TWO-PHONON CONTRIBUTIONS TO THE ENERGY ACCOMMODATION COEFFICIENT

J. R. Manson* and John Tompkins[†]
Clemson University, Clemson, S. C.

Abstract

We develop the theory of multiple-phonon surface scattering of neutral atoms in the first- and second-order distorted-wave Born Approximation (DWBA). Calculations are carried out for the thermal accommodation of helium at a tungsten surface. We find that the contribution due to the first DWBA is negligible even for temperatures as high as 400°K. The second DWBA, on the other hand, gives significant contributions to the accommodation for temperatures greater than 100°K and gives a much better agreement with experiment than theories that permit only a single phonon exchange.

Introduction

Although the theory of surface scattering of neutral atoms is a rather old subject,[1-4] it has received a great deal of renewed interest recently, largely because of improved experimental techniques[5-8] and the possibility of these investigations providing new information on the surface structure.[9,10] Most of the treatments of the inelastic surface scattering have included only the first-order or single-phonon contribution.[11-15] The work of Strachan[4] and Allen and Feuer[14] seems to indicate that multiple-phonon processes are not important for surface temperatures and particle energies in the neighborhood of

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room temperature and below. On the other hand, there are
several theories based on approximations other than pertur-
bation theory[16-19] which seem to indicate that multiphonon
processes are important and contribute over the same range of
scattering angles as the single-phonon contributions; hence
the many phonon effects cannot be treated as a "background."
However, these theories do not indicate clearly the conditions
of temperature and energy under which multiple-phonon process-
es become important. The work of Berry, Kaplan and Drauglis,[16]
and Levi et. al depends on the energies of the incoming parti-
cles being large compared to the total energy transfer (eikon-
al approximation), and the work of Beeby[18] similarly depends
on the deviation of the scattered particles from the specular
beam being small. The work of Liu[17] replaces the surface by
a simplified Einstein oscillator.

The work reported here is a calculation of the one- and
two-phonon contribution to the energy accommodation coeffi-
cient carried out in the first- and second-order distorted-
wave Born approximation (DWBA). The extension to higher-order
multiple-phonon processes is outlined. We represent the
averaged interaction between the particle and surface by a
Morse potential, and the phonon distribution is taken to be
the surface (Raleigh) modes of a semi-infinite isotropic con-
tinuum.

We find that in the first-order DWBA the two-phonon con-
tributions are unimportant for surface temperatures and parti-
cle energies as high as 400°K, consistent with the calcula-
tions of Strachan[4] and of Allen and Feuer.[14] However, the
contribution from the second-order DWBA, which has not been
taken into account previously, is an order of magnitude large
and becomes important at temperatures and energies around
100°K. Thus the basic conclusion of Strachan and of Allen an
Feuer is shown to be incorrect because they failed to include
all terms in the Born series which contribute to two-phonon
scattering. We find that the two-phonon contributions begin
to become important at very nearly the same conditions that
previous one-phonon "unitary" calculations[13,20] begin to
differ from the first-order DWBA.

This paper explains the discrepancy between those treat-
ments that claim that multiple-phonon effects are not import
and those that show that they are important. Furthermore, t
consistent approach indicates clearly the conditions of part
cle energy and surface temperature at which multiple-phonon
processes become an appreciable effect on the surface scatte
ing.

Accommodation Coefficient

The energy accommodation coefficient of Knudsen is given by

$$\alpha(T_s, T_g) = (E-E_g)/(E_s-E_g) \qquad (1)$$

where E is the average energy of a scattered gas molecule, E_g is the average energy of a particle in the incident gas, and E_s is the average energy of a particle in a gas with temperature equal to that of the surface. For theoretical convenience, a more useful quantity is the equilibrium accommodation coefficient defined by

$$\alpha(T) = \lim_{T_s \to T_g \to T} (E-E_g)/(E_s-E_g) \qquad (2)$$

We wish to develop an expression for $\alpha(T)$ in terms of the differential reflection coefficient $dR/d\varepsilon_f$. This describes the fraction of a beam of particles incident on the surface which is scattered into a range of final energies lying between ε_f and $\varepsilon_f + d\varepsilon_f$. For simplicity, we shall assume that the incoming gas is incident perpendicularly on the surface. However, after colliding with the surface, it will leave at any angle necessary to assure conservation of energy and momentum. It has been shown that under these conditions $\alpha(T)$ for single-phonon exchange processes can be expressed as[12]

