Surface Science 195 (1988) 513–534
North-Holland, Amsterdam

SIMPLE APPROXIMATION TO THERMAL ATTENUATION IN LOW ENERGY ATOM–SURFACE SCATTERING: MULTIPLE PHONON PROCESSES

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Received 20 August 1986; accepted for publication 14 September 1987

Within the context of a recently developed simple approximation model, we consider multiple phonon processes in the thermal attenuation of elastic peaks in atom–surface diffraction. A discussion of two phonon processes results in a set of parameters which indicate the relative importance of the three distinct types of multiphonon processes. We discuss multiple virtual phonon exchange, and the summation of certain classes of multiphonon transfers is carried out to all orders. This model illustrates clearly the distinction between thermal attenuation in atom–surface scattering and the more familiar Debye–Waller analysis valid for neutron or X-ray scattering. We obtain closed form expressions which are just as easy to apply as a Debye–Waller factor.

1. Introduction

In a recent paper, we have developed a simple approximation for the thermal attenuation of elastic diffraction intensities for low energy scattering of atoms from surfaces [1]. There, we restricted the development of the theory to processes involving the exchange of a single virtual phonon. Here, we consider, within the same model, processes involving multiple exchange of virtual phonons, including infinite resummation of certain classes of terms in the perturbation series.

The process of thermal attenuation in atom–surface scattering is inherently more complex than the case of more widely known diffraction experiments, such as neutron or X-ray scattering from bulk crystals [2–5]. There, 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

$$\exp(-2W) = \exp\left\{-\left\langle\left[(\boldsymbol{k}_i - \boldsymbol{k}_p)\cdot\boldsymbol{u}_\ell\right]^2\right\rangle\right\}, \tag{1}$$

where $\boldsymbol{k}_i - \boldsymbol{k}_p$ is the momentum exchanged and $\boldsymbol{u}_\ell$ is the thermal displacement of a crystal atom. The angular brackets imply a thermal average. In contrast to eq. (1), in atom–surface scattering, the interaction potential is extended and soft (particularly for metal surfaces) and the important contributions to the thermal attenuation come from higher order terms in perturbation theory. The simple model considered here allows us to demonstrate clearly the importance of these higher order contributions; furthermore, it demonstrates that the type of virtual phonon exchange giving rise to the ordinary Debye–Waller factor of eq. (1) is of negligible importance in atom–surface scattering.

In the next section, we restate very briefly the essential elements of this simple approximation as more detailed explanation has already been presented elsewhere. In section 3, we discuss the virtual exchange to two phonons. We show that these processes can be divided into three general classes, and the relative importance of each class of two phonon processes can be expressed in terms of simple parameters. For the most important class of events, we recover the well known parameter of Weare [6]. In section 4, we extend the model to multiple virtual phonon exchange. Section 5 contains a discussion of the summation of certain classes of terms in the perturbation series to all orders. We find that two different classes of processes can be resummed, resulting in particularly simple expressions for the scattered intensity as a function of temperature. In section 6, we draw a number of conclusions on multiphonon processes in general for the scattering of atoms by surfaces.

In the present paper, we consider the effects of phonon exchange on the elastic scattering from a flat surface which has no nonspecular diffraction beams. We have also considered the case of strongly diffractive systems, including inelastic effects in resonant interaction with the surface bound states. We discuss these more complex systems in a later paper [7], but we remark that the basic importance and effect of phonon exchange is quite similar to that exhibited by the model developed here.

2. Review of the simple model

We review very briefly here the theory of thermal attenuation in atom–surface scattering together with the reduction to our simple approximation. More detailed explanations are given in ref. [1].

It is appropriate to work in the distorted wave formalism with the total interaction potential between incoming atom and surface V expressed as

$$V = U + v, \tag{2}$$

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

$$T = v + vG_0^+ T, \tag{3}$$

where the Green function is

$$G_0^+ = \left(E_i + \mathscr{E}_i - H_0 - U - H^c + i\epsilon\right)^{-1}, \tag{4}$$

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

$$P(t) = \exp\left[i(E_i - H_0 + i\epsilon)t/\hbar\right]. \tag{5}$$

The transition operator becomes

$$T = v - \frac{i}{\hbar}\int_0^\infty dt\, v(t)P(t)T, \tag{6}$$

with $v(t)$ in the interaction picture

$$v(t) = \exp(iH^c t/\hbar)\, v\, \exp(-iH^c t/\hbar). \tag{7}$$

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

$$T = v - \frac{i}{\hbar}\int_0^\infty dt\langle v(t)P(t)v(0)\rangle + \left(-\frac{i}{\hbar}\right)^2 \int_0^\infty dt' \int_0^\infty dt \langle v(t'+t)P(t')v(t)P(t)v(0)\rangle + \cdots. \tag{8}$$

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

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

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

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

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 $|\langle F\rangle|^2$ [8,9].

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

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

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 of the form (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 [2–4] 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

$$U = \langle V(z, u') \rangle, \tag{12}$$

so that the average of the perturbing potential vanishes $\langle v \rangle = 0$. Then the first non-zero contribution to the thermally averaged transition matrix is

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

where $u(\tau) = \kappa u'(t)$ and e_n are the bound state energies of U. $f(p_i, q)$ and $l(p_i, n)$ are matrix elements of the perturbing 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 (13) can be carried out in the harmonic approximation giving

$$\left\langle \left\langle \left(e^{u(\tau)} - v_0\right)\left(e^{u(0)} - v_0\right) \right\rangle \right\rangle / v_0^2 = e^{Q(\tau)} - 1, \tag{14}$$

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 $n(\omega)$

$$Q(t) = 4\left\langle \left\langle u(\tau)u(0) \right\rangle \right\rangle = 4\frac{m}{M} \int_{-\infty}^{\infty} d\omega \frac{\rho(\omega)n(\omega)}{\omega} e^{i\omega t}, \tag{15}$$

where m and M are the masses of the projectile atom and crystal atom, 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 (13) gives the first non-vanishing contribution to lowest order in virtual phonon exchange:

$$\langle F^{(2,1)}(p_i)\rangle = \frac{m}{M}\int_0^\infty dq \int_{-\infty}^\infty d\omega \frac{\rho(\omega)}{\omega} f^2(p_i,q)\frac{n(\omega)}{p_i^2 - q^2 + \omega + i\epsilon}$$

$$+ \frac{m}{\pi^2 M}\sum_n \int_{-\infty}^\infty d\omega \frac{\rho(\omega)}{\omega} l^2(p_i,n)\frac{n(\omega)}{p_i^2 + e_n + \omega + i\epsilon}. \qquad (16)$$

This describes a single phonon virtual exchange process with positive values of ω giving phonon annihilation and negative values giving phonon creation. 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. As a useful visual aid, the phonon exchange process described by eq. (16) can be presented as a Feynman-type diagram, the single bubble as shown in fig. 1a. The notation used in eq. (16) is convenient for distinguishing between higher order and multiphonon terms. We write $\langle F^{(n,m)}\rangle$ where n is the order of perturbation theory and m is the number of virtual phonons exchanged. If the expression includes all numbers of phonon exchange we write it as $\langle F^{(n)}\rangle$ when n denotes the perturbation order, e.g. eq. (13).

