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Temperature effects in diffractive atom-surface scattering

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A theory is presented of the diffractive scattering of a light atom by a semi-infinite crystal in which the atoms are executing thermal vibrations about their equilibrium positions. The intensities of the diffracted beams can be expressed in terms of the average of the scattered wave function over the canonical ensemble defined by the vibrational Hamiltonian of the crystal (this is not true for the inelastic component of the scattered intensity). With the aid of projection operators we obtain the integral equation satisfied by the averaged atomic wave function. The effective potential entering this equation is nonlocal in space and time, complex, and temperature dependent. The change in intensity of each diffracted beam due to scattering out of the beam by the thermal vibrations of the atoms constituting the crystal is related to this effective potential.

I. INTRODUCTION

The following problem still hampers our understanding of the diffracted intensities in atom-surface scattering. If the scattering were due to an impulsive, two-body collision, the diffracted intensities could be computed by solving a purely elastic problem, and then multiplying the results by the usual Debye-Waller factor, $\exp[-\langle(\vec{q}\cdot\vec{u})^2\rangle][=\exp(-\sum_\alpha q_\alpha^2\langle u_\alpha^2\rangle)$ in situations of high symmetry], where $\vec{q}$ is the momentum transferred in the collision and $\langle u_\alpha^2\rangle$ is the mean-square displacement, in the direction $\hat{\alpha}$, of the surface atom involved in the collision. In reality, it is found that this formula applies fairly well (except when resonant scattering is important) with respect to the functional dependence on scattering parameters (through $\vec{q}$) and on temperature (through $\langle u_\alpha^2\rangle$). However, the effective $\langle u_\alpha^2\rangle$ is often about one-half of the expected value, which is that of the topmost surface atoms for a compact monatomic surface and some average over the topmost layer in other cases. Coincidentally, the effective $\langle u_\alpha^2\rangle$ is about equal to the value expected for bulk atoms.

The origin of the discrepancy is to be found in the facts that the collision is neither two body nor impulsive. A thorough discussion of the expected modifications in the theory of atom-surface scattering required by these facts, within a semiclassical approximation and with neglect of resonant scattering, has been given by Meyer.[1] He discusses four effects, which he calls the Beeby effect,[2] the Armand effect,[3] the Levi effect,[4] and the closed-channel effect.[5] The Beeby effect amounts to the fact that q is larger than the momentum transferred in the scattering, because the effective two-body repulsive collision takes place after the gas atom has been accelerated by the long-range attractive atom-surface potential. The Levi correction has a contrary effect: Because the repulsive collision is not impulsive, q may be smaller than expected. The Armand effect is a reduction of the effective $\langle u_\alpha^2\rangle$, due to the fact that the effective repulsive interaction is not simply two body (although it is a sum of two-body interactions). Finally, the closed-channel effect is the major correction due to the fact that multiple scattering must be taken into account. A limitation of the Meyer theory, in addition to the semiclassical approximation, is that the resonant processes are not included.

In earlier papers[5,6] we addressed the problem of multiple-scattering corrections (including the closed-channel effect) by an exact treatment of a simple model: the vibrating, corrugated hard wall. We found that, in some cases at least, the entire apparent decrease of $\langle u_\alpha^2\rangle$ could be attributed to multiple scattering. The model we used is incomplete, however, because in reality the presence of the attractive potential allows "closed-channel" transitions to take place through surface-bound states in the attractive well. Furthermore, recent work in atom-surface scattering has shown that the hard-wall model has only limited validity: Recent comparisons of theory and experiment for inelastic scattering show that there is a cutoff in parallel momentum transfer that can be described as an Armand effect, and is not present in the hard-wall model.[7,8] As long as inelastic scattering is weak, it is apparently well described by the distorted-wave Born approximation, using a sum of repulsive two-body potentials, and a long-range attraction. Such a description is certainly more realistic than the vibrating hard-wall model.

In this paper we extend the earlier formalism to handle these more realistic potentials. If diffractive scattering can be neglected, the result of the present treatment is simply equivalent to saying that the specular intensity is reduced by the total inelastic scattering, and in fact the present formulas are obtained, to lowest order, by summing the inelastic scattering intensity given by Manson and Celli.[9] More generally, the inelastic scattering leads to a redistribution of the specular and diffracted intensities. The total elastic intensity is decreased, but the individual intensities are affected differently, and may even increase at near-resonance conditions.

Although the treatment we give in Sec. II is in principle general, for practical evaluations it is most appropriate to the case where the inelastic scattering is weak and one-phonon processes dominate. The basic quantity to be

evaluated is the effective potential $\langle M \rangle$, which can be described as the position-dependent self-energy of the atom being scattering, or the optical potential for the scattering. General formulas for $\langle M \rangle$ are given in Sec. III; the effect of $\langle M \rangle$ on the scattered intensities is discussed in Sec. IV. The explicit evaluation of $\langle M \rangle$ and of the intensity to the lowest order in the phonon displacements is given in Sec. V. It is also shown how the formulas of this paper reduce to earlier results for simpler cases, including the hard wall. A discussion of the results obtained and of the need for further work is given in Sec. VI.

II. DIFFRACTIVE SCATTERING FROM A VIBRATING CRYSTAL

In the present work we develop a formalism that is generally valid, although it is particularly suitable for realistic calculations when the light incident atom has negligible effect on the heavier atoms constituting the semi-infinite crystal. Quite generally the problem becomes that of an atom moving in a time-dependent potential caused by the motion of the atoms of the crystal.

To define this potential we begin by defining the positions of the atoms in a semi-infinite crystal. We first introduce a two-dimensional Bravais lattice, parallel to the surface of the crystal (the plane $x_3=0$), that defines the translational symmetry of the semi-infinite crystal. The lattice points of this lattice are given by the vectors

$$\vec{x}_{||}(l)=l_1\vec{a}_1+l_2\vec{a}_2 , \tag{2.1}$$

where $\vec{a}_1$ and $\vec{a}_2$ are the noncollinear primitive translation vectors of the lattice, lying in the plane $x_3=0$. l_1 and l_2 are any two integers, positive, negative, or zero, that we denote collectively by l. The vectors $\vec{a}_1$ and $\vec{a}_2$ define a surface unit cell, whose area we denote by a_c.

Together with the two-dimensional Bravais lattice defined by Eq. (2.1) it is convenient to introduce the two-dimensional Bravais lattice reciprocal to it. The sites of this new lattice are given by the vectors

$$\vec{G}_{||}(h)=h_1\vec{b}_1+h_2\vec{b}_2 , \tag{2.2}$$

where the primitive translation vectors $\vec{b}_1$ and $\vec{b}_2$ are defined by the conditions

$$\vec{a}_i\cdot\vec{b}_h=2\pi\delta_{ij}, \quad i,j=1,2 . \tag{2.3}$$

In Eq. (2.2) h_1 and h_2 are any two integers that we denote collectively by h.

With each lattice point of the Bravais lattice we associate a basis, the points of which are defined by the vectors $\{\vec{x}(\kappa)\}$, with $\kappa=1,2,\ldots$. There is considerable arbitrariness in the definition of the basis. The chief requirement is that the equilibrium positions of all the atoms in the semi-infinite crystal be given by the vectors

$$\vec{x}(l\kappa)=\vec{x}_{||}(l)+\vec{x}(\kappa) . \tag{2.4}$$

On the assumption that the crystal occupies the lower half-space, we take $x_3(\kappa)\leq 0$.

The atom $(l\kappa)$ is now assumed to undergo an arbitrary, time-dependent displacement from its equilibrium position, described by the vector $\vec{u}(l\kappa;t)$. Then, if we denote the potential energy of interaction of the incident atom with an atom of type κ in the crystal by $U_\kappa(\vec{\rho})$, where $\vec{\rho}$ is the vector joining them, the time-dependent potential of the incident atom at position $\vec{r}$ will be written in the form

$$V(\vec{r},t)=\sum_{l\kappa} U_\kappa[\vec{r}-\vec{x}(l\kappa)-\vec{u}(l\kappa;t)] . \tag{2.5}$$

For simplicity, we will treat $\vec{u}(l\kappa;t)$ as a classical variable in the text of the paper. In the Appendix we show how the results obtained with these assumptions are still valid in a quantum-mechanical treatment of the crystal, and are not modified by the self-consistent inclusion of recoil due to the collision process. The only change is that in the final results the quantum-mechanical expressions for the displacement correlation functions must be used.[4]

The time-dependent Schrödinger equation for the atom being scattered is

$$ih\frac{\partial\psi(\vec{r},t)}{\partial t}=\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r},t)\right]\psi(\vec{r},t) , \tag{2.6}$$

where m is the mass of the atom. With the use of the Green function $G_0^+(\vec{r},\vec{r}';t-t')$ that satisfies the equation

$$\left[i\hbar\frac{\partial}{\partial t}+\frac{\hbar^2}{2m}\nabla^2\right]G_0^+(\vec{r},\vec{r}';t-t')=\delta(\vec{r}-\vec{r}')\delta(t-t') , \tag{2.7}$$

subject to outgoing wave or exponentially decaying boundary conditions at infinity, we convert Eq. (2.6) into an integral equation

$$\psi(\vec{r},t)=\psi_0(\vec{r},t)+\int d^3r'\int dt' G_0^+(\vec{r},\vec{r}';t-t')\times V(\vec{r}',t')\psi(\vec{r}',t') , \tag{2.8}$$

where $\psi_0(\vec{r},t)$ is a solution of the homogeneous equation,

$$\left[i\hbar\frac{\partial}{\partial t}+\frac{\hbar^2}{2m}\nabla^2\right]\psi_0(\vec{r},t)=0 , \tag{2.9}$$

and represents the incident wave. A convenient representation for $G_0^+(\vec{r},\vec{r}';t-t')$ is

$$G_0^+(\vec{r},\vec{r}';t-t')=\frac{2m}{\hbar^2}\int\frac{d^2k_{||}}{(2\pi)^2}\int\frac{d\omega}{2\pi}\frac{\exp[i\vec{k}_{||}\cdot(\vec{x}_{||}-\vec{x}'_{||})+i\alpha(k_{||}\omega)\,|\,x_3-x'_3\,|\,]}{2i\alpha(k_{||}\omega)}e^{-i\omega(t-t')} , \tag{2.7'}$$

where

$$\alpha(k_{\parallel}\omega)=\left[\frac{2m\omega}{\hbar}-k_{\parallel}^2\right]^{1/2}, \quad k_{\parallel}^2<\frac{2m\omega}{\hbar}$$
$$=i\left[k_{\parallel}^2-\frac{2m\omega}{\hbar}\right]^{1/2}, \quad k_{\parallel}^2>\frac{2m\omega}{\hbar}, \qquad (2.7'')$$

and $\vec{x}_{\parallel}=\hat{x}_1x_1+\hat{x}_2x_2$, $\vec{k}_{\parallel}=\hat{x}_1k_1+\hat{x}_2k_2$, with $\hat{x}_1$ and $\hat{x}_2$ unit vectors along the x_1 and x_2 directions, respectively.