$$\alpha_1(T) = \frac{\hbar^2}{k^3 T^3} \int_0^\infty d\varepsilon_i \int_0^{\omega_D} d\omega (\frac{d\varepsilon_f}{d\omega}) \omega^2 \exp(\frac{-\varepsilon_i}{kT}) \frac{dR^{(a)}}{d\varepsilon_f} \qquad (3)$$

where ω_D is the Debye cutoff frequency for the phonons. Contributions to the accommodation arise from processes in which a phonon is both created at the surface (energy given to the surface by the particle) or annihilated at the surface (energy given to the particle by the surface). The differential reflection coefficient describing single-phonon annihilation is $dR^{(a)}/d\varepsilon_f$, whereas that for creation is $dR^{(c)}/d\varepsilon_f$. These two contributions have been combined in Eq. (3) by making use of the principle of detailed balancing

$$dR^{(c)}/d\varepsilon_f = \exp(\hbar\omega/kT)(dR^{(a)}/d\varepsilon_f) \qquad (4)$$

where ω is the frequency of the transferred phonon. Equation (3) with $d\varepsilon_f/d\omega=\hbar$ is the expression for the accommodation coefficient given in the fundamental paper of Devonshire.[3]

The accommodation coefficient for two-phonon transfer can be derived in a similar manner, except that now we have to take into consideration the fact that there are three different classes of phonon transfers. A scattering event can occur in

which two phonons are created at the surface (denoted by the symbol cc), two phonons can be annihilated (aa), or there can be one phonon created and one phonon annihilated (ac). Again making use of detailed balancing, the additional contribution to $\alpha(T)$ for two-phonon transfer can be written in terms of the (aa) and (ac) processes as

$$\alpha(T) = \alpha_1(T) + \alpha_2(T) \tag{5}$$

where

$$\alpha_2(T) = \frac{1}{(kT)^3} \int d\epsilon_i \int_{\epsilon_i}^{\epsilon_i+2\hbar\omega_D} d\epsilon_f (\epsilon_f - \epsilon_i)^2 \exp\left[\frac{-\epsilon_i}{kT}\right]\frac{dR^{(aa)}}{d\epsilon_f}$$

$$+ \int_{\epsilon_i}^{\epsilon_i+\hbar\omega_D} d\epsilon_f (\epsilon_f - \epsilon_i)^2 \ \exp\left[\frac{-\epsilon_i}{kT}\right]\frac{dR^{(ac)}}{d\epsilon_f} \tag{6}$$

Numerous calculations of the single-phonon contributions to $\alpha(T)$ have been reported previously.[21] In this paper, we wish to consider contributions arising from two-phonon contributions, and, as evident from Eq. (6), we first must consider the differential reflection coefficients.

First-Order Distorted-Wave Born Approximation

The most direct approach to the problem of surface scattering is to divide the total interaction potential V into a "simple" part U exhibiting total specular reflection and a remainder v = V-U to be treated approximately in the framework of the Gell-Man and Goldberger two-potential formalism.[22] We choose V to be a sum over all lattice sites of two-body atomic potentials

$$V = \sum_\ell v^a(\vec{r} - \vec{r}_\ell - \vec{u}_\ell) \tag{7}$$

where $\vec{u}_\ell$ is the small displacement of the crystal ion at position $\vec{r}_\ell$. It can be shown readily that the thermal average of V takes the form

$$\langle V \rangle = \sum_{\vec{G}} e^{i\vec{G}\cdot\vec{R}} \ U_{\vec{G}}(z) \tag{8}$$

where the position vector $\vec{r}$ has the component $\vec{R}$ parallel to the surface and z perpendicular to the surface, $\vec{G}$ is a recirocal lattice vector of the surface, and

$$U_{\vec{G}}(z) = N \sum_m \sum_q e^{iq(z-z_m)} \ e^{-W(\vec{G},q)} \ v^a_{\vec{G},q} \tag{9}$$

In eq. (9), N is the number of surface lattice sites, $W_m(\vec{G},q)$ is the Debye-Waller factor for ions in the mth plane parallel

to the surface, and $v_{\vec{G},q}^{a}$ is the Fourier transform of the atomic two-body potential. The obvious choice for the potential U is $U_{\vec{G}=0}(z)$.

