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SIMPLE APPROXIMATION TO THERMAL ATTENUATION IN LOW ENERGY ATOM-SURFACE SCATTERING: SINGLE PHONON PROCESSES

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We consider a simple approximation to the general theory of thermal attenuation of elastic peaks, as a function of surface temperature in low energy atom surface scattering. 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. We find a new form for the corrections due to the adsorption well of the interaction potential. We consider the damping coefficient arising because the incoming atom interacts simultaneously with several surface atoms, and we develop a frequency cut-off factor which arises naturally due to the fact that low frequency phonons are the most important in thermal attenuation.

1. Introduction

The thermal attenuation of elastic diffraction intensities in atom scattering from surfaces has long been a problem of experimental and theoretical interest [1]. The typical experiment is to measure the intensity of a given diffracted beam as a function of surface temperature with the incident energy and angle held fixed, and the results are usually presented on a logarithmic plot. The rate of attenuation is found to depend strongly on the momentum of the incident and diffracted beams. This effect is common to all diffraction processes from crystals such as neutron or X-ray diffraction and low energy electron diffraction where it is called the Debye–Waller effect after those who first correctly described it theoretically [2]. In these bulk diffraction applications, the inten-

sity of each diffraction beam is multiplied by a Debye–Waller factor, which in its simplest form is

$$\exp\left\{-\tfrac{1}{3}\langle\langle[(\mathbf{k}_{fi}-\mathbf{k}_{iz})\cdot\mathbf{u}_l]^2\rangle\rangle\right\}.\tag{1}$$

where $\mathbf{k}_{fi}$ and $\mathbf{k}_{iz}$ are the incident and diffracted momentum, respectively, $\mathbf{u}_l$ is the thermal displacement of a crystal atom and the angular brackets denote the thermal average. Since for a harmonic crystal the mean $\langle u_l^2\rangle$ is proportional to the temperature T for sufficiently elevated temperatures, a typical logarithmic Debye–Waller plot is linear in T. The attractive simplicity of this approach has led to the use of eq. (1) for describing attenuation in atom surface scattering in spite of lack of theoretical justification except in the extreme semiclassical limit [3,4], or for the case of a very hard surface giving rise to an instantaneous collision [5,6]. In fact, careful measurements of the thermal attenuation of light atoms or molecules from metal surfaces usually give curved logarithmic plots even after correcting for zero point motion [7]. Nevertheless, eq. (1) often gives reasonable results, at least qualitatively, but usually only after making corrections for the well depth of the attractive atom surface potential [8] or various correlation effects due to the interaction of the incoming atom with a region of the surface which includes several crystal cores [9].

The case of low energy atom surface scattering is far less simple than most bulk diffraction because the interaction energies and the interaction potentials are relatively soft. For example, in X-ray or neutron diffraction from bulk crystals the scattering intensities can be adequately calculated in first-order perturbation theory which gives rise to the Debye–Waller factor of eq. (1). To get satisfactory results for the diffraction of atoms, usually many orders of perturbation theory need to be retained [10].

The authors have developed elsewhere a general method for treating thermal attenuation in atom surface scattering which up to the present has been applied to flat surfaces and works quite well [11,12]. In this paper, we use this general theory as a starting point for developing a simple approximation for explaining the salient features of the Debye–Waller effect in atom surface scattering. This simple model is capable of reproducing quite well the general features observed by the experiment. It is sufficiently sophisticated to show how inelastic effects must be treated in atom–surface scattering, and it often leads to useful expressions which are not much more complicated than the Debye–Waller factor of eq. (1). A correction for the depth of the surface adsorption well is obtained which is much more realistic than a simple refraction effect. Various cut-off factors which have been introduced in the past to account for the importance of the exchange of low frequency phonons [13] or for the spatial extent of the atom–surface interaction [9,14] arise quite

naturally. Multiple-phonon processes are also readily included in this model, but a discussion of these as well as infinite summations of certain classes of graphs is left for a separate paper.

The organization of the paper is as follows. In section 2 we review briefly the general theory of thermal attenuation and in section 3 we draw out of this theory the simple model. Section 4 is a discussion of the well depth correction that arises from the simple theory. In section 5 we show how the damping factor associated with the spatial extent of the atom surface interaction arises quite naturally in this model. Section 6 is a discussion of how the matrix elements of the interaction give rise to a frequency cut-off implying that mainly low frequency modes are responsible for the thermal attenuation. This frequency cut-off shows that it is possible for the thermal attenuation for materials with rather similar values of surface mean square displacement to have radically different thermal attenuation characteristics. Finally, all of these effects exposed by our simple model are reviewed and discussed in the concluding section 7.

