

Simple approximation to thermal attenuation in low-energy atom-surface scattering

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(Received 18 September 1986; accepted 3 November 1986)

We present a set of simple approximations for models of the thermal attenuation of elastic intensities as a function of surface temperature. The results illustrate the complexity of the strongly interacting atom-surface system, yet provide simple closed-form expressions which are no more difficult to apply than a standard Debye-Waller factor. Very good agreement is obtained with existing experimental data. The importance of the various types of multiphonon contributions is assessed and the resummation of bubble diagrams is demonstrated.

I. INTRODUCTION

In the scattering of low-energy atoms from surfaces inelastic processes become increasingly important as the surface temperature is raised. The increase in inelastically scattered atoms is paralleled by a decrease or attenuation of the elastic diffraction intensities.¹⁻³ This effect is common to all diffraction processes from crystals such as neutron or x-ray diffraction. In these latter cases, multiple scattering can usually be ignored and the diffraction intensities are well described by the Born approximation. The thermal attenuation appears as a Debye-Waller factor, which in its simplest form appears as

$$e^{-2W} = e^{-\langle [(\mathbf{k}_i - \mathbf{k}_f) \cdot \mathbf{u}_i]^2 \rangle}, \quad (1)$$

where $\mathbf{k}_i - \mathbf{k}_f$ is the exchanged momentum, \mathbf{u}_i is the thermal displacement of a crystal atom, and the angular brackets imply a thermal average. In contrast to Eq. (1), for atom-surface scattering the interaction potential is extended and soft (particularly for metal surfaces), and the important contributions come from higher-order perturbation theory. In this paper we develop a simple approximation for the thermal attenuation which allows us to demonstrate clearly the importance of these higher-order contributions.

In Sec. II we develop briefly the essential elements of the inelastic scattering formalism. In Sec. III we present the simple approximation and consider the single virtual phonon contribution for a flat surface model. Section IV is a comparison of single- and double-phonon contributions and a discussion of the relative importance of multiphonon inelastic scattering. In Sec. IV we also consider infinite summation of certain classes of multiphonon terms.

II. GENERAL DEVELOPMENT OF THERMAL ATTENUATION

We very briefly present here the theory of thermal attenuation in atom-surface scattering⁴⁻¹¹ together with the reduction to our simple approximation. It is appropriate to work in the distorted wave formalism with the total interaction potential V between incoming atom and surface expressed as

$$V = U + v, \quad (2)$$

with U a conveniently chosen distorting potential for a rigid lattice. Then the transition operator obeys the equation

$$T = v + vG_0^+ T, \quad (3)$$

where the Green function is

$$G_0^+ = (E_i + \epsilon_i - H_0 - U - H^c + i\epsilon)^{-1}, \quad (4)$$

where H_0 and H^c are the unperturbed Hamiltonians of the particle and crystal, respectively. Expressing the Green function as an integral representation and with the usual definition of the particle evolution operator,

$$P(t) = e^{i(E_i - H_0 + i\epsilon)t/\hbar}, \quad (5)$$

The transition operator becomes, for elastic processes,

$$T = v - (i/\hbar) \int_0^\infty dt v(t)P(t)T, \quad (6)$$

with $v(t)$ in the interaction picture,

$$v(t) = \exp(iH^c t/\hbar) v \exp(-iH^c t/\hbar). \quad (7)$$

Equation (6) can be iterated to yield the perturbation series in terms of time ordered operators

$$\begin{aligned} T = & v + (-i/\hbar) \int_0^\infty dt v(t)P(t)v(0) \\ & + (-i/\hbar)^2 \int_0^\infty dt' \int_0^\infty dt v(t')v(t) \\ & \times P(t')v(t)P(t)v(0) + \dots \end{aligned} \quad (8)$$

It is convenient to use the range parameter κ of the potential to obtain a dimensionless transition matrix. For the diagonal elements considered here this becomes

$$F(p_i) = (8m/\hbar^2 k^2) T_{ii}, \quad (9)$$

with m is the particle mass and $p_i = k_{iz}/\kappa$, with k_{iz} the particle wave vector normal to the surface. Then the intensity of the specular beam is given by

$$I_0 = |1 - (i\pi/4p_i) \langle F(p_i) \rangle|^2, \quad (10)$$

where we have used the fact that for elastic scattering the

thermal average $\langle |F(p)|^2 \rangle$ can be replaced by the simpler expression $|\langle F \rangle|^2$.^{6,9}

In order to proceed further, we must adopt a potential for the interaction process, and we choose a thermally vibrating exponential form

$$V(z, u') = D [e^{-2\kappa(z-u')/v_0} - A(z)], \quad (11)$$

where u' is the normal component of the thermal potential displacement,

$$v_0 = \langle \exp(2\kappa u') \rangle = \exp(2\kappa^2 \langle u'^2 \rangle),$$

and $A(z)$ is a static attractive part. The choice of an exponentially decreasing repulsive potential is justified by the fact that to a good approximation it is proportional to the electronic charge density outside the surface.