The eigenfunctions of U for outgoing (+) and incoming (-) wave boundary conditions will be denoted by $\chi_p^{(\pm)}$. They are products of a vibrational wave function for the solid, a plane wave for particle motion parallel to the surface, and a normal wave function $\chi^{(\pm)}(j_{zp};z)$ that obeys the equation

$$(\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + \frac{\hbar^2 k_{zp}^2}{2m} - U) \chi^{(\pm)} (k_{zp};z) = 0 \qquad (10)$$

where m is the mass of the scattered particle.

The transition rate w_{fi} from some initial state i to some final state f is given in terms of the transition matrix T_{fi} by

$$W_{fi} = (2\pi/\hbar) |T_{fi}|^2 \delta(E_f - E_i) \qquad (11)$$

where E_f and E_i are the final and initial energies of the entire system. The subscript f or i is a collective label for the wave vector $(\vec{K}, k_z)$ of the scattered particle and the number of phonons {n} in each vibrational mode of the crystal. The differential reflection coefficient is obtained by dividing Eq. (11) by the incident particle flux, multiplying by the available volume in phase space for a final scattered particle, averaging over initial phonon states, and summing over final phonon states

$$\frac{dR}{d\varepsilon_f d\Omega_f} = \frac{m^2 |\vec{k}_f|}{4\pi\hbar^3 k_{zi}} \sum_{\{n_f\}} \sum_{\{n_i\}} \rho(\{n_1\}) |T_{fi}|^2 \delta(E_f - E_1) \qquad (12)$$

where $\rho(\{n_i\})$ is the distribution of initial phonon states. The reflection coefficient used in Sec. II is the integral of (12) over all final scattered angles

$$\frac{dR}{d\varepsilon_f} = \int d\Omega_f \frac{dR}{d\varepsilon_f d\Omega_f} \qquad (13)$$

It is clear from Eq. (12) that all information on the scattering process depends on knowledge of the matrix element of the transition operator taken between initial and final states, ϕ_i and ϕ_f, of the unperturbed system. Gell-Mann and Goldberger have shown that this matrix element is equivalent to

$$T_{fi} = (\phi_f, U \chi^{(+)}) + t_{fi} \qquad (14)$$

where the reduced transition matrix t_{fi} obeys an integral equation involving only v

$$t_{fi} = (\chi_f^{(-)}, v\chi_i^{(+)}) + \sum_c (\chi_f^{(-)}, v\chi_c^{(-)}) \frac{1}{E_i - E_c + i\varepsilon} t_{ci} . (15)$$

We note here that, because U is chosen to contribute only to specular reflection, the outgoing wave eigenfunction $\chi_i^{(+)}$ (where i denotes the set of quantum numbers describing the incident beam) can differ from the incoming wave eigenfunction $\chi_s^{(-)}$ (where s denotes the quantum numbers of the specular beam only by a phase factor, depending on the absolute value of the perpendicular momentum, i.e.

$$\chi_i^{(+)} = e^{i\delta_i} \chi_s^{(-)} \qquad (16)$$

where

$$\delta_i = \delta_i(|k_{zi}|) = \delta_i(k_{zs}) \qquad (17)$$

In fact, $e^{i\delta_i}$ is the scattering matrix (S matrix) for the potential U.

The first term on the right-hand side of Eq. (14) is the transition matrix for U scattering and readily is shown to be given by

$$(\phi_f, U\chi_i^{(+)}) = \frac{i\hbar^2 |k_{zi}|}{m} e^{i\delta_i} \delta_{fs} \qquad (18)$$

where the Kronecker δ function implies that it contributes only to specular scattering.