2. General development of thermal attenuation

In order to consider the effects of surface temperature on elastic scattering it is appropriate to begin by writing the intensity of a diffraction peak I_{fi}, where G is its associated reciprocal lattice vector, in terms of the transition matrix T_{fi},

$$I_{fi}=\langle\langle|\langle1|\,(2\pi i m/\hbar^2)\sqrt{k_{iz}k_{iz}}\,|T_{fi}|\,1\rangle|^2\rangle\rangle.\tag{2}$$

where k_{iz} and k_{fz} are the perpendicular momenta of the incident and diffracted beam, respectively, and the angular brackets represent the thermal average. For elastic scattering an important simplification is provided [3,15] by the fact that $\langle\langle|T_{fi}|^2\rangle\rangle$ can be replaced by the simpler expression $|\langle\langle T_{fi}\rangle\rangle|^2$, thus we need to calculate the thermal average of the integral equation for the T-matrix,

$$T_{fi}=v_{fi}+\sum_j v_{fj}(E_i-E_j+\mathcal{E}_j-\mathcal{E}_i+i\epsilon)^{-1}T_{ji}.\tag{3}$$

We work in the distorted wave formalism where the total potential is

$$V=U+v,\tag{4}$$

with U a coveniently chosen distorting potential for a rigid lattice. The quantity E_i or E_j is the particle energy and $\mathcal{E}_i$ or $\mathcal{E}_j$ is the crystal energy. The thermal average is most readily carried out by expressing the Green operator in integral form

$$G^+=(E_i-\mathcal{E}_i-H_0-H_1+i\epsilon)^{-1}$$
$$=(-i/\hbar)\int_0^\infty\exp[i(E_i-\mathcal{E}_i-H_0-H_1+i\epsilon)/\hbar]\,d\tau,\tag{5}$$

where H_c is the crystal Hamiltonian and H_0 is that of the particle

$$H_0 = (-\hbar^2/2m)\nabla^2 + U.$$ (6)

Then, in terms of the particle evolution operator $P(t) = \exp[i(E_i - H_0 + i\epsilon)t/\hbar]$. The thermally averaged transition operator can be expressed as

$$\langle\langle T\rangle\rangle = \langle\langle v\rangle\rangle - (i/\hbar)\int_0^\infty dt\,\langle\langle v(t)P(t)T\rangle\rangle.$$ (7)

with $v(t)$ the potential expressed in the interaction picture

$$v(t) = \exp(iH_c t/\hbar)v\exp(-iH_c t/\hbar).$$ (8)

Iteration of eq. (7) leads to the perturbation expansion in time ordered operators

$$\langle\langle T\rangle\rangle = \langle\langle v\rangle\rangle + (-i/\hbar)\int_0^\infty dt\,\langle\langle v(t)P(t)v(0)\rangle\rangle + (-i/\hbar)^2\int_0^\infty dt_2$$
$$\times\int_0^\infty dt_1\,\langle\langle v(t_1+t_2)P(t_2)v(t_1)P(t_1)v(0)\rangle\rangle + \cdots.$$ (9)

The iterative series of eq. (9) is particularly adapted to a potential which is the pairwise sum of interactions between the incoming atom and those of the crystal, and we discuss this point further in section 5 where such considerations introduce a damping cut-off factor. For the present we consider a potential with a thermally corrugated exponential repulsion and a static attractive part.

$$v(z, u') = D\{\exp[-2\kappa(z - u')]/v_0 - A(z)\}.$$ (10)

where u' is the normal component of the thermal potential displacement, $v_0 = \exp[2\kappa^2\langle(u')^2\rangle)]$ is the thermal average of $\exp(2\kappa u')$ and $A(z)$ is the attractive part. The choice of a repulsive part of exponential form is justified by the fact that the repulsive interaction is, to a very good approximation, proportional to the electronic charge density outside the surface [16].

With the potential of eq. (10), all thermal averages to all orders can be readily carried out in the harmonic approximation. It is convenient to choose

$$U = \langle\langle V(z, u')\rangle\rangle$$ (11)

as this will cause the first-order term of eq. (9) to vanish. At this point it is useful to convert to dimensionless variables by scaling with the range parameter κ of the potential. The specular intensity, in terms of the dimensionless transition matrix $t_{fi}(p_z)$ is

$$I_0 = |1 - (i\pi/4p_z)\langle\langle t\rangle\rangle|^2.$$ (12)

where $p_z = k_{iz}/\kappa$ and $t'(p_z) = (8m/\hbar^2\kappa^2)t_{fi}$. Using the potential of eq. (10)

with the choice for U of eq. (11) gives for the leading, or second-order term of the perturbation series (9), after converting to dimensionless variables

$$\langle F(p_z)\rangle = (1/4!)\int_0^\infty dq\int_{-\infty}^\infty d\tau\,\exp[i(p_z^2 - q^2 + i\epsilon)\tau]$$
$$\times\langle\langle(e^{u(\tau)} - v_0)(e^{u(0)} - v_0)\rangle\rangle f^2(p_z, q)/v_0^2$$
$$i(1/4\pi^2 i)\sum_n\int_0^\infty d\tau$$
$$\times\exp[i(p_z^2 + e_n + i\epsilon)\tau]\langle\langle(e^{u(\tau)} - v_0)(e^{u(0)} - v_0)\rangle\rangle f^2(p_z, n)/v_0^2.$$ (13)

where $u(\tau) = \kappa u'(\tau)$ and e_n are the bound state energies of U, $f(p_z, q)$ and $f(p_z, n)$ are matrix elements of the distorted potential $e^{-2\kappa z}$ taken with respect to states of the perturbing 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

$$\langle\langle(e^{u(\tau)} - v_0)(e^{u(0)} - v_0)\rangle\rangle/v_0^2 = e^{Q(\tau)} - 1.$$ (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 $n(\omega)$

$$Q(\tau) = 4\langle\langle u(\tau)u(0)\rangle\rangle = 4\frac{m}{M}\int_0^\infty d\omega\frac{\rho(\omega)n(\omega)}{\omega}e^{i\omega\tau}.$$ (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 the transition matrix

$$\langle F(p_z)\rangle = \frac{m}{M}\int_0^\infty dq\int_{-\infty}^\infty d\omega\frac{\rho(\omega)}{\omega}f^2(p_z, q)\frac{n(\omega)}{p_z^2 - q^2 + \omega + i\epsilon}$$
$$+ \frac{m}{\pi^2 M}\sum_n\int_{-\infty}^\infty d\omega\frac{\rho(\omega)}{\omega}f^2(p_z, n)\frac{n(\omega)}{p_z^2 + e_n + \omega + i\epsilon}$$ (16)

