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Relating temperature dependence of atom scattering spectra to surface corrugation

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Abstract

It is suggested that a measurement of the temperature dependence of the most probable intensity of energy-resolved atom–surface scattering spectra can reveal the strength of the surface corrugation. To support this conjecture, a classical mechanical theory of atom scattering from a corrugated surface, valid in the weak corrugation limit, is developed. The general result for the scattering probability is expressed in terms of spatial integrals over the impact parameter within a surface unit cell. For the case of a one-dimensional corrugation, approximate expressions for the scattering probability are obtained in terms of analytic closed form expressions. As an indicator of its relation to experimental measurements, calculations using a one-dimensional corrugation model are compared with data for Ar scattering from a molten Ga surface and an approximate value of the corrugation height parameter is extracted.

1. Introduction

Many scattering experiments using atomic projectiles to investigate the properties of surfaces have been carried out in the classical regime which is characterized by the transfer of many phonon quanta in a typical collision [1, 2]. It has been suggested that in the classical regime the strength of the surface corrugation can be directly related to the temperature dependence of atom scattering spectra, and in particular to the temperature dependence of the most probable scattering intensity [3].

This concept can be visualized most easily by comparing two disparate expressions, one for the scattering from a smooth and uncorrugated surface and the other for a highly corrugated surface. For both cases, the differential reflection coefficient $dR(\mathbf{p}_f, \mathbf{p}_i)/dE_f d\Omega_f$ for scattering of an atomic projectile of initial momentum \mathbf{p}_i into the state \mathbf{p}_f has been determined in the classical limit within the impulse approximation.

For the case of a smooth, flat surface whose only corrugations are due to small thermal vibrations of the underlying atomic cores the differential reflection coefficient is given by [4-6]

$$\frac{\mathrm{d}R(\mathbf{p}_{\mathrm{f}},\mathbf{p}_{\mathrm{i}})}{\mathrm{d}\Omega_{\mathrm{f}}\mathrm{d}E_{\mathrm{f}}} = \frac{m^{2}v_{\mathrm{R}}^{2}|\mathbf{p}_{\mathrm{f}}|}{8\pi^{3}\hbar^{2}p_{iz}S_{\mathrm{uc}}}|\tau_{\mathrm{fi}}|^{2}\left(\frac{\pi}{k_{\mathrm{B}}T_{\mathrm{S}}\Delta E_{0}}\right)^{3/2} \times \exp\left\{-\frac{(E_{\mathrm{f}}-E_{\mathrm{i}}+\Delta E_{0})^{2}+2v_{\mathrm{R}}^{2}\mathbf{P}^{2}}{4k_{\mathrm{B}}T_{\mathrm{S}}\Delta E_{0}}\right\},\tag{1}$$

where *m* is the projectile atomic mass, p_{iz} is the surfacenormal component of the incident momentum, $T_{\rm S}$ is the temperature, $k_{\rm B}$ is Boltzmann's constant, the binary recoil energy is $\Delta E_0 = (\mathbf{p}_{\rm f} - \mathbf{p}_{\rm i})^2 / 2M_{\rm C}$ with $M_{\rm C}$ the target substrate mass, P is the parallel component of the scattering vector $\mathbf{p} = \mathbf{p}_{f} - \mathbf{p}_{i}$, and τ_{fi} is a transition matrix determined from the interaction potential. The incident energy is $E_i = \mathbf{p}_i^2/2m$, with a similar expression for the final energy $E_{\rm f}$. The factor $S_{\rm uc}$ is the surface area associated with a single surface atom and $v_{\rm R}$ is a parameter having dimensions of speed that is completely determined by the phonon spectral density at the classical turning point as discussed below in section 2, but which is usually treated as a parameter. In a purely classical derivation of equation (1) \hbar is a constant having dimensions of action [5], while if the same result is derived from quantum mechanical cross sections by taking the classical limit it is identified as Planck's constant divided by 2π [4].

Except for certain cases, such as very low incident energies equation (1), when viewed as a function of E_f with all other experimentally controllable parameters fixed, forms a single-peaked curve whose maximum or most probable intensity occurs when the argument of the exponential takes its minimum value. The dependence on surface temperature appears in two places, in the argument of the exponential and in the prefactor. The temperature appearing in the denominator of the argument of the exponential is largely responsible for

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determining the width of the peak. When the peak is nearly Gaussian in form, for example at incident energies that are large compared to the temperature, then this width increases nearly as $\sqrt{T_s}$, a behavior characteristic of classical scattering. The temperature dependence of the most probable intensity is mainly determined by the prefactor and thus is seen to vary approximately as $1/T_s^{3/2}$.