The first-order distorted-wave Born approximation is obtained upon replacing t_{fi} by v_{fi} in (14). Since the elastic scattering is of no interest in this approximation, the first term on the right of (14) never will enter, and we can replace v_{fi} by matrix elements of the true interaction potential V. Taking account of (16), the differential reflection coefficient now can be written as

$$\frac{dR}{d\varepsilon_f d\Omega_f} = \frac{m^2 |\vec{k}_f|}{(2\pi)^2 \hbar^3 k_{zi}} \sum_{\{n_f\}} \sum_{\{n_i\}} \rho(\{n_i\}) |(\chi_f^{(-)}, V\chi_s^{(-)})|^2 \delta(E_f - E_i) \quad (19)$$

The sums over phonon states can be carried out using the methods of many-body field theory as developed by Van Hove,[23] and the results are

$$
\frac{dR}{d\epsilon_f d\Omega_f} = \frac{m^2 |\vec{k}_f|}{(2\pi)^3 \hbar^4 k_{zi}} \int_\infty^\infty dt\, e^{i\hbar(k_f^{\,2}-k_i^{\,2})t/2m} \int d\vec{r} \int d\vec{r}^{\,\prime}\, \chi_s^*(\vec{r}) \chi_f(\vec{r})
$$

$$
\chi_f^{*(-)}(\vec{r}^{\,\prime}) \chi_s^{(-)}(\vec{r}^{\,\prime}) \sum_{\ell,\ell^\prime} \sum_{\vec{k},\vec{k}^\prime} e^{i[\vec{k}^\prime\cdot(\vec{r}^{\,\prime}-\vec{r}_\ell)\, -\vec{k}\cdot(\vec{r}-\vec{r}_\ell)]}
$$

$$
v_{\vec{k}}^{*a}\, v_{\vec{k}^\prime}^{a}\, e^{-W_\ell(\vec{k})}\, e^{-W_{\ell^\prime}(\vec{k})}\, e^{Q_{\ell\ell^\prime}(\vec{k},\vec{k}^\prime;t)} \tag{20}
$$

The term $W_\ell(\vec{k})$ is the Debye-Waller exponent and depends only on that component of ℓ which counts crystal planes parallel to the surface. The exponent $Q_{\ell\ell^\prime}(\vec{k}, \vec{k}^\prime;t)$ is essentially the surface-modified two-particle correlation function discussed in detail for bulk solids by Glauber.[24] For a Bravais lattice, it has the explicit form

$$
Q_{\ell\ell^\prime}(\vec{k},\vec{k}^\prime;t) = \frac{\hbar}{2NM} \sum_{\vec{Q},\nu} \frac{[\vec{k}\cdot e^*(\ell|\frac{\vec{Q}}{\nu})][\vec{k}^\prime\cdot e(\ell^\prime|\frac{\vec{Q}}{\nu})]}{\omega_\nu(\vec{Q})}
$$

$$
\{[n_\nu(\vec{Q}) + 1]e^{i\vec{Q}\cdot(\vec{R}_\ell-\vec{R}_{\ell^\prime}) \,+\, i\omega_\nu(\vec{Q})t}
$$

$$
+\, n_\nu(\vec{Q})e^{i\vec{Q}\cdot(\vec{R}_\ell-\vec{R}_{\ell^\prime})\, -\, i\omega_\nu(\vec{Q})t}\} \tag{21}
$$

where M is the mass of a lattice ion, $n_\nu(\vec{Q})$ is the Bose-Einstein occupation number, and $e(\ell|\frac{\vec{Q}}{\nu})$ is the unit polarization vector for a phonon of parallel wave vector $\vec{Q}$ and other labels ν (perpendicular wave vector, polarization, etc.). The polarization vector also depends only on the component of ℓ which counts planes parallel to the surface.

