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Atom-surface scattering in the classical limit: Temperature and energy dependence

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The backscattered intensity from a beam of atomic projectiles directed towards the surface of a many-body target can be expressed in terms of simple closed-form expressions in the single-collision classical regime. Two well-known limits, which exhibit significantly different dependence on the target temperature and incident energy, arise for the cases in which the target is considered either as a collection of discrete scattering points or as a flat repulsive surface. By examining a target potential that varies from the case of a weakly corrugated smooth repulsive surface to strongly corrugated cores a classical expression is derived that exhibits a continuous distribution of temperature dependencies that connect and bridge the extreme behavior of the two well-known classical limits. [S0163-1829(98)07827-8]

I. INTRODUCTION

The exchange of energy between a gas of particles and its containment vessel, whether the gas is in the low-energy regime such as thermal energy atoms or in the high-energy regime of an ionized plasma, is ultimately through exchange of vibrational modes of the surface in the form of heat. Historically, an important viewpoint for understanding this problem has been the study of the interaction of an isolated projectile with a surface. Energy transfer in single gas particle collisions with the surface has been discussed in quantitative mathematical terms since Knudsen's 1910 analysis of the accommodation coefficient,[1,2] a concept originally introduced by Maxwell.[3] The exchange of energy of a projectile with the surface is is important to an enormous range of experimentally measurable systems extending from the purely quantum-mechanical interaction of a low-energy, small mass atom[4] to the classical regime of heavy ion scattering with translational energies of keV.[5]

The experimental technique of He atom scattering from surfaces has been used extensively in recent years to gain a great deal of understanding about the energy exchange process at the microscopic level, and by extension has become a major method of investigating and characterizing surfaces.[4,6,7] In such systems the major mechanism for energy exchange is usually through single quantum interactions with the surface phonons,[8–10] although often large inelastic background intensities are observed due to multiple quantum exchanges.[11] The transition to the classical regime of multiple quantum exchange has been observed at high incident energies and high temperatures.[12,13]

Energy exchange in the scattering of heavier neutral atoms with surfaces has long been a subject of experimental study.[14,15] Recently, a series of high-precision energy-resolved experiments have demonstrated that the scattering of heavier rare-gas atoms with translational energies in the eV range from liquid metal surfaces can be described in completely classical terms.[16,17]

Inelastic exchange with vibrational modes plays a large role in the scattering of other projectiles such as electrons, ions and neutrons. Electron-energy-loss spectroscopy (EELS) has become a major tool for measuring surface phonons and other modes associated with surface adsorbates,[18] and there are significant inelastic backgrounds due to phonon exchange in EELS and in low-energy electron scattering (LEED).[18,19] In low-energy ion scattering the primary mechanism of energy loss is through excitation of elementary surface excitations,[5] and even in high-energy ion scattering this is still a major mechanism of energy exchange at glancing angles of incidence to the surface.[20–22]

There have been several different approaches to the theoretical description of the classical domain of projectile-surface scattering. One method is to use computer calculations in order to simulate the trajectory of the projectile as it interacts with the surface, and the many-body nature of the surface is treated with molecular-dynamics approaches[23–26] or other computationally intensive methods.[27] Another approach is to use purely analytical methods,[28] and using approaches originally applied to neutron scattering,[29] scattering intensities in the classical limit of exchange of many quanta of energy can be expressed in simple and elegant analytical forms.[30–34]

The analytic approaches give rise to two somewhat different classes of solutions that exhibit different dependencies on the incident energy of the projectile and on the surface temperature, depending on whether the surface is considered to be a smooth vibrating barrier or, alternatively, made up of a collection of discrete scattering centers. The main purpose of this paper is to discuss the origins of these these two types of classical solutions and to discuss how the differences in analytic form arise. It is shown that the differences can be explained in terms of the relative strengths of the surface corrugation, and in the process it is shown that classical expressions exist that exhibit the complete range of behavior between the two original solutions for discrete and smooth surfaces. A single analytic expression is exhibited that gives the discrete and smooth surface results as limiting cases of strong and weak surface corrugation and bridges these two limits for intermediate corrugation strengths.

