron-hole pairs to describe it.

An electron-hole pair excitation with energy ε is characterized by the electron state $\mid \varepsilon'' \rangle$ and the hole state $\mid \varepsilon' \rangle$ with $\varepsilon = \varepsilon'' - \varepsilon'$, and the operator W has the form[4,7]

$$W = \int_{-\infty}^{\infty} d\varepsilon'' \int_{-\infty}^{\infty} d\varepsilon'\, w(\varepsilon'', \varepsilon') C^\dagger(\varepsilon'') C(\varepsilon') \ , \tag{23}$$

where $C^\dagger(\varepsilon)$ [$C(\varepsilon)$] creates (destroys) an electron with energy ε;

$$C^\dagger(\varepsilon'')C(\varepsilon') + C(\varepsilon')C^\dagger(\varepsilon'') = \delta(\varepsilon'' - \varepsilon') \tag{24}$$

and w is dimensionless with the basic symmetry

$$w(\varepsilon'',\varepsilon') = -w(\varepsilon',\varepsilon'') . \tag{25}$$

Then we can show[11] that the matrix elements of W between two states $|\varepsilon_1'',\varepsilon_1'\rangle$, and $|\varepsilon_2'',\varepsilon_2'\rangle$ with the same number of electron-hole pairs, and which are identical except for the electron-hole pair displayed are

$$\langle \varepsilon_1',\varepsilon_1'' \mid W \mid \varepsilon_2'',\varepsilon_2'\rangle = w(\varepsilon_1'',\varepsilon_2'')\delta(\varepsilon_1'-\varepsilon_2') - w(\varepsilon_1',\varepsilon_2')\delta(\varepsilon_1''-\varepsilon_2') . \tag{26}$$

The matrix elements of W between the ground state, which we write with one electron-hole pair at ε_F, and an excited state with one electron-hole pair are

$$\langle \varepsilon',\varepsilon'' \mid W \mid \varepsilon_F,\varepsilon_F\rangle = \langle \varepsilon',\varepsilon'' \mid W \mid 0\rangle = w(\varepsilon'',\varepsilon')n(\varepsilon_F) , \tag{27}$$

where $n(\varepsilon)$ is the density of one-electron states. Of course w and n in Eqs. (26) and (27) depend on the gas atom's position $\mathbf{R}$, as do the adiabatic electron states, but for brevity we do not display this dependence. No other matrix elements of W are needed because of (i) and (iii) which have as their consequence that matrix elements of $\underline{T}_{fi}$ for final states with two or more electron-hole pairs are zero. Consequently, only final states with one electron-hole pair will appear in what follows.

The initial state $|i\rangle$ in Eq. (22) has the gas atom in the state $|\alpha\rangle$ say, with energy ε_α, and no electronic excitation present. The state $|f\rangle$ has the gas atom in $|\beta\rangle$ with energy ε_β, and there is one electron-hole pair excited. Therefore we write

$$|i\rangle = |\varepsilon_F,\varepsilon_F,\alpha\rangle/n(\varepsilon_F) = |0,\alpha\rangle/n(\varepsilon_F), \quad E_i=\varepsilon_\alpha , \tag{28}$$

$$|f\rangle = |\varepsilon_f'',\varepsilon_f',\beta\rangle/[n(\varepsilon_f'')n(\varepsilon_f')]^{1/2} , \quad E_f=\varepsilon_\beta+\varepsilon_f''-\varepsilon_f' , \tag{29}$$

and after making the change

$$\sum_f \rightarrow \sum_\beta \int_{\varepsilon_F}^{\infty} d\varepsilon_f'' \, n(\varepsilon_f'') \int_{-\infty}^{\varepsilon_F} d\varepsilon_f' \, n(\varepsilon_f') .$$