It is of interest at this point to develop explicitly some of the higher order terms in the perturbation series of eq. (8). The third order term, with the potential of (11) and after converting to dimensionless variables has the form

$$\langle F^{(3)}(p_i)\rangle = +\frac{1}{4i}\int_0^\infty dq_1 \int_0^\infty dq_2 \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \exp\left[i(p_i^2 - q_1^2 + i\epsilon)\tau_1\right]$$

$$\times \exp\left[i(p_i^2 - q_2^2 + i\epsilon)\tau_2\right] f(p_i,q_1) f(q_1,q_2) f(q_2,p_i)$$

$$\times \left\langle \left(e^{u(\tau_1+\tau_2)} - v_0\right)\left(e^{u(\tau_2)} - v_0\right)\left(e^{u(0)} - v_0\right)\right\rangle / v_0^3. \qquad (17)$$

For simplicity we have ignored the bound state contributions. The thermal average can again be carried out in terms of the phonon correlation function.

$$\left\langle \left(e^{u(\tau_1+\tau_2)} - v_0\right)\left(e^{u(\tau_2)} - v_0\right)\left(e^{u(0)} - v_0\right)\right\rangle / v_0^3$$

$$= e^{Q(\tau_1)+Q(\tau_2)+Q(\tau_1+\tau_2)} - e^{Q(\tau_1)} - e^{Q(\tau_2)} - e^{Q(\tau_1+\tau_2)} + 2, \qquad (18)$$

which when developed in a power series in Q gives as its first non-vanishing contribution

$$\approx Q(\tau_1)Q(\tau_2) + Q(\tau_1)Q(\tau_1+\tau_2) + Q(\tau_2)Q(\tau_1+\tau_2). \qquad (19)$$

Note that each Q is associated with an integration over ω, the integrand being proportional to $e^{i\omega\tau}$. Therefore, the integration over τ yields a propagator with ω responsible for the virtual phonon exchange. The fact that eq. (19) is quadratic in Q implies that the third order contribution begins with the exchange of two virtual phonons and contains no single phonon contributions

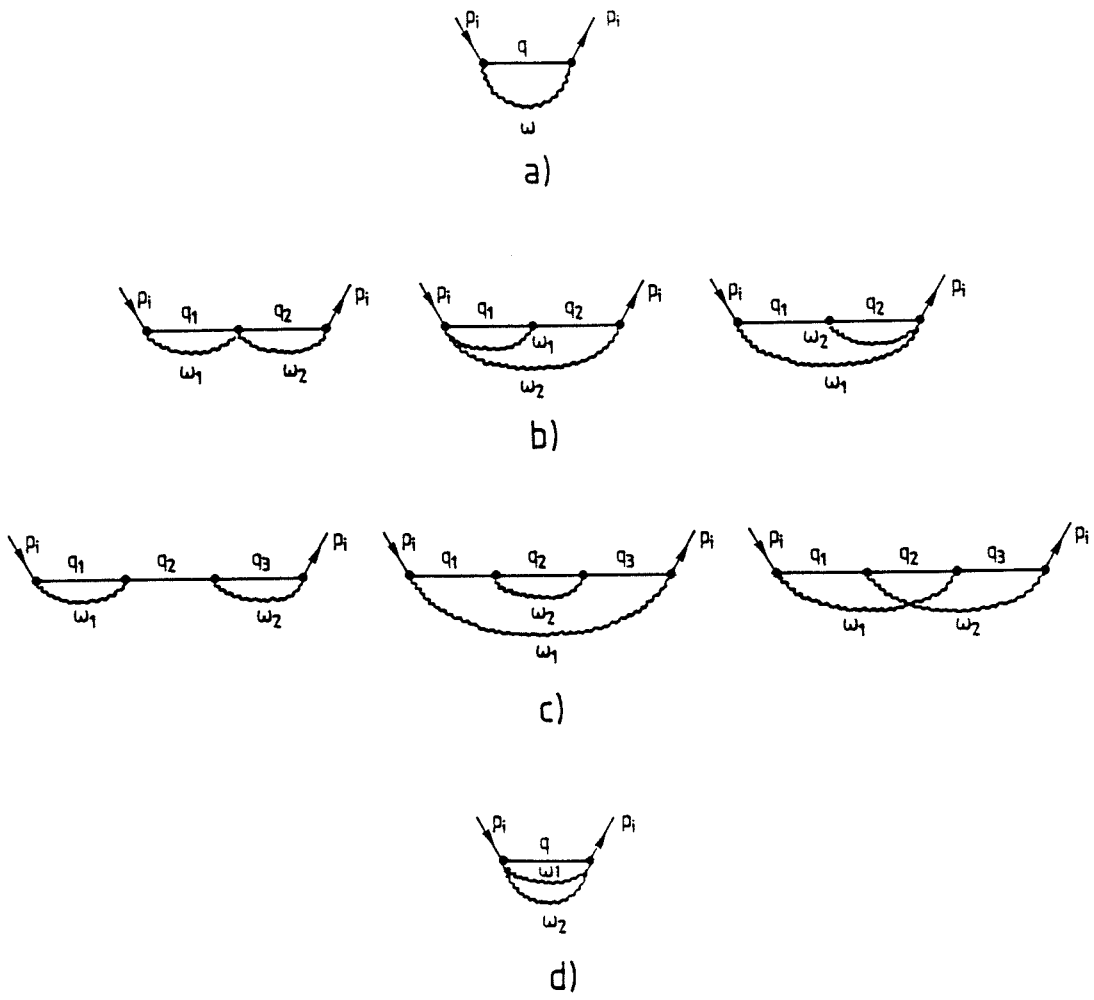

Fig. 1. Diagrams showing the various types of virtual phonon exchange in the first few orders of perturbation theory. (a) Single phonon exchange in second order. (b) The three, two phonon processes in third order. (c) The three, two phonon processes in fourth order. (d) The two phonon exchange process in second order.

at all. The three processes in eq. (19) are shown in graphs of fig. 1b. They are, in order, the touching bubble and then a symmetric pair of diagrams.

