

Inelastic Low-Energy Atom-Surface Scattering

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We present a fully quantum-mechanical theory of the inelastic scattering of low-energy atoms from surfaces, based on the perturbation series and an expansion in numbers of phonons exchanged. Numerical calculations are carried out with a simple potential model and good agreement is obtained for the thermal attenuation of a helium beam by a close-packed surface of copper.

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The decrease of diffracted beam intensity with increasing crystal temperature is a much more complicated problem in low-energy atom scattering from surfaces than it is for x-ray or neutron diffraction from bulk samples. In these latter two cases, the scattering intensities can be adequately calculated in first-order perturbation theory and the thermal attenuation is given by a multiplicative Debye-Waller factor, $\exp(-2W)$, and for sufficiently elevated temperatures T_s , W is proportional to T_s . The case of low-energy atom-surface diffraction is far less simple since the interaction energies are large compared to the incident particle energies. The experimental data, particularly for He scattered by metal surfaces, often give temperature dependencies of logarithmic diffraction intensities which show considerable deviation from linear behavior, even after account of anharmonic corrections.¹

In this Letter, we consider the elastic and inelastic intensities in atom-surface scattering and show

how these can be calculated exactly, complete with all necessary phonon averaging, term by term in perturbation theory. As an example of the application of this formalism, we consider elastic specular scattering of He from a simple model of a close-packed surface of Cu and obtain good agreement with experimental results.

In terms of the transition matrix, T_{fi} , the intensity of an elastic diffraction peak associated with the reciprocal-lattice vector \vec{G} is given by

$$I_G = \langle \langle |1 - (2\pi im/\hbar^2 k_{iz} k_{Gz}) T_{Gi}|^2 \rangle \rangle, \quad (1)$$

where k_{iz} is the perpendicular component of the incident particle momentum (capital letters will be used for parallel components) and the angular brackets represent the thermal average. For elastic scattering, it has been demonstrated that $\langle \langle |T_{Gi}|^2 \rangle \rangle$ can be replaced by the simpler expression $|\langle \langle T_{Gi} \rangle \rangle|^2$.² Thus, the thermal attenuation of a diffracted beam is obtained from (1) by replacing T_{Gi} by its thermal average

$$\langle \langle T_{Gi} \rangle \rangle = \langle \langle v_{Gi} \rangle \rangle + \langle \langle \sum_i v_{Gi} (E_i - E_l + \mathcal{E}_i - \mathcal{E}_l + i\epsilon)^{-1} T_{li} \rangle \rangle, \quad (2)$$

where the total potential is $V = U + v$, with U the distorting potential of a rigid lattice. The sum \sum_i runs over all possible intermediate states, both elastic and inelastic, E_q is the particle energy, and \mathcal{E}_q is the crystal energy. Extracting a Debye-Waller factor directly from the T matrix can be done only at the expense of making very severe approximations.² In fact, an approximation often made is to simplify the Green's-function denominator by assuming that the energy change of the crystal $\mathcal{E}_i - \mathcal{E}_l$ is negligible. In a separate calculation, we have shown directly that this leads to a perturbation series which is divergent.³ Briefly stated, the n th order term will contain the factor $\langle \langle \bar{u}^{2n} \rangle \rangle$ (or a more general function reducing to this for small \bar{u}), and this thermal average grows without bound as n increases. The treatment described below does not have this divergence problem.

A general method for evaluating the thermal average of the transition matrix in Eq. (2) is to start with the Green operator expressed in integral form, i.e.,

$$G^+ = (E_l + \mathcal{E}_l - H_0 - H_c + i\epsilon)^{-1} = (-i/\hbar) \int_0^\infty \exp[i(E_l - \mathcal{E}_l - H_0 - H_c + i\epsilon)t/\hbar] dt, \quad (3)$$

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

$$H_0 = (-\hbar^2/2m)\nabla^2 + U. \quad (4)$$

Then a short calculation allows one to write the thermally averaged transition operator as

$$\langle\langle T \rangle\rangle = \langle\langle v \rangle\rangle - (i/\hbar) \int_0^\infty dt \langle\langle v(t)P(t)T \rangle\rangle, \quad (5)$$

where $P(t) = \exp[i(E_i - H_0 + i\epsilon)t/\hbar]$ depends only on the particle coordinates and $v(t)$ is the potential in the interaction picture,

$$v(t) = \exp(iH_c t/\hbar)v \exp(-iH_c t/\hbar). \quad (6)$$

Iterating T in Eq. (5) leads to the perturbation expansion in time-ordered operators, the first few terms of which are

$$\begin{aligned} \langle\langle T \rangle\rangle = & \langle\langle v \rangle\rangle + (-i/\hbar) \int_0^\infty dt \langle\langle v(t)P(t)v(0) \rangle\rangle \\ & + (-i/\hbar)^2 \int_0^\infty dt_2 \int_0^\infty dt_1 \langle\langle v(t_1+t_2)P(t_2)v(t_1)P(t_1)v(0) \rangle\rangle + \dots \end{aligned} \quad (7)$$