If we denote the scattered wave function by $\psi_s(\vec{r},t)=\psi(\vec{r},t)-\psi_0(\vec{r},t)$, the 3 component of the scattered particle flux is given by

$$J_3^{(s)}(\vec{r},t)=\frac{\hbar}{2im}\left[\psi_s^*(\vec{r},t)\frac{\partial\psi_s(\vec{r},t)}{\partial x_3}-\psi_s(\vec{r},t)\frac{\partial\psi_s^*(\vec{r},t)}{\partial x_3}\right]. \qquad (2.10a)$$

In fact, since the atom is scattered by a random, time-dependent potential caused by the vibrations of the atoms of the crystal, what is of interest is the average of $J_3^{(s)}(\vec{r},t)$, $\langle J_3^{(s)}(\vec{x},t)\rangle$, over the canonical ensemble defined by the vibrational Hamiltonian of the crystal.

Similarly, the 3 component of the incident particle flux is

$$J_3^{(i)}(\vec{r},t)=\frac{\hbar}{2im}\left[\psi_0^*(\vec{r},t)\frac{\partial\psi_0(\vec{r},t)}{\partial x_3}-\psi_0(\vec{r},t)\frac{\partial\psi_0^*(\vec{r},t)}{\partial x_3}\right]. \qquad (2.10b)$$

The number of incident atoms crossing a plane $x_3=$const far above the scattering surface must equal the average number of scattered particles crossing the same plane:

$$\int d^3x_{\parallel}J_3^{(i)}(\vec{r},t)\,|_{x_3=\text{const}} = \int d^2x_{\parallel}\langle J_3^{(s)}(\vec{r},t)\rangle\,|_{x_3=\text{const}}. \qquad (2.11)$$

The average $\langle J_3^{(s)}(\vec{r},t)\rangle$ can always be written in the form

$$\langle J_3^{(s)}(\vec{r},t)\rangle=\frac{\hbar}{m}\mathrm{Im}\left\langle\psi_s^*(\vec{r},t)\frac{\partial\psi_s(\vec{r},t)}{\partial x_3}\right\rangle$$
$$=\frac{\hbar}{m}\mathrm{Im}\left[\langle\psi_s^*(\vec{r},t)\rangle\frac{\partial\langle\psi_s(\vec{r},t)\rangle}{\partial x_3}+\left\langle\psi_s^*(\vec{r},t)\frac{\partial\psi_s(\vec{r},t)}{\partial x_3}\right\rangle_{\text{corr}}\right]. \qquad (2.12)$$

The second term on the right-hand side of Eq. (2.12) gives the contribution to $\langle J_3^{(s)}(\vec{r},t)\rangle$ from all terms in which at least one displacement component $u_\alpha^*(l,t)$ appearing in $\psi_s^*(\vec{r},t)$ is contracted with a displacement component $u_\beta(l',t')$ appearing in $\partial\psi_s(\vec{r},t)/\partial x_3$.

If we confine ourselves to diffractive scattering, we need to be concerned with only the first term on the right-hand side of Eq. (2.12). The second term describes the inelastic scattering. This can be seen from the results of calculations based on simpler models.[5] It also follows from the fact that the averaging process restores periodicity and time translation invariance to our physical system, so that $\langle\psi_s(\vec{r},t)\rangle$ describes scattering from a static periodic crystal. Such scattering can only be diffractive. For a surface of area A, taking an integrated incident current

$$\int d^2x_{\parallel}J_3^{(i)}(\vec{r},t)=\hbar\alpha(k_{\parallel}\omega)A/m$$

[see Eq. (4.1) below], the diffracted beams have an integrated current of order $\alpha(k_{\parallel}\omega)A/m$ within a solid angle of order λ^2/A, where $2\pi/\lambda=\alpha(k_{\parallel}\omega)$. In the limit $A\to\infty$, such beams are unambiguously separated from the diffuse scattering that is described by the term $\langle\psi_s^*\partial\psi_s/\partial x_3\rangle_{\text{corr}}$ in Eq. (2.12).

Thus, in what follows we focus our attention on the averaged wave function $\langle\psi(\vec{r},t)\rangle$, from which $\langle\psi_s(\vec{r},t)\rangle$ is obtained according to

$$\langle\psi_s(\vec{r},t)\rangle=\langle(\vec{r},t)\rangle-\psi_0(\vec{r},t). \qquad (2.13)$$

We begin by introducing the operator P that averages everything that stands to its right over the canonical ensemble defined by the vibrational Hamiltonian of the crystal. We also introduce the complementary operator $Q=1-P$. Application of the operator P to both sides of Eq. (2.8) yields the equation

$$P\psi(\vec{r},t)=\psi_0(\vec{r},t)+\int d^3r'\int dt'G^+(\vec{r},\vec{r}';t-t')\times PV(\vec{r}',t')[P\psi(\vec{r}',t')+Q\psi(\vec{r}',t')]. \qquad (2.14)$$

Similarly, application of the operator Q to both sides of Eq. (2.8) yields

$$Q\psi(\vec{r},t)=\int d^3r'\int dt'G_0^+(\vec{r},\vec{r}';t-t')QV(\vec{r}',t')\times[P\psi(\vec{r}',t')+Q\psi(\vec{r}',t')]. \qquad (2.15)$$

We now formally solve Eq. (2.15) for $Q\psi(\vec{r},t)$, with the result that

$$Q\psi(\vec{r}',t')=\int d^3r''\int dt''\int d^3r'''\int dt'''R(\vec{r}',\vec{r}'',t't'')G_0^+(\vec{r}'',\vec{r}''';t''-t''')QV(\vec{r}''',t''')P\psi(\vec{r}''',t'''), \qquad (2.16)$$

where the function $R(\vec{r},\vec{r}';tt')$ is the solution of the equation

$$R(\vec{r},\vec{r}';tt')=\delta(\vec{r}-\vec{r}')\delta(t-t')+\int d^3\vec{r}''\int dt''G_0^+(\vec{r},\vec{r}'';t-t'')QV(\vec{r}'',t'')R(\vec{r}'',\vec{r}';t''t'). \qquad (2.17)$$

When the result given by Eq. (2.16) is substituted into Eq. (2.14), we find that $\langle\psi(\vec{r},t)\rangle$ satisfies the equation

$$\langle\psi(\vec{r},t)\rangle=\psi_0(\vec{r},t)+\int d^3\vec{r}'\int dt'\int d^3r''\int dt''G_0^+(\vec{r},\vec{r}';t-t')\langle M(\vec{r}',\vec{r}'';tt'')\rangle\langle\psi(\vec{r}'',t'')\rangle, \qquad (2.18)$$

where the function $M(\vec{r},\vec{r}';tt')$ satisfies the equation

$$M(\vec{r},\vec{r}';tt')=V(\vec{r},t)\delta(\vec{r}-\vec{r}')\delta(t-t')+V(\vec{r},t)\int d^3r''\int dt''G_0^+(\vec{r},\vec{r}'';t-t'')QM(\vec{r}'',\vec{r}';t''t') \ . \tag{2.19}$$

Thus $\langle\psi(\vec{r},t)\rangle$ satisfies an integral equation of the same form as $\psi(\vec{r},t)$, but with a nonlocal potential $\langle M(\vec{r}',\vec{r}'';t't'')\rangle$ in place of the local one $V(\vec{r}',t')\delta(\vec{r}'-\vec{r}'')\delta(t'-t'')$.

The straightforward way of obtaining $\langle M(\vec{r},\vec{r}';tt')\rangle$ is to solve Eq. (2.19) by iteration and then to average the solution term by term. However, by proceeding somewhat differently we can carry out a partial resummation of the terms in the straightforward iterative solution.

For this purpose we introduce the Green function $G^+(\vec{r},\vec{r}';tt')$ as the solution of the equation

$$G^+(\vec{r},\vec{r}';tt')=G_0^+(\vec{r},\vec{r}';t-t')+\int d^3r''\int dt''G_0^+(\vec{r},\vec{r}'';t-t'')\times V(\vec{r}'',t'')G^+(\vec{r}'',\vec{r}';t''t') \tag{2.20}$$

or, more concisely,

$$G^+=G_0^++G_0^+VG^+ \ . \tag{2.21}$$

We can rewrite this equation equivalently as

$$G^+=G_0^++G_0^+M\langle G^+\rangle \ , \tag{2.22}$$

and thus M can be defined alternatively by the equation

$$VG^+=M\langle G^+\rangle \ . \tag{2.23}$$

To establish this result we rewrite Eq. (2.21) in the form

$$G^+=G_0^++G_0^+V(PG^++QG^+) \tag{2.24}$$

and solve it formally to obtain

$$G^+=(I-G_0^+VQ)^{-1}G_0^++(I-G_0^+VQ)^{-1}G_0^+VPG^+ \ . \tag{2.25}$$

However, because G_0^+ is nonstochastic [i.e., it is independent of the displacements $\{\vec{u}(lk;t)\}$], the following relations are valid

$$(I-G_0^+VQ)^{-1}G_0^+=G_0^+ \ , \tag{2.26a}$$

$$(I-G_0^+VQ)^{-1}G_0^+VPG^+=G_0^+(I-VG_0^+Q)^{-1}VPG^+ \ . \tag{2.26b}$$

From Eq. (2.19) we see that M is given explicitly by

$$M=(I-VG_0^+Q)^{-1}V \ . \tag{2.27}$$

Therefore, on substituting Eqs. (2.26) and (2.27) into Eq. (2.25), we find that the latter becomes Eq. (2.22), which is what we wanted to prove.

It follows from Eq. (2.22) that

$$\langle G^+\rangle=G_0^++G_0^+\langle M\rangle\langle G^+\rangle \ . \tag{2.28}$$

Thus $\langle M\rangle$ is the self-energy, or effective potential that determines $\langle G^+\rangle$, just as it is the effective potential that determines $\langle\psi\rangle$.

We now use the fact that the single equation

$$G^+=G_0^++G_0^+(V_1+V_2)G^+ \tag{2.29}$$

is equivalent to the pair of equations

$$G_1^+=G_0^++G_0^+V_1G_1^+ \ , \tag{2.30a}$$

$$G^+=G_1^++G_1^+V_2G^+ \ . \tag{2.30b}$$

Thus, if we take $V_1=\langle M\rangle$ and $V_2=V-\langle M\rangle$, we obtain from Eqs. (2.30)

$$G_1^+=G_0^++G_0^+\langle M\rangle G_1^+ \ , \tag{2.31}$$

$$G^+=G_1^++G_1^+(V-\langle M\rangle)G^+ \ . \tag{2.32}$$

A comparison of Eqs. (2.28) and (2.31) shows that G_1^+ is $\langle G^+\rangle$. Consequently, Eq. (2.32) can be rewritten in the form

$$G^+=\langle G^+\rangle+\langle G^+\rangle(V-\langle M\rangle)G^+ \ . \tag{2.33}$$

Equation (2.33) is equivalent to

$$G^+=\langle G^+\rangle+G^+(V-\langle M\rangle)\langle G^+\rangle \ . \tag{2.34}$$

We multiply this equation from the left by V to obtain

$$VG^+=V\langle G^+\rangle+VG^+(V-\langle M\rangle)\langle G^+\rangle \ . \tag{2.35}$$

From Eq. (2.23) this is equivalent to

$$M\langle G^+\rangle=V\langle G^+\rangle+M\langle G^+\rangle(V-\langle M\rangle)\langle G^+\rangle \ , \tag{2.36}$$

whence it follows that

$$M=V+M\langle G^+\rangle(V-\langle M\rangle) \ . \tag{2.37}$$

This is the equation for M we seek. It contains the averaged Green function $\langle G^+\rangle$ instead of the free-particle Green function G_0^+.