The higher order terms in the perturbation series can now essentially be written down by extension. The fourth order term involves the following thermal average

$$\left\langle \left(e^{u(\tau_1+\tau_2+\tau_3)} - v_0\right)\left(e^{u(\tau_2+\tau_3)} - v_0\right)\left(e^{u(\tau_3)} - v_0\right)\left(e^{u(0)} - v_0\right)\right\rangle / v_0^4$$

$$\approx Q(\tau_1)Q(\tau_3) + Q(\tau_2)Q(\tau_1+\tau_2+\tau_3) + Q(\tau_1+\tau_2)Q(\tau_2+\tau_3). \tag{20}$$

The first order development again is quadratic in Q which implies that it is involved with two phonon virtual transfers. The first non-vanishing contribution to the fourth order term now appears as

$$\begin{aligned}\langle F^{(4,2)}(p_i)\rangle &= +\left(\frac{1}{4i}\right)^3 \int_0^\infty dq_1 \int_0^\infty dq_2 \int_0^\infty dq_3 \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \\ &\times \exp\left[i(p_i^2 - q_1^2 + i\epsilon)\tau_1\right] \exp\left[i(p_i^2 - q_2^2 + i\epsilon)\tau_2\right] \\ &\times \exp\left[i(p_i^2 - q_3^2 + i\epsilon)\tau_3\right] f(p_i, p_1) f(q_1, q_2) f(q_2, q_3) f(q_3, p_i) \\ &\times \left[Q(\tau_1)Q(\tau_3) + Q(\tau_2)Q(\tau_1 + \tau_2 + \tau_3) + Q(\tau_1 + \tau_2)Q(\tau_2 + \tau_3)\right]. \end{aligned} \quad (21)$$

The three contributions are shown in fig. 1c and are, in order, the bubble diagram, the direct term and the exchange term.

Higher order terms in the perturbation series will be of interest when we discuss the infinite summation of selected classes of diagrams in section 7, but we need go no further at this point. We mention only that for a potential of the form of eq. (11) with U chosen as the thermal average that the next or fifth order in perturbation theory will involve at least three phonon exchange. In general, the minimum number of virtual phonons exchanged at each order in the perturbation series is $n/2$ if the order n is even, or $(n+1)/2$ if n is odd.

We now briefly review the essentials of what we describe as the "simple approximation" to atom–surface scattering. These approximations eliminate the cumbersome integrals involved in obtaining the transition matrix, yet all of the important and salient features of the thermal attenuation process are retained. The approximation consists of the following steps:

(1) Replace all time dependent phonon correlation functions by the mean square amplitude, i.e.

$$Q(\tau) = 4\langle u(\tau)u(0)\rangle \to 4\langle u^2(0)\rangle = Q(0).$$

(It will also be convenient to use a Debye phonon spectral density for evaluating $Q(0)$.)

(2) In all integrals over intermediate perpendicular momenta, we retain only the imaginary or δ-function, energy conserving contribution.

(3) Ignore the contributions of bound states in the intermediate sums. (This is quite justified except at very low incident energies or very grazing incident angles [1,2] or in cases of elastic bound state resonance.)

We illustrate by example. Consider the lowest order contribution in the perturbation theory, the second order term of eq. (13). With $Q(t)$ in eq. (14) replaced by $Q(0)$ and neglecting the bound state contributions we have

$$\langle F^2(p_i)\rangle = \tfrac{1}{4}(e^{Q(0)} - 1)\int_0^\infty dq \frac{f^2(p_i, q)}{p_i^2 - q^2 + i\epsilon}. \quad (22)$$

Retaining only the imaginary contribution to the integral over normal momenta leaves us with

$$\langle F^2(p_i)\rangle = (-i\pi/8p_i)(e^{Q(0)}-1)f^2(p_i,p_i), \tag{23}$$

and the term for exchange of m phonons is obtained by expanding the exponential

$$\langle F^{(2,m)}(p_i)\rangle = (-i\pi/8p_i)f^2(p_i,\,p_i)Q^m(0)/m!. \tag{24}$$

The intensity of the specular beam is obtained from eq. (10)

$$I_0 = \left[1 - \frac{1}{2}\left(\frac{\pi}{4}\right)^2\left(\frac{f(p_i,\,p_i)}{p_i}\right)^2\left(Q(0) + \sum_{j=2}^{\infty}\frac{Q^j(0)}{j!}\right)\right]^2. \tag{25}$$

It is interesting at this point to make a comparison with standard Debye–Waller theory. In spite of the fact that the thermal average $\langle u^2(0)\rangle$ appears in the exponential of eq. (23) this is not at all a Debye–Waller factor (in fact the exponential in (23) in an increasing, rather than a decreasing function). The higher order virtual phonon transfers appear in the summation in eq. (25), and as we will show in the next section, they are totally negligible except for very high temperatures.

We find in this example drawn from second order perturbation theory that only the diagonal matrix element of the potential is needed, and this result will hold for all other orders as well. Diagonal matrix elements are often relatively simple in form and a number of useful general theorems can be demonstrated [10]. A convenient model which can be evaluated explicitly is to choose $U(z)$ as a Morse potential

$$U(z) = D(e^{-2\kappa z} - 2\,e^{-\kappa z}), \tag{26}$$

which implies that the attractive potential $A(z)$ of eq. (11) is the attractive exponential of (26). The diagonal matrix elements are

$$\begin{aligned} f(p_i,\,p_i) &= (p_i|e^{-2\kappa z}|p_i) \\ &= (4/\pi)\{p_i^2 + p_i d\ \mathrm{Im}[\psi(\tfrac{1}{2} - d + ip_i)]\}, \end{aligned} \tag{27}$$

where $d^2 = 2mD/\hbar^2\kappa^2$ and $\psi(z)$ is the di-gamma function of complex argument. In most instances, the imaginary part of the di-gamma function can be evaluated to sufficient accuracy by using a few terms of its asymptotic series

$$\psi(z) \sim \ln(z) - \frac{1}{2z} - \frac{1}{12z^2} + \frac{1}{120z^4} + \cdots. \tag{28}$$

Combining the Morse potential matrix elements of (27) with a Debye phonon spectrum and the lowest order development of the specular intensity in eq. (25) leads to excellent agreement with available experimental data at low surface temperatures [1,2].