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. (10), including all phonon assisted bound state resonances. Higher-order terms in the perturbation series contribute to multiphonon processes and these are considered elsewhere [17]. Eq. (16) has been used to explain the thermal attenuation of the specular beam of He or H$_2$ scattering
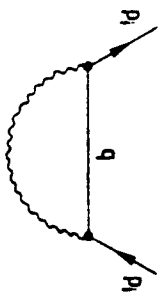
Fig 1. Diagrams showing the single virtual phonon exchange process which comes from the second order of perturbation theory.

from smooth Cu surfaces and excellent agreement with experiment has been obtained [11]. As a useful visual aid, the phonon exchange process described by eq. (14) can be prevented as a Feynman-type diagram, the single bubble as shown in fig. 1.

3. Simple approximation

We now outline a 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. These approximations consist of the following:

(1) Replace the time dependent phonon correlation functions by an effective mean square amplitude, i.e. in the simplest case

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

(2) In integrals over intermediate perpendicular momenta, retain only the imaginary or δ-function, energy conserving contribution.
There are also two further approximations which are less stringent but quite useful:

(3) Ignore the contribution of bound states in the intermediate sums.

(4) Approximate the spectral density $\rho(\omega)$ by that appropriate to a Debye phonon model. (This is certainly not a necessary approximation but is very useful in obtaining numerical estimates when no better $\rho(\omega)$ is available.)

Of these approximations (1) is the most severe and least justifiable. However, comparison with our detailed calculations [11,12,18] indicate that it works rather well. We note by comparison that only $\langle u^2(0)\rangle$ appears in the Debye–Waller factor of eq. (1). Approximations (2) and (3) are both well justified by our more detailed calculations. The neglect of off-energy-shell contributions in the sum over intermediate state is justified by the fact that they contribute less than 20% of the total in all systems we have investigated. These contributions are not always negligible in atom–surface scattering, in fact for elastic scattering from highly corrugated surfaces they can be dominant It appears here that in single phonon regime the thermal roughening is

sufficiently small that off-shell contributions are not large. A similar argument appears to hold for the intermediate sum contribution from the bound states. They are negligible except for grazing angles, for example even at $\theta_i = 75°$ they contribute only a few percent to the total intensity. This again seems to be due to the smallness of the thermal roughening.

These approximations are readily applied to eq. (16). Neglecting the term involving bound states and retaining only the imaginary contribution from the continuum states gives

$$\langle F(p_i)\rangle = -\frac{i\pi}{2}\frac{m}{M}\int_{-\infty}^{\infty} d\omega\,\frac{\rho(\omega)}{\omega}\frac{f^2(p_i, p)}{p}\,n(\omega),\qquad(17)$$

with $p^2 = p_i^2 + \omega$.
We can write this in the form

$$\langle F(p_i)\rangle = -i\pi|f^2(p_i, p)/8p_i]Q_{eff}\qquad(18)$$

where the effective mean square displacement is

$$Q_{eff} = 4(m/M)\int_{\infty}^{\infty} d\omega[\rho(\omega)/\omega]\Lambda(\omega),\qquad(19)$$

with

$$\Lambda(\omega) = p_i f^2(p_i, p)/p f^2(p_i, p_i).$$

The simplest choice for Q_{eff} is to set $\Lambda(\omega) = 1$ which from eq. (15) is equivalent to

$$Q_{eff} = Q(0) = 4\langle u^2(0)\rangle.$$

An alternative approach is to replace $Q(\tau)$ by $Q(0)$ in eq. (14) and after insertion into (13) and neglecting bound states one obtains

$$\langle F(p_i)\rangle = \tfrac{1}{2}(e^{Q(0)} - 1)\int_0^{\infty} dq\,\frac{f^2(p_i, q)}{p_i^2 - q^2 + i\varepsilon}.\qquad(20)\qquad(21)$$

Retaining only the imaginary contribution to the remaining integral leaves us with

$$\langle F_R(p_i)\rangle = -\frac{i\pi}{\kappa p_i}f^2(p_i, p)(e^{Q(0)} - 1),\qquad(22)$$

which, upon expanding the exponential, is equivalent to (18) with $Q_{eff} = Q(0)$. This expression involves only the diagonal matrix elements of the potential and the temperature dependence is entirely in the factor $Q(0)$.

