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Multiphonon scattering from surfaces: comparison of approximations

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We consider the inelastic interaction of a neutral atomic projectile scattering from a solid surface and develop several theoretical models appropriate for describing the diffuse multiphonon contribution to the scattered intensity. Through extensive numerical calculations and comparisons with experiment, we determine the limits of validity of some of the various approximations and the scattering regimes in which each is applicable.

1. INTRODUCTION

In energy resolved experiments of atom-surface scattering a diffuse background is observed even under conditions for which quantum mechanical features such as diffraction and single phonon peaks should dominate the backscattered intensity [1, 2]. This diffuse intensity is in part due to incoherent scattering from defects and impurities on the surface, but for clean surfaces it is mostly due to the coherent process of multiphonon exchanges. The sharp quantum mechanical peaks in the intensity contain information on the structure and dynamics of the surface, but in order to correctly interpret these peaks it is necessary to have a good understanding of the diffuse inelastic intensity in order to perform a proper background subtraction. The theory describing this inelastic background must also be capable of spanning the range from purely quantum mechanical conditions to extreme semiclassical and classical scattering conditions. Even in the case of thermal energy He atom scattering from surfaces, where the He atom is usually considered as a quantum mechanical projectile, one can readily find examples of situations in which the scattering distribution is very nearly classical.

We have recently developed a theory of multiquantum atom-surface scattering which satisfies the above conditions, but which is still sufficiently tractable for carrying out numerical calculations [3]. The theoretical model is fundamentally quantum mechanical in its treatment of the projectile motion, and phonon effects are treated exactly within the model of a linear coupling of the projectile to a harmonic crystal. The main approximation is the assumption of a quick scattering collision in which the scattering time is shorter than that of the small frequency and long wavelength phonons which are the major contributors to multiquantum exchanges for low mass thermal energy atomic projectiles. The theory admits to several distinct degrees of approximation. Starting from an exact numerical solution of the model, we present a first order semiclassical approximation and an extreme semiclassical approximation, and each of these cases has forms appropriate to low and high surface temperatures.

The object of this work is to define the range of validity of each of the regimes of approximation through numerical calculations and comparisons with experiment. In the next section we give a brief development of the theory and its various approximate forms. In Sec. 3 we present the results of calculations and consider general conditions as to the range of validity of these approximations. A few conclusions are drawn in Sec. 4.

2. THEORY

The interaction between the atomic projectile and the surface can be described by a Hamiltonian of the form

$$H = H^p + H^c + V \tag{1}$$

where H^p is the Hamiltonian of the free particle, H^c is the Hamiltonian of the unperturbed crys-

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tal, and V is the interaction coupling the projectile and crystal. It is convenient to divide the interaction potential into two parts

$$V = V^0 + V^1 \tag{2}$$

where the "strong" part V^0 contains the terms which backscatter the projectile and prevent it from penetrating appreciably into the bulk, and the remainder V^1 contains the major terms describing interactions with the lattice vibrations.

A standard approach is to start from the probability density of the particle to exchange an amount of energy ΔE and an amount $\hbar\mathbf{K}$ of parallel momentum upon colliding with the surface. Such a probability is defined by

$$P(\mathbf{K},\Delta E) = \sum_{\mathbf{G}} \times \; << (n_i,\mathbf{k}_i|S^\dagger\,\delta(H^c - E_i^c - \Delta E) \times \delta(\hat{\mathbf{K}}^c - \mathbf{K}^c + \mathbf{K} + \mathbf{G})\,S|\mathbf{k}_i,n_i) >> \tag{3}$$

where $\hbar\hat{\mathbf{K}}^c$ is the momentum operator for the crystal, and the sum over reciprocal lattice vectors $\mathbf{G}$ appears because momentum is not conserved in the collision. The symbol $<<\ >>$ defines an ensemble average over the initial crystal states. The differential reflection coefficient, which is usually compared to the experimentally measured intensities, is related to Eq. (3) by a simple density of states:

$$\frac{dR}{d\Omega_f\,dE_f} = k_f k_{fz} P(\mathbf{K},\Delta E) \tag{4}$$

where $\hbar\mathbf{k}_f$ is the final projectile momentum and $\hbar k_{fz}$ is its component in the direction normal to the surface.