II. THEORY

In the classical limit of large incident energies and high surface temperatures the scattering of an atomic projectile by a continuous, smooth, vibrating surface can be described by a transition rate $w(\mathbf{p}_f,\mathbf{p}_i)$ for scattering an incident beam of particles with momentum $\mathbf{p}_i$ into a final momentum state of $\mathbf{p}_f$. The result is given by the following expression;[31–34]

$$w(\mathbf{p}_f,\mathbf{p}_i)=\frac{2\hbar v_R^2}{S_{\text{u.c.}}}\,|\tau_{fi}|^2\left(\frac{\pi}{\Delta E_0 k_B T_S}\right)^{3/2}\times\exp\left\{-\frac{(E_f-E_i+\Delta E_0)^2+2v_R^2\mathbf{P}^2}{4k_BT_S\Delta E_0}\right\},\qquad(1)$$

where E_f and E_i are the final and initial energy of the projectile whose energy in a given momentum state $\mathbf{p}_q$ is given by $E_q=\mathbf{p}_f^2/2m$ with m the projectile mass. T_S is the surface temperature and k_B is the Boltzmann constant, $S_{\text{u.c.}}$ is the area of a surface unit cell, v_R is a weighted average of phonon velocities at the surface,[31] $|\tau_{fi}|^2$ is the scattering form factor, $\hbar$ is the Planck constant, and ΔE_0 is the recoil energy. The momentum of a projectile is decomposed into components parallel and perpendicular to the surface according to $\mathbf{p}_q=(\mathbf{P}_q,p_{qz})$ with the z axis taken as normal to the surface. Then $\mathbf{P}=\mathbf{P}_f-\mathbf{P}_i$ is the parallel momentum transfer. The recoil energy appearing in Eq. (1) is in the simplest case given by $\Delta E_0=\mathbf{p}^2/2M$ where $\mathbf{p}=\mathbf{p}_f-\mathbf{p}_i$ is the scattering vector and M is the mass of a surface atom, although several other forms have been suggested.[11,33] The Gaussian-like term in the parallel momentum transfer $\mathbf{P}$ in Eq. (1) arises from the correlations of vibrations parallel to the surface, and is the only dependence of Eq. (1) on the actual form of the surface phonon spectral density. In the limit as $v_R\rightarrow\infty$ Eq. (1) agrees with previous theories such as the classical hard cubes model, in which parallel momentum is assumed to remain constant, i.e., $\mathbf{P}=0$.[35]

If, instead of a smooth continuous barrier, the surface is regarded as a collection of discrete scattering centers, the transition rate becomes a somewhat simpler expression than Eq. (1):[29,34]

$$w(\mathbf{p}_f,\mathbf{p}_i)=\frac{1}{\hbar}\,|\tau_{fi}|^2\left(\frac{\pi}{\Delta E_0 k_B T_S}\right)^{1/2}\times\exp\left\{-\frac{(E_f-E_i+\Delta E_0)^2}{4k_BT_S\Delta E_0}\right\}.\qquad(2)$$

The essential differences between the smooth surface limit of Eq. (1) and the discrete target limit (2) is that Eq. (1) has the additional Gaussian-like term in the parallel momentum transfer $\mathbf{P}$ arising from correlated vibrations parallel to the surface, and it has an envelope function varying as $(\Delta E_0 T_s)^{-3/2}$ rather than $(\Delta E_0 T_s)^{-1/2}$. This classical limit depends on the interaction potential between the projectile and the surface cores only through the form factor $|\tau_{fi}|^2$, and it is independent of the form of the vibrational spectrum at the surface. It depends on the surface temperature through equipartition of kinetic energy and on the recoil energy through the choice of ΔE_0.

Although both Eqs. (1) and (2) can be derived from purely classical arguments, it is more germane to the discussion here to derive them from quantum-mechanical theory taken to the classical limit using the correspondence principle of large quantum numbers. Within a forced harmonic oscillator approximation, and assuming that the collisions is short compared to vibrational periods, the transition rate takes on the following form:[6,36]

$$\begin{aligned}w(\mathbf{p}_f,\mathbf{p}_i)=&\frac{1}{\hbar^2S_{\text{u.c.}}^2}\int_{-\infty}^{+\infty}dt\,e^{-i(E_f-E_i)t/\hbar}\sum_l e^{i\mathbf{P}\cdot\mathbf{R}_l/\hbar}\\&\times\int_{\text{u.c.}}d\mathbf{R}\int_{\text{u.c.}}d\mathbf{R}'\,e^{i\mathbf{P}\cdot(\mathbf{R}-\mathbf{R}')/\hbar}\tau(\mathbf{R})\tau(\mathbf{R}')\\&\times e^{ip_z[z(\mathbf{R})-z(\mathbf{R}')]}e^{-W(\mathbf{R},p_f,\mathbf{p}_i)}e^{-W(\mathbf{R}',\mathbf{p}_f,\mathbf{p}_i)}\\&\times e^{\mathcal{W}_l(\mathbf{R},\mathbf{R}';\mathbf{p}_f,\mathbf{p}_{i,l})},\end{aligned}\qquad(3)$$