To solve Eq. (2.37) we expand M formally in powers of V,

$$M=M_1+M_2+M_3+\cdots \ , \tag{2.38}$$

where the subscript denotes the order of the corresponding term in V. When Eq. (2.38) is substituted into Eq. (2.37), and terms of the same order in V on both sides are equated, we obtain the set of equations

$$M_1=V \ , \tag{2.39a}$$

$$M_2=M_1\langle G^+\rangle(V-\langle M_1\rangle) \ , \tag{2.39b}$$

$$M_3=-M_1\langle G^+\rangle\langle M_2\rangle+M_2\langle G^+\rangle(V-\langle M_1\rangle) \ , \quad \vdots \ . \tag{2.39c}$$

If we average each of these equations in turn, we find that

$$\langle M_1\rangle=\langle V\rangle \ , \tag{2.40a}$$

$$\langle M_2\rangle=\langle V\langle G^+\rangle V\rangle-\langle V\rangle\langle G^+\rangle\langle V\rangle \ , \tag{2.40b}$$

$$\langle M_3\rangle=\langle V\langle G^+\rangle V\langle G^+\rangle V\rangle-\langle V\rangle\langle G^+\rangle\langle V\langle G^+\rangle V\rangle$$
$$-\langle V\langle G^+\rangle\langle V\rangle\langle G^+\rangle V\rangle$$
$$-\langle V\langle G^+\rangle V\rangle\langle G^+\rangle\langle V\rangle$$
$$+2\langle V\rangle\langle G^+\rangle\langle V\rangle\langle G^+\rangle\langle V\rangle$$
$$\vdots \quad . \tag{2.40c}$$

We see that the $\langle M_n\rangle$ have the form of cumulant averages.

It should be noted that Eqs. (2.38) and (2.40) constitute highly nonlinear integral equations for $\langle M\rangle$, because according to Eq. (2.29) the Green function $\langle G^+\rangle$ that enters the latter equations is itself a functional of $\langle M\rangle$.

We conclude this section by pointing out that either by studying the first few terms in the iterative solutions of Eqs. (2.19) and (2.20), or more generally from the periodicity properties of the time-averaged crystal, one can establish the results that $\langle M(\vec{r},\vec{r}';tt')\rangle$ and $\langle G^+(\vec{r},\vec{r}';tt')\rangle$ can be written in the forms

$$\langle M(\vec{r},\vec{r}';tt')\rangle=\sum_{\vec{G}_{\parallel},\vec{G}'_{\parallel}}\int_{BZ}\frac{d^2k_{\parallel}}{(2\pi)^2}\int\frac{d\omega}{2\pi}e^{i(\vec{k}_{\parallel}+\vec{G}_{\parallel})\cdot\vec{x}_{\parallel}}\hat{M}_{\omega}(\vec{k}_{\parallel}+\vec{G}_{\parallel},\vec{k}_{\parallel}+\vec{G}'_{\parallel}\,|\,x_3x'_3)e^{-i(\vec{k}_{\parallel}+\vec{G}'_{\parallel})\cdot\vec{x}'_{\parallel}}e^{-i\omega(t-t')}\,, \tag{2.41a}$$

$$\langle G^+(\vec{r},\vec{r}',tt')\rangle=\sum_{\vec{G}_{\parallel},\vec{G}'_{\parallel}}\int_{BZ}\frac{d^2k_{\parallel}}{(2\pi)^2}\int\frac{d\omega}{2\pi}e^{i(\vec{k}_{\parallel}+\vec{G}_{\parallel})\cdot\vec{x}_{\parallel}}\hat{G}_{\omega}(\vec{k}_{\parallel}+\vec{G}_{\parallel},\vec{k}_{\parallel}+\vec{G}'_{\parallel}\,|\,x_3x'_3)e^{-i(\vec{k}_{\parallel}+\vec{G}'_{\parallel})\cdot\vec{x}'_{\parallel}}e^{-i\omega(t-t')}\,. \tag{2.41b}$$

The integration over $\vec{k}_{\parallel}$ in both of these expressions is restricted to the two-dimensional Brillouin zone for the surface we are considering. It then follows from Eqs. (2.7), (2.28), and (2.41), that $\hat{G}^{+}_{\omega}(\vec{k}_{\parallel}+\vec{G}_{\parallel},\vec{k}_{\parallel}+\vec{G}'_{\parallel}\,|\,x_3x'_3)$ and $\hat{M}_{\omega}(\vec{k}_{\parallel}+\vec{G}_{\parallel},\vec{k}_{\parallel}+\vec{G}'_{\parallel}\,|\,x_3x'_3)$ are related by the following matrix integral equation:

$$\hat{G}^{+}_{\omega}(\vec{k}_{\parallel}+\vec{G}_{\parallel},\vec{k}_{\parallel}+\vec{G}'_{\parallel}\,|\,x_3x'_3)=\hat{G}^{+}_{0\omega}(\vec{k}_{\parallel}+\vec{G}_{\parallel},\vec{k}_{\parallel}+\vec{G}'_{\parallel}\,|\,x_3x'_3)$$
$$+\sum_{\vec{G}''_{\parallel},\vec{G}'''_{\parallel}}\int dx''_3\int dx'''_3\hat{G}^{+}_{0\omega}(\vec{k}_{\parallel}+\vec{G}_{\parallel},\vec{k}_{\parallel}+\vec{G}''_{\parallel}\,|\,x_3x''_3)$$
$$\times\hat{M}_{\omega}(\vec{k}_{\parallel}+\vec{G}''_{\parallel},\vec{k}_{\parallel}+\vec{G}'''_{\parallel}\,|\,x''_3x'''_3)\hat{G}^{+}_{\omega}(\vec{k}_{\parallel}+\vec{G}'''_{\parallel},\vec{k}_{\parallel}+\vec{G}'_{\parallel}\,|\,x'''_3x'_3)\,, \tag{2.42}$$

where

$$\hat{G}^{+}_{0\omega}(\vec{k}_{\parallel}+\vec{G}_{\parallel},\vec{k}_{\parallel}+\vec{G}'_{\parallel}\,|\,x_3x'_3)$$
$$=\delta_{\vec{G}_{\parallel},\vec{G}'_{\parallel}}\frac{2m}{\hbar^2}\frac{e^{i\alpha(|\vec{k}_{\parallel}+\vec{G}_{\parallel}|\omega)|x_3-x'_3|}}{2i\alpha(|\vec{k}_{\parallel}+\vec{G}_{\parallel}|\omega)}\,. \tag{2.43}$$

What remains to be established is the relation between

$$\hat{M}_{\omega}(\vec{k}_{\parallel}+\vec{G}_{\parallel},\vec{k}_{\parallel}+\vec{G}'_{\parallel}\,|\,x_3x'_3)$$

and

$$\hat{G}^{+}_{\omega}(\vec{k}_{\parallel}+\vec{G}_{\parallel},\vec{k}_{\parallel}+\vec{G}'_{\parallel}\,|\,x_3x'_3)$$

that follows from Eqs. (2.38) and (2.40), and which when combined with Eqs. (2.42) and (2.43) yields a complete solution of the problem of the temperature effects in diffractive scattering. It is to the determination of this relation that Sec. IV is devoted.

III. EFFECTIVE SCATTERING POTENTIAL

In this section we outline the derivation of the equation satisfied by the effective potential $\langle M(\vec{r},\vec{r}';tt')\rangle$ in the lowest approximation that contributes an imaginary part to it. Our starting point is therefore the equation

$$\langle M\rangle\cong\langle V\rangle+[\langle V\langle G^+\rangle V\rangle-\langle V\rangle\langle G^+\rangle\langle V\rangle]\,, \tag{3.1}$$

where the potential $V(\vec{r},\vec{r}';t-t')$ is given by

$$V(\vec{r},\vec{r}';t-t')=V(\vec{r},t)\delta(\vec{r}-\vec{r}')\delta(t-t')\,, \tag{3.2}$$

while $V(\vec{r},t)$ has been defined in Eq. (2.5). We assume that the potential $U_{\kappa}(\vec{\rho})$ entering the latter equation can be Fourier expanded according to

$$U_{\kappa}(\vec{\rho})=\int\frac{d^3k}{(2\pi)^3}\hat{U}_{\kappa}(\vec{k}_{\parallel}\,|\,k_3)e^{i\vec{k}\cdot\vec{\rho}}\,. \tag{3.3}$$

Since, as we will presently see, the projection of the three-dimensional wave vector $\vec{k}$ onto the plane $x_3=0$, $\vec{k}_{\parallel}$, enters the effective scattering potential in a different way from the normal component k_3, we have indicated the dependence of the Fourier coefficient of $U_{\kappa}(\vec{\rho})$ on both of these components of $\vec{k}$ explicitly in writing Eq. (3.3).

It follows therefore that

$$\langle V(\vec{r},t)\rangle=\sum_{l\kappa}\int\frac{d^3k}{(2\pi)^3}U_{\kappa}(\vec{k}_{\parallel}\,|\,k_3)e^{-i\vec{k}\cdot[\vec{r}-\vec{x}(l\kappa)]}\,. \tag{3.4}$$

It is a standard result of lattice dynamics that in the harmonic approximation

$$\langle e^{-i\vec{k}\cdot\vec{u}(l\kappa;t)}\rangle=e^{-(1/2)\langle[\vec{k}\cdot\vec{u}(\kappa)]^2\rangle}\,. \tag{3.5}$$

The expression on the right-hand side of this equation is independent of the time and, because of the periodicity of the semi-infinite crystal in directions parallel to the surface, is independent of the cell index l, although it does depend on the basis index κ. To simplify the following results, we will assume that the symmetry at the site κ is sufficiently high that

$$\langle u_\alpha(\kappa)u_\beta(\kappa)\rangle=\delta_{\alpha\beta}\langle u_\alpha^2(\kappa)\rangle\ , \tag{3.6}$$

and that

$$\langle u_1^2(\kappa)\rangle=\langle u_2^2(\kappa)\rangle\equiv\langle u_{||}^2(\kappa)\rangle\ , \tag{3.7a}$$

$$\langle u_3^2(\kappa)\rangle\equiv\langle u_\perp^2(\kappa)\rangle\ . \tag{3.7b}$$

Under these assumptions Eq. (3.4) takes the form

$$\langle V(\vec{r},t)\rangle=\sum_{l\kappa}\int\frac{d^2k_{||}}{(2\pi)^2}\int\frac{dk_3}{2\pi}U_\kappa(\vec{k}_{||}\,|\,k_3)e^{i\vec{k}_{||}\cdot[\vec{x}_{||}-\vec{x}_{||}(\kappa)]}\exp[-i\vec{k}_{||}\cdot\vec{x}_{||}(l)-\tfrac{1}{2}k_{||}^2\langle u_{||}^2(\kappa)\rangle]e^{ik_3[x_3-x_3(\kappa)]}e^{-(1/2k_3^2\langle u_\perp^2(\kappa)\rangle}\ . \tag{3.8}$$

If, finally, we use the result that

$$\sum_l e^{-i\vec{k}_{||}\cdot\vec{x}_{||}(l)}=\frac{(2\pi)^2}{a_c}\sum_{\vec{G}_{||}}\delta(\vec{k}_{||}-\vec{G}_{||})\ , \tag{3.9}$$

we obtain

$$\langle V(\vec{r},t)\rangle=\sum_{\vec{G}_{||}}e^{i\vec{G}_{||}\cdot\vec{x}_{||}}\hat{V}(\vec{G}_{||}\,|\,x_3)\ , \tag{3.10a}$$

where

$$\hat{V}(\vec{G}_{||}\,|\,x_3)=\frac{1}{a_c}\sum_\kappa\exp[-i\vec{G}_{||}\cdot\vec{x}_{||}(\kappa)-\tfrac{1}{2}G_{||}^2\langle u_{||}^2(\kappa)\rangle]\int\frac{dk_3}{2\pi}\hat{U}_\kappa(\vec{G}_{||}\,|\,k_3)e^{ik_3[x_3-x_3(\kappa)]}e^{-(1/2)k_3^2\langle u_\perp^2(\kappa)\rangle}\ . \tag{3.10b}$$

This is clearly a local, periodic, temperature-dependent potential.