The scattering operator S appearing in Eq.(3) can be represented in several forms, but perhaps the most convenient is the time dependent exponential in the interaction picture

$$S = \mathcal{T} \lim_{t_0\to\infty} e^{(-i/\hbar)\int_{-t_0}^{+t_0}[V^0(t)+V^1(t)]dt} \tag{5}$$

where $\mathcal{T}$ is the time ordering operator.

In order to make further progress toward readily calculable expressions we make the trajectory approximation. The trajectory approximation consists in assuming that the projectile follows a classical trajectory from its initial state characterized by momentum $\hbar\mathbf{k}_i$ to its final state $\hbar\mathbf{k}_f$. This approximation effectively decouples the two potentials appearing in Eq.(5) and leads to a greatly simplified expression for the differential reflection coefficient. We write it here in its simplest form for the case of a surface of Bravais unit cells [4, 5]:

$$\frac{dR}{d\Omega_f\,dE_f} = \frac{m^2 k_f}{(2\pi)^3\hbar^5 k_{iz}}\,|\tau_{fi}|^2 \int_{-\infty}^{+\infty} dt \times e^{-i\Delta E t/\hbar} \sum_l e^{-i\mathbf{k}\cdot\mathbf{r}_l} e^{-2W(\mathbf{k})}\; e^{2\mathcal{W}_l(\mathbf{k};t)} \tag{6}$$

where m is the projectile mass, $\mathbf{k} = \mathbf{k}_f - \mathbf{k}_i$ and the scattering amplitude is identified as

$$\sigma_{fi} = (\mathbf{k}_f|\mathcal{T}e^{(-i/\hbar)\int_{-\infty}^{+\infty} V^0(s)\,ds}|\mathbf{k}_i)_{u.c.} \tag{7}$$

which is the unit cell (u.c.) contribution to the off-energy-shell transition matrix of the elastic part of the potential V^0 taken with respect to the initial and final states of the projectile. The function $\mathcal{W}_l(\mathbf{k};t)$ is a somewhat complicated correlation function involving the inelastic part of the potential V^1 and the displacement operators of the crystal. The Debye-Waller exponent is $W(\mathbf{k}) = \mathcal{W}_{l=0}(\mathbf{k};t=0)$.

The trajectory approximation is equivalent to application of the Feynman path integral approach, but limited to a single classically allowed path. Choosing and then calculating the appropriate classically allowed path for the situation at hand is not a simple matter in general. However, there is one case in which the choice becomes quite simple indeed, and this is the quick collision approximation in which the collision time of the particle is assumed short compared to a typical vibration time of the surface. For many purposes the quick collision approximation would not be appropriate for atom-surface scattering because typical collision times are comparable to the higher frequency phonon periods. In the case of multiphonon exchange, however, the energy exchange is due mainly to transfers of large numbers of small energy and long wavelength quanta and the quick collision approximation appears quite reasonable in many instances. In this approximation the classically allowed path is characterized

only by the initial and final momentum states of the projectile, and the correlation function becomes the displacement correlation function:

$$\mathcal{W}_l(\mathbf{k};t) = << \mathbf{k}\cdot\mathbf{u}_0^*(0)\ \mathbf{k}\cdot\mathbf{u}_l(t) >> \qquad (8)$$

Equation (6), with the above quick collision approximation is in a form that can be calculated directly when the displacement correlation function of (8) is expressed in its well known form for a harmonic crystal.