3. Comparison of single and double phonon exchange

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 with the two phonon exchange terms which can be divided into three distinct types according to whether they come from second order, third order, or fourth order perturbation theory. As explained above, there are no other two phonon contributions from higher order in the perturbation expansion. What we are able to demonstrate is that the higher number phonon processes coming from second order in perturbation theory are negligible. The most important two phonon contribution comes from fourth order while that from third order, although not always negligible, is clearly less important.

We begin with the second order term in the perturbation expansion and its two phonon contribution is the $m = 2$ term of (24):

$$\left\langle F^{(2,2)}(p_i)\right\rangle = (-i\pi/16p_i)f^2(p_i, p_i)Q^2(0). \tag{29}$$

This term is the one illustrated in the diagram of fig. 1d.

Next we look at the third order term from the perturbation series. The two phonon contribution is obtained by inserting eq. (19) into eq. (17). With the approximation of replacing all $Q(\tau)$ by $Q(0)$ the integrals over τ in (17) become trivial, and retaining only the δ-function contribution to the q-integrals gives the result

$$\left\langle F^{(3,2)}(p_i)\right\rangle = -\tfrac{3}{64}(\pi/p_i)^2 f^3(p_i, p_i)Q^2(0). \tag{30}$$

Note that there is a phase difference between eqs. (29) and (30), and the essential difference in their magnitudes is the factor $f(p_i, p_i)/p_i$, the ratio of the diagonal matrix element to the perpendicular momentum. We note in passing that the approximation of replacing all displacement correlation operators $Q(\tau)$ by $Q(0)$ eliminates any distinction between the different diagrams of a given perturbation order. Thus this approximation is surely an overestimate since usually $Q^2(0) > Q^2(\tau)$, and furthermore it will overestimate the relative importance of many diagrams within a given order since it sets them all equal.

Moving on to fourth order in the perturbation series, we obtain the two phonon contribution from eq. (21) again by replacing all $Q(\tau)$ by $Q(0)$. The result is

$$\left\langle F^{(4,2)}(p_i)\right\rangle = i\tfrac{3}{512}(\pi/p_i)^3 f^4(p_i, p_i)Q^2(0). \tag{31}$$

Again there is a difference in phase with the other two phonon terms and the major variation in magnitude is the same factor of $f(p_i, p_i)/p_i$.

The relative importance of these three contributions is best expressed by comparing them to the single phonon contribution from eq. (24)

$$\left\langle F^{(2,1)}(p_i)\right\rangle = (-i\pi/8p_i)f^2(p_i, p_i)Q(0). \tag{32}$$

The three ratios then become, making use of eq. (26):

$$\frac{\langle F^{(2,2)}\rangle}{\langle F^{(2,1)}\rangle} = \frac{Q(0)}{2} = 12\frac{m}{M}\frac{\hbar^2\kappa^2}{2m}\frac{T}{k_B\Theta_D^2}, \tag{33}$$

$$\frac{\langle F^{(3,2)}\rangle}{\langle F^{(2,1)}\rangle} = -i\frac{3}{8}\frac{\pi}{p_i}f(p_i, p_i)Q(0) = -i9\frac{m}{M}\frac{\hbar^2\kappa^2}{2m}\frac{\pi f(p_i, p_i)}{p_i}\frac{T}{k_B\Theta_D^2}, \tag{34}$$

$$\frac{\langle F^{(4,2)}\rangle}{\langle F^{(2,1)}\rangle} = -i\frac{3}{64}\left(\frac{\pi}{p_i}\right)^2 f^2(p_i, p_i)Q(0) = \frac{9}{8}\frac{m}{M}\frac{\hbar^2\kappa^2}{2m}\left(\frac{\pi f(p_i, p_i)}{p_i}\right)^2\frac{T}{k_B\Theta_D^2}. \tag{35}$$

In order to write the above ratios explicitly in terms of the surface temperature, we have made use of the Debye model for the phonon spectrum as follows. From eq. (15) with $\rho(\omega) = 3\omega^2/\omega_D^2$ we have for sufficiently high temperatures such that $n(\omega) \to k_B T/\omega$,

$$Q(0) = \frac{12}{\omega_D^3}\frac{mk_B}{M}\int_{-\omega_D}^{\omega_D} d\omega = 24\frac{m}{M}\frac{T}{k'_B\Theta_D^2}, \tag{36}$$

where $k'_B = 2mk_B/\hbar^2\kappa^2$.

Representative values of $f(p_i, p_i)/p_i$, for typical He/metal systems are in the neighborhood of 10 or larger, therefore clearly the fourth order two phonon contribution is the largest while the contribution from second order is negligible. In the case of the scattering of H_2 from the surface the well depth is typically a factor of five larger and this can substantially increase the value of f/p_i, and consequently make the difference in the above two phonon contributions even larger. On the other hand, if the scattering potential is purely a repulsive exponential with no attractive well then $f(p_i, p_i) = 4p_i^2/\pi$ and $f/p_i = 4p_i/\pi$, which is usually larger than unity, but not necessarily large. The importance of the n-phonon contribution coming from the $2n$-order of perturbation theory has been recognized previously [11,12]. However, in some older calculations erroneous conclusions have been drawn about the relative importance of single to double phonon processes when the most important process was thought to be that coming from second order perturbation [13,14].

Another interesting observation is that the ratio for the second order two phonon contribution of eq. (33) is independent of the mass or velocity of the incoming particle, and depends only on the parameters of the crystal and the interaction potential.