Equation (21) for the matrix elements of $\underline{T}_{fi}(E_i)$ assumes the form

$$\langle \beta,\varepsilon_f',\varepsilon_f'' \mid T \mid 0,\alpha\rangle = \langle \beta,\varepsilon_f'\varepsilon_f'' \mid W \mid 0,\alpha\rangle - i\pi \sum_\gamma \int_{\varepsilon_F}^{\infty} d\varepsilon'' \int_{-\infty}^{\varepsilon_F} d\varepsilon' \langle \beta,\varepsilon_f',\varepsilon_f'' \mid W \mid \varepsilon'',\varepsilon',\gamma\rangle \delta(\varepsilon_\alpha-\varepsilon_\gamma-\varepsilon''+\epsilon') \times \langle \gamma,\varepsilon',\varepsilon'' \mid T \mid 0,\alpha\rangle . \tag{30}$$

Using Eqs. (26) and (27), Eq. (30) becomes

$$\langle \beta,\varepsilon_f'\varepsilon_f'' \mid T \mid 0,\alpha\rangle = \langle \beta \mid w(\varepsilon_f'',\varepsilon_f') \mid \alpha\rangle n(\varepsilon_F) - i\pi \sum_{\gamma<\alpha} \{ \langle \beta \mid w(\varepsilon_f'',\varepsilon_\alpha-\varepsilon_\gamma+\varepsilon_f') \mid \gamma\rangle \langle \gamma,\varepsilon_f',\varepsilon_f'+\varepsilon_\alpha-\varepsilon_\gamma \mid T \mid 0,\alpha\rangle - \langle \beta \mid w(\varepsilon_f',\varepsilon_f''-\varepsilon_\alpha+\varepsilon_\gamma) \mid \gamma\rangle \langle \gamma,\varepsilon_f''-\varepsilon_\alpha+\varepsilon_\gamma,\varepsilon_f'' \mid T \mid 0,\alpha\rangle \} . \tag{31}$$

A further slight simplification of Eq. (31) is possible by taking account of the antisymmetry of w, and by noting that, on the energy shell, $\varepsilon_f''-\varepsilon_f'=\varepsilon_\alpha-\varepsilon_\beta$. But the most important simplification for practical computations comes because energy losses in sticking are generally small on the scale of electronic energies so only electron-hole pairs close to the Fermi level are excited. In this case, i.e., when $\varepsilon''-\varepsilon'$ is small, w depends only on the difference of its two arguments; $w(\varepsilon'',\varepsilon') \simeq w(\varepsilon''-\varepsilon')$,[4] and if we make this simplification, Eq. (31) can be written in the form

$$\langle \beta \mid T \mid \alpha\rangle = \langle \beta \mid w(\varepsilon_\alpha-\varepsilon_\beta) \mid \alpha\rangle n(\varepsilon_F) - 2\pi i \sum_{\gamma<\alpha} \langle \beta \mid w(\varepsilon_\gamma-\varepsilon_\beta) \mid \gamma\rangle \langle \gamma \mid T \mid \alpha\rangle . \tag{32}$$

The corresponding result for Eq. (22) is

$$\Gamma_i(\varepsilon_\alpha) = \pi \sum_{\beta<\alpha} (\varepsilon_\alpha-\varepsilon_\beta) \, |\langle \beta \mid T \mid \alpha\rangle|^2/[n(\varepsilon_F)]^2 \tag{33}$$

and Eq. (32) shows explicitly that the required T-matrix elements are obtained by inverting a matrix of dimension N, the number of gas atom states in the vessel with energy below that of the initial state $|\alpha\rangle$. N always includes the bound states of the gas-metal potential U, which holds the stuck atom, but unbound states with energy greater than ε_α are not accessible in a collision with a cold metal. We note that $\langle \alpha \mid T \mid \alpha\rangle$ is excluded from Eq. (32); it is not an element of the gettering T matrix defined by Eq. (18).