Although Eq. (6) can be treated directly, it is a cumbersome and lengthy form to handle for numerical calculations, and it can be well approximated by several expressions which are much more convenient. In keeping with the assumption that only long wavelength and small frequency phonons contribute strongly to the multiphonon part of the inelastic intensity, a further important simplification is possible. This consists of making an expansion in small wave vectors for the the displacement correlation function of (8). Again for case of a Bravais surface unit cell, and including terms through third order in $\mathbf{Q}\cdot\mathbf{R}_l$ where $\mathbf{R}_l$ is a surface lattice vector and $\mathbf{Q}$ is the parallel wave vector of the phonon, leads to a form for the differential reflection coefficient which is expressed quite simply as

$$\frac{dR}{d\Omega_f\, dE_f} = \frac{\rho m^2 k_f}{(2\pi)^3\hbar^5 k_{iz}}|\tau_{fi}|^2 e^{-2W(\mathbf{k})} S(\mathbf{K},\Delta E)\, I(\mathbf{K},\Delta E) \qquad (9)$$

where ρ is the surface density of unit cells and

$$S(\mathbf{K},\Delta E) = \sum_l e^{-i\mathbf{K}\cdot\mathbf{R}_l} e^{-F_l} \qquad (10)$$

with

$$F_l = \sum_{\alpha,\alpha'=1}^{3} k_\alpha\, k_{\alpha'} \sum_{\mathbf{Q},\nu} \frac{\hbar(\mathbf{Q}\cdot\mathbf{R}_l)^2}{2NM\omega_\nu(\mathbf{Q})} \times e_\alpha\begin{pmatrix}\mathbf{Q}\\ \nu\end{pmatrix} e^*_{\alpha'}\begin{pmatrix}\mathbf{Q}\\ \nu\end{pmatrix} [2n(\omega_\nu(\mathbf{Q}))+1] \qquad (11)$$

where M is the mass of a crystal atom, e_α is the phonon polarization vector, and $n(\omega_\nu(\mathbf{Q}))$ is the Bose-Einstein function for the phonon of frequency $\omega_\nu(\mathbf{Q})$. The final factor in Eq. (9) is

$$I(\mathbf{K},\Delta E) = \int_{-\infty}^{+\infty} dt\, e^{-i\Delta E t/\hbar} \times e^{<<\mathbf{k}\cdot\mathbf{u}_0^*(0)\ \mathbf{k}\cdot\mathbf{u}_0(t)>>} \qquad (12)$$

The transition rate of Eq.(9) is the product of a form factor $|\tau_{fi}|^2$, a Debye-Waller factor, a structure factor $S(\mathbf{K},\Delta E)$ arising from the periodic distribution of surface atoms, and an energy exchange factor $I(\mathbf{K},\Delta E)$. At high temperatures and large momentum transfers the structure factor is a rapidly convergent sum over lattice sites, since Eq.(11) shows that F_l varies as $\mathbf{R}_l^2$.

At high temperatures for which the Bose-Einstein function can be expanded in terms of small arguments, Eq.(9) remains valid but the terms become simpler. Writing explicitly for the case of a Debye phonon model, the energy exchange factor becomes

$$I(\mathbf{K},\Delta E) = \int_{-\infty}^{+\infty} dt\, e^{-i(\Delta E/\hbar+\omega_0)t} \times e^{2W(\mathbf{k})sin(\omega_D t)/t} \qquad (13)$$

and Eq.(11) simplifies to

$$F_l = \frac{\omega_0 k_B T \mathbf{R}_l^2}{2\hbar v_R^2} \qquad (14)$$

where ω_D is the Debye frequency and v_R is a weighted average of parallel phonon velocities. The Debye-Waller exponent takes the familiar form

$$2W(\mathbf{k}) = \frac{3\mathbf{k}^2 k_B T}{M\omega_D^2} \qquad (15)$$

and the energy shift is given by

$$\omega_0 = \frac{\hbar k^2}{2M} \qquad (16)$$

This energy shift has its origins in the zero-point motion of the lattice. It is interesting that even though the zero-point motion is usually considered a low-temperature effect, here it has an important manifestation in the semiclassical limit of high temperature and incident energy.

Equations (9) through (12) represent the first order semiclassical approximation in its full temperature form which we will refer to as FT. We denote by HT the form using the simpler high temperature expressions of Eqs.(13) through (16).

We now consider the extreme semiclassical limit of very high energies which we denote by

CL. Under such near classical and classical scattering conditions the Debye-Waller factor is so small that elastic and single phonon peaks are completely suppressed, and only multiple phonon exchanges occur. It is of interest to consider the present theory in this limit as it leads to closed form expressions for the scattering intensities, and gives specific criteria for the validity of the classical limit.