Thus the first term on the right-hand side of Eq. (3.1) can be written in the form

$$\langle M_1(\vec{r},\vec{r}';tt')\rangle=\sum_{\vec{G}_{||},\vec{G}'_{||}}\int_{\mathrm{BZ}}\frac{d^2k_{||}}{(2\pi)^2}\int\frac{d\omega}{2\pi}e^{i(\vec{k}_{||}+\vec{G}_{||})\cdot\vec{x}_{||}}\hat{M}_{1\omega}(\vec{k}_{||}+\vec{G}_{||},\vec{k}_{||}+\vec{G}'_{||}\,|\,x_3x_3')e^{-i(\vec{k}_{||}+\vec{G}'_{||})\cdot\vec{x}'_{||}}e^{-i\omega(t-t')}\ , \tag{3.11a}$$

where

$$\hat{M}_{1\omega}(\vec{k}_{||}+\vec{G}_{||},\vec{k}_{||}+\vec{G}'_{||}\,|\,x_3x_3')=\hat{V}(\vec{G}_{||}-\vec{G}'_{||}\,|\,x_3)\delta(x_3-x_3')\ . \tag{3.11b}$$

The second-order contribution to $\langle M(\vec{r},\vec{r}';tt')\rangle$ can be written as

$$\langle M_2(\vec{r},\vec{r}';tt')\rangle=\langle G^+(\vec{r},\vec{r}';tt')\rangle[\langle V(\vec{r},t)V(\vec{r}',t')\rangle-\langle V(\vec{r},t)\rangle\langle V(\vec{r}',t')\rangle]\ . \tag{3.12}$$

We consider first the difference in square brackets. With the use of Eqs. (2.5) and (3.3), as well as the result

$$\langle e^{-i\vec{k}\cdot\vec{u}(l\kappa;t)}e^{-i\vec{k}'\cdot\vec{u}(l'\kappa';t')}\rangle=\exp\{-\tfrac{1}{2}\langle[\vec{k}\cdot\vec{u}(\kappa)]^2\rangle-\tfrac{1}{2}\langle[\vec{k}'\cdot\vec{u}(\kappa)]^2\rangle-\langle\vec{k}\cdot\vec{u}(l\kappa;t)\vec{k}'\cdot\vec{u}(l'\kappa';t')\rangle\} \tag{3.13}$$

that is valid in the harmonic approximation, we find that

$$\begin{aligned}\langle V(\vec{r},t)V(\vec{r}',t')\rangle-\langle V(\vec{r},t)\rangle\langle V(\vec{r}',t')\rangle&=\sum_{l\kappa}\sum_{l'\kappa'}\int\frac{d^2k_{||}}{(2\pi)^2}\int\frac{dk_3}{2\pi}\int\frac{d^2k'_{||}}{(2\pi)^2}\int\frac{dk'_3}{2\pi}\hat{U}_\kappa(\vec{k}_{||}\,|\,k_3)\exp\{i\vec{k}_{||}\cdot\vec{x}_{||}(l)+i\vec{k}_{||}\cdot[\vec{x}_{||}-\vec{x}_{||}(\kappa)]-\tfrac{1}{2}k_{||}^2\langle u_{||}^2(\kappa)\rangle\}\\&\quad\times\exp\{ik_3[x_3-x_3(\kappa)]-\tfrac{1}{2}k_3^2\langle u_\perp^2(\kappa)\rangle\}\hat{U}_{\kappa'}(\vec{k}'_{||}\,|\,k'_3)\\&\quad\times\exp\{ik'_3[x'_3-x_3(\kappa')]-\tfrac{1}{2}k_3'^2\langle u_\perp^2(\kappa')\rangle\}\\&\quad\times\{\exp[-\langle\vec{k}\cdot\vec{u}(l\kappa;t)\vec{k}'\cdot\vec{u}(l'\kappa';t')\rangle]-1\}\ .\end{aligned} \tag{3.14}$$

The displacement correlation function can be written formally as

$$\begin{aligned}\langle\vec{k}\cdot\vec{u}(l\kappa;t)\vec{k}'\cdot\vec{u}(l'\kappa';t')\rangle&=\sum_{\alpha\beta}k_\alpha k'_\beta\langle u_\alpha(l\kappa;t)u_\beta(l'\kappa';t')\rangle\\&=\sum_{\alpha\beta}k_\alpha k'_\beta\int_{\mathrm{BZ}}\frac{d^2q_{||}}{(2\pi)^2}\int\frac{d\Omega}{2\pi}C_{\alpha\beta}(\vec{q}_{||}\Omega\,|\,\kappa\kappa')e^{i\vec{q}_{||}\cdot[\vec{x}_{||}(l)-\vec{x}_{||}(l')]}e^{-i\Omega(t-t')}\ .\end{aligned} \tag{3.15}$$

In what follows we will make the approximation of replacing the last factor on the right-hand side of Eq. (3.14) by the negative of the correlation function (3.15). This is not an essential approximation; it is a reasonable one, but also one that can be improved systematically; and it simplifies the subsequent results. With this result we find that

$$\langle V(\vec{r},t)V(\vec{r}',t')\rangle - \langle V(\vec{r},t)\rangle\langle V(\vec{r}',t')\rangle$$
$$= \sum_{\kappa\alpha}\sum_{\kappa'\beta}\sum_{\vec{G}_{\parallel}}\sum_{\vec{G}'_{\parallel}}\int_{\mathrm{BZ}}\frac{d^2q_{\parallel}}{(2\pi)^2}\int\frac{d\Omega}{2\pi}e^{-i\Omega(t-t')}e^{-i(\vec{q}_{\parallel}+\vec{G}_{\parallel})\cdot\vec{x}_{\parallel}}W^*_{\kappa\alpha}(\vec{q}_{\parallel}+\vec{G}_{\parallel}\,|\,x_3)C_{\alpha\beta}(\vec{q}_{\parallel}\Omega\,|\,\kappa\kappa')$$
$$\times W_{\kappa'\beta}(\vec{q}_{\parallel}+\vec{G}'_{\parallel}\,|\,x'_3)e^{i(\vec{q}_{\parallel}+\vec{G}'_{\parallel})\cdot\vec{x}'_{\parallel}}, \tag{3.16a}$$

where

$$W_{\kappa\alpha}(\vec{q}_{\parallel}+\vec{G}_{\parallel}\,|\,x_3)=\exp[-i(\vec{q}_{\parallel}+\vec{G}_{\parallel})\cdot\vec{x}_{\parallel}(\kappa)-\tfrac{1}{2}(\vec{q}_{\parallel}+\vec{G}_{\parallel})^2\langle u^2_{\parallel}(\kappa)\rangle]$$
$$\times\frac{1}{a_c}\int\frac{dq_3}{2\pi}\hat{U}_{\kappa}(\vec{q}_{\parallel}+\vec{G}_{\parallel}\,|\,q_3)\exp\{iq_3[x_3-x_3(\kappa)]-\tfrac{1}{2}q_3^2\langle u^2_{\perp}(\kappa)\rangle\}[(1-\delta_{\alpha 3})(q_{\alpha}+G_{\alpha})+\delta_{\alpha 3}q_3]\,. \tag{3.16b}$$

If we now combine this result with $\langle G^+(\vec{r},\vec{r}';tt')\rangle$ according to Eq. (3.12), and make use of Eq. (2.41b), we obtain finally the result that

$$\langle M_2(\vec{r},\vec{r}',tt')\rangle = \sum_{\vec{G}_{\parallel},\vec{G}'_{\parallel}}\int_{\mathrm{BZ}}\frac{d^2k_{\parallel}}{(2\pi)^2}\int\frac{d\omega}{2\pi}e^{i(\vec{k}_{\parallel}+\vec{G}_{\parallel})\cdot\vec{x}_{\parallel}}\hat{M}_{2\omega}(\vec{k}_{\parallel}+\vec{G}_{\parallel},\,\vec{k}_{\parallel}+\vec{G}'_{\parallel}\,|\,x_3x'_3)e^{-i(\vec{k}_{\parallel}+\vec{G}'_{\parallel})\cdot\vec{x}'_{\parallel}}e^{-i\omega(t-t')}, \tag{3.17a}$$

where

$$\hat{M}_{2\omega}(\vec{k}_{\parallel}+\vec{G}_{\parallel},\,\vec{k}_{\parallel}+\vec{G}'_{\parallel}\,|\,x_3x'_3)$$
$$=\sum_{\vec{H}_{\parallel}}\sum_{\vec{H}'_{\parallel}}\int_{\mathrm{BZ}}\frac{d^2p_{\parallel}}{(2\pi)^2}\int\frac{d\omega'}{2\pi}\Bigg[\sum_{\kappa\alpha}\sum_{\kappa'\beta}W_{\kappa\alpha}(\vec{k}_{\parallel}+\vec{G}_{\parallel}-\vec{p}_{\parallel}-\vec{H}_{\parallel}\,|\,x_3)$$
$$\times C_{\alpha\beta}(\vec{p}_{\parallel}-\vec{k}_{\parallel},\omega-\omega'\,|\,\kappa\kappa')W^*_{\kappa'\beta}(\vec{k}_{\parallel}+\vec{G}'_{\parallel}-\vec{p}_{\parallel}-\vec{H}'_{\parallel}\,|\,x'_3)\Bigg]$$
$$\times\hat{G}_{\omega'}(\vec{p}_{\parallel}+\vec{H}_{\parallel},\,\vec{p}_{\parallel}+\vec{H}'_{\parallel}\,|\,x_3x'_3)\,. \tag{3.17b}$$

The relation between $\hat{M}_{\omega}(\vec{k}_{\parallel}+\vec{G}_{\parallel},\,\vec{k}_{\parallel}+\vec{G}'_{\parallel}\,|\,x_3x'_3)$ and $\hat{G}_{\omega}(\vec{k}_{\parallel}+\vec{G}_{\parallel},\,\vec{k}_{\parallel}+\vec{G}'_{\parallel}\,|\,x_3x'_3)$ that we seek is now obtained by combining Eq. (3.1) with Eqs. (2.40a), (3.11), and (3.17):

$$\hat{M}_{\omega}(\vec{k}_{\parallel}+\vec{G}_{\parallel},\,\vec{k}_{\parallel}+\vec{G}'_{\parallel}\,|\,x_3x'_3)$$
$$=\hat{V}(\vec{G}_{\parallel}-\vec{G}'_{\parallel}\,|\,x_3)\delta(x_3-x'_3)$$
$$+\sum_{\hat{H}_{\parallel}}\sum_{\hat{H}'_{\parallel}}\int_{\mathrm{BZ}}\frac{d^2p_{\parallel}}{(2\pi)^2}\int\frac{d\omega'}{2\pi}\Bigg[\sum_{\kappa\alpha}\sum_{\kappa'\beta}W_{\kappa\alpha}(\vec{k}_{\parallel}+\vec{G}_{\parallel}-\vec{p}_{\parallel}-\vec{H}_{\parallel}\,|\,x_3)$$
$$\times C_{\alpha\beta}(\vec{p}_{\parallel}-\vec{k}_{\parallel},\omega-\omega'\,|\,\kappa\kappa')W^*_{\kappa'\beta}(\vec{k}_{\parallel}+\vec{G}'_{\parallel}-\vec{p}_{\parallel}-\vec{H}'_{\parallel}\,|\,x'_3)\Bigg]$$
$$\times\hat{G}^{+}_{\omega'}(\vec{p}_{\parallel}+\vec{H}_{\parallel},\vec{p}_{\parallel}+\vec{H}'_{\parallel}\,|\,x_3x'_3)\,. \tag{3.18}$$

Together with Eq. (2.41), Eq. (3.18) gives a complete prescription for the determination of $\langle M(\vec{r},\vec{r}';tt')\rangle$, within the approximations indicated above.