The formalism exhibited in Eq. (7) is particularly adapted to a potential which is the sum of pairwise interactions between the incoming atom and those of the crystal³; however, for the sake of brevity, we specialize to the following model potential with a thermally corrugated exponential repulsion and a static attractive part:

$$V(z, u) = D [e^{-2\kappa(z-u)/v_0} - 2e^{-\kappa z}], \quad (8)$$

where u is the normal component of the thermal potential displacement and $v_0 = \exp(2\kappa^2 \langle\langle u^2 \rangle\rangle)$ is the thermal average of the $\exp(2\kappa u)$. All of the essential features of the formalism are retained starting from Eq. (8), and furthermore, this model, with an appropriate static corrugation, gives excellent agreement with elastic diffraction intensities from metal surfaces when the experimental intensities are extrapolated to zero temperature.⁴

With this potential, all the phonon averages to all

orders can be readily carried out in the harmonic approximation. With $U = \langle\langle V(z, u) \rangle\rangle$, the first-order term of Eq. (7) vanishes, while the second-order term involves

$$\begin{aligned} \langle\langle (e^{2\kappa u(t)} - v_0)(e^{2\kappa u(0)} - v_0)/v_0^2 \rangle\rangle \\ = e^{Q(t)} - 1, \end{aligned} \quad (9)$$

where $Q(t) = 4\kappa^2 \langle\langle u(t)u(0) \rangle\rangle$ is the displacement correlation function which, in the usual way, can be expressed as an integral over the phonon spectral density $\rho(\omega)$ and the Bose-Einstein function $n(\omega)$. Expanding $\exp[Q(t)]$ in powers of $Q(t)$ is equivalent to an expansion in the number of intermediate virtual phonons transferred. The specular intensity for this potential is most conveniently written in terms of a dimensionless transition matrix as $I_0 = |1 - (i\pi/4p_i)F_0|^2$ and the first nonvanishing contribution is

$$\begin{aligned} F_0(p_i) = & \frac{m}{M} \int_0^\infty dq \int_0^\infty d\omega \frac{\rho(\omega)}{\omega} f^2(p_i, q) \left(\frac{n(\omega)}{p_i^2 - q^2 + \omega + i\epsilon} + \frac{n(\omega) + 1}{p_i^2 - q^2 - \omega + i\epsilon} \right) \\ & + \frac{m}{\pi^2 M} \sum_j \int_0^\infty d\omega \frac{\rho(\omega)}{\omega} L^2(p_i, j) \left(\frac{n(\omega)}{p_i^2 + (d-j-\frac{1}{2})^2 + \omega + i\epsilon} + \frac{n(\omega) + 1}{p_i^2 + (d-j-\frac{1}{2})^2 - \omega + i\epsilon} \right), \end{aligned} \quad (10)$$

and the higher phonon terms can be readily written down. In Eq. (10), $d^2 = 2mD/\hbar^2\kappa^2$, $\omega = 2m\nu/\hbar\kappa^2$, $p_i = k_{iz}/\kappa$, M is the crystal atom mass, and the functions $f(q, p)$ and $L(q, j)$ are the Morse potential matrix elements of an exponential perturbation for continuum-continuum and continuum-bound transitions, respectively.⁵ We note that Eq. (10) contains exactly all possible single-phonon virtual-exchange processes for the potential of (8), and

furthermore includes all phonon-assisted bound-state resonances.

It is straightforward exercise to extend Eq. (10) to higher orders, and we note that our calculations indicate that the two-phonon contribution coming from the second term in the expansion of $\exp[Q(t)] - 1$ is negligible. The important two-phonon effects come from the next higher order of

perturbation theory, an effect which has been pointed out previously.⁶ We note that the perturbation series seems to be convergent, and this is to be expected, since the thermal corrugations at these temperatures are small compared to a typical static corrugation.