A potential in the form of Eq. (11) is extremely convenient for carrying out the thermal averages as will be shown below. Its major disadvantage is that it describes a flat vibrating surface and hence the phonons will not give rise to an exchange of momentum parallel to the surface. As we have shown^{8,10} this is not a fundamental difficulty for the problem of thermal attenuation where most of the phonons involved are of low energy and hence long wavelength. It is convenient to choose

$$U = \langle V(z, u') \rangle, \quad (12)$$

so that the average of the perturbing potential vanishes $\langle v \rangle = 0$. Then the first nonzero contribution to the thermally averaged transition matrix is from second order in Eq. (8):

$$\begin{aligned} \langle F^{(2)}(p_i) \rangle &= (1/4i) \int_0^\infty dq \int_0^\infty d\tau e^{i(p_i^2 - q^2 + i\epsilon)\tau} \\ &\times \langle [e^{u(\tau)} - v_0] [e^{u(0)} - v_0] \rangle f^2(p_i, q) / v_0^2 \\ &+ (1/4\pi^2 i) \sum_n \int d\tau e^{i(p_i^2 + e_n + i\epsilon)\tau} \\ &\times \langle [e^{u(\tau)} - v_0] [e^{u(0)} - v_0] \rangle l^2(p_i, n) / v_0^2, \quad (13) \end{aligned}$$

where $u(\tau) = \kappa u'(t)$ and e_n are the bound-state energies of U . Here, $f(p_i, q)$ and $l(p_i, n)$ are matrix elements of the per-

turbing potential $e^{-2\kappa z}$ taken with respect to states of the distorted potential U , with q representing continuum states and n the bound states. The thermal averages in Eq. (13) can be carried out in the harmonic approximation giving

$$\langle [e^{u(\tau)} - v_0] [e^{u(0)} - v_0] \rangle / v_0^2 = e^{Q(\tau)} - 1, \quad (14)$$

where $Q(\tau)$ is the displacement correlation function, which in the usual way can be expressed in terms of an integral over the phonon spectral density $\rho(\omega)$ and the Bose-Einstein function $n(\omega)$:

$$Q(\tau) = 4 \langle u(\tau) u(0) \rangle = 4 \frac{m}{M} \int_0^\infty d\omega \frac{\rho(\omega) n(\omega)}{\omega} e^{i\omega\tau}, \quad (15)$$

where m and M are the masses of the projectile and crystal atoms, respectively. (The mass of the projectile atom appears because of our choice of dimensionless variables.) Expanding Eq. (14) to first order in $Q(\tau)$ and inserting back into Eq. (13) gives the first nonvanishing contribution to lowest order in virtual phonon exchange:

$$\begin{aligned} \langle F^{(2,1)}(p_i) \rangle &= \frac{m}{M} \int_0^\infty dq \int_0^\infty d\omega \frac{\rho(\omega)}{\omega} \\ &\times f^2(p_i, q) \frac{n(\omega)}{p_i^2 - q^2 + \omega + i\epsilon} \\ &+ \frac{m}{\pi^2 M} \sum_n \int_{-\infty}^\infty d\omega \frac{\rho(\omega)}{\omega} \\ &\times l^2(p_i, n) \frac{n(\omega)}{p_i^2 + e_n + \omega + i\epsilon}. \quad (16) \end{aligned}$$

This describes a single-phonon virtual exchange process with positive values of ω giving phonon creation and negative values giving phonon annihilation. In fact Eq. (16) contains exactly all possible single-phonon virtual processes for the potential of Eq. (11), including all phonon assisted bound-state resonances.

We now consider some of the higher-order terms in the perturbation series of Eq. (8). The third-order term, with the potential of Eq. (11) and after converting to dimensionless variables has the form

$$\begin{aligned} \langle F^{(3)}(p_i) \rangle &= + \left(\frac{1}{4i} \right) \int_0^\infty dq_1 \int_0^\infty dq_2 \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 e^{i(p_i^2 - q_1^2 + i\epsilon)\tau_1} e^{i(p_i^2 - q_2^2 + i\epsilon)\tau_2} \\ &\times f(p_i, q_1) f(q_1, q_2) f(q_2, p_i) (e^{Q(\tau_1) + Q(\tau_2) + Q(\tau_1 + \tau_2)} - e^{Q(\tau_1)} - e^{Q(\tau_2)} - e^{Q(\tau_1 + \tau_2)} + 2), \quad (17) \end{aligned}$$

where bound-state contributions have been ignored. The expansion of the factor involving the phonon correlation functions $Q(\tau)$ begins with the quadratic term, implying that the third-order contribution must involve the exchange of at least two virtual phonons. A similar calculation shows that the fourth-order contribution to the perturbation series also exchanges at least two virtual phonons.