It is apparent from (21) that the factor $\exp[Q_{\ell\ell^\prime}(\vec{k},\vec{k}^\prime;t)]$, through its dependence on t, contains all of the possibilities

for energy transfer. The elastic (zero phonon) and inelastic (one-phonon, two-phonon, etc.) reflection coefficients are obtained by expanding $\exp[Q_{\ell\ell'}(k,k';t)]$ in powers of $Q_{\ell\ell'}(k,k';t)$. The elastic and one-phonon case have been treated previously.[20] The result for the two-phonon case is

$$\frac{dR}{d\epsilon_f d\Omega_f} = \frac{m^2}{8\hbar^2 N^2 M^2 k_{zi}} \sum_{\vec{G}} \sum_{\vec{Q},\nu} \sum_{\vec{Q'},\nu'} \frac{|\vec{k}_f|}{\omega_\nu(\vec{Q})\omega_{\nu'}(\vec{Q'})}$$

$$\{|(\chi(k_{zf};z), [\vec{\nabla}\cdot U_{-\vec{Q}-\vec{Q'}-\vec{G}}(z) \cdot \overleftarrow{\vec{\nabla}}]\ \chi(k_{zs}:z))|^2 (n_\nu(\vec{Q})+1)(n_{\nu'}(\vec{Q'})+1)$$

$$\delta(\vec{K}_f-\vec{K}_i+\vec{Q}+\vec{Q'}+\vec{G})\ \delta(\hbar^2(k_f^2-k_i^2)/2m+\hbar\omega_\nu(\vec{Q})+\hbar\omega_{\nu'}(\vec{Q'}))$$

$$+2|(\chi(k_{zf};z), [\vec{\nabla}\cdot\overleftrightarrow{U}_{-\vec{Q}+\vec{Q'}-\vec{G}}(z)\cdot\overleftarrow{\vec{\nabla}}]\ \chi(k_{zs};z))|^2 (n_\nu(\vec{Q})+1)n_{\nu'}(\vec{Q'})$$

$$\delta(\vec{K}_f-\vec{K}_i+\vec{Q}-\vec{Q'}+\vec{G})\ \delta(\hbar^2[k_f^2-k_i^2]/2m+\hbar\omega_\nu(\vec{Q})+\hbar\omega_{\nu'}(\vec{Q'}))$$

$$+|(\chi(k_{zf};z), [\vec{\nabla}\cdot\overleftrightarrow{U}_{\vec{Q}+\vec{Q'}-\vec{G}}(z)\cdot\overleftarrow{\vec{\nabla}}]\ \chi(k_{zs};z))|^2 n_\nu(\vec{Q})n_{\nu'}(\vec{Q'})$$

$$\delta(\vec{K}_f-\vec{K}_i-\vec{Q}-\vec{Q'}+\vec{G})\ \delta(\hbar^2[k_f^2-k_i^2]/2m-\hbar\omega_\nu(\vec{Q})-\hbar\omega_{\nu'}(\vec{Q'}))\}\qquad(22)$$

The dyadic potential and divergence operator are defined by

$$\overleftrightarrow{U}_{\vec{Q}+\vec{Q'}+\vec{P}}(z) = N \sum_m \sum_q e^{iq(z-z_m)} e^{-W_m(\vec{Q}+\vec{Q'}+\vec{P},q)}$$

$$\vec{e}(m|\genfrac{}{}{0pt}{}{\vec{Q}}{\nu})\ \vec{e}(m|\genfrac{}{}{0pt}{}{\vec{Q'}}{\nu'})\ v^a_{\vec{Q}+\vec{Q'}+\vec{P},q} \qquad(23)$$

$$-i\vec{\nabla}\cdot\overleftrightarrow{U}_{\vec{A}}(z) = (\vec{A},-i\partial/\partial z)\cdot\overleftrightarrow{U}_{\vec{A}}(z) \qquad(24)$$

The physical significance of each of the terms in (22) can be seen by examining the δ functions in energy and momentum. The first term containing the factor $[n_\nu(\vec{Q})+1][n_\nu(\vec{Q'})+1]$ describes scattering processes in which two phonons are created at the surface (cc). The next term represents processes in which one phonon is created and one phonon annihilated (ac), for which the final energy of the particle can be less or greater than the initial energy. The last term represents the annihilation of two phonons (aa), whose energy and momenta are transferred to the scattered particle. The appearance of two differential

operators acting on the dyadic potential shows that the effective potential for two-phonon scattering is essentially the second-order term in the Taylor series expansion of the thermally averaged potential.

It is clear that higher-order phonon processes can be handled readily by extending the process just outlined. However, since it is necessary to sum over all of the internal degrees of freedom of each phonon exchanged, the extension of this process would be practical only for very simple models.