For scattering of a point projectile with a lattice of discrete atomic centers, the differential reflection coefficient of Eq. (6) can be evaluated by the method of steepest descents. The result is independent of the phonon frequency distribution because in this limit the initial energy exchange is simply through the recoil of the surface atoms upon impact:

$$\frac{dR}{d\Omega_f\, dE_f} = \frac{m^2\,|\mathbf{k}_f|}{8\pi^3\hbar^5 k_{iz}}\,|\tau_{fi}|^2\left(\frac{\hbar\pi}{\omega_0 k_B T}\right)^{1/2} \times \exp\left\{-\frac{(\Delta E+\hbar\omega_0)^2}{4k_B T\hbar\omega_0}\right\} \qquad (17)$$

The Debye-Waller factor no longer appears explicitly in this expression because it has been canceled by a term arising from the energy exchange factor. We have also assumed the high temperature limit, but it is straightforward to obtain a similar expression that is valid for low temperatures.

The scattering intensity of (17) is a Gaussian-like function in the energy exchange ΔE, but shifted to the energy loss side by the energy shift $\hbar\omega_0$ of Eq.(16). However, we note that this function is not a true Gaussian because ω_0 is a function of k. The intensity is limited on the energy loss side by the fact that the projectile may lose no more energy than it had initially, and it is skewed towards the energy gain side by the energy dependence of ω_0. The width of the differential reflection coefficient in energy exchange is roughly $2\sqrt{k_B T\hbar\omega_0}$ in energy units, and the peak amplitude decays with increasing temperature as $(k_B T\hbar\omega_0)^{1/2}$. This behavior of the width and peak intensity of the differential reflection coefficient is understandable in terms of the unitarity condition, which guarantees the equality of the number of scattered particles to the number of incident particles. At higher temperatures the intensity spreads over a larger range of ΔE, consequently in order to preserve the number of particles, the peak intensity must decrease accordingly.

The steepest descent evaluation of Eq.(17) implies a criterion for the validity of the semiclassical result which is

$$2W(\mathbf{k})/6 \gg 1 \qquad (18$$

This is a very stringent criterion, and is in fact rarely satisfied in typical He-scattering experiments, and often not satisfied even when the projectile is a heavier atom such as Ne or Ar. The average number of phonons exchanged in a collision process is approximately equal to $2W$, thus (18) implies that for the classical approximation to be valid, a truly large number of quanta must be exchanged.

Equation (17) is the extreme semiclassical limit for a point particle scattering from a lattice of discrete scattering centers. There is a second limit for the case of an incident projectile which interacts with many surface atoms, and the surface can be treated as a continuum. This is the limit that should be applicable, for example, in the completely classical case of a projectile that is large compared to the interatomic lattice spacing. This expression is obtained by replacing the summation over lattice sites in (6) or (10) by an integral. The result is a differential reflection coefficient of the following form:

$$\frac{dR}{d\Omega_f\, dE_f} = \frac{m^2\,|\mathbf{k}_f| v_R^2}{4\pi^3\hbar^5 k_{iz} S_{u.c.}}\left(\frac{\hbar\pi}{\omega_0 k_B T}\right)^{3/2} \times |\tau_{fi}|^2 \exp\left\{-\frac{(\Delta E+\hbar\omega_0)^2+2\hbar^2 v_R^2 K^2}{4k_B T\hbar\omega_0}\right\} \qquad (19$$

There is a clear difference between the two CL limits (17) and (19). In the latter, the temperature dependence of the peak in the inelastic intensity varies as $1/T^{3/2}$ as opposed to $1/T^{1/2}$ and there is the extra skewed Gaussian-like behavior in parallel momentum exchange. Eq. (19) with the form factor $|\tau_{fi}|^2$ taken to be constant is essentially the expression developed by Brako and Newns [6] and can be arrived at by purely classical thermodynamical treatments of scattering from an isotropic continuum surface [7].