where $\mathbf{R}_l$ is the position of the surface atom in the lth unit cell (u.c.), $\tau(\mathbf{R})$ is the source function, and $z(\mathbf{R})$ is the position of the classical turning point of the projectile. $\exp\{-W(\mathbf{R},\mathbf{p}_f,\mathbf{p}_i)\}$ is the Debye-Waller factor and $\mathcal{W}_l(\mathbf{R},\mathbf{R}';\mathbf{p}_f,\mathbf{p}_i,t)$ is a generalized displacement correlation function, related to the Debye-Waller factor through the relation $W(\mathbf{R},\mathbf{p}_f,\mathbf{p}_i)=\mathcal{W}_{l=0}(\mathbf{R}=\mathbf{R}';\mathbf{p}_f,\mathbf{p}_i,t=0)$. Within the approximation of a harmonic system with linear coupling, the correlation function depends only on the difference $\mathbf{R}-\mathbf{R}'$ and takes the form $\mathcal{W}_l(\mathbf{R};\mathbf{p}_f,\mathbf{p}_i,t)=\langle\boldsymbol{\mathcal{F}}\cdot\mathbf{u}_0(0,0)\boldsymbol{\mathcal{F}}\cdot\mathbf{u}_l(\mathbf{R},t)\rangle$, where $\boldsymbol{\mathcal{F}}$ is a generalized force that in the classical limit becomes the momentum transfer $\boldsymbol{\mathcal{F}}\rightarrow\mathbf{p}/\hbar$.

Equation (3) can be related easily to other forms for the transition rate that have been successfully used in multiphonon inelastic scattering. For example, in the exponentiated distorted wave Born approximation[37,38] $\boldsymbol{\mathcal{F}}$ becomes a matrix element, taken between quantum states $\mathbf{p}_f$ and $\mathbf{p}_i$, of the gradient of the interaction potential with respect to the vibrational displacement $\mathbf{u}$. On the other hand, the widely used eikonal approximation is recovered when the source function is given by the simple form $\tau(\mathbf{R})\propto(k_{iz}/k_{fz})^{1/2}$.[6]

The classical scattering intensities of Eqs. (1) and (2) are readily derived from the general expression of Eq. (3) upon recognizing that in the classical limit of exchange of large numbers of quanta, the coherence region in both time and space becomes small. Thus, in the correlation function only small times and small R are important and only a single term in the sum over unit cells contributes. The two classical limits of Eqs. (1) and (2) are now recovered upon making an expansion in small times and displacements and carrying out the corresponding integrals by the method of steepest descents. Choosing $\tau(\mathbf{R})$ to be a constant, which is consistent with a continuous surface sheet that is flat when evaluated at the position of vibrational equilibrium $\tau(\mathbf{R})=\tau_{fi}$, the double integral over space in Eq. (3) reduces to a single integral and the result is the smooth surface limit of Eq. (1). Similarly, if the source function is chosen to be consistent with an isolated point particle at the center of each unit cell, $\tau(\mathbf{R})=\tau_{fi}S_{\text{u.c.}}\delta(\mathbf{R})$, where $\delta(\mathbf{R})$ is the Dirac δ function in the two dimensions parallel to the surface, then the classical limit of Eq. (3) is the discrete particle surface model of Eq. (2).

This exercise shows that the differences apparent in Eqs. (1) and (2) are due entirely to the corrugation of the source function $\tau(\mathbf{R})$. These two classical expressions represent the extreme limits of surfaces which, at their vibrational equilibrium, are either a hard flat sheet or a collection of discrete point masses. This implies that it should be possible, with appropriate choice of the corrugation of the source function, to obtain a continuous distribution of classical limit expressions that exhibit a continuous range of temperature and energy dependence between the limits of Eqs. (1) and (2).