For the two-phonon calculations presented below, we choose the averaged interaction between the particle and surface to be a Morse potential, and the phonon distribution is taken to be the surface (Raleigh) modes of a semi-infinite isotropic continuum. The results of this model applied to the single-phonon case have been presented previously.[12,13] For two-phonon scattering, the matrix elements of Eq. (22) reduce to matrix elements of the second derivative of the Morse potential taken between Morse potential eigenstates. These have been considered by Devonshire[3] and Strachan[4] and are well known.

Second-Order Distorted-Wave Born Approximation

The second-order distorted-wave Born approximation is obtained by replacing t_{fi} in (14) with

$$t_{fi} = (\chi_f^{(-)}, v\chi_i^{(+)}) + \sum_\ell (\chi_f^{(-)}, v\chi_\ell^{(-)}) \frac{1}{E_i - E_\ell + i\epsilon} (\chi_f^{(-)}, v\chi_i^{(+)}) \qquad (25)$$

Since the Van Hove technique for carrying out the phonon averaging has not been applied successfully to higher-order Born approximations, it will be necessary to approach this with a less direct technique. Also, the sum over intermediate states in the second term of (25) is very cumbersome to handle, and to obtain a simpler expression we neglect the principal part contribution. Considering only nonspecular processes and taking account of (16), the transition matrix of (14) now becomes

$$T_{fi} = t_{fi} = (\chi_f^{(-)}, v\chi_s^{(-)}) - i\pi \sum_\ell (\chi_f^{(-)}, v\chi_\ell^{(-)}) \, \delta(E_i - E_\ell)(\chi_\ell^{(-)}, v\chi_s^{(-)}) \qquad (26)$$

This approximation is identical with that used previously to obtain a unitary transition matrix for elastic and one-phonon scattering.[20,25] The principal part contribution has been estimated for the models used below, and its contribution is small compared to the δ function part.

The second reason for making this principal part approxi mation now becomes obvious. When (26) is substituted into th transition rate (11), there is no interference between the first and second DWBA terms. This can be seen explicitly by noting that for real potentials it is possible to choose a gauge in which the matrix elements are also real.

As mentioned previously, the sums over phonon states in (12) cannot be carried out readily in the second-order DWBA. Thus, instead of using the techniques of Sec. III, we thermally average the matrix elements appearing in (26) before (26) is inserted into the reflection coefficient (12). This approximation is essentially the same as that used previously in obtaining a unitary approximation to the transition matrix for elastic and one-phonon surface scattering.[20,25] This approach to the averaging problem can be used to reproduce th same results obtained for single-phonon transfers in (17). For simplicity, we specialize to the type of potentials to be considered in Sec. IV, i.e., those exhibiting no diffraction and having vibrations perpendicular to the surface. The extension to the general case is lengthy but straightforward ar need not be considered here. The potential between the parti cle and surface can be expanded in a Taylor series as

$$V = U(z) + (dU/dz)\, u_z + \cdots \qquad (27)$$

where u_z is the deviation from equilibrium and can be expanded in terms of the phonon amplitudes as

$$u_z = \sum_{\vec{Q},\nu} \left[\frac{1}{2NM\omega_\nu(\vec{Q})}\right]^{\frac{1}{2}} e_z\!\left(\frac{\vec{Q}}{\nu}\right) \{a_{\vec{Q},\nu}\, e^{-i\omega t} + a^{\dagger}_{\vec{Q},\nu}\, e^{+i\omega t}\} \qquad (28)$$

where $e_z\!\left(\frac{\vec{Q}}{\nu}\right)$ is the perpendicular component of the phonon polarization vector, and $a^{\dagger}_{\vec{Q},\nu}$ and $a_{\vec{Q},\nu}$ are, respectively, the phonon creation and destruction operators. The part of the potential contributing to inelastic scattering is

$$v = <V> - U = u_z(dU/dz) + \cdots \qquad (29)$$

We now insert (29) into the transition matrix (26) and procee to evaluate the differential reflection coefficient (12). We omit the first DWBA contribution, since it has been considere in detail previously. The second-order DWBA can contribute only to processes transferring greater than one phonon, since