If we let $\rho(\omega)$ be a Debye spectral density

$$\rho(\omega) = 3\omega^2/\omega_D^3,\qquad(23)$$

and using the fact that for sufficiently high temperatures

$$n(\omega) \to k_B T/\omega,\qquad(24)$$

we have from eq. (15)

$$Q(0) = 4\frac{m}{M}\int_{\omega_D}^{\omega_D}\frac{d\omega}{\omega}\frac{3\omega^2}{\omega_D^3}\frac{k_B'T}{\omega} = 24\frac{m}{M}\frac{T}{k_B'\theta_D^2},\qquad(25)$$

where θ_D is the Debye temperature and k_B' is related to Boltzmann's constant k_B by $k_B' = 2mk_B/\hbar^2$.

In spite of the fact that the mean square displacement $\langle u^2(0)\rangle$ is found in the exponential of eq. (21) this is not at all of the form of a Debye Waller factor as in eq. (1). In fact, to compare with previous results involving single phonon transfer we expand the exponential and insert (22) into expression (12) for the specular intensity to obtain

$$I_0 = \left[1 - \frac{1}{2}\left(\frac{\pi}{4}\right)^2\left|\frac{f(p_i,p_i,p_i)}{p_i}\right|^2\left|\langle u^2(0)\rangle\right|^2\right].\qquad(26)$$

In order to see how well this approximation works we proceed to make some comparisons with previous theoretical results as well as with experiment. In previous work [11,12] the authors have found it convenient to approximate the distorted potential by a Morse potential

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

which implies that the attractive potential of $A(z)$ of eq. (10) is simply the attractive exponential in (27). The diagonal matrix elements of the perturbing potential are then rather simple

$$f(p_i,p_i) = (p_i|e^{-2\kappa z}|p_i) = (4/\pi)|p_i^2 + p_i d \, \operatorname{Im}\psi(\tfrac{1}{2} - d + ip_i)|.\qquad(28)$$

where $d^2 = 2mD/\hbar^2\kappa^2$ and $\psi(z)$ is the di-gamma function of complex argument.

Some care must be taken in evaluating the mean square surface displacement $\langle u^2(0)\rangle$. This should not be the mean square displacement of a single surface atom, but instead the weighted mean square displacement averaged over the surface atoms simultaneously "seen" by the incoming projectile atom. In previous work this number of crystal atoms is best taken to be four for close-packed metal surfaces (more exactly, the spectral density is taken to be the average spectral density of four neighboring crystal atoms). The effect of this averaging process on $\langle u^2(0)\rangle$ is, to a very good approximation, to multiply it by a factor $1/4$. An equivalent statement is that $\langle u^2(0)\rangle$ is the effective mean square displacement which is approximately $1/4$ that of a single surface atom. The need for this spatial averaging is discussed further in section 5 where we consider the damping factor that arises when we assume that the potential is a pairwise sum of atomic interactions.

A further factor of $1/4$ arises because of the use of the Morse potential. The static attractive part of the Morse potential enhances the isopotential

corrugation of the total potential. That is to say, a potential of the form of eq. (10) with only the repulsive part thermally corrugated will find its constant energy corrugation enhanced with respect to the actual corrugation amplitude of the function u'. For the Morse potential this enhancement is a factor of two at low energies, decreasing slowly to unity at large energies. To account for this enhancement we multiply $\langle u^2(0)\rangle$ by another factor $\alpha = 1/4$ as was done in previous work [11,12]. Now, using eq. (26) for the specular intensity and the above discussed Debye phonon model we can compare with the experimental data. This is done in fig. 2 for the case of He scattering from the close-packed Cu(100) face. The parameters for the Morse potential are $D = 6.35$ meV and
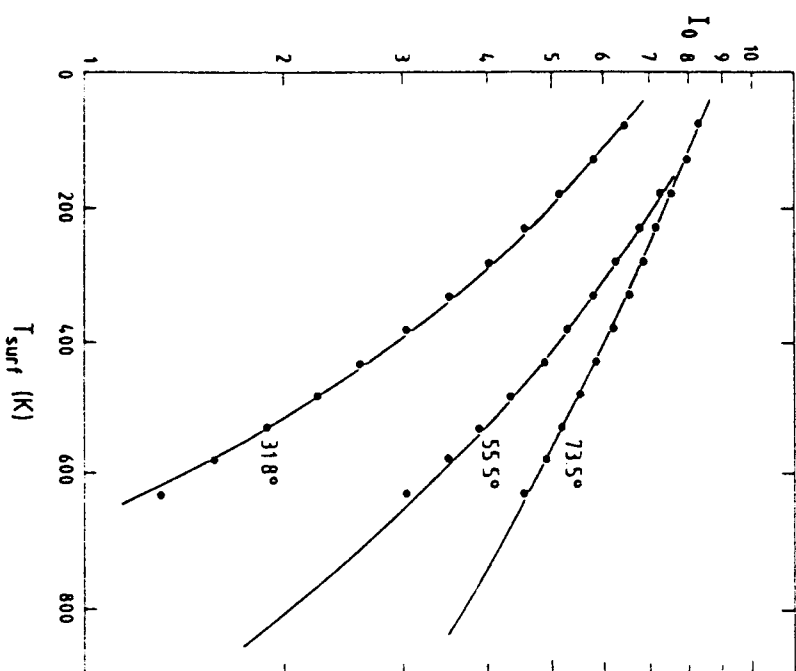

Fig. 2. Thermal attenuation of the specular beam for the He/Cu(100) system with incident energy 21 meV and three different angles of incidence. The points are from experiment [7] and the curves are the single phonon calculation of eq. (27). The surface Debye temperature for $\theta_i = 73.5°$ is 276 K, for $\theta_i = 55.5°$ is 240 K and for $\theta_i = 31.8°$ is 220 K.