The parameter involving the most important contribution, that of eq. (35) can be put into an interesting form upon recognizing that

$$\frac{\hbar^2\kappa^2}{2m}(\pi f(p_i, p_i)/p_i) \equiv 16\frac{\hbar^2(k_i^*)^2}{2m} = 16E^*, \tag{37}$$

where E^* can be considered as the energy associated with normal particle motion corrected for the well depth. Then eq. (35) becomes

$$\frac{\langle F^{(4,2)}(p_i)\rangle}{\langle F^{(2,1)}(p_i)\rangle} = -18\frac{m}{M}\frac{E^*}{k_B\Theta_D}\frac{T}{\Theta_D}. \tag{38}$$

Apart from the numerical factor, the right hand side of (38) is the well known Weare criterion [6] for the importance of two phonon terms. However, it appears here with a correction for the depth of the adsorption well coming from the appearance of the diagonal matrix element in eq. (37). For example, with the Morse potential matrix elements of eq. (27)

$$k_i^{*2} = (\kappa\pi f(p_i, p_i)/4p_i)^2 = k_{iz}^2\left\{1 + \left(\sqrt{D/E_i}\right)\mathrm{Im}\left[\psi\left(\tfrac{1}{2} - d + ip_i\right)\right]\right\}^2, \tag{39}$$

where E_i is the energy associated with normal motion far from the surface. This well depth correction is considerably stronger than the usual correction [1] of simply assuming that the well merely refracts the particles as expressed by

$$k_i^{*2} = k_{iz}^2(1 + D/E_i). \tag{40}$$

It is interesting to note that the Weare criterion is not simply a gauge for the importance of two phonon processes but essentially the same expression is obtained for all phonon contributions. For example, the specular intensity as expressed in eq. (10) shows that the ratio of single phonon scattering to the elastic intensity is given by the parameter

$$(-i\pi/4p_i)\langle F^{(2,1)}(p_i)\rangle \approx -\tfrac{1}{32}(\pi/p_i)^2 f^2(p_i, p_i)Q(0), \tag{41}$$

which, again apart from a small difference in numerical factor, is the same parameter as eqs. (35) or (37). Thus the Weare parameter is essentially a quantity which can be used to gauge when inelastic scattering of any type is important.

A significant and very interesting observation appears when we compare the single phonon transition matrix (32) directly to the most important two phonon contribution of eq. (31). The two are of opposite sign, which means that the two phonon contribution subtracts from the single phonon contribution consequently enhancing the elastic intensity. This result is not surprising as a similar property appears when the thermal attenuation is described by a Debye–Waller factor as in eq. (1) or (30).

$$I(T) = I_0\, e^{-2W(T)} \approx I_0\left[1 - 2W(T) + 2W^2(T) + \cdots\right]. \tag{42}$$

In the expansion, the term $-2W(T)$ is essentially due to single virtual phonon exchange and subtracts from the elastic contribution. The term in $W^2(T)$ corresponds to double virtual phonon exchange and it enhances the elastic intensity. Otherwise stated, the principal effect of double virtual phonon exchange is to subtract from the single phonon contribution to the scattering amplitude just as the single phonon subtracts from the elastic scattering amplitude. The net result is to increase the total elastic scattering intensity.

In another paper, we have presented numerous exact calculations for the one and two phonon contributions arising from all of the diagrams shown in fig. 1 for several different projectiles and surfaces [4]. These detailed calculations show that for the systems examined the observations made based on the very simple model presented here essentially hold true. In general, the two phonon processes from fourth order perturbation theory are the most important while those arising from second order are nearly always negligible. Those contributions coming from third order, while not always as small as would be indicated by the parameter of eq. (34), are usually considerably smaller than the fourth order term, the exceptions usually occurring for very low surface temperatures when multiphonon contributions are relatively small. The fact observed here that two phonon contributions tend to enhance the elastic scattering holds true also for the exact calculations except again sometimes at very low surface temperatures.

4. Multiphonon contributions

At this point it is worthwhile to extend the discussion of the preceding section with a few comments about multiple phonon contributions in general. As we will shortly see, it is not reasonable to stretch the simple model being developed in this paper very much further in terms of numbers of phonons exchanged, but several interesting points arise.

Within a given order of perturbation theory, we have seen from the preceding section that all multiphonon effects can be included by simply retaining all terms of the form $\exp[Q(0)]$ resulting from the phonon averaging, rather than expanding these exponentials to first non-vanishing order. However, we also saw that this led to negligible additional contributions in second order as shown in eq. (33) and, since the value of $Q(0)$ is relatively small, this conclusion holds true for all perturbation orders.

The most important contributions to multiphonon exchange come from higher orders in perturbation theory. We have seen in section 2 that the higher order terms can, in principle, be written down in a rather straightforward but lengthy manner. Our simple approximation allows these expressions to be evaluated in a closed form.

Since this evaluation is rather straightforward, again depending only on letting $Q(\tau) \to Q(0)$ and retaining only the δ-function contribution of the q-integrals, we present the final result:

$$\left\langle F^{(N,m)}(p_i)\right\rangle = (-i\pi/8p_i)^{N-1} f^N(p_i, p_i) P_m^N Q^m(0), \tag{43}$$

where N is the order of perturbation theory and m is the number of virtual phonons exchanged. The numerical factor P_m^N is derived in the appendix. Its value is

$$P_m^N = \sum_{k=0}^{N} \frac{1}{m!2^m} \binom{N}{k} (-1)^k (N-k)^m (N-k-1)^m. \tag{44}$$

P_m^N is the total number of distinct diagrams contributing if the number of phonons is the minimum for the given perturbation order, i.e. if N is even, $m = N/2$ and $P_m^{2m} = (2m-1)!!$; or if N is odd $m = (N+1)/2$ and $P_m^n = (m-1)(2m-1)!!$. Otherwise P_m^N is a number less than the total number of diagrams for more than the minimum number of phonons transferred at a given order, since in this case different classes of diagrams enter with different weights.

Not surprisingly, the perturbation series with each term given by eq. (43) diverges, even if we retain only the minimum number of phonon transfers at each order. The reason for this divergence is obvious, our simple model when applied to the case of minimum numbers of phonons transferred at each order, treats all diagrams within the order as equal. This number of diagrams diverges very strongly as the order of perturbation increases. The problem is in replacing $Q(\tau)$ by $Q(0)$. As shown for example in eq. (21) or (17), many of the diagrams for a given perturbation order will be associated with a displacement correlation operator evaluated at very large times and consequently their contribution will be very small. The question of the convergence properties of this phonon exchange series is an interesting point. The series of eq. (43) can be summed using a Borel transformation, in which case the thermal attenuation is expressed in terms of solutions of Schrödinger's equation with temperature dependent, effective potentials [7,15].

Two interesting results do come out of eq. (42), however. The first is that for a given multiphonon exchange it is the n-phonon contribution from the $2n$-order of perturbation theory which is most important. The second observation is that these most important contributions alternate in sign as the order of perturbation increases. This means that the elastic intensity alternately decreases and increases as each new even order of perturbation is added to the series. This is, in fact, a behavior similar to that seen in the Debye–Waller expansion of eq. (41). Both of the above observations are logical extensions of the two phonon results obtained in section 3 above. They also appear to be reasonably well verified by more sophisticated calculations [3].