III. WEAK CORRUGATION LIMIT

In order to examine the temperature and energy dependence induced by different degrees of corrugation of the source function, it is of interest to look first at a weakly corrugated surface for which $\tau(\mathbf{R})$ appearing in Eq. (3) can be expanded in a Taylor series about its maximum point. For simplicity, consider $\tau(\mathbf{R})$ to be a real function, although the general case is straightforward. A suitable expansion is

$$\tau(\mathbf{R})=\tau(0)+\boldsymbol{\nabla}\tau(0)\cdot\mathbf{R}+\frac{1}{2}\sum_{\beta=1}^{2}\sum_{\beta'=1}^{2}\times\frac{\partial^2\tau(0)}{\partial R_\beta\partial R_{\beta'}}R_\beta R_{\beta'}+\cdots . \tag{4}$$

The turning point locus is also expanded

$$z(\mathbf{R})=z(0)+\boldsymbol{\nabla}z(0)\cdot\mathbf{R}+\cdots , \tag{5}$$

although it is expected that the expansion point $\mathbf{R}=0$ will usually be an extremum of $\tau(\mathbf{R})$ and $z(\mathbf{R})$ in which case the first derivatives will vanish. The spatial dependence of the Debye-Waller factors in Eq. (3) will be neglected.

For simplicity it will be convenient to assume isotropy of $z(\mathbf{R})$ and $\tau(\mathbf{R})$ in a region about the point of expansion so that the derivatives with respect to R_β are the same in all directions parallel to the surface. When the expansions of Eqs. (4) and (5) are substituted into the general expression (3) the integrals can be evaluated in the classical limit using the method of steepest descents as before and the result is

$$w(\mathbf{p}_f,\mathbf{p}_i)=2\hbar v_R^2|\tau(0)|^2\left(\frac{\pi}{\Delta E_0 k_B T_S}\right)^{3/2}\exp\left\{-\frac{(E_f-E_i+\Delta E_0)^2+2v_R^2[\mathbf{P}+p_z\boldsymbol{\nabla}z(0)]^2}{4k_BT_S\Delta E_0}\right\}$$
$$\times\left\{1-\gamma^2\frac{2\hbar^2v_R^2}{k_BT_S\Delta E_0}\left[1-\frac{2v_R^2[\mathbf{P}+p_z\boldsymbol{\nabla}_z(0)]^2}{4k_BT_S\Delta E_0}+\cdots\right]+\cdots\right\}. \tag{6}$$

The symbol γ is the corrugation range parameter of the source function in this weak corrugation limit:

$$\gamma^2=-\frac{1}{2\tau(0)}\frac{\partial^2\tau(0)}{\partial R^2}, \tag{7}$$

and this is expected to be a positive number if the point of expansion is at the maximum of $\tau(\mathbf{R})$.

Clearly, with the identification $\tau(0)=\tau_{fi}$ the leading term in Eq. (6) is the same as the smooth surface limit of Eq. (1) except that the Gaussian-like term in parallel momentum transfer P^2 has been replaced by $[\mathbf{P}+p_z\boldsymbol{\nabla}z(0)]^2$. Thus the effect of the parallel momentum transfer is strengthened by the term involving the gradient of the classical turning point position. The effect of the corrugation of the source function is to weaken the temperature dependence. The envelope function of Eq. (6) is of the form

$$\left(\frac{1}{\Delta E_0 k_B T_S}\right)^{3/2}\left(1-\frac{|\mathrm{const}|}{\Delta E_0 k_B T_S}\right). \tag{8}$$

Viewed as a function of surface temperature for fixed energy, the correction factor in Eq. (8) weakens the $1/T_S^{3/2}$ temperature dependence of the leading factor. Thus the temperature dependence of the envelope function for the intensity of particles scattered from a surface with a weakly corrugated source function is less strong than that of the uncorrugated surface.

IV. STRONG CORRUGATION LIMIT

Having examined the weak corrugation limit in Sec. III above, it is now of interest to examine the opposite limit of a source function, which is nearly a point δ-function source corresponding to a strongly corrugated surface. This can be accomplished by choosing the source to be a localized function which reduces to a δ function in an appropriate limit, such as

$$\tau(\mathbf{R})=\mathcal{N}\frac{2\gamma^2}{\tau}\tau_{fi}e^{-2\gamma^2R^2}, \tag{9}$$

where $\mathcal{N}$ is a normalization constant that will be simply $S_{\mathrm{u.c.}}$ if the range parameter is large, i.e., if $S_{\mathrm{u.c.}}\gg 1/\gamma^2$.