The opposing case of a highly corrugated surface can be viewed as a model in which the surface is so corrugated that each core atom appears as an individual scattering center. The well-known differential reflection coefficient, calculated within the impulse approximation, for an atomic projectile colliding with a collection of discrete scattering centers whose initial momenta are in an equilibrium distribution at temperature T_S is given by [6–8]

$$\frac{\mathrm{d}R(\mathbf{p}_{\mathrm{f}},\mathbf{p}_{\mathrm{i}})}{\mathrm{d}E_{\mathrm{f}}\mathrm{d}\Omega_{\mathrm{f}}} = \frac{m^{2}|\mathbf{p}_{\mathrm{f}}|}{8\pi^{3}\hbar^{4}p_{iz}}|\tau_{\mathrm{fi}}|^{2}\left(\frac{\pi}{k_{\mathrm{B}}T_{\mathrm{S}}\Delta E_{0}}\right)^{1/2}$$
$$\times \exp\left\{-\frac{(E_{\mathrm{f}}-E_{\mathrm{i}}+\Delta E_{0})^{2}}{4k_{\mathrm{B}}T_{\mathrm{S}}\Delta E_{0}}\right\}.$$
(2)

This expression is similar to, but somewhat simpler than equation (1) for the smooth surface. For $E_{\rm f}$ much larger than $k_{\rm B}T_{\rm S}$ it appears as a single-peaked structure when viewed as a function of $E_{\rm f}$, although it is not a true Gaussian shape and can be highly skewed because of the energy dependence of ΔE_0 . The width of the peak again goes with temperature approximately as $\sqrt{T_{\rm S}}$. However, the temperature dependence of the most probable intensity, which occurs when $E_{\rm f} - E_{\rm i} + \Delta E_0 = 0$, is entirely governed by the prefactor and goes as $1/\sqrt{T_{\rm S}}$.

Comparison of equations (1) and (2) shows that there is a very distinct difference in behavior of the most probable intensity with temperature, with the intensity of an uncorrugated surface behaving approximately as $1/T_s^{3/2}$ while that of a highly corrugated surface going as $1/T_s^{1/2}$. A logical conclusion is that a moderately corrugated surface will exhibit behavior somewhere between these two extreme limits. Consequently, a measurement of the temperature dependence of the most probable intensity, when compared with an appropriate theory, can be used to extract the strength of the corrugation function.

It should also be noted that the temperature in both equations (1) and (2) always appears multiplied by the classical recoil energy ΔE_0 . Consequently, for both types of surface corrugation the behavior of the reflected intensity as a function of ΔE_0 for fixed T_S should be similar to that of the temperature dependence for fixed ΔE_0 (or equivalently for fixed initial and final momenta). This implies that similar information about the corrugation strength could be obtained by examining the most probable intensity as a function of ΔE_0 , although such an experiment is normally more difficult to perform. However, there are circumstances for which $\Delta E_0 \propto E_i$, notably the case in which the incident energy is large compared to the surface temperature [2]. Under such conditions measurements of the scattered intensity as a function of incident energy E_i could be used to get the same information on the corrugation as could be obtained from a temperature dependent measurement at fixed energy. However, in view of the fact that most experiments appear to more easily measure good relative intensities as a function of temperature than as a function of incident energy, it is expected that temperature dependent measurements would be the first method of choice.

In this paper we develop a classical theory of atom scattering from a corrugated surface and apply it to a surface having a one-dimensional corrugation. The starting point is a semiclassical quantum theory valid for small corrugations in which the collision is treated within the impulsive approximation. The classical limit is obtained by invoking the Bohr correspondence principle of large numbers of phonon quanta excited. The general result is expressed as a two-dimensional spatial integral over the one-dimensional surface unit cell. The general result lends itself to an approximate solution that can be expressed in terms of closed form analytic expressions. Comparisons of the general result and the approximate solution with the limited available data allows an approximate evaluation of the average corrugation height of liquid metal surfaces as measured by Ar atom scattering.

The organization of the remainder of this paper is as follows. Section 2 presents the general theory and the special case of application to a one-dimensional corrugation. Section 3 develops the approximate solution for a one-dimensional corrugated surface, section 4 gives the comparison with experimental data for molten metal surfaces, and discussion and conclusions are presented in section 5.

2. Classical scattering probability for a corrugated surface

Although the objective of this section is to develop a theory of scattering from corrugated surfaces in the classical mechanical limit it is of interest to begin from a semiclassical quantum mechanical treatment and then take the classical limit of large energies, high temperatures and heavy mass projectiles. This procedure assures that quantum features that persist in the classical decoherence limit, such as recoil and zero point thermal motion, are automatically and correctly included.

A good starting point is the generalized Fermi golden rule for the transition rate

$$w(\mathbf{p}_{\rm f}, \mathbf{p}_{\rm i}) = \frac{2\pi}{\hbar} \left\langle \sum_{\{n_{\rm f}\}} |T_{\rm fi}|^2 \delta(\mathcal{E}_{\rm f} - \mathcal{E}_{\rm i}) \right\rangle,\tag{3}$$

where $T_{\rm fi}$ is the transition matrix element taken between final and initial states of the system of projectile plus target surface, and $\mathcal{E}_{\rm i}$ and $\mathcal{E}_{\rm f}$ are the initial and final global energies of the entire system. The angular brackets are an average over all initial states of the target surface and the $\sum_{\{n_f\}}$ indicates a sum over all final states of the target.