5. Summation of bubble diagrams

There are certain classes of diagrams which can be summed to all orders. The most obvious of these classes are the bubble diagrams, that is to say those processes for which the corresponding diagrams have non-overlapping phonon lines. In the case of our simple model the summation can be carried out readily and the result provides a particularly interesting closed form expression for the elastic intensity as a function of temperature.

Let us begin by considering the bubble diagrams arising from even orders of perturbation theory. These are shown in fig. 1a, the first diagrams of fig. 1c and the corresponding diagrams for higher even orders. This means that for each even order of the perturbation expansion we are selecting only a single diagram. The first two terms in the series for the transition matrix are obtained by adding eq. (32) and one third of eq. (31).

$$\langle F(p_i)\rangle = (-i\pi/8p_i)f^2(p_i,p_i)Q(0) + (-i\pi/8p_i)^3 f^4(p_i,p_i)Q^2(0) + \cdots, \tag{45}$$

and the general expression can be written down from eq. (43) with $P_m^N = 1$ and $N = 2m$:

$$\begin{aligned}\langle F(p_i)\rangle &= \sum_{m=1}^{\infty} (-i\pi/8p_i)^{2m-1} f(p_i,p_i)^{2m} Q^m(0) \\ &= \sum_{m=1}^{\infty} (-i\pi/8p_i)^{m-1} \left[\left\langle F^{(2,1)}(p_i)\right\rangle\right]^m \\ &= \frac{\left\langle F^{(2,1)}(p_i)\right\rangle}{1 + (i\pi/8p_i)\left\langle F^{(2,1)}(p_i)\right\rangle},\end{aligned} \tag{46}$$

which can also be written in the form

$$\langle F(p_i)\rangle = \left\langle F^{(2,1)}(p_i)\right\rangle + (-i\pi/8p_i)\left\langle F^{(2,1)}(p_i)\right\rangle\langle F(p_i)\rangle, \tag{47}$$

where we have cast the result in terms of the lowest or second order contribution of eq. (32). For the specular intensity of eq. (10) this gives the particularly simple form

$$I_0 = \left(\frac{1 - (i\pi/8p_i)\left\langle F^{(2,1)}(p_i)\right\rangle}{1 + (i\pi/8p_i)\left\langle F^{(2,1)}(p_i)\right\rangle}\right)^2, \tag{48}$$

which, since $\langle F^{(2,1)}(p_i)\rangle$ is negative imaginary, is of the form of a Padé approximant in the temperature

$$I_0 = (1 - AT)^2/(1 + AT)^2. \tag{49}$$

There is another series of diagrams which can quite readily be summed and this is the series of touching bubbles, exemplified by the first diagram in fig. 1b and all corresponding touching bubbles in higher orders. This series can be developed similarly to the above by starting with the second order term of eq. (32) and adding to it the third order diagram which is given by one third of eq. (30), and so on for the higher orders. Alternatively, since there is only one diagram in each perturbation order in which all the bubbles are touching and this diagram involves a number of phonons equal to one less than the order, we can get the result by summing eq. (5) with $P_m^N = 1$ and $m = N - 1$ which leads to a series which can be expressed as

$$\langle F(p_i)\rangle = \langle F^{(2,1)}(p_i)\rangle - (-i\pi/8p_i) f(p_i, p_i) Q(0) \langle F(p_i)\rangle, \tag{50}$$

$$\langle F(p_i)\rangle = \frac{\langle F^{(2,1)}(p_i)\rangle}{1 + (i\pi/8p_i) Q(0) f(p_i, p_i)}. \tag{51}$$

The general case including all combinations of touching and separated bubbles can now readily be written down

$$\langle F(p_i)\rangle = \langle F^{(2,1)}(p_i)\rangle + (-i\pi/8p_i)\left[Q(0) f(p_i, p_i) + \langle F^{(2,1)}(p_i)\rangle\right]\langle F(p_i)\rangle, \tag{52}$$

with the solution

$$\langle F(p_i)\rangle = \frac{\langle F^{(2,1)}(p_i)\rangle}{1 + [i\pi/8p_i - 1/f(p_i, p_i)]\langle F^{(2,1)}(p_i)\rangle}, \tag{53}$$

and the resummed expression for the intensity (12) is of the form

$$I_0 = \left(\frac{1 + [-i\pi/8p_i - 1/f(p_i, p_i)]\langle F^{(2,1)}(p_i)\rangle}{1 + [i\pi/8p_i - 1/f(p_i, p_i)]\langle F^{(2,1)}(p_i)\rangle}\right)^2. \tag{54}$$

Although it is interesting to exhibit the expression in which the touching bubbles are also summed, it is clear from eqs. (51) or (50) that their contribution compared to the separated bubbles from the next higher order is small by the factor $p_i/f(p_i, p_i)$. Thus, in general, their contribution will not be important for the same reasons as discussed above for the two phonon contributions of eqs. (34) and (35). Basically, any diagram with a touching bubble has at least one vertex involving double phonon exchange, and such vertices are always small, in our model, being multiplied by a factor of $p_i/f(p_i, p_i)$ compared to a vertex having only one phonon line eminating from it.

It is of interest at this point to look at the above two resummation processes from a somewhat more formal viewpoint. The resummation of disconnected

bubbles, approximated in eqs. (45) through (47), can be written exactly in operator form as

$$\langle F\rangle = \langle F^{(2)}\rangle + \tfrac{1}{4}\langle F^{(2)}\rangle G_0\langle F\rangle, \tag{55}$$

where G_0 is the elastic or bare propagator Green function. The simple geometric series expression of eq. (46) or (47) is obtained by keeping only the δ-function part of G_0 and neglecting the principal part. However, in general (55) can be summed to convergence by simply iterating the equation [16].

The resummation equation for all bubbles, both connected and disconnected, can be presented by introducing a second Green function into (55):

$$\langle F\rangle = \langle F^{(2)}\rangle + \tfrac{1}{4}\langle F^{(2)}\rangle\{G_\omega + G_0\}\langle F\rangle. \tag{56}$$

The approximation to the above consistent with the intent of this paper is eq. (52). The Green function G_ω is the propagator which links together two vertices with a virtual phonon exchange. For example, it is precisely the propagation operator linking the two vertices shown graphically in fig. 1a. Just as in the case of eq. (55), eq. (56) can be summed to convergence by iteration. The only added nuance is that all terms linked by G_ω involve an additional summation over the phonon quantum numbers [3].