III. SIMPLE APPROXIMATION AND SINGLE-PHONON CONTRIBUTIONS

We now present the following series of approximations which greatly simplify the work of calculating the thermally

averaged transition matrix but which retain almost all of the salient features of the method: (1) Replace the time-dependent phonon correlation functions by an effective mean-square amplitude, i.e., in the simplest case $Q(\tau) = Q(0) = 4\langle u^2(0) \rangle$. (2) In integrals over intermediate perpendicular momenta, retain only the imaginary or δ function, energy-conserving contribution. (This is justified by the fact that for most temperatures of interest the surface thermal roughening is small, as demonstrated in more exact calculations.^{8,10}) (3) Ignore the contribution of bound states in the intermediate sums. (This is justified except at very low incident energies or very grazing incident angles.^{8,10})

We illustrate by example. Consider the lowest-order contribution in perturbation theory, the second-order term of Eq. (16). Applying the above three approximations leaves us with

$$\langle F^2(p_i) \rangle = (-i\pi/8p_i) [e^{Q(0)} - 1] f^2(p_i, p_i) \quad (18)$$

and the term for exchange of m phonons is expressed as

$$\langle F^{(2,m)}(p_i) \rangle = (-i\pi/8p_i) f^2(p_i, p_i) [Q^m(0)/m!]. \quad (19)$$

The single virtual phonon contribution to the thermal attenuation [the $m = 1$ term of Eq. (19) together with Eq. (10)] is compared with experimental data for the specular scattering of He from the close-packed Cu(100) face in Fig. 1. The attractive part of the potential of Eq. (11) is chosen to be an exponential so that the average potential $U(z)$ is a Morse potential. The parameters are $D = 6.35$ meV and $\kappa = 1.05 \text{ \AA}^{-1}$, values fixed by previous comparison of theory and experiment for elastic diffraction intensities from stepped Cu surfaces.¹² For evaluating the correlation function $Q(0) = 4\langle u^2 \rangle$ we use a Debye spectral density averaged over four surface atoms to account for the number of surface atoms actually "seen" by the incoming atom in the region of its turning point¹³; $\rho(\omega) = 3\omega^2/4\omega_D^3$. The static attractive part of the potential enhances the isopotential corrugation of the total potential and to account for this we multiply $\rho(\omega)$ by an additional factor $\alpha = \frac{1}{4}$ as in previous work.⁸ The agreement shown in Fig. 1 is remarkably good. Although the Debye temperature (the only variable parameter) changes somewhat with incident angle, the values obtained, 200 K $< \theta_D < 280$ K, are within the expected range for the sur-

face Debye temperature of Cu. Measurements have also been made at the higher incident energy of 63 meV and our simple model gives equally good agreement for these data.

IV. MULTIPLE-PHONON CONTRIBUTIONS

This simple model allows us to discuss clearly and simply the relative importance of the various types of multiphonon events that contribute to atom-surface scattering. We begin by comparing to the single-phonon contribution the three different types of two-phonon processes. The two-phonon amplitude from second-order perturbation is obtained from Eq. (19) with $m = 2$:

$$\langle F^{(2,2)}(p_i) \rangle = -(i\pi/16p_i) f^2(p_i, p_i) Q^2(0). \quad (20)$$

The third- and fourth-order perturbation contributions start with double-phonon exchange terms which are, respectively,

$$\langle F^{(3,2)}(p_i) \rangle = -\frac{3}{64} (\pi/p_i)^2 f^3(p_i, p_i) Q^2(0), \quad (21)$$

$$\langle F^{(4,2)}(p_i) \rangle = -\frac{3}{512} (\pi/p_i)^3 f^4(p_i, p_i) Q^2(0). \quad (22)$$