3. COMPARISONS

The theoretical expressions presented in the preceding section have been used to interpret the multiphonon background observed in a number of experimental time-of-flight measurements over a wide range of conditions, especially for the case of He as the atomic projectile [8, 9]. We wish to present here some of the results of a large number of numerical calculations that have been done in order to test the range of validity, as a function of experimentally adjustable incident conditions, of all levels of theoretical approximations from the exact solution of the model through the first order semiclassical approximation, to the extreme semiclassical expression. For these calculations we have used a Debye model for the phonon frequency spectrum in order to calculate the displacement correlation functions of the crystal unit cells.

We will concentrate here on the comparison of the first order semiclassical and the extreme semiclassical approximations. It is found that these approximations work reasonably well for all but the very lowest incident projectile energies and surface temperatures. As discussed above in Sec. 2, exact numerical solutions for the multiple phonon transfers are quite tractable starting from Eq.(6) after first subtracting off the singular elastic lines, and possibly the single phonon contribution for quicker convergence. However, such calculations are substantially more lengthy in computer time than the approximate results, and discussions of them will be left for a later paper.

Under typical conditions where the multiphonon background can be readily observed in the energy resolved measurements, it usually takes the form of a smooth and broad foot upon which appear the elastic and single phonon quantum peaks. This multiphonon foot usually has a well defined maximum peak intensity and full width at half maximum (FWHM). An example of such a measurement is shown in Fig. 1. This is the case of He incident at an angle of $\theta_i = 60°$ and an energy of 30 meV on a mica substrate coated with a Langmuir-Blodgett film of arachidic acid and methyl sterate (AAMS, in the molar ratio 9:1) with a surface temperature of 130 K [10]. In this case there is no specular or other quantum mechanical peak in the scattered intensity, as evidenced by comparison with the width of the incident beam profile shown in the insert. Because of the softness of this ordered layer of long chain molecules, and because of the small mass of the methyl end group which terminates the chain, the scattering is dominated by multiphonon exchanges and appears as a very classical intensity. The solid line is the result of calculations [9] using the extreme semiclassical expression of Eq. (17) with an effective crystal mass equal to the $15 amu$ of the terminating methyl group.

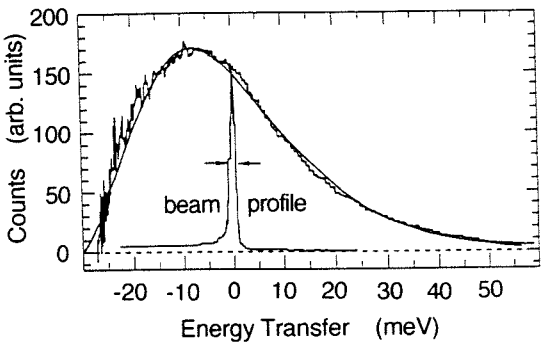


Figure 1. The time-of-flight spectrum converted to energy gain and loss for a monoenergetic He atom beam of energy 30 meV scattered from an AAMS monolayer surface at a temperature of 130 K. The narrow peak shows the energy width of the incident He beam including all broadening by the instrument. The solid smooth curve is the theoretical fit with an effective end group mass of $M = 15$ amu.

In the process of evaluating the validity of the various approximations we have carried out many calculations of the type shown in Fig. 1 and we find that the easiest manner to make quantitative assessments of different examples is through comparisons of the maximum of the multiphonon intensity foot and its FWHM.

An example of the types of comparison that can be made is given in Fig. 2 which shows the maximum intensity of the multiphonon foot as

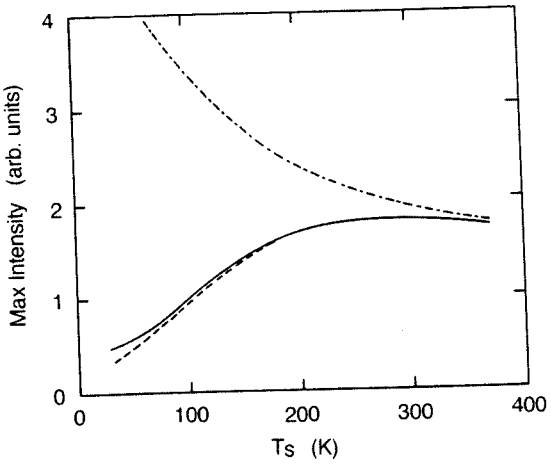


Figure 2. Maximum of the multiphonon inelastic intensity plotted as a function of surface temperature. The solid curve is the FT approximation, the dashed curve is the HT approximation, and the dash-dot curve is the CL calculation. The incident parameters are $k_i = 9.2\,\mathring{A}^{-1}$ (or $E_i = 44.23\,meV$), $m = 4\,amu$, $M = 35.5\,amu$, $\theta_i = \theta_f = 45°$, and $\Theta_D = 215\,K$.