The differential reflection coefficient is obtained from the transition rate by dividing by the incident flux which is proportional to p_{iz} and multiplying by the density of states in final energy

$$\frac{\mathrm{d}R}{\mathrm{d}E_{\mathrm{f}}\mathrm{d}\Omega_{\mathrm{f}}} = \frac{m^2 L^4}{(2\pi\hbar)^3} \frac{p_{\mathrm{f}}}{p_{iz}} w(\mathbf{p}_{\mathrm{f}}, \mathbf{p}_{\mathrm{i}}). \tag{4}$$

A very useful semiclassical approximation for the transition matrix is to assume that the interaction potential for the static surface is a strongly repulsive or hard wall barrier located at the position $z = \xi(\mathbf{R})$, where $\xi(\mathbf{R})$ is the corrugation function. Applying the eikonal approximation to this model leads to [11, 12]

$$T_{\rm fi} = i \mathrm{e}^{\mathrm{i}\delta_{\rm f}} \frac{\hbar p_{\rm fz}}{mL} \frac{1}{L^2} \int \mathrm{d}\mathbf{R} \, \mathrm{e}^{-\mathrm{i}\mathbf{P}\cdot\mathbf{R}/\hbar} \mathrm{e}^{-\mathrm{i}\Delta p_z \xi(\mathbf{R})/\hbar} \mathrm{e}^{\mathrm{i}\mathbf{p}\cdot\mathbf{u}(\mathbf{R},t)/\hbar}, \quad (5)$$

where Δp_z is the component of **p** normal to the surface, **u**(**R**, *t*) is the displacement of the surface due to thermal vibrations, *L* is a quantization length and δ_f is a phase shift produced by the potential. This phase factor is unimportant because it disappears in the modsquare of the transition rate in equation (3). The sum and average over target states in equation (3) are carried out using the Glauber–van Hove transformation [9, 10] which leads to

$$w(\mathbf{p}_{f}, \mathbf{p}_{i}) = \left(\frac{p_{fz}}{mL}\right)^{2} \int_{-\infty}^{+\infty} dt e^{i(E_{i}-E_{f})t/\hbar} \\ \times \frac{1}{L^{4}} \int d\mathbf{R} \int d\mathbf{R}' e^{-i\mathbf{P}\cdot(\mathbf{R}-\mathbf{R}')/\hbar} \\ \times e^{-i\Delta p_{z}[\xi(\mathbf{R})-\xi(\mathbf{R}')]/\hbar} e^{-2W(\mathbf{p})} e^{2W(\mathbf{p};\mathbf{R},\mathbf{R}',t)}.$$
(6)

The argument of the Debye–Waller factor $exp\{-2W\}$ is given by

$$2W(\mathbf{p}) = \langle (\mathbf{p} \cdot \mathbf{u})^2 \rangle / \hbar^2 \approx \frac{3\mathbf{p}^2 T_{\rm S}}{M_{\rm C} k_{\rm B} \Theta_{\rm D}^2},\tag{7}$$

where the final expression on the right-hand side is the standard approximation for a bulk solid in the Debye model with Θ_D the Debye temperature.

The position and time dependent correlation function appearing in the exponential of equation (6) is given by

$$2\mathcal{W}(\mathbf{p};\mathbf{R},\mathbf{R}',t) = \langle \mathbf{p} \cdot \mathbf{u}(\mathbf{R},t)\mathbf{p} \cdot \mathbf{u}(\mathbf{R}',0) \rangle / \hbar^2.$$
(8)

Within the same approximations as for the Debye–Waller factor of equation (7) above this correlation function can be evaluated in the classical limit for small time and parallel displacements

$$2\mathcal{W}(\mathbf{p}; \mathbf{R}, \mathbf{R}', t) \approx 2W(\mathbf{p}) - i\Delta E_0 t/\hbar - \Delta E_0 k_B T_S t^2/\hbar^2 - \frac{\Delta E_0 k_B T_S (\mathbf{R} - \mathbf{R}')^2}{2\hbar^2 v_{\mathrm{R}}^2} + \cdots, \qquad (9)$$

where the velocity parameter $v_{\rm R}$ is given by the relation [4]

$$\frac{1}{v_{\rm R}^2} = \frac{1}{k_{\rm B}T_{\rm S}} \sum_{\alpha,\alpha'=1}^{3} \hat{p}_{\alpha} \hat{p}_{\alpha'} \sum_{\mathbf{Q},\nu} \frac{\hbar(\mathbf{Q}\cdot\hat{\mathbf{R}})^2}{2N_{\rm C}\omega_{\nu}(\mathbf{Q})} \times e_{\alpha}(\mathbf{Q},\nu)e_{\alpha'}(\mathbf{Q},\nu)[2n_{\nu}(\mathbf{Q})+1],$$
(10)

where $\hat{\mathbf{R}}$ is a unit vector in the direction of $\mathbf{R} - \mathbf{R}'$. The parameter $v_{\rm R}$ is evaluated in terms of the surface phonon polarization vectors $e_{\alpha}(\mathbf{Q}, \nu)$ for a phonons of frequency $\omega_{\nu}(\mathbf{Q})$ with \mathbf{Q} the parallel wavevector and additional quantum number ν , $N_{\rm C}$ is the number of phonon modes and $n_{\nu}(\mathbf{Q})$ is the Bose–Einstein factor.