Substituting Eq. (9) into the general expression (3) and assuming isotropy in the spatial variables as above in Sec. III it is again possible to evaluate the integrals with the method of steepent descent. The result is

$$w(\mathbf{p}_f,\mathbf{p}_i)=\frac{1}{\hbar}|\tau_{fi}|^2e^{[\boldsymbol{\nabla}W(0)]^2/4\gamma^2}\left(\frac{\pi}{\Delta E_0k_BT_S}\right)^{1/2}$$
$$\times\exp\left\{-\frac{(E_f-E_i+\Delta E_0)^2}{4k_BT_S\Delta E_0}\right\}\left[\frac{\gamma^2}{\frac{k_BT_S\Delta E_0}{2\hbar^2v_R^2}+\gamma^2}\right]$$
$$\times\exp\left\{-\frac{[\mathbf{P}+p_z\boldsymbol{\nabla}_z(0)]^2}{4\left(\frac{k_BT_S\Delta E_0}{2v_R^2}+\hbar^2\gamma^2\right)}\right\}. \tag{10}$$

Equation (10) is an interesting expression because it contains as limiting cases both the discrete model and the smooth surface model. Taking the limit as $\gamma^2 \to \infty$ one obtains the discrete limit together with correction terms:

$$w(\mathbf{p}_f,\mathbf{p}_i)=\frac{1}{\hbar}\,|\tau_{fi}|^2\left(\frac{\pi}{\Delta E_0 k_B T_S}\right)^{1/2}\exp\left\{-\frac{(E_f-E_i+\Delta E_0)^2}{4k_B T_S \Delta E_0}\right\}$$
$$\times\left\{1-\frac{1}{\gamma^2}\left[\frac{k_B T_S \Delta E_0}{2\hbar^2 v_R^2}+\frac{[\mathbf{P}+p_z\boldsymbol{\nabla}z(0)]^2}{4\hbar^2}\right.\right.$$
$$\left.\left.-[\boldsymbol{\nabla}W(0)]^2\right]+\cdots\right\}. \tag{11}$$

This has Eq. (2) as the leading term. The temperature and energy dependence of the envelope function, if the term involving the gradient of the Debye-Waller argument is ignored, is of the form

$$\left(\frac{1}{\Delta E_0 k_B T_S}\right)^{1/2}(1-|\mathrm{const}|\Delta E_0 k_B T_S), \tag{12}$$

which if viewed as a function of T_S at fixed energy describes a more rapid decay with temperature than the uncorrected $1/T_S^{-1/2}$ envelope, contrary to the behavior of Eq. (8). Thus when the source function corrugation is less strong than that of a collection of discrete scattering centers, the most probable intensity decays faster with increasing temperature.

On the other hand, if one takes the limit of Eq. (10) as $\gamma^2 \to 0$ the result, after choosing the correct normalization constant $\mathcal{N}$ and ignoring the spatial dependence of the Debye-Waller exponent, is identical with Eq. (6) with the same physical definition relating γ^2 to the curvature of the source function as in Eq. (7). Thus, Eq. (10) is more than just an expression that produces the limiting case of the intensity for a nearly discrete corrugation of the source function. Equation (10), as a function of the surface corrugation through the range parameter γ^2, gives a continuous distribution of temperature and energy dependence which completely bridges the limiting behaviors of Eqs. (1) and (2).

V. COMPARISON WITH EXPERIMENT

It is of interest to compare the results calculated here and contained in Eq. (10) with available experimental data. However, in most classical scattering experiments the intensity observations are reported in terms of relative intensities or even in arbitrary units because of the difficulties of maintaining a consistent normalization for experiments done at different incident energies or surface temperatures. However, there are a small number of experiments for which comparisons can be made with the temperature dependence of the most probable intensity of the scattered peak for fixed incident beam energy and angle.

One such experiment is the scattering of He atoms from a clean and ordered single crystal surface of Cu(001) at incident energies of about 100 meV.[12,39] Similar experiments have been done at somewhat higher energies 100–250 meV for both He and D_2 scattering from the same Cu(001) surface.[13] The scattered intensities observed in both of these experiments consisted of small and sharply peaked quantum-mechanical features due to elastic diffraction or single surface phonon transfer, superimposed on a single broad multiphonon peak. At higher energies and surface temperatures, the quantum peaks disappeared completely leaving only the broad classical inelastic peak. Both of these experiments are in agreement with a temperature dependence of the most probable intensity of the classical peak going as $1/T_S^{-3/2}$ in agreement with Eq. (1) for a smooth vibrating surface. The work on comparisons of He and D_2 scattering also measured the energy dependence of the most probable intensity and this also was consistent with the $1/\Delta E_0^{-3/2}$ dependence of the continuum model (1) (Ref. 13) This behavior is not surprising, because the repulsive part of the He-metal surface potential is known to be smooth and to have a very weak corrugation,[9,40] which are the conditions for Eq. (1) to be valid.