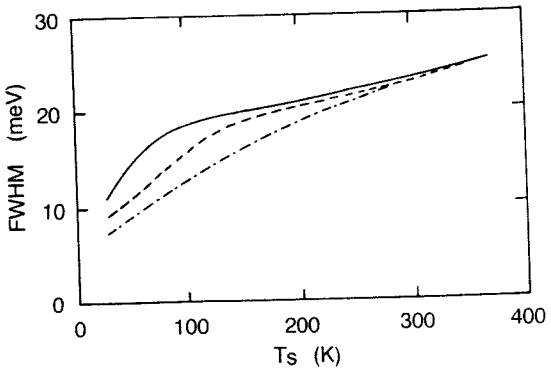
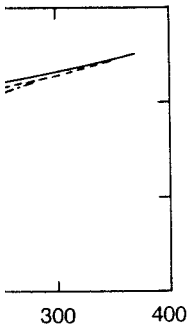


Figure 3. The FWHM of the multiphonon in elastic intensity plotted as a function of surfac temperature. The order of the curves, and th parameters are the same as in Fig. 2

a function of surface temperature for three different approximations, the full temperature first order semiclassical, the high temperature first order semiclassical, and the high temperature version of the extreme semiclassical of Eq. (17). The various parameters are, incident wave vector $9.2\,\mathring{A}^{-1}$ (corresponding to an incident energy of $44.23\,meV$), projectile mass $4\,amu$ (incident He beam), crystal mass $35.5\,amu$, incident and final angles $\theta_i = \theta_f = 45°$, and Debye temperature $\Theta_D = 215\,K$. It is clear that the FT curve is quite well approximated by the HT approximation starting around $T \approx 100\,K$, and the two are nearly identical at temperatures higher than $T \approx 200\,K$. The extreme semiclassical approximation, however, does not agree with the more exact FT and HT curves except for temperatures considerably higher than $300K$. At lower temperatures the CL approximation strongly overestimates the maximum intensity of the multiphonon contribution.

The type of comparison provided by th FWHM is shown in Fig. 3 This is for the sam set of parameters as in 2. Here it is clear tha the HT calculation does not fully agree with th FT calculation until the surface temperature i relatively close to the Debye temperature. Th CL calculation, just as in Fig. 2, does not be gin to agree with the FT approximation until th temperature is over $300K$. At temperatures lowe than this the CL approximation gives a predictio of multiphonon intensities which is considerabl too narrow.

In general we find the conditions for the valid ity of the HT approximation to the FT calculatio easiest to characterize. In principle this should b the case since, in general, the region of high tem peratures is defined by the validity of the expan sion of the Bose-Einstein distribution function $n(\omega) \to k_B T/\hbar\omega$. We find that for all parameter studied (E_i, m, M, θ_i, θ_f and Θ_D) that the in tensities predicted by the HT approximation be gin to approach the FT values when the surfac temperature reaches a value of $\Theta_D/2$, or some what higher. For $T \approx \Theta_D$ and higher the tw treatments give quite similar results. This sam statement holds for the low and high temperatur



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versions of the extreme semiclassical approximation, they are essentially the same for $T > \Theta_D$.

For the extreme semiclassical CL version to give dependable results, the conditions are not so clear as for the high and low temperature HT and FT approximations. The derivation of this approximate expression depends rigorously on the condition for the Debye-Waller exponent $2W(\mathbf{k}) >> 6$, however, often it is found that the CL expression works quite satisfactorily if $2W(\mathbf{k}) \geq 4$ in the neighborhood of zero energy exchange $\Delta E \approx 0$.