The model used to generate Eq. (10) for the specular scattering amplitude is a potential with a rigidly vibrating exponential repulsive part. The results of calculations are compared with experiment in Figs. 1 and 2 for both low-energy (21 meV) and high-energy (63 meV) He incident on Cu(100). In these calculations, we have used the spectral density $\rho(\omega)$ corresponding to the incident He atom interacting with the average over a cell containing four Cu atoms of the (100) face,⁷ to account for the geometrical effect that the atom interacts simultaneously with several surface atoms as is found, for instance, with a pairwise summation potential.⁸ In addition, the spectral density is multi-

plied by a factor of $\alpha = \frac{1}{4}$, a parameter which accounts primarily for the fact that the isopotentials of the Morse interaction of Eq. (8) have a vibrational amplitude $2u$ at low energies, diminishing to u at high energies. This factor also accounts for the interactions with atoms outside of the four atoms of the cell, and for the fact that the model does not have the physical constraint of conservation of parallel momentum, both of these being effects which would tend to reduce the effective spectral density. Inclusion of nonadditive contributions to the potential, and averaging over the size of the He atom,⁹ would further reduce the strength of the interaction potential, but since the scattering amplitude of Eq. (10) is quadratic in both the matrix elements and the thermal displacement, these seemingly widely different effects can be accounted for by the same parameter. Even with the simple and restricted model that we have used the agreement with experiment is good; the important point is that the deviation from linear behavior in the experimental points is well matched, particularly at the higher energy.

The effect of the attractive well is very dramatic. Shown in Fig. 3(a) are examples of calculations with $\alpha = 1$ of the specular intensity versus tempera-

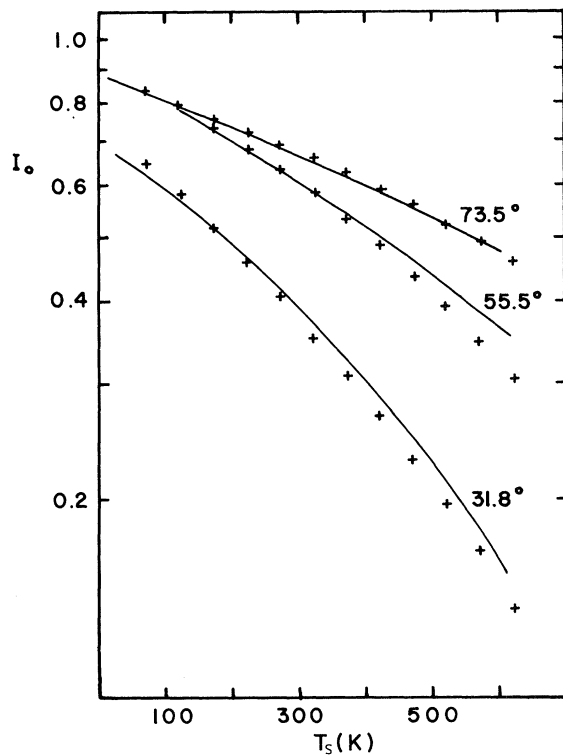


FIG. 1. Specular intensity as a function of temperature for 21-meV He scattered by a Cu (100) surface; $D = 6.35$ meV and $\kappa = 1.05 \text{ \AA}^{-1}$. Experimental points are those of Lapujoulade and co-workers for angles of incidence 73.5° , 55.5° , and 31.8° as shown. Since the experimental intensities do not extrapolate to unity for each incidence angle, the calculated intensities have been multiplied by the corresponding experimental unitarity.

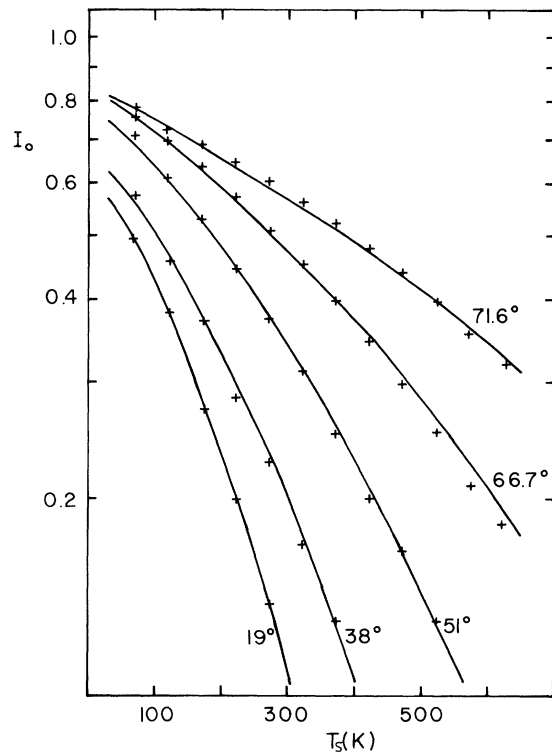


FIG. 2. Same as Fig. 1 except for an incident energy of 63 meV and different incident angles.