The T matrix in Eqs. (32) and (33) has dimensions (energy)$^{-1}$. To obtain a dimensionless T matrix, we divide Eq. (32) through by $n(\varepsilon_F)$. This removes $n(\varepsilon_F)$ from the first term on the right-hand side in Eq. (32), and from the right-hand side in Eq. (33), and incorporates it instead in the new dimensionless T matrix.

Turning now to the case where a gas atom loses energy to the phonons,[12] let[13] the phonon states of the solid in the presence of the gas atom at $\mathbf{R}$ be denoted $|m;\mathbf{R}\rangle$, and let $E_m(\mathbf{R})$ be the corresponding atom-solid interaction potential. A gas atom moving on $E_m(\mathbf{R})$ can transfer energy to the phonons, and make transitions to states on $E_n(\mathbf{R})$. The operator causing these transitions is[14]

$$W_{nm}(\mathbf{R}) = \langle n;\mathbf{R} \mid W \mid m;\mathbf{R}\rangle = (\hbar^2/M)(\langle n;\mathbf{R} \mid \nabla_R \mid m;\mathbf{R}\rangle \nabla_R + \tfrac{1}{2}\langle n;\mathbf{R} \mid \nabla_R^2 \mid m;\mathbf{R}\rangle) , \tag{34}$$

where M is the mass of the gas atom, and ∇_R the gradient operator with respect to its position. We note that this operator is zero if $|n;\mathbf{R}\rangle$ and $|m;\mathbf{R}\rangle$ differ by more than a two-phonon excitation. To parallel the electron-hole pair case, we confine attention to one-phonon final states, but this is an approximation which may be expected to fail for a light gas atom on a heavy solid because the relevant mass ratio[14] is unfavorable. We note that phonon excitation cannot alter the shape of the gas-solid interaction, but only shifts the potential vertically by the phonon excitation energy. Then the Hamiltonian has the form of Eqs. (10)–(12) with $E_0(\mathbf{R})$ the elastic potential, and the operator W defined by Eq. (34). Passing to a continuum of phonon states, and suppressing the $\mathbf{R}$ dependence for brevity

$$W_{nm}(\mathbf{R})\rightarrow w(\varepsilon_1,\varepsilon_2)/[n(\varepsilon_1)n(\varepsilon_2)]^{1/2} ,$$

where $n(\varepsilon)$ is the density of phonon states, enables us to write the matrix elements of Eq. (21) in the form

$$\begin{aligned}\langle\beta,\varepsilon_f\,|\,T\,|\,0,\alpha\rangle &= \langle\beta\,|\,w(\varepsilon_f,0)\,|\,\alpha\rangle \\ &\quad -i\pi\sum_{\gamma}\int d\varepsilon\,\langle\beta\,|\,w(\varepsilon_f,0\,|\,\gamma\rangle\delta(\varepsilon_\alpha-\varepsilon_\gamma-\varepsilon)\langle\gamma,\varepsilon\,|\,T\,|\,0,\alpha\rangle \\ &= \langle\beta\,|\,w(\varepsilon_f,0)\,|\,\alpha\rangle - i\pi\sum_{\gamma<\alpha}\langle\beta\,|\,w(\varepsilon_f,\varepsilon_\alpha-\varepsilon_\gamma)\,|\,\gamma\rangle\langle\gamma,\varepsilon_\alpha-\varepsilon_\gamma\,|\,T\,|\,0,\alpha\rangle\ . \end{aligned} \tag{35}$$

On the energy shell $\varepsilon_f=\varepsilon_\alpha-\varepsilon_\beta$ so we can write Eq. (35) in the form

$$\begin{aligned}\langle\beta\,|\,T\,|\,\alpha\rangle &= \langle\beta\,|\,w(\varepsilon_\alpha-\varepsilon_\beta,0)\,|\,\alpha\rangle \\ &\quad -i\pi\sum_{\gamma<\alpha}\langle\beta\,|\,w(\varepsilon_\alpha-\varepsilon_\beta,\varepsilon_\alpha-\varepsilon_\gamma)\,|\,\gamma\rangle \\ &\quad\times\langle\gamma\,|\,T\,|\,\alpha\rangle\ , \end{aligned} \tag{36}$$