In order to understand the regime of validity of the CL expression it is of interest to discuss the general nature of the multiphonon background. Under quantum mechanical conditions, where the sharp quantum diffraction and single phonon peaks dominate the scattered intensity, the diffuse multiphonon part forms a very small background under these peaks. For a given surface and projectile, as the temperature and/or incident energy are increased, the multiphonon background grows in intensity and broadens over a larger and larger range of energy exchange while at the same time the quantum peaks are reduced by the Debye-Waller factor. The growth of the inelastic background with energy and temperature continues up to the point where the Debye-Waller factor becomes so small that the diffraction and single phonon peaks are negligible, in which case nearly all of the scattering is in the diffuse inelastic background. It is under these conditions of increasing inelastic background intensity that the CL approximation is not valid and the FT or HT (or the exact calculation in the extreme quantum mechanical limit) must be used. Now if the temperature and incident energy are further increased, the classical regime is approached for which there is essentially nothing but multiple quantum inelastic scattering. With still higher energies and temperatures, more and more inelastic channels of scattering open up over a broader range of energy exchange. Since the width of the scattered distribution increases, the maximum intensity must decrease in order to assure that the total number of scattered particles always equals the number in the incident beam, i.e., to assure the unitarity condition. It is only in this latter regime, where the maximum intensity of the multiphonon background is decreasing, that the CL approximation begins to become valid.

One would expect that if $2W(\mathbf{k}) \approx 6$, in which case the Debye-Waller factor is of the order 10^{-3}, that the CL case should work rather well, but this does not tell the whole story. The Debye-Waller factor is a function of energy exchange through its momentum dependence, and is generally larger at small energy exchange than it is at larger energy exchanges. For very low incident energies, and especially for small mass ratios m/M this asymmetry can be very pronounced. It is this same energy dependence appearing in the energy shift $\hbar\omega_0$ that makes the Gaussian-like CL expression (17) very skewed towards positive energy exchange when the temperature is large and for small mass ratios.

As a general statement, the results of our calculations indicate that if $2W(\mathbf{k}) > 6$ over the entire range of ΔE for which there is appreciable inelastic intensity, then the CL expression works quite well in predicting the form of the diffuse inelastic background. Under most conditions it is adequate to test the value of $2W$ at $\Delta E = 0$. However, when E_i or m/M is small, the value of $2W$ will vary strongly from small to large energy exchange, and its value at $\Delta E = 0$ may need to be substantially larger than 6 in order for the CL expression to be valid.

4. CONCLUSIONS

We have presented the essential features of the theory of multiple phonon inelastic scattering of atomic projectiles by surfaces. Several approximations are developed which lead to straightforward and tractable numerical calculations. Three of these approximations are examined here, the first order semiclassical in both its full temperature and high temperature forms and the extreme semiclassical limit. A large number of numerical calculations have been carried out in order to establish the regimes of validity of each approximation. We find that over a very large range of initial parameters the HT approximation gives a good representation of the FT results as long as the surface temperature is greater than the Debye

temperature of the surface.

The regime of the extreme semiclassical approximation is somewhat more complicated. As suggested by its theoretical development in Eq.(18), one finds that the CL expression is good if the Debye-Waller argument $2W(\mathbf{k})$ is greater than 6 over the entire range of energy exchange for which the scattered intensity is non-negligible. However, a casual test of $2W(\mathbf{k})$ under elastic conditions of zero energy exchange is not always a good test of the validity of the CL model. The exponent $2W(\mathbf{k})$ is an increasing function of energy exchange, and for small incident energies and particularly for low crystal masses it can be a strongly varying function. Thus, although the condition $2W(\mathbf{k}) > 6$ may be met for some values of energy exchange, it may not be met at others.

When used with a Debye frequency distribution for determining the displacement correlation function, the HT approximation for the multiphonon intensity is rather simple, the numerical calculation involving primarily a Fourier transformation over time. The CL approximation is even simpler, it is a closed-form expression that does not even depend on the form of the phonon spectral density. These two approximations taken together cover, for many systems, virtually the entire range for which the multiphonon contribution to the scattered intensity is significant. Thus they can be used to estimate the importance of the multiphonon background in a variety of atom-surface scattering systems.

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