In practice, the method of solution could proceed in the following manner. Equation (2.41) is first solved for $\hat{G}^{+}_{\omega}(\vec{k}+\vec{G}_{\parallel},\,\vec{k}_{\parallel}+\vec{G}'_{\parallel}\,|\,x_3x'_3)$ on the basis of the approximation for $\langle\hat{M}_{\omega}(\vec{k}_{\parallel}+\vec{G}_{\parallel},\,\vec{k}_{\parallel}+\vec{G}'_{\parallel}\,|\,x_3x'_3)\rangle$, given by the first term on the right-hand side of Eq. (3.18). The result is then substituted into the second term on the right-hand side of Eq. (3.18) to yield an improved approximation to $\hat{M}_{\omega}(\vec{k}_{\parallel}+\vec{G}_{\parallel},\,\vec{k}_{\parallel}+\vec{G}'_{\parallel}\,|\,x_3x'_3)$, and the process is continued until convergence is achieved.

An important result of the discussion in this and the preceding section is that the effective potential $\langle M\rangle$ is complex, i.e., it is an optical potential.[10] In what follows we shall express this result by writing $\langle M\rangle$ in the form

$$\langle M\rangle=\langle M_R\rangle+i\langle M_I\rangle\ , \tag{3.19}$$

where $\langle M_R\rangle$ and $\langle M_I\rangle$ are real quantities. The existence of $\langle M_I\rangle$ ultimately derives from the fact that $\langle G^+\rangle$ is complex, and it is the existence of $\langle M_I\rangle$ that in turn gives rise to the decrease in the integrated intensity of the diffracted beams.

IV. THE DEBYE-WALLER FACTOR

Given $\langle M\rangle$, we can, in principle, solve the Lippman-Schwinger equation (2.18), or the equivalent Schrödinger equation, and compute the scattered fluxes according to the first term on the right-hand side of Eq. (2.12). As usual, $\psi_0(\vec{r},t)$ is taken to be a plane wave:

$$\psi_0(\vec{r},t)=\exp[i\vec{k}_{||}\cdot\vec{x}_{||}-i\alpha(k_{||}\omega)x_3-i\omega t]\ , \tag{4.1}$$

where $\alpha(k_{||}\omega)$ is defined in Eq. (2.7''). Then $\langle\psi(\vec{r},t\rangle$ has the form

$$\langle\psi(\vec{r},t)\rangle=\sum_{\vec{G}_{||}}\psi_\omega(\vec{k}_{||}+\vec{G}_{||},\vec{k}_{||}\,|\,x_3)e^{i(\vec{k}_{||}+\vec{G}_{||})\cdot\vec{x}_{||}-i\omega t}\ , \tag{4.2}$$

and for sufficiently large x_3 we have

$$\psi_\omega(\vec{k}_{||}+\vec{G}_{||},\vec{k}_{||}\,|\,x_3)\sim e^{-i\alpha(k_{||}\omega)x_3}\delta_{\vec{G}_{||},\vec{0}}+A_\omega(\vec{k}_{||}+\vec{G}_{||},\vec{k}_{||})\times e^{i\alpha(|\vec{k}_{||}+\vec{G}_{||}|\omega)x_3}\ . \tag{4.3}$$

More generally, if the incident wave vector is $[\vec{k}_{||}+\vec{G}'_{||},-\alpha(|\vec{k}_{||}+\vec{G}'_{||}|\omega)]$, the reflected amplitude will be denoted by $A_\omega(\vec{k}_{||}+\vec{G}_{||},\vec{k}_{||}+\vec{G}'_{||})$. In the rest of this section, $\vec{k}_{||}$ and ω are fixed quantities. We can then simplify the notation by defining

$$A(\vec{G}_{||},\vec{G}'_{||})\equiv A_\omega(\vec{k}_{||}+\vec{G}_{||},\vec{k}_{||}+\vec{G}'_{||})\ , \tag{4.4a}$$

$$\psi(\vec{G}_{||},\vec{G}'_{||}\,|\,x_3)\equiv\psi_\omega(\vec{k}_{||}+\vec{G}_{||},\vec{k}_{||}+\vec{G}'_{||}\,|\,x_3)\ , \tag{4.4b}$$

$$\alpha(\vec{G}_{||})\equiv\alpha(|\vec{k}_{||}+\vec{G}_{||}|\omega)\ . \tag{4.4c}$$

By computing the incoming and reflected fluxes according to Eq. (2.18), we find that the reflection coefficient for the diffracted beam $\vec{G}_{||}$ is, as usual,

$$\frac{\alpha(\vec{G}_{||})}{\alpha(\vec{0})}\,|A(\vec{G}_{||},\vec{0})|^2\ . \tag{4.5}$$

One can also solve the scattering problem by using only $\langle M_R\rangle$, instead of $\langle M\rangle$. The resulting scattering amplitudes will be called $A_R(\vec{G}_{||},\vec{0})$, in the compact notation exemplified by Eq. (4.4a).

More commonly, the scattering problem is solved for the static potential $V_{\rm st}(\vec{r})$, that is obtained by setting $\vec{u}(lk;t)=0$ in $V(\vec{r},t)$ [see Eq. (2.5)]; the resulting scattering amplitudes $A_{\rm st}(\vec{G}_{||},\vec{0})$ are then temperature independent.

The task of this section is to obtain a relation among the three sets of amplitudes $\{A\}$, $\{A_R\}$, and $\{A_{\rm st}\}$, in a form that generalizes the Debye-Waller relation for an impulsive collision:

$$A(\vec{G}_{||},\vec{G}'_{||})=e^{-(1/2)\langle(\Delta\vec{k}\cdot\vec{u})^2\rangle}A_{\rm st}(\vec{G}_{||},\vec{G}'_{||})\ . \tag{4.6}$$

Here $\Delta\vec{k}$ is the momentum transferred in the collision and $\vec{u}$ is the phonon-induced displacement of the harmonically bound scattering center. In atom-surface scattering, semiclassical arguments suggest that to a first approximation

$$\langle(\Delta\vec{k}\cdot\vec{u})^2\rangle=(\vec{G}_{||}-\vec{G}'_{||})^2\langle u_{||}^2(0)\rangle+[\alpha(\vec{G}_{||})+\alpha(\vec{G}'_{||})]^2\langle u_\perp^2(0)\rangle \tag{4.7}$$

in the notation of Eq. (3.7), where $\kappa=0$ labels the surface atom involved in the collision. The most widely used corrections to and generalizations of Eq. (4.6) have been discussed in the Introduction.

We discuss first the relation between $A(\vec{G}_{||},\vec{G}'_{||})$ and $A_R(\vec{G}_{||},\vec{G}'_{||})$. General formulas can be obtained by using the two-potential formalism, which we review here in a form adapted to the diffraction problem. Using Eqs. (4.1) and (4.2), and proceeding as in the derivation of Eq. (2.41), we rewrite Eq. (2.18) as the matrix integral equation

$$\psi(\vec{G}_{||},\vec{0}\,|\,x_3)=\delta_{\vec{G}_{||}\vec{0}}e^{-i\alpha(\vec{0})x_3}+\sum_{\vec{G}'_{||}\vec{G}''_{||}}\int dx'_3\int dx''_3 G_0^+(\vec{G}_{||},\vec{G}'_{||}\,|\,x_3x'_3)M(\vec{G}'_{||},\vec{G}''_{||}\,|\,x'_3x''_3)\psi(\vec{G}''_{||},\vec{0}\,|\,x''_3)\ . \tag{4.8}$$

Here, as in Eq. (4.4), we use the compact notation

$$G_0^+(\vec{G}_{||},\vec{G}'_{||}\,|\,x_3x'_3)\equiv\hat{G}^+_{0\omega}(\vec{k}_{||}+\vec{G}_{||},\vec{k}_{||}+\vec{G}'_{||}\,|\,x_3x'_3)\ , \tag{4.9}$$

and similarly for $M(G'_{||},G''_{||}\,|\,x'_3x''_3)$ and other quantities of the same kind to be defined below. Symbolically, we may write Eq. (4.8) in the form

$$\psi=\psi_0+G_0^+M\psi\ . \tag{4.8'}$$

Next, we set $M=M_R+iM_I$, in an obvious notation, and assume that we are able to solve the equations

$$\psi_R^+=\psi_0+G_0^+M_R\psi_R^+\ , \tag{4.10}$$

$$G_R^+=G_0^++G_0^+M_RG_R^+\ . \tag{4.11}$$

Formally, we have that $\psi_R^+=(I-G_0^+M_R)^{-1}\psi_0$ and $G_R^+=(I-G_0^+M_R)^{-1}G_0^+$.