The classical limit for which equation (9) is valid is defined by the recoil energy ΔE_0 being large, and in this limit the Debye–Waller factor is exactly canceled by the

leading term in (9). This cancelation of the Debye–Waller factor signals the disappearance of all quantum peaks and the integrals in equation (6) become separable and converge at small times and displacements. The time integral is trivial and (6) becomes

$$w(\mathbf{p}_{f}, \mathbf{p}_{i}) = \left(\frac{p_{fz}}{mL}\right)^{2} \frac{2\pi\hbar}{\sqrt{4\pi\Delta E_{0}k_{B}T_{S}}}$$

$$\times \exp\left\{-\frac{(E_{f} - E_{i} + \Delta E_{0})^{2}}{4\Delta E_{0}k_{B}T_{S}}\right\} \times \frac{1}{L^{4}} \int d\mathbf{R}$$

$$\times \int d\mathbf{R}' e^{-i\mathbf{P}\cdot(\mathbf{R}-\mathbf{R}')/\hbar} e^{-i\Delta p_{z}[\xi(\mathbf{R})-\xi(\mathbf{R}')]/\hbar}$$

$$\times \exp\left\{-\frac{\Delta E_{0}k_{B}T_{S}(\mathbf{R}-\mathbf{R}')^{2}}{2\hbar^{2}v_{R}^{2}}\right\}.$$
(11)

The leading terms in equation (11) are identical to the transition rate of equation (2), showing that if the corrugation function $\xi(\mathbf{R})$ and the spatial correlations in the last term in the expansion of equation (9) are ignored the transition rate becomes that of equation (2) for a discrete surface.

A second interesting limit occurs if the corrugation function $\xi(\mathbf{R})$ is set equal to a constant in equation (11), corresponding to a flat surface, then the spatial integrals become trivial and the result is just that first obtained by Brako and Newns of equation (1).

Equation (11) as it stands can be regarded as an extension of the results of Brako and Newns [4] to the case of a vibrating surface that is repulsive and has a static corrugation given by the corrugation function $\xi(\mathbf{R})$. The physical significance of this Gaussian-like term in $(\mathbf{R}-\mathbf{R}')$ is that it denotes the limitation of influence of the correlations in surface vibrations. In fact, the factor $\ell = \sqrt{2\hbar^2 v_{\rm R}^2 / \Delta E_0 k_{\rm B} T_{\rm S}}$ appearing in the argument of the exponential can be regarded as a correlation length over which surface vibrational correlations are important in the classical limit.

3. One-dimensional corrugated surface

For certain simple forms of two-dimensional corrugation functions the spatial integrals appearing in the result of equation (11) can be reduced to a three-dimensional integral, but in general it appears easier to treat it numerically as a fourdimensional integral. However, if the corrugation function is one-dimensional, a case that has many useful applications in the scattering of rare gases from stepped surfaces [13], equation (11) becomes significantly simplified and in some cases lends itself to approximations that can be cast into closed form expressions.

In order to show some of these simplifications it is useful to rewrite the transition rate of equation (11) as the product of the transition rate for the highly corrugated discrete surface and a structure factor contribution arising due to the corrugation function:

$$w(\mathbf{p}_{\rm f}, \mathbf{p}_{\rm i}) = w_{\rm disc}(\mathbf{p}_{\rm f}, \mathbf{p}_{\rm i})S(\mathbf{p}_{\rm f}, \mathbf{p}_{\rm i}), \qquad (12)$$

where obviously

$$S(\mathbf{p}_{\rm f}, \mathbf{p}_{\rm i}) = \frac{1}{L^4} \int d\mathbf{R} \int d\mathbf{R}' e^{-i\mathbf{P}\cdot(\mathbf{R}-\mathbf{R}')/\hbar} \\ \times e^{-i\Delta p_z[\xi(\mathbf{R})-\xi(\mathbf{R}')]/\hbar} \exp\left\{-\frac{\Delta E_0 k_{\rm B} T_{\rm S}(\mathbf{R}-\mathbf{R}')^2}{2\hbar^2 v_{\rm R}^2}\right\}.$$
(13)

Now, if the corrugation function is one-dimensional, such as a sinusoidal function of period *a* that we will make use of below, i.e.,

$$\xi(x) = ha \cos\left(\frac{2\pi x}{a}\right),\tag{14}$$

the structure factor simplifies to

$$S(\mathbf{p}_{\rm f}, \mathbf{p}_{\rm i}) = \frac{1}{L^3} \sqrt{\frac{2\pi \hbar^2 v_{\rm R}^2}{\Delta E_0 k_{\rm B} T_{\rm S}}} \exp\left\{-\frac{2v_{\rm R}^2 P_y^2}{4k_{\rm B} T_{\rm S} \Delta E_0}\right\} \\ \times \int dx \int dx' e^{-iP_x(x-x')/\hbar} e^{-i\Delta p_z[\xi(x)-\xi(x')]/\hbar} \\ \times \exp\left\{-\frac{\Delta E_0 k_{\rm B} T_{\rm S}(x-x')^2}{2\hbar^2 v_{\rm R}^2}\right\}.$$
 (15)