which shows again that a finite-order matrix inversion is needed to calculate the T matrix. In this respect the phonon, and electron-hole pair cases are similar. But there are two important differences. Firstly there is no factor 2 multiplying the sum on γ in Eq. (36), and secondly for phonons, the energy losses in sticking are not small on the scale of phonon energies, with the result that Eq. (36) is slightly more complicated than Eq. (32). The basic reason for the factor 2 in Eq. (32) is that W can change either the electron state or the hole state. For phonons there is no such dual action; W simply causes one-quantum transitions in a normal mode.

V. CONCLUDING REMARKS

Gettering theory provides a powerful route to the calculation of the sticking coefficient, and we have developed this approach to the point where the calculation of the exact sticking coefficient for a nontrivial model is seen to involve the inversion of a finite-order matrix. Detailed computations will be reported in another paper.[6]

Finally, we remark that gettering is a collision process with some unusual features. To understand them we observe that the wave function representing the system at time t can be partitioned into two orthogonal components, one representing the "reactants" is the only component present at $t=0$, but is absent as $t\rightarrow\infty$, the other, representing the "products" is the only component remaining as $t\rightarrow\infty$, but is absent at $t=0$. A stationary scattering state $|i+\rangle$ is only established as $t\rightarrow\infty$ when $\langle\psi_i\,|\,\psi_i^+(t)\rangle=0$. Consequently the elastic reflection coefficient calculated as $|\langle i\,|\,i+\rangle|^2$ is zero. Of course this tells us nothing of importance about the collision of an atom with a solid; the ratio $\nu_{\rm coll}/(R_{\rm stick}+R_{\rm inel}+\nu_{\rm coll})$ is the gettering-theory definition of the elastic reflection coefficient.

The distribution of "products when the gettering collision is over can be calculated from

$$\langle\psi_f\,|\,\psi_i^+(t)\rangle=-\frac{1}{\pi}\int_{-\infty}^{+\infty}d\varepsilon\,e^{-i\varepsilon t/\hbar}{\rm Im}\langle f\,|\,G^+(\varepsilon)\,|\,i\rangle\ . \tag{37}$$

From Eq. (13) we find $\underline{G}_{fi}=\underline{G}_f^0\underline{T}_{fi}\underline{G}_i$, and using this in Eq. (37), it is not difficult to show that

$$\langle\psi_f\,|\,\psi_i^+(\infty)\rangle=\langle f\,|\,T(E_f)\,|\,i\rangle/[E_f-E_i-q_i(E_f)] . \tag{38}$$

On the energy shell, this reads

$$\langle\psi_f\,|\,\psi_i^+(\infty)\rangle=-\langle f\,|\,T(E_i)\,|\,i\rangle/q_i(E_i)\ .$$

The same results are obtained from the Lippmann-Schwinger equation[1] $|i+\rangle=|i\rangle+GW\,|\,i\rangle$, namely $\langle i\,|\,i+\rangle=0$, and

$$\langle f\,|\,i+\rangle=-\langle f\,|\,T(E_i)\,|\,i\rangle/q_i(E_i)$$

for $|f\rangle$ on the energy shell. These results for the elements of the S matrix, whilst of some theoretical interest, have no bearing on the calculation of the sticking, and reflection coefficients, and we shall not therefore give more details of their derivation here.

The "products" of the gettering reaction are gas atoms either stuck to, or reflecting off, the solid in its various quantum states, and of course states $|f\rangle$ off the energy shell are populated as Eq. (38) shows. The gettering is not complete in the sense that the system wave function as $t\rightarrow\infty$ does not lie totally in the stuck subspace, because we have not included a relaxation mechanism on the states $|f\rangle$.

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*Permanent address: Dipartimento di Fisica dell'Università degli Studi di Milano and Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, via Celoria 16, I-20133 Milano, Italy.

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