Equation (4.8') can be rewritten as $(I-G_0^+M_R)\psi=\psi_0+iG_0^+M_I\psi$, and gives at once $\psi=\psi_R+iG_R^+M_I\psi$, or explicitly,

$$\psi(\vec{G}_{\parallel},\vec{0}\,|\,x_3)=\psi_R^+(\vec{G}_{\parallel},\vec{0}\,|\,x_3)+i\sum_{\vec{G}'_{\parallel}\vec{G}''_{\parallel}}\int d^3x'_3\int dx''_3 G_R^+(\vec{G}_{\parallel},\vec{G}'_{\parallel}\,|\,x_3x'_3)M_I(\vec{G}'_{\parallel},\vec{G}''_{\parallel}\,|\,x'_3x''_3)\psi(\vec{G}''_{\parallel},\vec{0}\,|\,x''_3)\ . \tag{4.12}$$

To proceed, we need to know the asymptotic behavior of $G_R^+(\vec{G}_{\parallel},\vec{G}'_{\parallel}\,|\,x_3x'_3)$ for $x_3\to\infty$ and finite x'_3 (we are assuming that M_I has finite range). When written out explicitly, Eq. (4.11) has the form of Eq. (2.42), and $G_0^+(\vec{G}_{\parallel},\vec{G}'_{\parallel}\,|\,x_3x'_3)$ is given by Eq. (2.43). We find, then for $x_3\to\infty$,

$$G_R^+(\vec{G}_{\parallel},\vec{G}'_{\parallel}\,|\,x_3x'_3)\sim\frac{2m}{\hbar^2}\frac{e^{i\alpha(\vec{G}_{\parallel})x_3}}{2i\alpha(\vec{G}_{\parallel})}\left[\delta_{\vec{G}_{\parallel},\vec{G}'_{\parallel}}e^{-i\alpha(\vec{G}'_{\parallel})x'_3}+\sum_{\vec{G}''_{\parallel}}\int dx''_3\int dx'''_3 e^{-i\alpha(\vec{G}_{\parallel})x''_3}\right.$$
$$\left.\times M_R(\vec{G}_{\parallel},\vec{G}''_{\parallel}\,|\,x''_3x'''_3)G_R^+(\vec{G}''_{\parallel},\vec{G}'_{\parallel}\,|\,x'''_3x'_3)\right]\ . \tag{4.13}$$

The quantity in large parentheses is the Hermitian conjugate of $\psi_R^-(\vec{G}_{\parallel}\vec{G}'_{\parallel}\,|\,x'_3)$, which is the eigenfunction of M_R that satisfies the equation

$$\psi_R^-(\vec{G}_{\parallel},\vec{G}'_{\parallel}\,|\,x_3)=\delta_{\vec{G}_{\parallel}\vec{G}'_{\parallel}}e^{i\alpha^*(\vec{G}_{\parallel})x_3}+\sum_{\vec{G}''_{\parallel}\vec{G}'''_{\parallel}}\int dx'_3\int dx''_3 G_0^-(\vec{G}_{\parallel},\vec{G}''_{\parallel}\,|\,x_3x'_3)M_R(\vec{G}''_{\parallel},\vec{G}'''_{\parallel}\,|\,x'_3x''_3)\psi_R^-(\vec{G}'''_{\parallel},\vec{G}'_{\parallel}\,|\,x''_3)\ . \tag{4.14a}$$

Here $G_0^-(\vec{G}_{\parallel},\vec{G}'_{\parallel}\,|\,x_3x'_3)$ comes from a $G_0^-(\vec{r},\vec{r}\,';t-t')$, which is defined by the same equation as $G_0^+(\vec{r},\vec{r}\,';t-t')$, Eq. (2.7a), but is subject to incoming wave or exponentially decaying boundary conditions at infinity. In practice, we use

$$G_0^-(\vec{G}_{\parallel},\vec{G}'_{\parallel}\,|\,x_3x'_3)=G_0^+(\vec{G}_{\parallel}\vec{G}'_{\parallel}\,|\,x_3x'_3)^* \tag{4.14b}$$

with $G_0^+(\vec{G}_{\parallel},\vec{G}'_{\parallel}\,|\,x_3x'_3)$ given by Eq. (2.43). To show explicitly that $\psi_R^-(\vec{G}'_{\parallel}\vec{G}_{\parallel}\,|\,x'_3)^*$ appears in Eq. (4.13), we must transform Eqs. (4.14) into the equivalent set of equations:

$$\psi_R^-=\psi_0^*+G_R^-M_R\psi_0^*\ , \tag{4.15a}$$

$$G_R^-=G_0^-+G_0^-M_RG_R^-\ . \tag{4.15b}$$

We then use the fact that G_R^- is the Hermitian conjugate of G_R^+, and we must also remember that M_R is Hermitian.

The two-potential formula follows from Eqs. (4.12) and (4.13), from the asymptotic behavior of ψ, given by Eq. (4.3), and from the analogous formula for ψ_R^+. It is

$$A(\vec{G}_{\parallel},\vec{0})=A_R(\vec{G}_{\parallel},\vec{0})+\frac{im}{i\hbar^2\alpha(\vec{G}_{\parallel})}\sum_{\vec{G}'_{\parallel}\vec{G}''_{\parallel}}\int dx'_3\int dx''_3\psi_R^-(\vec{G}'_{\parallel},\vec{G}_{\parallel}\,|\,x'_3)^*M_I(\vec{G}'_{\parallel},\vec{G}''_{\parallel}\,|\,x'_3x''_{\parallel})\psi(\vec{G}''_{\parallel},\vec{0}\,|\,x''_3)\ . \tag{4.16}$$

This result can be recast in a form analogous to Eq. (4.6) by using the fact that $\psi_R^+(\vec{G}_{\parallel},\vec{F}_{\parallel}\,|\,x_3)$ and $\psi_R^-(\vec{G}_{\parallel},\vec{F}_{\parallel}\,|\,x_3)$ are linearly related to each other, because they are expansion coefficients of two sets of solutions of the same eigenvalue problem. Specifically, let us define

$$\psi_R^{\pm}(\vec{k}_{\parallel}+\vec{F}_{\parallel},\vec{r})=\sum_{\vec{G}_{\parallel}}\psi_R^{\pm}(\vec{G}_{\parallel},\vec{F}_{\parallel}\,|\,x_3)e^{i(\vec{k}_{\parallel}+\vec{G}_{\parallel})\cdot\vec{x}_{\parallel}}\ . \tag{4.17}$$

Then we must have

$$\psi_R^+(\vec{k}_{\parallel}+\vec{F}_{\parallel},\vec{r})=\sum_{\vec{F}'_{\parallel}}\psi_R^-(\vec{k}_{\parallel}+\vec{F}'_{\parallel},\vec{r})A_R(\vec{F}'_{\parallel},\vec{F}_{\parallel})\ , \tag{4.18}$$

as can be seen by comparing the coefficients of $\exp[i(\vec{k}_{\parallel}+\vec{F}'_{\parallel})\cdot\vec{x}_{\parallel}+i\alpha(\vec{F}'_{\parallel})x_3]$ on the two sides of Eq. (4.17) for $x_3\to\infty$. The sum over $\vec{F}'_{\parallel}$ is restricted to open channels, i.e., those with $\alpha^2(\vec{F}'_{\parallel})>0$. It follows that

$$\psi_R^+(\vec{G}_{\parallel},\vec{F}_{\parallel}\,|\,x_3)=\sum_{\vec{F}'_{\parallel}}\psi_R^-(\vec{G}_{\parallel}\vec{F}'_{\parallel}\,|\,x_3)A_R(\vec{F}'_{\parallel},\vec{F}_{\parallel})\ . \tag{4.19}$$

It is convenient to introduce the S matrix for the scattering from M_R: $S_R(\vec{F}_{\parallel},\vec{F}'_{\parallel})$ is defined for the open channels only and is given by [see Eq. (4.5)]

$$S_R(\vec{F}_{\parallel},\vec{F}'_{\parallel})=-\left[\frac{\alpha(\vec{F}'_{\parallel})}{\alpha(\vec{F}_{\parallel})}\right]^{1/2}A_R(\vec{F}_{\parallel},\vec{F}'_{\parallel}) \tag{4.20}$$

or, symbolically, $\alpha^{1/2}S_R=-A_R\alpha^{1/2}$. Because M_R is Hermitian, S_R is unitary; it follows then that Eq. (4.19), which is rewritten as $\psi_R^+=-\psi_R^-\alpha^{1/2}S_R^{1/2}$, can be inverted to give $\psi_R^+\alpha^{1/2}S_R^+=-\psi_R^-\alpha^{1/2}$. Using $S_R^+=-\alpha^{1/2}\times A_R^+\alpha^{1/2}$, this yields

$$\psi_R^-(\vec{G}'_{||},\vec{F}_{||}\,|\,x_3)=\sum_{\vec{F}'_{||}}\psi_R^+(\vec{G}'_{||},\vec{F}'_{||}\,|\,x_3)\frac{\alpha(\vec{F}_{||})}{\alpha(\vec{F}'_{||})}A_R^*(\vec{F}_{||},\vec{F}'_{||})\,. \tag{4.21}$$

Inserting Eq. (4.21) into Eq. (4.16), we obtain

$$A(\vec{F}_{||},\vec{0})=\sum_{\vec{F}'_{||}}A_R(\vec{F}_{||},\vec{F}'_{||})D(\vec{F}'_{||},\vec{0})\,, \tag{4.22}$$

where the effective Debye-Waller matrix D is defined by

$$D(\vec{F}'_{||},\vec{F}_{||})=\delta_{\vec{F}'_{||}\vec{F}_{||}}+\frac{m}{\hbar^2\alpha(\vec{F}'_{||})}\sum_{\vec{G}'_{||}\vec{G}''_{||}}\int dx'_3\int dx''_3\,\psi_R^+(\vec{G}'_{||}\vec{F}'_{||}\,|\,x'_3)^*M_I(\vec{G}'_{||}\vec{G}''_{||}\,|\,x'_3x''_3)\psi(\vec{G}''_{||},\vec{F}\,|\,x''_3)\,. \tag{4.23}$$

Here the Debye-Waller correction factor appears only in the entrance channel, labeled by $\vec{0}$, and not in the exit channel. It is also possible to obtain a formula where the correction factor appears only in the exit channel. To do so, one starts from the equivalent expression for $A(\vec{G}_{||},\vec{0})$ that is obtained from Eq. (4.16) by allowing $\psi_R^-\to\psi^-$ and $\psi\to\psi_R^+$. Here ψ^- is related to ψ in the same way as ψ_R^- is related to ψ_R^+. Using Eq. (4.19), one finds

$$A(\vec{F}_{||},\vec{0})=\sum_{\vec{F}'_{||}}D^-(\vec{F}_{||},\vec{F}'_{||})A_R(\vec{F}'_{||},\vec{0})\,, \tag{4.22'}$$

$$D^-(\vec{F}_{||},\vec{F}'_{||})=\delta_{\vec{F}_{||}F'_{||}}+\frac{m}{\hbar^2\alpha(F_{||})}\sum_{\vec{G}_{||}\vec{G}'_{||}}\int dx_3\int dx'_3\,\psi_R^-(\vec{G}_{||},\vec{F}_{||}\,|\,x_3)^*M_I(\vec{G}_{||},\vec{G}'_{||}\,|\,x_3x'_3)\psi^-(\vec{G}'_{||},\vec{F}'_{||}\,|\,x'_3)\,. \tag{4.23'}$$

Other formulas are obtained by taking suitable averages of Eqs. (4.23) and (4.23').

To first order in M_I we can replace ψ by ψ_R^+ in Eq. (4.16), or in Eq. (4.23). This, of course, is the distorted-wave Born approximation (DWBA) for M_I with $\langle M_R\rangle$ as the "large" potential and $\langle M_I\rangle$ as the perturbation.

If diffraction is completely negligible, Eq. (4.22) gives the specular intensity as

$$|A(\vec{0},\vec{0})|^2=|D(\vec{0},\vec{0})|^2 \tag{4.24}$$

because $A_R(\vec{0},\vec{0})$, describing total reflection, has unit modulus. This formula is discussed in detail in the next section.