In the classical limit in which the correlation length ℓ is smaller than the period a the integrals in (15) can be reduced to integrals over a single period multiplied by the number of periods. As in the case of the full expression of equation (11)the one-dimensional case presented in equation (15) cannot be integrated in closed form for a general one-dimensional corrugation function. However, in the case of a onedimensional corrugation function the dominant contributions to the scattering come from the portions of the corrugation function that are nearly straight lines, namely the flat parts that contribute strongly in the specular direction, such as the top and bottom (e.g., for the corrugation of equation (14) near x = 0 and $\pm a/2$), and the inflection points that contribute strong intensity in the directions of the classical rainbows (e.g., for equation (14) near $x = \pm a/4$ where the slope is given by $d\xi/dx = 2\pi h$). This suggests the approximation of replacing the smoothly varying corrugation function such as equation (14) by a combination of straight line segments having zero slope and slopes equal to that of the inflection point as illustrated in figure 1. The relative lengths along the x-axis of the straight line segments can be chosen in a variety of ways, but the most reasonable is to choose these relative lengths according to the Taylor series expansion of the corrugation function at the critical points. For example, in the case of the sinusoidal corrugation function of equation (14) the Taylor series expansion at the maximum is $\xi(x)/hb \approx$ $1 - (2\pi x/b)^2/2!$ while the expansion for small deviations x around the inflection point is $\xi(x)/2\pi hx \approx 1 - (2\pi x/b)^2/3!$ which would imply that the zero slope and inflection point slopes would occupy lengths along the x-axis in the ratio $1:\sqrt{3}$ as shown in figure 1. Along these straight line segments the structure factor of equation (15) can be integrated to a closed form expression when the correlation length ℓ is small. For example, along the zero slope it is identical to the Brako-Newns result

$$S^{0}(\mathbf{p}_{\rm f}, \mathbf{p}_{\rm i}) = \frac{1}{L^2} \frac{2\pi\hbar^2 v_{\rm R}^2}{\Delta E_0 k_{\rm B} T_{\rm S}} \exp\left(-\frac{2v_{\rm R}^2 \mathbf{P}^2}{4k_{\rm B} T_{\rm S} \Delta E_0}\right), \quad (16)$$



Figure 1. An example of a one-dimensional sinusoidal corrugation function and its approximation by straight line segments having either zero slope or the slopes at the inflection points.

while along the straight line portion having the slope at the inflection point the result is similar, but with a shifted x-component of the parallel momentum

$$S^{\pm}(\mathbf{p}_{\rm f}, \mathbf{p}_{\rm i}) = \frac{1}{L^2} \frac{2\pi \hbar^2 v_{\rm R}^2}{\Delta E_0 k_{\rm B} T_{\rm S}} \times \exp\left(-\frac{2v_{\rm R}^2 [(P_x \pm 2\pi h \Delta k_z)^2 + P_y^2]}{4k_{\rm B} T_{\rm S} \Delta E_0}\right), \tag{17}$$

where the \pm signs refer to the two inflection points with positive and negative slopes.

The above discussion illustrates that for any onedimensional corrugation function a closed form approximation can be obtained by approximating the corrugation function by a combination of straight line segments. The combination approximation for the sinusoidal corrugation function of equation (14) is

$$S_{\text{combo}}(\mathbf{p}_{\text{f}}, \mathbf{p}_{\text{i}}) = \left(\frac{2S^{0}(\mathbf{p}_{\text{f}}, \mathbf{p}_{\text{i}}) + AS^{+}(\mathbf{p}_{\text{f}}, \mathbf{p}_{\text{i}}) + AS^{-}(\mathbf{p}_{\text{f}}, \mathbf{p}_{\text{i}})}{2(1+A)}\right),$$
(18)

where according to the choice based on the Taylor series expansions at the critical points $A = \sqrt{3}$.

For a repulsive surface with a one-dimensional corrugation function of the type such as equation (14) an analytic closed form approximation to the full three-dimensional transition rate of equation (11) is then

$$w(\mathbf{p}_{\rm f}, \mathbf{p}_{\rm i}) = \left(\frac{p_{fz}}{mL}\right)^2 \frac{2\pi\hbar}{\sqrt{4\pi\Delta E_0 k_{\rm B} T_{\rm S}}}$$
$$\times \exp\left\{-\frac{(E_{\rm f} - E_{\rm i} + \Delta E_0)^2}{4\Delta E_0 k_{\rm B} T_{\rm S}}\right\} S_{\rm combo}(\mathbf{p}_{\rm f}, \mathbf{p}_{\rm i}).$$
(19)