Table 1
Values of the diagonal matrix element $f(p_i, p_i)$ and the Debye temperature for the system He/Cu(100) at the two energies $E_i = 21$ and 63 meV, and for several incident angles $θ_i$

E_i (meV)	$θ_i$ (deg)	P_i	$f(p_i, p_i)$	$θ_D$ (K)
21	73.5	1.73	23	276
21	55	3.45	49	240
21	31.8	5.18	80	220
63	71.6	3.31	47	255
63	19	9.91	204	202

$κ = 1.05$ Å^{-1}, these values being fixed by elastic scattering data from stepped Cu surfaces [19]. The values of matrix elements and Debye temperatures are given in table 1. For all of the three difference incident angles excellent agreement with the experimental points is obtained. It is found that the Debye temperature (the only variable parameter) must change somewhat with incident angle but the values which are obtained, $200 < θ_D < 280$ K are within the expected range of the surface 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. The Debye temperatures and other parameters for two different angles of incidence at this higher energy are also shown in table 1.

4. Well depth correction

The effect of the attractive adsorption well in the potential has long been recognized as sufficiently important to introduce a substantial correction in the thermal attenuation. This has usually been done as a "refraction" effect, by simply adding in the depth of the well to the energy associated with the normal motion of the incident particle, and is often referred to as the Beeby correction [8]. The Debye Waller factor of eq. (1) applied to the specular beam of a flat surface gives

$$I_0 = \exp[-2W(T)] = \exp[-(\Delta k_z)^2 \langle u^2(0)\rangle].$$ (29)

where $\Delta k_z = 2k_{iz}$. The Beeby correction is to replace k_{iz} by an effective value

$$k_{iz} \rightarrow k_{iz}^* = k_{iz}\sqrt{1 + (D/E)}.$$ (30)

where D is the well depth and E is the energy associated with normal motion

$$E = \hbar^2 k_{iz}^2 / 2m.$$ (31)

Our simple approximation as expressed in eq. (26) provides a more sophisticated and easily justifiable well depth correction. We can write eq. (26)

in the Debye Waller form $\exp[-2W(T)]$ by performing the first-order cumulant expansion

$$I_0 = \left[1 - \frac{1}{2}\left(\frac{\pi}{4}\right)^2 \left(\frac{f(p_i, p_i)}{p_i}\right)^2 κ^2 \langle u^2(0)\rangle\right]^2$$

$$= 1 - \left(\frac{\pi}{4}\right)^2 \left(\frac{f(p_i, p_i)}{p_i}\right)^2 κ^2 \langle u^2(0)\rangle + \dots$$ (32)

and make the identification

$$W(T) = \frac{1}{2}\left(\frac{\pi}{4}\right)^2 \left(\frac{f(p_i, p_i)}{p_i}\right)^2 κ^2 \langle u^2(0)\rangle.$$ (33)

Comparison with the Debye–Waller expression of eq. (30) shows that our effective perpendicular momentum is

$$k_{iz}^{*2} = \left(\frac{\pi}{4}\right)^2 \left(\frac{f(p_i, p_i)}{p_i}\right)^2 κ^2$$ (34)

or from eq. (28)

$$k_{iz}^* = k_{iz}\left[1 + \sqrt{D/E}\; \mathrm{Im}\,\psi(\tfrac{1}{2} - d + i p_i)\right].$$ (35)

This well depth correction is considerably stronger than the Beeby correction of eq. (30) and is in better agreement with most experimental observations, i.e. use of the Beeby correction almost always leads to an overestimate of the depth of the adsorption well.

One thing that appears a bit forbidding in our correction expression (35) is the presence of the di-gamma function $\psi(\tfrac{1}{2} - d + i p_i)$. This poses no problem at all in practice because for practically all systems $d > 1$ and $p_i > 1$ and we can make use of a rapidly converging asymptotic series [20]:

$$\psi(z) \sim \ln(z) - \frac{1}{2z} - \frac{1}{12z^2} + \frac{1}{120z^4} - \frac{1}{252z^6} + \dots$$ (36)

Usually two or three terms will give several decimals of precision and often just the logarithm term will suffice as a good estimate. Since $\tfrac{1}{2} - d$ is negative for all well depths having at least one bound level, eq. (36) shows that for most systems we will have

$$\pi/2 \le \mathrm{Im}\,\psi(\tfrac{1}{2} - d + i p_i) \le \pi,$$ (37)

with the upper limit approached for small p_i and the lower limit for large p_i.

Of course, the well depth correction obtained here is based on the Morse potential but one would not expect the results to change drastically if the attractive part of the potential is replaced by a more realistic $-1/z^2$ form, although the dependence of D might be somewhat weaker.