More generally, it is always true that $S_R(\vec{F}_{||},\vec{F}'_{||})$ [defined in Eq. (4.20)] is unitary:

$$\sum_{\vec{F}_{||}}S_R^*(\vec{F}_{||},\vec{F}'_{||})S_R(\vec{F}_{||},\vec{F}''_{||})=\delta_{\vec{F}'_{||}\vec{F}''_{||}}\,, \tag{4.25}$$

and therefore

$$\sum_{\vec{F}_{||}}|A(\vec{F}_{||},\vec{0})|^2\frac{\alpha(\vec{F}_{||})}{\alpha(\vec{0})}=\sum_{\vec{F}_{||}}|D(\vec{F}_{||},\vec{0})|^2\,. \tag{4.24'}$$

The decrease in the total diffracted intensity (including the specular) can then be computed from $|D(\vec{F}_{||},\vec{0})|^2$ alone. However, the inelastic scattering also causes a redistribution of the elastic intensity among the diffracted beams, and to compute this we need to know how $A_R(\vec{F}_{||},\vec{0})$ is related to $A_{st}(\vec{F}_{||},\vec{0})$ or to $A_R(\vec{F}_{||},\vec{0})$, at some reference temperature.

The individual diffracted intensities can be obtained as follows, in the limit where diffraction is weak. It is convenient to regard $V(\vec{0}\,|\,x_3)$ as the unperturbed potential and the rest of $\langle M\rangle$ as the perturbation. Let $A_0(\vec{F}_{||}\,|\,\vec{F}_{||})$ be the reflection amplitude from the potential $\hat{V}(\vec{0}\,|\,x_3)$, and let $\chi^+(\vec{F}_{||}\,|\,x_3)$ be the corresponding wave function. The equation for $\chi^\pm(\vec{G}_{||}\,|\,x_3)$, consistent with the prototype equation (4.8), is

$$\chi^\pm(\vec{F}_{||}\,|\,x_3)=e^{\mp i\alpha(\vec{F}_{||})x_3}+\int dx'_3G_0^\pm(\vec{F}_{||}\,|\,x_3x'_3)\times\hat{V}(\vec{0}\,|\,x'_3)\chi^\pm(\vec{F}_{||}\,|\,x'_3)\,, \tag{4.26}$$

where we have simplified the notation by setting

$$G_0^\pm(\vec{G}_{||},\vec{G}'_{||}\,|\,x_3x'_3)=\delta_{\vec{G}_{||}\vec{G}'_{||}}G_0^\pm(\vec{G}_{||}\,|\,x_3x'_3) \tag{4.27}$$

[see Eq. (2.43) and recall Eq. (4.14)]. It is usually more convenient, however, to compute $\chi^\pm(\vec{G}_{||}\,|\,x_3)$ as the solutions of the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx_3^2}+\hat{V}(\vec{0}\,|\,x_3)\right]\chi(\vec{G}_{||}\,|\,x_3)=\frac{\hbar^2\alpha^2(\vec{G}_{||})}{2m}\chi(\vec{G}_{||}\,|\,x_3)\,, \tag{4.28}$$

with boundary conditions consistent with Eq. (4.26). This equation also has bound-state solutions, for negative values of $\alpha^2(\vec{G}_{||})$, corresponding to solutions of the homogeneous part of Eq. (4.26).

The relation between $A(\vec{F}_{||},\vec{0})$ and $A_0(\vec{F}_{||},\vec{0})$ is given by the analogs of Eqs. (4.16) and (4.12):

$$A(\vec{F}_{||},\vec{0})=A_0(\vec{F}_{||},\vec{F}_{||})\delta_{\vec{F}_{||}\vec{0}}+\frac{m}{\hbar^2 i\alpha(\vec{F}_{||})}\left[\sum_{\vec{G}_{||}\neq\vec{0}}\int dx_3\chi^-(\vec{F}_{||}\,|\,x_3)^*\hat{V}(\vec{F}_{||}-\vec{G}_{||}\,|\,x_3)\psi^+(\vec{G}_{||},\vec{0}\,|\,x_3)+\sum_{\vec{G}_{||}}\int dx_3\int dx'_3\chi^-(\vec{F}_{||}\,|\,x_3)^*M_2(\vec{F}_{||},\vec{G}_{||}\,|\,x_3x'_3)\psi^+(\vec{G}_{||},\vec{0}\,|\,x'_3)\right], \tag{4.29a}$$

$$\psi^{\pm}(\vec{G}_{||},\vec{0}\,|\,x_3)=\chi^{\pm}(\vec{0}\,|\,x_3)\delta_{\vec{G}_{||}\vec{0}}+\sum_{\vec{G}'_{||}\neq\vec{G}_{||}}\int dx'_3\,\Gamma^{\pm}(\vec{G}_{||}\,|\,x_3x'_3)\hat{V}(\vec{G}_{||}-\vec{G}'_{||}\,|\,x'_3)\psi^{\pm}(\vec{G}'_{||},\vec{0}\,|\,x'_3)$$

$$+\sum_{\vec{G}'_{||}}\int dx'_3\int dx''_3\,\Gamma^{\pm}(\vec{G}_{||}\,|\,x_3x'_3)M_2(\vec{G}_{||},\vec{G}'_{||}\,|\,x'_3x''_3)\psi^{\pm}(\vec{G}'_{||},\vec{0}\,|\,x''_3)\,, \tag{4.29b}$$

where $\Gamma^{\pm}(\vec{G}_{||}\,|\,x_3x'_3)\delta_{\vec{G}_{||}\vec{G}'_{||}}$ are the Fourier coefficients of the Green functions for the potential $\hat{V}(\vec{0}\,|\,x_3)$, and satisfy the analog of Eq. (4.11):

$$\Gamma^{\pm}(\vec{G}_{||}\,|\,x_3x'_3)=G_0^{\pm}(\vec{G}_{||}\,|\,x_3x'_3)+\sum_{\vec{G}'_{||}}\int dx''_3\,G_0^{\pm}(\vec{G}_{||}\,|\,x_3x''_3)\hat{V}(\vec{G}_{||}-\vec{G}'_{||}\,|\,x''_3)\Gamma^{\pm}(\vec{G}'_{||}\,|\,x''_3x'_3)\,. \tag{4.30}$$

In practice, it is sufficient to find χ^+ and Γ^+ and to use

$$\chi^-(\vec{G}_{||}\,|\,x_3)=\chi^+(\vec{G}_{||}\,|\,x_3)^*\,, \tag{4.31a}$$

$$\Gamma^-(\vec{G}_{||}\,|\,x_3x'_3)=\Gamma^+(\vec{G}_{||}\,|\,x_3x'_3)^*\,. \tag{4.31b}$$

It should also be noted that the analog of Eq. (4.21) reduces to

$$\chi^-(\vec{F}_{||}\,|\,x_3)=A_0(\vec{F}_{||},\vec{F}_{||})\chi^+(\vec{F}_{||}\,|\,x_3)\,. \tag{4.32}$$

Using Eqs. (4.29) and (4.32) we obtain, to leading order in V and in M_2:

$$\frac{A(\vec{F}_{||},\vec{0})}{A_0(\vec{F}_{||},\vec{F}_{||})}=\delta_{\vec{F}_{||},\vec{0}}\left[1+\frac{m}{\hbar^2\alpha(\vec{0})}\int dx_3\int dx'_3\,|\chi^+(\vec{0}\,|\,x_3)|^2M_2(\vec{0},\vec{0}\,|\,x_3x'_3)\right]$$

$$+(1-\delta_{\vec{F}_{||},\vec{0}})\frac{m}{i\hbar^2\alpha(\vec{F}_{||})}\Bigg[\int dx_3\chi^+(\vec{F}_{||}\,|\,x_3)^*\hat{V}(\vec{F}_{||}\,|\,x_3)\chi^+(\vec{0}\,|\,x_3)$$

$$+i\int dx_3\int dx'_3\int dx''_3\chi^+(\vec{F}_{||}\,|\,x_3)^*M_2(\vec{F}_{||},\vec{F}_{||}\,|\,x_3x'_3)\Gamma^+(\vec{F}_{||}\,|\,x'_3x''_3)$$

$$\times\hat{V}(\vec{F}_{||}\,|\,x''_3)\chi^+(\vec{0}\,|\,x''_3)$$

$$+i\int dx_3\int dx'_3\int dx''_3\chi^+(\vec{F}_{||}\,|\,x_3)^*\hat{V}(\vec{F}_{||}\,|\,x_3)\Gamma^+(\vec{0}\,|\,x_3x'_3)$$

$$\times M_2(\vec{0},\vec{0}\,|\,x'_3x''_3)\chi^+(\vec{0}\,|\,x''_3)$$

$$+\int dx_3\int dx'_3\chi^+(\vec{F}_{||}\,|\,x_3)^*M_2(\vec{F}_{||},\vec{0}\,|\,x_3x'_3)\chi^+(\vec{0}\,|\,x'_3)\Bigg]\,. \tag{4.33}$$

In the next two sections, we give approximate evaluations and discussions of these formulas.

V. APPROXIMATE RESULTS

We evaluate the formulas of Sec. IV when diffraction is completely negligible. In this case, we need only be concerned with the specular intensity, i.e., we can set $\vec{F}_{||}=\vec{0}$ in Eq. (4.33) or $\vec{F}_{||}=\vec{F}'_{||}=\vec{0}$ in Eqs. (4.22) and (4.23), and we can compute $A_R(\vec{0},\vec{0})$, $A_{\rm st}(\vec{0},\vec{0})$, and $A_0(\vec{0},\vec{0})$ as follows. $A_{\rm st}(\vec{0},\vec{0})$ is the specular scattering amplitude from the zero Fourier component of the static potential

$$\hat{V}_{\rm st}(\vec{0}\,|\,x_3)=\frac{1}{a_c}\sum_{\kappa}\int\frac{dk_3}{2\pi}\hat{U}_{\kappa}(\vec{0}\,|\,k_3)e^{ik_3[x_3-x_3(\kappa)]}\,. \tag{5.1a}$$

$A_0(\vec{0},\vec{0})$ is the specular scattering amplitude from the zero Fourier component of the average potential $\langle V(\vec{r},t)\rangle$, as given by Eq. (3.10b):

$$\hat{V}(\vec{0}\,|\,x_3)=\frac{1}{a_c}\sum_{\kappa}\int\frac{dk_3}{2\pi}\hat{U}_{\kappa}(\vec{0}\,|\,k_3)e^{-(1/2)k_3^2\langle u_1^2(\kappa)\rangle}\times e^{ik_3[x_3-x_3(\kappa)]}\,. \tag{5.1b}$$

Comparison of Eqs. (5.1a) and (5.1b) shows that, although $\hat{V}(\vec{0}\,|\,x_3)$ is more slowly varying than $V_{\rm st}(\vec{0}\,|\,x_3)$, both potentials give total specular reflection, which implies that both $A_0(\vec{0},\vec{0})$ and $A_{\rm st}(\vec{0},\vec{0})$ represent simply a phase factor. $A_R(\vec{0},\vec{0})$ is computed using the exact expression for the real part of $\hat{M}_\omega(\vec{k}_{||},\vec{k}_{||}\,|\,x_3x_3')$, instead of the leading approximation $\hat{V}(\vec{0}\,|\,x_3)\delta(x_3-x_3')$. It is also simply a phase factor. The phase of $A_R(\vec{0},\vec{0})/A_0(\vec{0},\vec{0})$ can be deduced by comparing Eqs. (4.22) and (4.23) with Eq. (4.32), but it is of no interest here. Therefore, in the absence of diffraction, the Debye-Waller factor, to second order in the phonon-induced displacements, is simply

$$\left|\frac{A(\vec{0},\vec{0})}{A_{\rm st}(\vec{0},\vec{0})}\right|=\left|\frac{A(\vec{0},\vec{0})}{A_0(\vec{0},\vec{0})}\right|=\left|\frac{A(\vec{0},\vec{0})}{A_R(\vec{0},\vec{0})}\right|\equiv|D(\vec{0},\vec{0})|=1+d(\vec{k}_{||},\vec{k}_{||})\,, \tag{5.2}$$

$$d(\vec{k}_{||},\vec{k}_{||})=\frac{m}{\hbar^2\alpha(k_{||}\omega)}\int dx_3\int dx_3'\chi^+[\alpha(k_{||}\omega)\,|\,x_3]^*\hat{M}_{I\omega}(\vec{k}_{||},\vec{k}_{||}\,|\,x_3x_3')\chi^+[\alpha(k_{||}\omega)\,|\,x_3']\,, \tag{5.3}$$

where we have reverted to the more explicit notation of Sec. III, so that in general $D(\vec{F}_{||},\vec{F}_{||}')$ will now be denoted by $D(\vec{k}_{||}+\vec{F}_{||},\vec{k}_{||}+\vec{F}_{||}')$, and $\chi^+(\vec{G}_{||}\,|\,x_3)$ will be denoted by $\chi^+[\alpha(\,|\,\vec{k}_{||}+\vec{G}_{||}\,|\,\omega)\,|\,x_3]$.