4. Comparison with experimental measurements

It is of interest to compare the intensities calculated from the theory developed in section 3 above in order to see if such calculations can explain the dynamical scattering of atoms



Figure 2. Energy-resolved spectrum for Ar scattering from molten Ga with $\theta_i = \theta_f = 55^\circ$, $E_i = 95$ kJ mol⁻¹ and $T_S = 673$ K. The calculations shown as a dashed–dotted curve are for the smooth surface of equation (1), the combination approximation with h = 0.08 is shown as a solid curve, and the full 1D corrugation calculation with h = 0.08 is the dotted curve. The data points shown as open circles are from [14].

from surfaces, and in particular to see if reasonable values of the corrugation height can be extracted through comparisons with the temperature dependence of the most probable intensities, as anticipated in the discussion of section 1 above. However, the available experimental data for comparison with a model of classical scattering from a one-dimensionally corrugated surface is quite limited. There is an extensive history of experiments involving scattering of molecular beams from surfaces under classical conditions, and many of these used stepped or otherwise nearly one-dimensionally corrugated surfaces combined with measurements over a range of surface temperatures. However, due to experimental difficulties in most such published papers the information on the relative intensities taken at different temperatures was not reported. In fact, to our knowledge, there is only one series of experiments that reported carefully measured relative intensities for the energy-resolved spectra taken over a large range of surface temperatures and was also in the classical mechanical regime. These are measurements of Ar atoms scattering from the molten metal surfaces of In and Ga by Nathanson *et al* [14, 15]. Although the amorphous nature of liquid metal surfaces is quite different from the one-dimensional corrugation model developed in section 3 above, since this is the only data available that provides relative scattering intensities over a range of temperatures we use this data as a guide for comparison with our calculations. It should be stressed, however, that this comparison can only be regarded as indicative of the behavior of the scattered spectra as functions of the controllable experimental parameters. Comparisons of calculations with this data can be expected to be qualitative, but not quantitative.

In addition to the energy-resolved spectra taken at fixed incident and detector angles Nathanson *et al* also reported



Figure 3. In-plane angular distribution for Ar/Ga with $\theta_i = 55^\circ$ and $E_i = 92 \text{ kJ mol}^{-1}$. The calculations are for the smooth surface of equation (1), dashed–dotted curve; combination approximation with h = 0.08, solid curve; and full 1D corrugation calculation with h = 0.08, dotted curve. The data points shown as open circles are from [14].

angular distributions taken both in and out of the scattering plane. The angular distributions are taken for fixed incident beam angles, are functions of final in-plane scattering angle, and are the integrated intensity over all final scattered energies. Thus, for these systems there are four distinctly different types of measurements available for comparison with the theory. These are energy-resolved spectra taken with a timeof-flight (TOF) detector, in-plane angular distributions, outof-plane angular distributions and temperature dependence measurements of the energy-resolved spectra.

The energy-resolved spectra are plots of intensity as a function of final energy and are single-peaked structures with the most probable intensity at a final energy significantly less than the incident energy, and a typical example is shown for the case of Ar scattering from Ga in figure 2. The in-plane angular distributions give the measured intensity as a function of final detector polar angle with fixed incident angle, and an example for Ar/Ga is shown in figure 3. The out-of-plane angular distributions are taken with both the incident and final polar angles fixed and the detector was moved perpendicularly to the scattering plane, and the intensities as shown in figure 4 are presented as a function of an angle α_f that is measured perpendicular to the scattering plane. Comparison of calculations with all of these measurements provides a redundant test of the predictive behavior of a theory.

Figure 5 gives an example of the type of comparison with experimental data from which this work argues that a measure of the surface corrugation height can be extracted. This shows the behavior as a function of surface temperature T_S of the most probable intensity, or peak intensity, of a series of energy-resolved spectra such as that shown in figure 2 for Ar scattered from liquid Ga. The incident Ar translational energy is 95 kJ mol⁻¹ (0.98 eV) and the incident and final angles are



Figure 4. Out-of-plane angular distributions for Ar/Ga with $\theta_i = 55^{\circ}$ and $E_i = 92 \text{ kJ mol}^{-1}$. The data points for $T_S = 308 \text{ K}$ (circles), 436 K (squares) and 586 K (triangles) are from [14]. The calculations are for the smooth surface of equation (1), dashed–dotted curves; combination approximation with h = 0.08, solid curves; and full 1D corrugation calculation with h = 0.08, dotted curves.

 $\theta_i = \theta_f = 55^\circ$. The experimental points shown as circles [14] show a monotonic decrease with T_S that lies in between the dash-dotted curve for the smooth surface model of equation (1) and the highly corrugated discrete model of equation (2) shown as a dashed curve. The solid curve is the calculation using the approximate closed form expression for the combination model of equation (19) using the one-dimensional corrugation function of equation (14) with a corrugation height parameter h = 0.08. The dotted curve is the result for the full calculation of equation (11) with the one-dimensional corrugation function of equation (14) and the same value of h. All calculations were carried out using a velocity parameter $v_{\rm R} = 600 \text{ m s}^{-1}$. As mentioned above a one-dimensional corrugation function is a crude approximation to the type of two-dimensional corrugation function that would be needed to properly describe an amorphous liquid surface, however, the agreement between the data and the calculated curves indicates that the behavior of the theory is qualitatively correct. The calculated curves lie between the extreme limits provided by the smooth and discrete models, roughly in agreement with the experimental points, and the corrugation height value h = 0.08 can be regarded as an approximation to the average corrugation height of the liquid surface provided by the crude model of a onedimensional corrugation.