Quite recently Ronk *et al.* reported a new series of experiments for atom scattering at surfaces in the classical domain but for incident energies intermediate between the He projectiles and the Na^+ ions discussed above.[16] These experiments were carried out for the scattering of the heavier rare gases Ne, Ar, and Xe from the surfaces of the molten metals Ga, In, and Bi, with incident energies in the range 0.1–2 eV. The observed intensities consisted, in every case, of a broad inelastic intensity peak with its maximum at a position of substantial energy loss by the incident projectiles, and with a long tail in the direction of energy loss and another long tail on the energy gain side extending out to energies larger than the incident projectile energy. These intensities were well explained by an analysis based on the discrete model of Eq. (2) with the inclusion of successive multiple scattering events with more than one liquid metal atom.[17]

In these experiments it was possible to carry out a series of measurements for the temperature dependence of the most probable intensity for the case of Ar scattering from liquid Ga and liquid In. Although in each case the temperature range was limited to a variation of approximately 100–150 K above the melting temperature, the data were quite adequate to demonstrate that the temperature dependence was intermediate to the two limiting cases of $1/T_S^{-3/2}$ and $1/T_S^{-1/2}$ given by Eqs. (1) and (2).[16,17]

Figure 1 shows these data together with calculations carried out using Eqs. (10) of Sec. IV above. The data shown in Fig. 1 are for Ar with incident energy $E_i = 0.44$ eV, incident angle θ_i and final angle θ_f given by $\theta_i = \theta_f = 55°$, and the data points are the values of the most probable intensity as a function of surface temperature T_S. The points shown by circles (○) are for gallium and those shown as squares (□) are for indium.[16] The $T_S^{-3/2}$ and $T_S^{-1/2}$ behaviors predicted by Eqs. (1) and (2) are shown by the dash-dotted and the dashed lines, respectively. The solid lines are calculations using Eq. (10). For these calculations we have assumed that $\boldsymbol{\nabla}z(0) = 0$, the value of the range parameter for the source function is $\gamma = 20\ \text{Å}^{-1}$ and $v_R = 400$ m/s. Because the experimental data were measured only over a limited range, the fit of the theory to the data cannot be considered definitive evidence for the validity of Eq. (10), however, the agreement is quite good.

The value of v_R is expected to be of the same order of magnitude as the surface wave velocity in the case of smooth

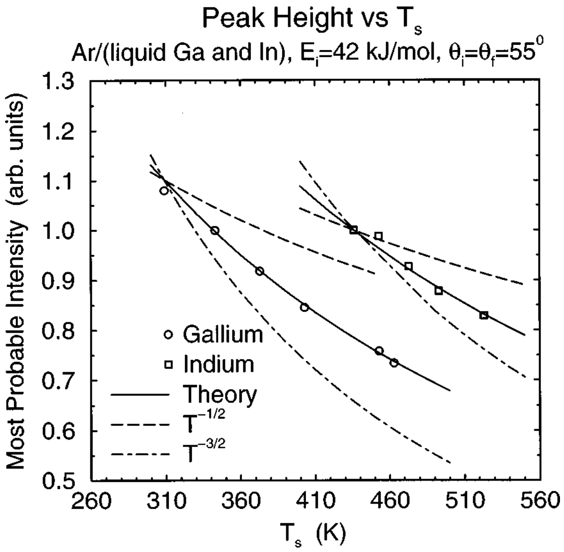

FIG. 1. Temperature dependence of the intensity at the most probable energy transfer for Ar with incident energy $E_i = 0.44$ eV and incident angle $\theta_i = 55°$ scattering from liquid Ga and In. The data points shown by circles (○) are for gallium and the data points shown as squares (□) are for indium (Ref. 16). The $T_S^{-3/2}$ and $T_S^{-1/2}$ behavior predicted by Eqs. (1) and (2) are shown by the dash-dotted and the dashed lines, respectively. The solid line is the result predicted by the general Eq. (10) with a range parameter value $\gamma = 20$ Å^{-1} and $v_R = 400$ m/s.