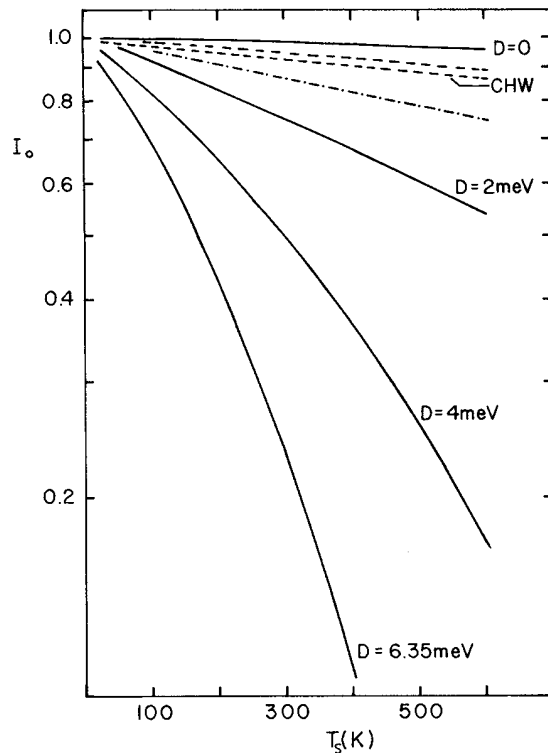


FIG. 3. Effects of well depth and the hard-wall limit in the specular intensity as a function of temperature for 21-meV He scattered by a Cu (100) surface at $\theta_i = 73.5^\circ$. Solid lines, calculations for different values of the well depth D , $\kappa = 1.05 \text{ \AA}^{-1}$; dashed lines, calculations for the exponential repulsive potential ($D = 0$) with values of $\kappa = 2.5 \text{ \AA}^{-1}$ and $\kappa \rightarrow \infty$ (CHW) showing the approach to the hard-wall limit; dash-dotted line, the exponential repulsive potential with the Beeby correction for $D = 6.35 \text{ meV}$ and $\kappa = 1.05 \text{ \AA}^{-1}$.

ture for several values of the well depth, including the case of the exponential repulsive potential ($D = 0$). The exponential repulsive model gives a specular intensity that is always far larger than experiment, the difference increasing with temperature. Note that as κ increases, the corrugated-hard-wall¹⁰ (CHW) limit is approached. Even the exponential repulsion potential with the well simulated by a Beeby correction, also shown in Fig. 3 (i.e., the only effects of the well are to enhance the perpendicular momentum and refract the incident beam), gives intensities which are too large. Thus

we must conclude that a simple exponential potential is certainly an inadequate model, even when the well is simulated in a semiclassical manner.

Similar methods can be used to calculate the inelastic scattering intensities, and in fact, the inelastic transition rate is contained in the elastic scattering amplitudes through the optical theorem. For strongly diffractive systems, one develops the inelastic scattering amplitudes starting from a strong scattering elastic formalism using projection techniques similar to those used to handle bound-state resonances in purely elastic scattering.

The calculations presented here serve to underscore our introductory statement that thermal attenuation is a much more involved problem in atom-surface diffraction than in many other diffraction experiments. The fact that a logarithmic plot of the experimentally observed intensities from metal surfaces is not linear in temperature for large temperatures points out that it is inconvenient to attempt to represent the thermal attenuation by a Debye-Waller-type factor, and we have demonstrated that agreement can be readily obtained by direct calculation of the inelastic scattering.

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¹J. Lapujoulade, J. Perreau, and A. Kara, *Surf. Sci.* **129**, 59 (1983).

²A. C. Levi and H. Suhl, *Surf. Sci.* **88**, 221 (1979); V. Celli and A. A. Maradudin, to be published.

³G. Armand and J. R. Manson, to be published.

⁴J. Perreau and J. Lapujoulade, *Surf. Sci.* **119**, L292 (1982).

⁵C. Strachan, *Proc. Roy. Soc. London, Ser. A* **150**, 456 (1935); A. R. Devonshire, *Proc. Roy. Soc. London, Ser. A* **158**, 269 (1937).

⁶Everett Thiele and John Weare, *J. Chem. Phys.* **48**, 2324 (1968); J. R. Manson and John Tompkins, *Prog. Astronaut. Aeronaut.* **51**, 603 (1977).

⁷G. Armand, *J. Phys. (Paris)* **38**, 989 (1977).

⁸J. Lapujoulade, *Surf. Sci.* **134**, 529 (1983).

⁹N. D. Lang and J. K. Norskov, *Phys. Rev. B* **15**, 4612 (1983).

¹⁰G. Armand and J. R. Manson, *Surf. Sci.* **80**, 532 (1979); N. Garcia and G. Benedek, *Surf. Sci.* **80**, 543 (1979).