Figure 6 shows a graph for Ar/Ga similar to figure 5 except for a lower incident energy of 42 kJ mol⁻¹ (0.44 eV). Again, the two curves for the one-dimensional corrugation considered here agree with the data calculated with the slightly smaller corrugation height h = 0.07. This is again in qualitative agreement with the intuitive expectation that at smaller incident energies the Ar projectiles would penetrate less into the surface and hence experience a smaller corrugation strength.

Although the qualitative agreements with experimental data exhibited in the intensity versus temperature graphs of



Figure 5. Temperature dependence of the most probable intensity of energy-resolved spectra for Ar scattering from molten Ga with $\theta_i = \theta_f = 55^\circ$ and $E_i = 95 \text{ kJ mol}^{-1}$. The solid curve shows calculations for the closed form combination approximation with h = 0.08, the dotted curve is the result for the full one-dimensional corrugation also with h = 0.08, the dashed curve is the $1/\sqrt{T_S}$ behavior of the highly corrugated discrete model of equation (2), and the dashed–dotted curve gives the results for the smooth surface approximation of equation (1). The data points shown as circles for temperature values $T_S = 313$, 483 and 673 K are from [14].



Figure 6. Same as figure 5 except for a lower incident energy $E_i = 42 \text{ kJ mol}^{-1}$ and the calculations are for h = 0.07. The data points shown as circles for temperature values $T_s = 309, 343, 373, 403, 453$ and 463 K are from [15].

figures 5 and 6 are satisfying, that alone is not sufficient to lend confidence in the validity of the theory. A satisfactory model of the scattering process should also explain all of the observed spectra and an illustration of this is the objective of figures 2– 4. Figure 2 shows a complete TOF spectrum converted to final energy for $T_{\rm S} = 673$ K. The experimental point at this value of $T_{\rm S}$ in the most probable intensity versus temperature plot of figure 5 comes from this data. As before the dash-dotted curve shows the results of the smooth surface model, the solid curve is for the combination model with a one-dimensional corrugation with h = 0.08, and the dotted curve is for the full one-dimensional corrugation calculation with the same h value. All three calculated curves, each representing the results of a single collision with the surface, show reasonable qualitative agreement with the data, and with each other.

The angular distributions are shown in figure 3. Plotted is the total incident intensity, summed over all final energies, as a function of final scattering angle for incident angle fixed at $\theta_i =$ 55°. The experimental points show a broad angular distribution with the most probable intensity at a slightly supraspecular position of a little larger than 60° and a width of more than 40° . For comparison of calculations with the angular distribution data, the energy-resolved differential reflection coefficients are integrated over all final energies. The dash-dotted, solid and dotted curves are, respectively, the same model calculations as described above in connection with figures 2 and 5. All three calculations are in reasonable qualitative agreement with experiment. The two calculations for the corrugated surface exhibit a somewhat broader angular distribution than that of the smooth surface, and this is to be expected since a corrugated surface would tend to scatter particles out to larger angles as compared to a flat surface. In fact, as discussed below in section 5 the comparison of calculated results for the corrugated versus uncorrugated surfaces helps to answer a fundamental question of which is more important in forming the angular spread of the scattering distribution, energy transfer through phonons or surface corrugation. The present calculations would indicate that both phonons and corrugation can cause roughly equivalent angular spreads.

A comparison with out-of-plane angular distributions is shown in figure 4. These were taken for an incident energy $E_i = 92 \text{ kJ mol}^{-1}$ (0.95 eV) with fixed $\theta_i = \theta_f = 55^\circ$. Measurements at three different temperatures are exhibited [14], 308 K are shown as square points, 436 K as circles and 586 K as triangles. The smooth, dashdotted and dotted curves are the present calculations as described in the previous figures. Again, for these out-ofplane angular distributions the calculations give reasonable qualitative agreement with the measurements. The results for the corrugated surfaces show a slightly larger angular spread in the intensity as intuitively expected.

It should be again emphasized that the data used for comparison in this section is for Ar scattering from a liquid metal surface, and is not expected to be fully explained by the present calculations for corrugations restricted to a single linear dimension on the surface. Thus the results of calculations can be regarded only as indicative of the general trends expected in the measurements. However, out of the four different types of comparisons shown in figures 2–6 comes a reasonably consistent picture illustrating the predictions of the scattering theory for a corrugated surface. The theory provides a qualitative explanation of the behavior of the observed energy-resolved spectra as well as the angular distributions over a wide range of energies and temperatures, and it provides a prediction of the corrugation strength parameter h that is reasonable.