the matrix elements of (29) transfer at least one phonon. After using the completeness relation for phonon eigenstates and carrying out the trivial sums, the two-phonon contribution to the second DWBA can be written as

$$\frac{dR}{d\varepsilon_f d\Omega_f} = \sum_{k_{z\ell'}} \frac{\pi^2 m^4 \sqrt{2m\varepsilon_f}}{4(2\pi)^4 \hbar^7 k_{zi} k_{z\ell} k_{z\ell'} N^2 M^2} \sum_{\vec{Q},\vec{\nu}} e_z^2(\vec{Q}) \; e_z^2(\vec{P})$$

$$\{ v'_{f\ell} v'_{\ell i} v'_{f\ell'} v'_{\ell' i} \; n_\nu(\vec{Q}) \; n_\nu(\vec{P}_{aa})$$

$$+ 2 \, v'_{f\ell} v'_{\ell i} v'_{f\ell'} v'_{\ell' i} \; [n_\nu(\vec{Q}) + 1] \; n_{\nu'}(\vec{P}_{ac})$$

$$+ v'_{f\ell} v'_{\ell i} v'_{f\ell'} v'_{\ell' i} \; [n_\nu(\vec{Q}) + 1] \; [n_{\nu'}(\vec{P}_{cc}) + 1] \}$$

$$(30)$$

where the single-phonon matrix elements $v'_{\ell m}$ are given by

$$v'_{\ell m} = \int_{-\infty}^{} dz \; \chi^*(k_{z\ell};z) \; \frac{dU}{dz} \chi(k_{zm};z) \qquad (31)$$

The intermediate parallel phonon wave vector is defined for the three cases by

$$\vec{P} = \begin{cases} \vec{K}_f - \vec{Q} - \vec{K}_{i'} \equiv \vec{P}_{aa} \text{ for (aa) case} \\[2ex] \vec{K}_i - \vec{Q} - \vec{K}_{f'} \equiv \vec{P}_{cc} \text{ for (cc) case} \\[2ex] \vec{K}_f - \vec{Q} - \vec{K}_{i'} \equiv \vec{P}_{ac} \text{ for (ac) case} \end{cases} \qquad (32)$$

The sum over $k_{z\ell'}$ indicates that there are two pairs of intermediate momentum states to be summed over. These are

$$k_{z\ell'} = \{ (2m\varepsilon_i/\hbar^2) + [2m\omega_{\nu'}(\vec{P})/\hbar] - P^2 \}^{\frac{1}{2}} \qquad (33a)$$

$$k_{z\ell'} = \{ (2m\varepsilon_i/\hbar^2) + [2m\omega_\nu(Q)/\hbar] - P^2 \}^{\frac{1}{2}} \qquad (33b)$$

Finally, the value of $k_{z\ell}$ is

$$k_{z\ell} = \{(2m\varepsilon_i/\hbar^2) + [2m\omega_\nu \cdot (\vec{P})/\hbar] - P^2\}^{\frac{1}{2}} \qquad (34)$$

The extension of Eq. (30) for the case of more general potentials or to higher-order multiphonon processes is straightforward.

Calculations and Discussion

Calculations have been carried out for the accommodation of helium at a tungsten surface. The averaged interaction between the particles and the surface is the Morse potential:

$$U(z) = D(e^{-2\kappa z} - 2e^{-\kappa z}) \qquad (35)$$

where D is the well depth and κ is the range parameter. Values of the sound velocities and density of tungsten are taken from the American Institute of Physics Handbook.[26]

When the two-phonon first-order DWBA of Eq. (22), together with (13), is inserted into the accommodation coefficient of Eq. (6), it is found that the results are very small compared to the single-phonon contribution. It readily can be shown that this contribution varies as T^4 for small temperatures and is linear at large temperatures. At a temperature of 300°K, this two-phonon part is only about 0.5% of the single-phonon contribution calculated by Gaffney[13] using the same model and parameters. Thus, the two-phonon contribution from the first-order DWBA appears to be completely negligible, even at temperatures higher than room temperature. This compares favorably with the results of Allen and Feuer, who calculated the accommodation within the framework of the Devonshire model using a repulsive exponential interaction. They found that the two-phonon contribution at 300°K was 0.46% of the one-phonon part. Strachan also has shown, in his studies of the desorption of surface adatoms, that two-phonon transfers in the first-order DWBA should be negligible