In a recent paper, Celli and Maradudin have developed an alternative approach to the problem of thermal attenuation [9]. Rather than obtaining the thermally averaged transition matrix as done here, they replace the many body problem by a single particle Schrödinger equation with a temperature dependent optical potential, with the imaginary part of this potential simulating the decrease of elastic intensity due to thermal attenuation. In principle, both approaches are equivalent. Celli and Maradudin present in their paper a resummation of phonon bubbles which is equivalent to eq. (48) above.

As an illustration of the usefulness of the expressions found here, we show in fig. 2 a comparison with the experimental data [17] for the thermal attenuation of H_2 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°. At these energies and incidence angles rotational excitation of the hydrogen molecules is observed to be a negligible effect [17]. At $\theta_i = 75.5°$ the energy associated with motion normal to the surface is well below the $j = 0 \to j = 2$ rotational threshold of 42.5 meV for H_2, and that at $\theta_i = 31°$. The normal energy $E_z = E_i \cos^2\theta_i \approx 56$ meV which is only slightly above threshold. There is a unitary loss in the experimental points due to scattering by other mechanisms such as disorder or impurities on the surface. To account for this the theoretical curves have been shifted downward by a multiplicative constant. The parameters appropriate to the Morse potential for this system are a well depth $D = 21.6$ meV and a range $\kappa = 1.0$ Å^{-1}, as determined by comparison of elastic diffraction calculations with experiment [16]. For each angle of incidence the theoretical curves show the single phonon contribution

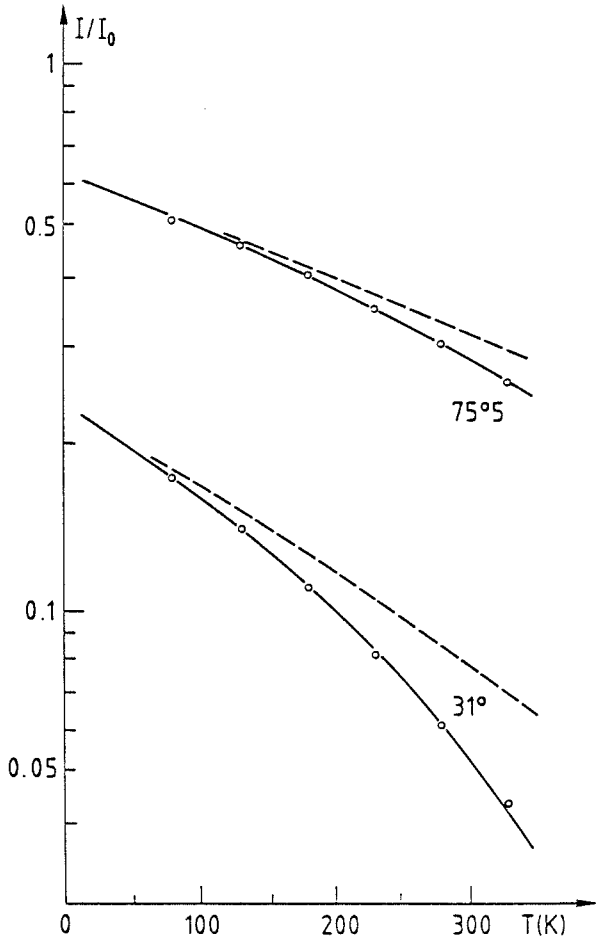

Fig. 2. Thermal attenuation of the specular beam for the H_2/Cu(100) system with energy 77.2 meV and two angles of incidence $\theta_i = 75.5°$ and $\theta_i = 31°$. The points are from experiment [7]. The solid curves are the single phonon result of eq. (32), and the dashed curves are the summation of bubbles expression of eq. (48). The Debye temperature for $\theta_i = 75.5°$ is 242 K and for $\theta_i = 31°$ is 217 K.

of eq. (32) and the summation expression of eq. (46). The single phonon curve matches the experimental points with a surface Debye temperature of 242 K for $\theta_i = 75.5°$ and 217 K for $\theta_i = 31°$. The summation of bubble diagrams increases the elastic scattering, implying that at high temperatures a single phonon calculation overestimates the total inelastic scattering. It is interesting to note that the summation expression (46) gives results that are relatively close to being linear, as would be expected from the Debye–Waller form, but they are still somewhat curved. If we presented the one plus two phonon contribution on fig. 2 the curve would lie above the resummation calculation at higher temperatures. This is equivalent to keeping only the first two terms in eq. (45) where it is clear that the two phonon correction subtracts from the single phonon amplitude and as discussed above in section 3. This leads to an

underestimate of the total inelastic scattering. Perhaps the most important conclusion to be drawn from these calculations is that they clearly delineate the domain where single phonon exchange is dominant and multiple phonon effects are negligible. Fig. 2 shows that for the $H_2/Cu(100)$ system at this incident energy two phonon exchange is not appreciable until the surface temperature is above 100 K, while at 200 K and particularly for more normal incidence there will be an important multiphonon background.

In a separate paper, we consider the question of infinite summation based on exact calculations of each term in the perturbation series [3]. In general, it is possible to sum all orders of touching and separated bubbles. However, it is no longer possible to obtain expressions in closed form but the results are expressed in terms of a simple integral equation which can be solved to convergence by iterative methods.

One can go much further with these summation techniques. If any group of lower order graphs is calculated (either exactly or approximately) this group can be considered as a sort of "generalized bubble". This "generalized bubble" can then be coupled with all other higher order diagrams in which it repeats, either touching or separated by a bare propagator line, and the summation operation applied. Within the simple approximation treated in this paper, the results look formally very similar to eq. (50) or (51) except the second order transition matrix $\langle F^{(2,1)}(p_i)\rangle$ is replaced by the corresponding expression for the "generalized bubble". This generalized summation procedure has been carried out using as the basis "generalized bubble" all of the diagrams in fig. 1 calculated exactly with the Morse potential [3].

6. Conclusions

In this paper, we have extended to processes involving multiple virtual phonon transfers, a straightforward and simple approximation to the general treatment of thermal attenuation in atom–surface scattering.