However, there is one very interesting effect that occurs with the well depth correction, namely that it completely disappears if both the attractive and repulsive parts of the Morse potential vibrate in phase with each other. To see this we consider a potential of the form

$$V(z, u') = D(\exp[-2\kappa(z - u')]/v_0 - 2\exp[-\kappa(z - u')]/v_0),$$ (38)

with $v_0 = \langle\langle\exp(\kappa u')\rangle\rangle = v_0^{1/4}$. If we now carry through the same simple approximation we will obtain exactly the same form for the specular intensity as in eq. (26) except that the perpendicular matrix element will be of the form

$$f(p_i, p_s) = (p_s|e^{-2\kappa z}|p_i) - (p_s|e^{-\kappa z}|p_i) = (4/\pi)p_s^2.$$ (39)

The part of the matrix element coming from the attractive part of the potential exactly cancels the term containing the di-gamma function in eq. (28) and the net result is to leave us with no well depth correction at all. Incidentally, it is of interest to note that the matrix element of eq. (39) above is exactly the same result which would be obtained if there were no attractive part at all, i.e. if the potential consists only of a vibrating exponential repulsive part. This is, in fact, a special case of a general result valid for any one dimensional potential. It can be shown that for a appropriate to the surface scattering problem. It can be shown that for a distorted potential $U(z)$ of the general form of eq. (11) the diagonal matrix elements of dU/dz taken with respect to the eigenstates of U are the same as eq. (39) [21].

The results expressed in the above paragraph lead to a very significant observation on the attractive part of the potential. If the attractive part vibrates with the repulsive part, eq. (39) implies that there would be no well depth correction associated with the thermal attenuation. The fact that analyses of the experimental data from essentially all surfaces have needed to include a well depth correction [1,7] leads to the conclusion that the attractive part of the potential does not vibrate strongly. In general, one does not expect the potential to the attractive potential to vibrate very much in comparison long-range part of the attractive potential to vibrate very much in comparison with the repulsive part. This is because the repulsive potential is predominantly the result of an interaction with a small number of surface atoms, whereas the long-range $1/z^3$ term arises from the pairwise sum of the polarization interactions with all the crystal atoms including those in the bulk. However, shorter-ranged corrections to the attractive potential may vibrate more or less strongly and the above observation would seem to indicate that this would tend to reduce somewhat the actual well depth correction.

5. Damping coefficient

The simple model presented in this paper affords an illustrative way to introduce the damping factor associated with the inelastic atom surface

interaction that arises because the incoming beam interacts simultaneously with more than one surface atom. This effect has been discussed previously by the authors and others [5,9] and has recently been put on a more rigorous foundation by Celli et al. [14] using a pairwise summation of atomic potentials. The essence of their result is that the probability of single phonon exchange is multiplied by a damping factor $\exp(-Q^2\bar{z}/2\kappa)$ where Q is the momentum transferred by the phonon, $\bar{z}$ is the classical turning point of the incoming atom and κ is the range parameter of the atom–surface potential as in eq. (10).

This result arises from the assumption that the repulsive potential can be written as a sum of pairwise exponentially decaying atomic interactions between the incoming atom and those of the crystal. For simplicity, consider a sum of Yukawa potentials (other forms can be obtained by appropriate differentiation with respect to the range parameter κ)

$$V(z, R) = \sum_i \frac{\exp(-2\kappa|r - r_i|)}{|r - r_i|} = C\sum_Q \exp(-\beta_Q z)\exp(iQ \cdot R),$$ (40)

where C is a constant [14] and $\beta_Q = \sqrt{4\kappa^2 + Q^2}$. Expanding β_Q to first order gives

$$V(z, R) = C\exp(-2\kappa z)\sum_Q \exp(iQ \cdot R)\exp(-Q^2z/4\kappa).$$ (41)

The damping coefficient of ref. [14] is recovered by approximating z by the classical turning point $\bar{z}$ in the factor $\exp(-Q^2z/4\kappa)$.

$$V(z, R) = C\exp(-2\kappa z)\sum_Q \exp(iQ \cdot R)\exp(-Q^2\bar{z}/4\kappa).$$ (42)

Eq. (42) is to be regarded as the static repulsive part of the interaction potential of eq. (10) arising from a pairwise summation. If we now assume phonons for which the momentum transfer is negligible we can still retain the damping coefficient by replacing Q^2 by ω^2/c^2 where c is a representative phonon wave velocity. This implies that the perpendicular matrix elements are of the form

$$(p_s|V'|q) \approx (p_s|\exp(-2\kappa z)|q)\exp(-\omega^2\bar{z}/4\kappa^2)$$

$$= f(p_s, q)\exp(-\omega^2\bar{z}/4\kappa^2),$$ (43)

where $f(p_s, q)$ is the same matrix element defined after eq. (13), and with ω being the dimensionless frequency of section 2 we must have $\bar{z} = 2mc/\hbar^2\kappa^2$.

If we now go back and develop the general formalism for the thermal attenuation as in section 2 above using the potential of eq. (42) we would

obtain, for the first non-vanishing contribution to the transition matrix, eq. (16) with $f(p_i, q)$ replaced by eq. (43):

$$\langle F(p_i) \rangle = \frac{m}{M} \frac{1}{\rho_i} \int_{\infty} dq \int_{\infty}^{\infty} d\omega \frac{\rho(\omega)}{\omega} n(\omega) \frac{f^2(p_i, q) \exp(-\omega^2 \bar{z}/2 c^2 \kappa)}{p_i^2 - q^2 + \omega + i\epsilon},$$ (44)

where we have ignored the bound state contribution. We now apply the central approximation developed in this paper which is equivalent to setting $\omega = 0$ in the denominator of (44) and retaining only the δ-function contribution to the integral over q:

$$\langle F(p_i) \rangle = -\frac{i\pi}{8\rho_i} f^2(p_i, p_i) Q_{eff}(0).$$ (45)

where

$$Q_{eff}(0) = 4\langle u^2(0) \rangle_{eff} = 4 \frac{m}{M} \int_{\infty}^{\infty} d\omega \frac{\rho(\omega)}{\omega} n(\omega) \exp(-\omega^2 \bar{z}/2 c^2 \kappa).$$ (46)