The relative importance of these contributions is best expressed by comparing them to the single-phonon term from Eq. (19). Again we make use of a Debye spectral density and we take the high-temperature limit where $\langle u^2 \rangle \propto T$, the surface temperature:

$$\langle F^{(2,2)} \rangle / \langle F^{(2,1)} \rangle = 12 \frac{m}{M} \left[\frac{\hbar^2 \kappa^2}{2m} \right] \frac{T}{k_B \theta_D^2}, \quad (23)$$

$$\langle F^{(3,2)} \rangle / \langle F^{(2,1)} \rangle = -i \frac{9m}{M} \left[\frac{\hbar^2 \kappa^2}{2m} \right] \frac{\pi f(p_i, p_i)}{p_i} \frac{T}{k_B \theta_D^2}, \quad (24)$$

$$\langle F^{(4,2)} \rangle / \langle F^{(2,1)} \rangle = \frac{9}{8} \frac{m}{M} \left[\frac{\hbar^2 \kappa^2}{2m} \right] \left[\frac{\pi f(p_i, p_i)}{p_i} \right]^2 \frac{T}{k_B \theta_D^2}. \quad (25)$$

Representative values of $f(p_i, p_i)/p_i$ for typical systems are of the order of 10 or larger, therefore clearly the fourth-order double-phonon term is the largest while the double-phonon contribution from second order is small. This prediction is borne out by detailed exact model calculations¹⁰ which show that among the three different types of two-phonon contributions the fourth order is dominant, the second order is negligible, and the third order is substantially smaller than the fourth order but not always negligible.

Another interesting point is the difference in phase between the second- and fourth-order terms of Eqs. (19) and (22). The fourth-order amplitude subtracts from the single-phonon contribution which has the effect of increasing the elastic intensity. A similar effect is noted with an ordinary Debye-Waller factor.

The parameter involving the most important contribution, that of Eq. (25), can be put into an interesting form upon recognizing that

$$(\hbar^2 \kappa^2 / 2m) [\pi f(p_i, p_i) / p_i]^2 \equiv 16 (\hbar^2 k_i^2 / 2m) = 16E^*, \quad (26)$$

where E^* can be considered as the energy associated with normal particle motion corrected for the well depth. Then Eq. (25) becomes

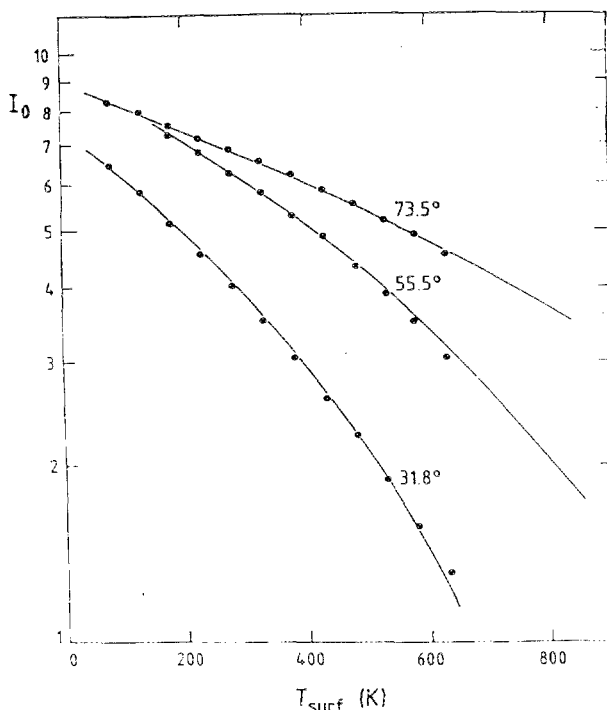


FIG. 1. Thermal attenuation of the specular beam for the He/Cu(100) system with incident energy 21 meV and three different angles of incidence. The experimental points are from Ref. 2 and the curve is the single-phonon calculation. The surface Debye temperature for $\theta_i = 73.5^\circ$ is 276 K, for $\theta_i = 55.5^\circ$ is 240 K, and for $\theta_i = 31.8^\circ$ is 220 K.

$$\langle F^{(4,2)}(p_i) \rangle / \langle F^{(2,1)}(p_i) \rangle = -18 \frac{m}{M} \frac{E^*}{k_B \theta_D} \frac{T}{\theta_D}. \quad (27)$$

Apart from the numerical factor, the right-hand side of Eq. (27) is the well-known Weare criterion¹⁴ for the importance of two-phonon terms. However, it appears here with a correction for the depth of the adsorption well coming from appearance of the diagonal matrix element in Eq. (26). This well depth correction is considerably stronger than the usual correction¹⁵ of simply assuming that the well merely refracts the particles as expressed by $E^* = E + D$.