We address the question of two phonon exchange in manner which is applicable to both thermal attenuation and multiphonon inelastic effects. There are three types of double phonon processes in a flat surface model coming from the second, third and fourth order of the perturbation expansion, respectively. We find parameters expressing the relative importance of each of these contributions. The most important contribution is that from fourth order perturbation theory and the associated parameter is the same as that found by Weare [6] with the addition of our bound state correction on the energy associated with normal motion of the particle. The interesting distinction between these three processes appears to be the number of phonons associated with each interaction vertex. The fourth order contribution has only one phonon associated with each vertex, as in fig. 1c. The two phonon contribution

from second order, fig. 1d has two phonons associated with each vertex and we find these processes to be negligible in atom–surface scattering. The third order contribution has at least one vertex involving two phonon lines and we find its contribution is substantially less than the fourth order but not always negligible. The two phonon contribution tends to enhance the elastic scattering rather than to decrease it. This is due to the fact that the major effect is to subtract amplitude from the single phonon scattering which in turn increases the elastic term. An extension of the discussion to multiphonon contributions shows that, consistent with the results found for double phonons, the most important n-phonon scattering amplitude comes from $2n$-order in perturbation theory. This statement is based on the elastic transition amplitude. If we look at the inelastic intensity via the optical theorem, the equivalent statement would rather be that the most important n-phonon contribution to the total inelastic intensity comes from n-order perturbation theory. The important point being that multiphonon scattering amplitudes coming from lower orders of perturbation will be substantially less important.

As a further treatment of multiphonon effects, we consider the question of summation of all bubble diagrams in the perturbation series. This produces some useful closed form expressions for the elastic intensity as a function of surface temperature which are essentially in the form of Padé approximants. Furthermore, we discuss how any general group of lower order processes can be considered a part of an infinite series which can be readily summed to all orders.

The basic importance of this work is twofold. First, we have demonstrated that this simple approximation to the general formalism provides simple closed form expressions for the thermal attenuation which agree quite well with experiment. Secondly, in spite of its simplicity, this approximation provides a clear model for describing the salient features and complexities of thermal attenuation in atom–surface scattering. Particularly, it demonstrates the contrasts between a highly multiple scattering process such as this and the usual Debye–Waller factor applicable to neutron or X-ray diffraction. The Debye–Waller factor is usually obtained from a resummation of virtual phonon transfers in first order perturbation theory. We show here that the equivalent processes in atom–surface scattering, that is to say multiple virtual phonon transfers at a single vertex, are completely negligible. The major contributions here come from the lowest order phonon exchange in higher orders of perturbation theory. This major difference is reflected in the fact that we do not obtain an exponential behavior in surface temperature for the thermal attenuation, as opposed to the standard Debye–Waller plot. Several experiments which have been performed over a sufficiently large temperature range confirm this point [16–18].

The difference in behavior with the Debye–Waller expression becomes even more apparent in considerations of inelastic scattering. General calculations

show that the thermal attenuation of a single phonon inelastic peak intensity can be much stronger than that of an elastic peak [7]. This is in sharp contrast with Debye–Waller theory, where all intensities, elastic or inelastic, are multiplied by an attenuation factor of the same functional form.

Acknowledgements

The authors would like to thank Drs. J. Lapujoulade, B. Salanon, F. Fabre and D. Gorse, as well as A. Nourtier for many helpful discussions.

Appendix

We wish to derive the numerical factor of P_m^n appearing in eq. (42), where N is the order of perturbation theory and m is the number of phonons exchanged. From the development of the multiphonon expressions in section 2, it is clear that the Nth order of perturbation theory will involve the following time ordered correlation function

$$A_N = v_0^{-N}\left\langle \left(e^{u(t_1)} - v_0\right)\left(e^{u(t_2)} - v_0\right)\cdots\left(e^{u(t_N)} - v_0\right)\right\rangle$$

$$= v_0^{-N}\left\langle \prod_{j=1}^{N}\left(e^{u(t_j)} - v_0\right)\right\rangle, \tag{A.1}$$

where we recall that $v_0 = \langle e^u \rangle$. The result of the thermal averaging process can be expressed in terms of the pair correlation functions of eq. (15)

$$A_N = \sum_{k=0}^{N}\binom{N}{k}(-1)^k \exp\left(\sum_{j}^{(N-k)(N-k-1)/2} Q(t_j)\right) \tag{A.2}$$

where $\binom{N}{k}$ is a binomial coefficient.

Our major approximation in this paper consists in replacing $Q(t)$ by $Q(0)$, which leaves

$$A_N = \sum_{k=0}^{N}\binom{N}{k}(-1)^k \exp\left[(N-k)(N-k-1)Q(0)/2\right]. \tag{A.3}$$

We develop each order of perturbation theory in a series in numbers of phonons exchanged by expanding the exponential

$$A_N^m = \frac{Q^m(0)}{m!2^m}\sum_{k=0}^{N}\binom{N}{k}(-1)^k(N-k)^m(N-k-1)^m, \tag{A.4}$$

where m is now to be considered as the number of exchanged phonons. From the zero sum relation for the binomial coefficients

$$\sum_{k=0}^{N} \binom{N}{k} (-1)^k k^m = 0, \quad m \leqq N-1, \tag{A.5}$$

we see that

$$A_N^m = 0, \quad \text{if } m < N/2 \text{ for } N \text{ even} \tag{A.6}$$

and

$$A_N^m = 0, \quad \text{if } m < (N+1)/2 \text{ for } N \text{ odd}. \tag{A.7}$$

The result expressed in (A.6) and (A.7) holds true even if we do not approximate $Q(t_j)$ by $Q(0)$, i.e. it also applies if we expand the exponential of eq. (A.2) directly.

Eq. (A.4) gives directly the numerical factor to be associated with the N-order, m-phonon transition matrix of eq. (42)

$$P_m^N = \frac{1}{m!2^m} \sum_{k=0}^{N} \binom{N}{k} (-1)^k (N-k)^m (N-k-1)^m. \tag{A.8}$$

When m is the smallest number of phonons that can be exchanged for a given perturbation order ($m = N/2$ for N even or $m = (N+1)/2$ for N odd), eq. (A.8) gives the total number of distinct diagrams for m-phonon exchange in order N. If m is greater than the smallest number of phonons that can be exchanged for the given order N, then P_m^N is a number smaller than the total number of distinct (N,m) diagrams because certain diagrams are multiplied by a relative weighting factor. In particular

$$P_m^{2m} = (2m-1)!! \tag{A.9}$$

and

$$P_m^{2m-1} = (m-1)(2m-1)!!. \tag{A.10}$$

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