To make a numerical estimate of the size of $\langle u^2(0) \rangle_{eff}$ we can approximate $\rho(\omega)$ by a Debye spectral density as in eq. (23). The integrals in the high temperature limit are trivial and comparing to $\langle u^2(0) \rangle$ of eq. (25) we have

$$\frac{Q(0)_{eff}}{Q(0)} = \frac{\langle u^2(0) \rangle_{eff}}{\langle u^2(0) \rangle} = \left(\frac{\pi c^2 \kappa}{2 \omega_D^2 \bar{z}} \right)^{1/2}.$$ (47)

For a typical metal and a helium beam we would have the Debye frequency approximately 7×10^{12} Hz, $\bar{z} \approx 3$ Å, $\kappa \approx 1$ Å^{-1}, and $c \approx 1000$ m/s which would give a value of about 0.2 to eq. (47). This compares quite favorably with the value of ~ 0.25 obtained by considering $\langle u^2(0) \rangle_{eff}$ to be the average over four surface atoms as discussed above in section 3.

The damping factor in eqs. (43) and (44) is a cut-off in Q-space but this implies that it is also a damping factor in real space since the Fourier transform of the Gaussian form is also a Gaussian. Consequently, this damping factor is essentially the same as the so-called "Armand effect" in which one averages the thermal displacement over several surface atoms. In other words, it accounts for the fact that the incoming atom actually "sees" several crystal atoms in the region of its classical turning point and the relative vibrations of these crystal atoms tend to cancel leaving a net effective surface vibration which is smaller than that of any individual crystal atom.

We note in passing that this damping factor will be essentially the same for atoms or light molecules scattered by all noble metals. This is readily seen

from the fact that the relevant parameter is $\omega_D^2 \bar{z}/2 c^2 \kappa$. The range parameter κ is, for a given projectile, essentially the same for all metals and the same can be said for $\bar{z}$. The ratio ω_D/c^2 also remains essentially the same since the sound velocity scales approximately with the maximum crystal frequency.

6. Frequency cut-off correction

In addition to the damping factor of the above section there is also a frequency cut-off correction which arises because the relevant matrix elements decrease rapidly in magnitude with the frequency of the phonon exchanged. This effect has been introduced previously to explain the decrease in inelastic intensity with increasing phonon frequency [13] for the exchange of Rayleigh mode quanta.

This frequency cut-off can be of real importance in the thermal attenuation of elastic diffraction beams. For example, in the noble metals the mean square displacement $\langle u^2(0) \rangle$ remains relatively constant as one goes from Cu to Ag to Au. The effect of the increased spectral density $\rho(\omega)$ is cancelled by the decrease in the mass ratio m/M and this would imply that the thermal attenuation would vary very little. However, because Au and Ag have a larger proportion of low frequency phonons in their spectral density relative to Cu, the frequency cut-off developed here gives rise to the prediction that there will be substantially increased thermal attenuation as we progress from Cu to Ag to Au, regardless of the projectile atom.

The starting point is the expression for the thermally averaged transition matrix of eq. (17), which is written in terms of the effective mean square surface displacement of eq. (19). The frequency cut-off factor is quite simply the factor $\Lambda(\omega)$ appearing in eq. (19)

$$f^2(p_i, p_i)/\rho = f^2(p_i, p_i) \Lambda(\omega)/\rho_i.$$ (48)

For the Morse potential a good approximation to $\Lambda(\omega)$ can be obtained readily. The Morse matrix elements are given by

$$f(p, q) = (p | \exp(-2\kappa z) | q) = \frac{\sqrt{2p} \sinh(2\pi p) 2q \sinh(2\pi q)}{\sinh[\pi(p+q)] \sinh[\pi(p-q)]}$$

$$\times \left\{ (p^2 - q^2 + 2d) \left| \frac{\Gamma(\tfrac{1}{2} - d + iq)}{\Gamma(\tfrac{1}{2} - d + ip)} \right| \right.$$

$$\left. - (p^2 - q^2 - 2d) \left| \frac{\Gamma(\tfrac{1}{2} - d + ip)}{\Gamma(\tfrac{1}{2} - d + iq)} \right| \right\}.$$ (49)

where $\Gamma(z)$ is the gamma function of complex argument and the diagonal matrix elements are given by eq. (28). To first order in the parameter $\Omega = \pi\omega/2\rho_t$, we have

$$\Lambda(\omega) = \left(\frac{\pi\omega/2\rho_t}{\sinh(\pi\omega/2\rho_t)}\right)^2 (1 + \theta(\Omega) + \dots).$$ (50)

Under most circumstances the parameter Ω will be small even in the range where $\pi\omega/2\rho_t$ is fairly large. We note in passing that eq. (50) is also recovered for the case in which the potential is a purely repulsive exponential with no attractive part, i.e. the exponential repulsive potential.