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5. Discussion and conclusions

This paper discusses how relatively straightforward measurements of the temperature dependence of atom-surface scattering spectra taken in the classical or multiphonon regime can be used to extract physical information on the corrugation strength of the surface. We develop a semiclassical quantum theory of atom-surface scattering from a corrugated surface that is valid in the weak corrugation limit. The most general form of the final result is expressed in terms of a double surface integral over all possible impact parameters on the surface, that is to say a four-dimensional integral over the surface. This theory is extended to the regime of classical mechanics by taking the limit in which large numbers of vibrational quanta are transferred in the collision process, providing an example of the application of the Bohr correspondence principle for relating quantum to classical physics. In this classical limit all quantum correlations disappear and the surface integrals can be limited to a single surface unit cell. The theory can be regarded as an extension of the well-known classical atomsurface scattering theory of Brako and Newns [4] to the case where the surface is corrugated.

Using the classical theory, we make the prediction that a simple measurement of the most probable intensity in energyresolved scattering spectra can be directly related to the corrugation strength. More precisely, the temperature dependence of the most probable intensity is a monotonic function of the height parameter of the corrugation function, and this dependence ranges between that of a flat and uncorrugated surface and that of a highly corrugated surface resembling a collection of discrete scattering centers. Consequently, such measurements of the temperature dependence of the most probable intensity can be used to extract the value of the corrugation height parameter.

Calculations are carried out for the case of a simple one-dimensional sinusoidal corrugation function. For onedimensional corrugations it is shown that the general form of the theory lends itself to a useful approximation based on the assumption that the most important regions of the surface for forming the scattered spectrum are those that contribute to the classical rainbow patterns, i.e., the flat portions of the surface where the first derivative of the corrugation function vanishes and the inflection regions where the second derivative of the corrugation function vanishes. This approximation can be expressed in terms of analytic closed form expressions.

Calculations are carried out with both the full version of the theory for a one-dimensional corrugation function of equation (11) and the closed form approximation of equation (19). These calculations are compared with data for the scattering of Ar atoms at hyperthermal energies from molten Ga surfaces. Although a liquid metal surface is expected to be rather poorly represented by a one-dimensional periodic corrugation, we use these data because they are the only measurements available that include consistent temperature dependence of the energy-resolved spectra. Thus we would expect at best only qualitative agreement with this data, but it should indicate general trends expected as functions of the controllable experimental parameters. Comparisons of calculations with this data do show qualitative agreement with the measurements. For the Ar/Ga liquid metal system the calculated energy-resolved spectra, the in-plane angular distributions, and the out-of-plane distributions are reasonably well depicted. Furthermore, the approximate closed form result of equation (19) is shown to provide very good numerical approximations to the full theoretical expression of equation (11) in the weak corrugation limit.

Comparisons of calculations with the measurements of the temperature dependence of the most probable intensity of the available energy-resolved spectra for the Ar/Ga system allow us to extract a value for the corrugation height parameter. Even though the use of a one-dimensional corrugation function to describe the amorphous liquid metal surface is a relatively crude representation of reality, the value of the extracted corrugation parameter is reasonable. Furthermore, it has the intuitively correct property that for larger incident Ar energies the corrugation height increases. More than doubling the energy from 42 to 92 kJ mol⁻¹ gives a small increase in the predicted height parameter from approximately h = 0.07 to 0.08 for a sinusoidal corrugation function.

These calculations can also help to answer a very fundamental question in the field of molecular beams scattering from surfaces, and this question is the following: is the major contributor to the width of the measured angular distributions due mainly to surface corrugation or to energy transfer via the exchange of many phonons? Two competing theoretical approaches seem to indicate that both mechanisms can explain the rather large angular widths over which molecular beams can be scattered under classical conditions. The washboard model of Tully [16] has been extensively used to interpret experimental data, and this model has in many cases been shown to describe reasonably well the angular spread of the scattered distributions in spite of the fact that it does not include a mechanism for energy transfer with the surface. On the other hand, theories based on the Brako-Newns approach for a flat and non-corrugated surface have also been successful in explaining the observed widths of measured The results of the calculations angular distributions [2]. carried out here indicate that both static corrugations, and energy and momentum transfer to phonons can contribute to similar angular spreads in the measured spectra. Thus, to separate out the effects of static corrugation versus those due to phonons requires more extensive comparison with a larger range of data. In particular what is needed is comparisons of calculations with energy-resolved data taken over large ranges of incident projectile energies and angles as well as surface temperatures. Particularly important in this endeavor would be studies of atom–surface scattering under conditions in which rainbow behavior can be observed, because rainbow behavior can be produced not only through static corrugations of the surface [17–20], but also through inelastic scattering [21].

Future work on this and related problems will include considerations of systems and incident conditions in which rainbow behavior, both due to static corrugations and inelastic effects, can be observed. Calculations using the full theory for two-dimensional corrugations, more appropriate for application to the data available for rare gases scattering from amorphous liquid metal surfaces, are planned [22].

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