solid surfaces.[31] For many solids it has been determined to be smaller than the Rayleigh phonon velocity.[39] For rougher solid surfaces it is expected to be smaller than for smooth solid surfaces due to lessened vibrational correlation, and similarly for liquids it is expected to be even smaller compared to the velocity of sound in the bulk. The value of $v_R = 400$ m/s chosen here can be compared with the respective sound velocities, which are $u = 2740$ m/s for Ga at its melting temperature of $T_M = 303$ K and $u = 2215$ m/s for In at its melting temperature of $T_M = 429$ K.[41]

The value of $\gamma = 20$ Å^{-1} implies a full width at half maximum (FWHM) of the source function of Eqs. (9) given by FWHM$= 2\sqrt{\ln 2}/\gamma = 0.08$ Å. Compared to the mean nearest-neighbor distance between metal atoms in the liquid, which is $D = 2.78$ Å for Ga and $D = 3.14$ Å for In,[42] this value is small, which implies a strong corrugation of the source function and hence very localized scattering centers.

Earlier, it was empirically observed that the data points in Fig. 1 were reasonably fit by a curve varying as $1/T_S$.[17] The calculated curves in Fig. 1 are nearly indistinguishable from a $1/T_S$ fit over the range of temperatures shown, however, over a larger range of temperatures the present calculated curve is less concave than a $1/T_S$ curve.

It is possible to obtain equally good fits to the data of Fig. 1 for larger values of γ, as long as v_R is reduced according to the relation $\gamma v_R =$ const as suggested by the envelope factor of Eq. (10). The chosen values of $\gamma = 20$ Å^{-1} and $v_R = 400$ m/s correspond to the smallest value of γ for which the entire curves of the calculated intensities at all energy transfers agree with the experimental measurements of Ref. 16. For these values of γ and v_R the comparisons with the experimental time of flight (TOF) measurements, which were taken just above the melting points of Ga and In, are indistinguishable from the previously published calculations based on the discrete scattering center model of Eq. (2).[17]

Good fits to the data of Fig. 1 can also be obtained for smaller values of γ, and in this case v_R must be increased but not as much as would be indicated by the relation $\gamma v_R =$ const. However, the resulting curves for the calculated energy distributions become too narrow to agree with the broad peaks observed in the full TOF measurements, therefore $\gamma = 20$ Å^{-1} must be considered as the smallest value permitted by this model.

VI. CONCLUSIONS

In this paper two well-known classical mechanical expressions for describing the intensity of atomic projectiles scattering from surfaces have been reexamined. One of these models treats the surface target as a collection of point scattering centers and its intensity gives a characteristic signature dependence on temperature and incident energy for the most probable intensity, which varies as $1/(\Delta E_0 T_S)^{1/2}$. The other model assumes that the target surface is a smooth vibrating sheet and it produces a most probable intensity which varies as $1/(\Delta E_0 T_S)^{3/2}$. By treating the scattering problem semiclassically within a source function formalism, in which the source function describes the reflectivity properties of the surface at each point, a new classical expression is obtained in the correspondence principle limit of transfer of large numbers of phonon quanta. This expression interpolates between the discrete and smooth-surface models, and as a function of a single parameter, gives a continuous gradation of temperature and energy dependencies for the most probable intensity which bridges the gap between the $1/(\Delta E_0 T_S)^{1/2}$ and $1/(\Delta E_0 T_S)^{3/2}$ cases of the two extreme models.

Interestingly, the intensity derived from the smooth-surface model of Eq. (1) is not normalizable due to the singularity in the envelope function at small incident energy and in the forward direction. However, the new expression obtained here in Eq. (10) is no more singular than the discrete model function of Eq. (2), and is normalizable.

The theoretical expression Eq. (10) is applied to two available sets of data for the scattering of Ar from the surfaces of liquid Ga and In,[16] and good agreement is obtained, not only for the temperature dependence of the most probable intensity, but also for the complete TOF intensity curves. Clearly, the comparison with the very limited data currently available does not allow for the unambiguous conclusion that Eq. (10) is the only correct expression connecting the two well-known classical transition rates. However, this work demonstrates that theoretical comparisons with the full temperature and incident energy dependence of the scattered intensity for such systems, even in the classical scattering regime, can provide valuable information on the amplitude and statistics of the surface corrugation.

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