The effective mean square displacement of eq. (19) now appears as

$$Q(0)_{eff} = 4\langle u^2(0)\rangle_{eff} = \frac{m}{M}\int_{-\infty}^{\infty} d\omega\, \frac{\rho(\omega)}{\omega} n(\omega) \frac{\pi\omega/2\rho_t}{\sinh(\pi\omega/2\rho_t)}$$
$$\times \exp(-\omega^2 z/2z^2\kappa).$$ (51)

where we have included the damping factor of the preceding section. To compare with the Debye mean square displacement of eq. (25)

$$Q(0) = 24\frac{m}{M}\frac{T}{k_r\theta_D^2}.$$ (52)

we write eq. (51) at large temperatures as

$$Q_{eff}(0) = 48\frac{m}{M}\frac{k_r T}{\omega_D}\frac{\rho_t}{\pi}\int_x^{\infty} dx\, \frac{x^2}{\sinh^2 x}\exp(-x^2/a^2).$$ (53)

where $a^2 = 2\rho_t^2 z/(\pi z^2\kappa)$.

In table 2 we show a comparison of $Q(0)$ and $Q(0)_{eff}$ for the three noble metals: copper, silver and gold. For a given light projectile such as He or H$_2$ the ratio of $Q(0)$ to that of copper is given by the ratio of $M\theta_D^2$ and, as shown in table 2, this does not vary much from unity. This result would imply that the use of the uncorrected mean square displacement of eq. (52) would give an elastic thermal attenuation which is only slightly larger for gold or silver as it is for copper. However, use of the effective mean square displacement of eq. (53) gives a much more physically reasonable result. Since, as mentioned in the

Table 2
The ratio of Debye mean square displacement and effective mean square displacement of the noble metals: $R_1 = (m\theta_D)_{Cu}/(m\theta_D)^2$; $R_2 = (m\theta_D^2)_{Cu}/(m\theta_D^2)$

	θ_D (K)	M	R_1	R_2
Cu	326	64	1	1
Ag	226	108	1.23	1.78
Au	170	197	1.19	2.29

preceding section the quantity α is essentially the same for all these metals for the same projectile and incident conditions, the ratio of $Q(0)_{eff}$ to that of Cu is approximately the same as the corresponding ratio of $M\theta_D^3$. From table 2 we see that this ratio is roughly 1.81 and 2.31 for silver and gold, respectively. This implies that silver and gold have a greatly enhanced thermal attenuation over that of copper. This prediction is quite understandable and is due to the fact that the spectral densities of silver and gold have more low frequency phonons, and it is specifically the low frequency modes which contribute most to thermal attenuation.

7. Conclusions

Starting from the general formalism for the thermal attenuation of the elastic intensities in atom-surface scattering, we have developed here a very simple and useful approximation. Although the general formalism requires extensive numerical calculation, this approximation, while still retaining most of the general features, allows many results to be obtained in simple closed form expressions. The main approximation in this method consists of two parts, replacing time dependent phonon displacement correlation functions $\langle u(\tau)u(0)\rangle$ by an effective mean square amplitude which in its simplest form is $\langle u^2(0)\rangle$, and retaining only the energy conserving contributions to integrals over intermediate perpendicular momenta. In this paper, we consider only processes involving the exchange of a single virtual phonon. A complete discussion of multiphonon exchange within the confines of this simple model, including infinite resummation of selected classes of multiphonon processes is given in another paper [17]. Numerical comparisons with experimental data are made using a Morse interaction potential with a vibrating repulsive part and a Debye spectral density for the phonons.

We arrive at a number of new and interesting results. We obtain a well depth correction that is much stronger than the simple refraction effect as applied to the Debye-Waller formula. In fact, the refraction or Beeby correction usually overestimates the depth of the adsorption well, whereas the stronger correction developed here appears to be in better qualitative agreement with experiment.

We discuss how damping factors and the frequency cut-off affect atom surface scattering. The damping factor arises naturally in the theory when we consider a potential which is a pairwise summation of atomic interactions. It takes into account the fact that the incoming atom interacts simultaneously with several surface atoms and the interference between their correlated vibrations decreases the net inelastic scattering amplitude. For light atom scattering at metal surfaces, this reduces the inelastic contribution in essentially the same proportion for all metals examined.

The frequency cut-off, on the other hand, can vary strongly from one metal surface to another for a given incident atom. This is because the thermal attenuation is largely the result of low frequency phonon transfers, and the attenuation is largely the result of low frequency phonon transfers, and the metals with low Debye temperatures have many more low energy phonons in their spectral densities. The frequency cut-off correction takes account of the fact that the matrix elements for a particular interaction decay rapidly with the difference between the magnitudes of incident and scattered normal momentum. Thus those processes associated with a small matrix element and are large phonon frequency) are associated with a small matrix element and are strongly damped.

The importance of this work is twofold. First it provides a simple model for treating the complexities of thermal attenuation in atom-surface scattering. In general, because of the large strength of the interaction, thermal attenuation in low energy atom surface scattering is substantially more complicated than that predicted by a simple Debye–Waller factor. This simple model provides a way to illustrate these complexities, yet still produces closed form expressions for the elastic intensity which are not much more difficult to apply than the Debye–Waller factor. Secondly, this model and the general theory from which it is derived [11,12,18], have demonstrated the ability to give excellent agreement with experiment.

Acknowledgements

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