When the contribution of the second-order DWBA of Sec. is calculated, a different picture emerges. Figure 1 shows a plot of the first- and second-order DWBA contributions to $\alpha(T)$, together with the corresponding one-phonon results calculated by Gaffney. The Debye temperature for this graph is 300°K, the well depth is 60°K, and range parameter is 1.3×10^{11} m^{-1}, all reasonably accepted values. That part due to two-
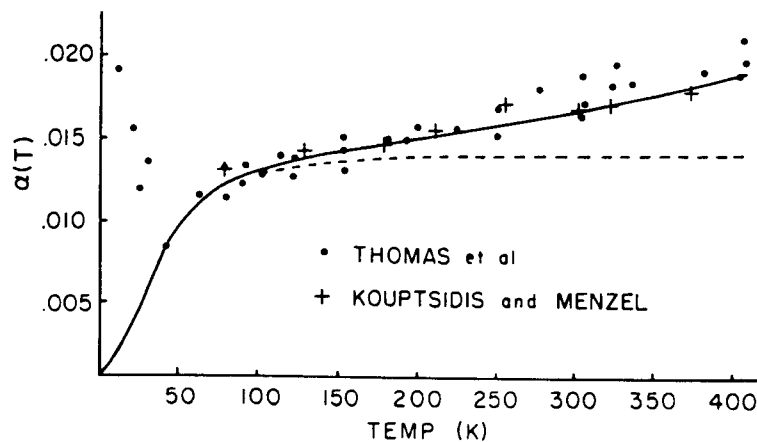
Fig. 1 The accommodation coefficient $\alpha(T)$ as a function of temperature for He at a W surface (---- single-phonon calculation; ____ one-and two-phonon contributions). The experimental data are those of Thomas et. al[29] and Kouptsidis and Menzel.[28]

phonon transfer is due almost entirely to the second-order DWBA. The graph shows that the two-phonon contribution becomes important at about 100°K and becomes more important for large temperatures, as one would expect. At large temperatures, the two-phonon contribution increases as T^2, whereas the one-phonon contribution essentially goes to a constant. For small T, the second-order DWBA varies as T^5.

These calculations seem to indicate clearly the point at which two-phonon effects become important. By varying all of the parameters, including the surface and gas temperature independently, it always appears that the two-phonon contribution becomes an appreciable fraction of the total scattering when either temperature reaches about 100°K. When these calculations are compared with the unitary one-phonon calculations of Goodman[27] and Gaffney,[13] it is found that the two-phonon contribution becomes important at almost the same point that the unitary calculations differ from the one-phonon DWBA calculations. This also is in agreement with what one would expect; i.e., when the scattering is strong enough for unitary corrections to be important, then there should be contributions from higher-order phonon processes.

The preceding comparison between the first- and second-order DWBA contributions appears to clarify a discrepancy in the published literature concerning the importance of two-phonon effects in surface scattering. The earlier work of Strachan and of Allen and Feuer which is based strictly on a first-order DWBA approach concludes that two-phonon effects are unimportant. On the other hand, several more recent

papers, which are not based on a perturbation approach, show that multiple-phonon effects can be very important even at relatively low temperatures.

Our present work, which is a perturbation theory approac shows that the work of Strachan and of Allen and Feuer is not complete, since they failed to include the second-order Born approximation. It is clear that, if one wishes to calculate multiple-phonon effects self-consistently, it also is necessary to consider the contributions from the higher-order terms in the Born series. We have shown that, for the case two-phonon surface scattering, the contribution of the secon order DWBA can be more than an order of magnitude larger tha the first-order DWBA.

The importance of higher Born terms in the perturbation series can be illustrated further by a comparison of our work with that of Kaplan and Drauglis.[16] Their work is of such a nature that it can be interpreted only qualitatively, but it shows that multiple-phonon effects are important in surface scattering at temperatures of the order 100°K. However, all of their multiple-phonon contribution must come from higher-order Born processes, because their interaction potential is capable of only single-phonon transfers at each collision between the particle and surface.

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