Another interesting situation in which multiple-phonon contributions can be considered is in the infinite summation of the various classes of bubble diagrams. The approximation of neglecting the time correlation of the phonon displacements [i.e., putting $\langle u(t)u(0) \rangle = \langle u^2 \rangle$] has the effect of setting, at any given perturbation order, all phonon exchange processes equivalent. Otherwise stated, all Feynman diagrams corresponding to a particular order are equal. The simplest and most important of all possible infinite summations is the summation of nontouching bubbles. This consists of summing the amplitudes from the one such diagram of each even perturbation order. The summation is a geometric series and the resummed amplitude is given by

$$\langle F(p_i) \rangle = \langle F^{(2,1)}(p_i) \rangle / (1 + i\pi/8p_i \langle F^{(2,1)}(p_i) \rangle), \quad (28)$$

which gives the following particularly simple and interesting form for the specular intensity:

$$I_0 = \left\{ \frac{[1 - (i\pi/8p_i) \langle F^{(2,1)} \rangle]}{[1 + (i\pi/8p_i) \langle F^{(2,1)} \rangle]} \right\}^2. \quad (29)$$

As an illustration of the usefulness of the expressions found here, we show in Fig. 2 a comparison with the experimental data for the thermal attenuation of H₂ at a Cu(100) surface. The incident beam has an energy of 77.2 meV, and shown is the specular intensity for two angles of incidence, 75.5° and 31°. The parameters appropriate to the Morse potential for this system are a well depth $D = 21.6$ meV and $\kappa = 1.0 \text{ \AA}^{-1}$.¹² These results are very close to those obtained by the exact summation of bubbles.¹⁰

As a further note on multiphonon effects, with the approximation $\langle u(t)u(0) \rangle = \langle u^2 \rangle$, the entire perturbation series can be summed using a Borel transformation. In this case the thermal attenuation can be most simply expressed in terms of solutions to Schrödinger's equation with temperature-dependent, effective potentials. Furthermore, if the entire potential, both repulsive and attractive parts, vibrates in phase [i.e., if $V(z, u) = V(z - u)$] then the Debye-Waller factor of Eq. (1) is recovered.¹⁶

The set of approximations considered here permits a clear demonstration of the important and relevant inelastic processes. Not only does it establish the conditions for the importance of multiphonon events in general, but it distinguishes between those which are important and those which are negligible, and gives rise to simple closed form expressions for the elastic intensities.

ACKNOWLEDGMENTS

The authors would like to thank Dr. J. Lapujoulade, Dr. B. Salanon, Dr. F. Fabre, Dr. D. Gorse, Dr. A. Nourtier, and Dr. C. S. Jayanthi for many helpful discussions.

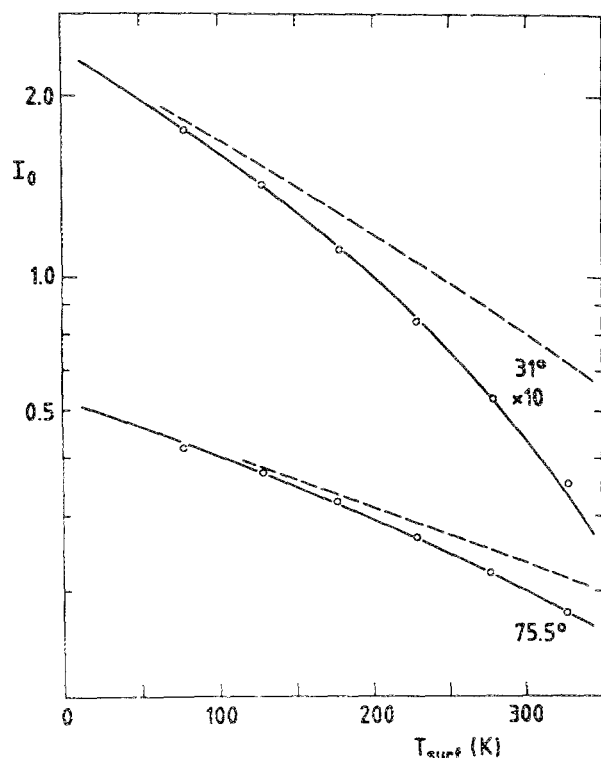


FIG. 2. Thermal attenuation of the specular beam for the H₂/Cu(100) system with energy 77.2 meV and two angles of incidence $\theta_i = 75.5^\circ$ and $\theta_i = 31^\circ$. The crosses are experimental points (Ref. 2), the solid curve is the single-phonon result, and the dashed curve is the summation of bubbles expression of Eq. (29). The Debye temperature for $\theta_i = 75.5^\circ$ is 242 K and for $\theta_i = 31^\circ$ is 217 K. (This latter curve is multiplied by a factor of 10.)

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