We can also simplify Eq. (3.18) by neglecting all Fourier components of $W_{\kappa\alpha}(\vec{k}_{||}+\vec{G}_{||}\,|\,x_3)$ except those for $\vec{G}_{||}=0$ ($\vec{k}_{||}$ is in the first Brillouin zone). According to Eq. (3.16b), this approximation is consistent with the neglect of the $\vec{G}_{||}\neq 0$ Fourier components of $\hat{U}_\kappa(\vec{q}_{||}+\vec{G}_{||})$, which in turn is consistent with the replacement of $\langle V(\vec{r},t)\rangle$ by $\hat{V}(\vec{0}\,|\,x_3)$, Eq. (5.1b). We have then

$$\hat{M}_{I\omega}(\vec{k}_{||},\vec{k}_{||}\,|\,x_3x_3')=\int\frac{d^2p_{||}}{(2\pi)^2}\int\frac{d\omega'}{2\pi}\sum_{\kappa\alpha}\sum_{\kappa'\beta}W_{\kappa\alpha}(\vec{k}_{||}-\vec{p}_{||}\,|\,x_3)C_{\alpha\beta}(\vec{p}_{||}-\vec{k}_{||},\omega-\omega'\,|\,\kappa\kappa')W^*_{\kappa'\beta}(\vec{k}_{||}-\vec{p}_{||}\,|\,x_3')$$
$$\times\,{\rm Im}\hat{G}^+_\omega(\vec{p}_{||},\vec{p}_{||}\,|\,x_3x_3')\,. \tag{5.4}$$

In order to evaluate ${\rm Im}\,\hat{G}^+_\omega$ we start from Eqs. (2.41) and (2.42), and we use the fact that

$$\frac{\hbar^2}{2m}\left[\alpha^2(\,|\,\vec{k}_{||}+\vec{G}_{||}\,|\,\omega)+\frac{d^2}{dx_3^2}\right]\hat{G}^+_{0\omega}(\vec{k}_{||}+\vec{G}_{||},\vec{k}_{||}+\vec{G}_{||}'\,|\,x_3x_3')=\delta_{\vec{G}_{||}\vec{G}_{||}'}\delta(x_3-x_3') \tag{5.5}$$

to obtain a set of coupled differential equations for $\hat{G}^+_\omega(\vec{k}_{||}+\vec{G}_{||},\vec{k}_{||}+\vec{G}_{||}'\,|\,x_3x_3')$. In the approximation where $\hat{M}_\omega(\vec{k}_{||}+\vec{G}_{||}'',\vec{k}_{||}+\vec{G}_{||}\,|\,x_3''x_3)$ is replaced by $\hat{V}_\omega(\vec{0}\,|\,x_3'')\delta_{\vec{G}_{||}''\vec{G}_{||}}\delta(x_3''-x_3)$, these equations decouple if we set

$$\hat{G}^+_\omega(\vec{k}_{||}+\vec{G}_{||},\vec{k}_{||}+\vec{G}_{||}'\,|\,x_3x_3')=\delta_{\vec{G}_{||}\vec{G}_{||}'}\hat{G}^+_\omega(\vec{k}_{||}+\vec{G}_{||},\vec{k}_{||}+\vec{G}_{||}\,|\,x_3x_3')\,, \tag{5.6}$$

as is to be expected in view of the translational invariance of $\hat{V}_\omega(\vec{0}\,|\,x_3)$. Only the $\vec{G}_{||}=0$ component is now of interest, and it satisfies the equation

$$\left[\frac{\hbar^2}{2m}\left[\alpha^2(\vec{k}_{||}\omega)+\frac{d^2}{dx_3^2}\right]-\hat{V}(\vec{0}\,|\,x_3)\right]\hat{G}^+_\omega(\vec{k}_{||},\vec{k}_{||}\,|\,x_3x_3')=\delta(x_3-x_3') \tag{5.7}$$

with the solution

$$\hat{G}^+_\omega(\vec{k}_{||},\vec{G}_{||}\,|\,x_3x_3')=\sum_\nu\frac{\chi_\nu(x_3)\chi_\nu^*(x_3')}{[\hbar^2\alpha^2(\vec{k}_{||}\omega)/2m]+i0^+-E_\nu}\,, \tag{5.8}$$

where the $\{\chi_\nu\}$ are a complete orthonormal set of eigenfunctions of the potential $\hat{V}(\vec{0}\,|\,x_3)$, with energies E_ν. As usual, the imaginary part of $\hat{G}^+_\omega$ involves only states on the energy shell, $E_\nu=\hbar^2\alpha^2(k_{||}\omega)/2m>0$. Since the scattering states $\chi^+(k_3\,|\,x_3)$ form a complete set for positive energies, $E_\nu=\hbar^2k_3^2/2m$, it follows that

$${\rm Im}\hat{G}^+_\omega(\vec{p}_{||},\vec{p}_{||}\,|\,x_3x_3')=-\pi\int\frac{dk_3}{2\pi}\delta\left[\frac{\hbar^2}{2m}[\alpha^2(p_{||}\omega')-k_3^2]\right]\chi^+(k_3\,|\,x_3)\chi^+(k_3\,|\,x_3')^*$$
$$=-\frac{m\,{\rm Re}\alpha(p_{||}\omega')}{2\hbar^2\alpha(p_{||}\omega')}\chi^+[\alpha(p_{||}\omega')\,|\,x_3]\chi^+[\alpha(p_{||}\omega')\,|\,x_3']^*\,. \tag{5.9}$$

We remark that, in this approximation, $\hat{G}^{+}_{\omega}(\vec{k}_{||}+\vec{G}_{||},\vec{k}_{||}+\vec{G}_{||}\,|\,x_3x_3')$ is identical to $\Gamma^{+}(\vec{G}_{||}\,|\,x_3x_3')$ as defined by Eq. (4.30).

We are now in a position to evaluate $d(\vec{k}_{||},\vec{k}_{||})$, Eq. (5.3), by using Eqs. (5.4) and (5.9). It is convenient to define the matrix elements

$$W_{\kappa\alpha}(\vec{q}_{||}\,|\,\alpha\alpha')=\int dx_3\chi^{+}(\alpha\,|\,x_3)^{*}W_{\kappa\alpha}(\vec{q}_{||}\,|\,x_3)\chi^{+}(\alpha'\,|\,x_3)\,, \tag{5.10}$$

in terms of which we have

$$d(\vec{k}_{||},\vec{k}_{||})=-\frac{m^2}{\hbar^2\alpha(\vec{k}_{||}\omega)}\int\frac{d^2p_{||}}{(2\pi)^2}\int\frac{d\omega'}{2\pi}\sum_{\kappa\alpha}\sum_{\kappa'\beta}\frac{\mathrm{Re}\alpha(p_{||}\omega')}{\alpha^2(p_{||}\omega')}W_{\kappa\alpha}[\vec{k}_{||}-\vec{p}_{||}\,|\,\alpha(k_{||}\omega),\alpha(p_{||}\omega')]$$

$$\times C_{\alpha\beta}(\vec{p}_{||}-\vec{k}_{||},\omega-\omega'\,|\,\kappa\kappa')W^{*}_{\kappa'\beta}[\vec{k}_{||}-\vec{p}_{||}\,|\,\alpha(k_{||}\omega),\alpha(p_{||}\omega')]\,. \tag{5.11}$$

This is a rather general result of the consistent application of lowest-order perturbation theory in the DWBA. It can be obtained by summing all the inelastic transition intensities as given, for example, by Manson and Celli,[9] and subtracting them from unity, to account for the decrease in specular intensity due to the opening of the inelastic channels. To proceed farther, we need to make assumptions about the atom-surface potential. It is possible, however, to make the following general statements.

It should be clear from the above discussion and from the form of Eq. (5.4) that $(\vec{p}_{||}-\vec{k}_{||})$ and $(\omega-\omega')$ represent the transfer of lateral momentum and total energy in inelastic collisions. In the limit of small $\vec{q}_{||}$, it is seen from Eq. (3.16b) that $W_{\kappa3}(\vec{q}_{||}\,|\,x_3)$ is larger than $W_{\kappa1}(\vec{q}_{||}\,|\,x_3)$ and $W_{\kappa2}(\vec{q}_{||}\,|\,x_3)$, and can be approximated by $W_{\kappa3}(\vec{0}\,|\,x_3)$. Furthermore, if $W_{\kappa\alpha}(\vec{0}\,|\,x_3)$ decays rapidly with increasing $|\,x_3-x_3(\kappa)\,|$, the major contribution to the sums in Eqs. (5.2) and (5.4) comes from $\kappa=\kappa'=0$, i.e., from the top atomic layer on the surface. We can then replace $C_{\vec{p}_{||}}(\vec{p}_{||}-\vec{k}_{||},\omega-\omega'\,|\,\kappa\kappa')$ by its value for $\kappa=\kappa'=0$, and the approximation will become exact in the limit $\vec{p}_{||}-\vec{k}_{||}\to0$, $\omega-\omega'\to0$, because the range of C_{33}, as a function of $|\,x_3(\kappa)-x_3(\kappa')\,|$, is of the order of $[\,|\,\vec{p}_{||}-\vec{k}_{||}\,|^2+(\omega-\omega')^2/c^2]^{-1/2}$, where c is a typical sound velocity, and thus much larger than the range of $W_{\kappa3}(\vec{0}\,|\,x_3)$. With all these approximations, Eq. (5.11) reduces to

$$d(\vec{k}_{||},\vec{k}_{||})=-\frac{m^2}{2\hbar^4\alpha(k_{||}\omega)}\int_{\mathrm{BZ}}\frac{d^2p_{||}}{(2\pi)^2}\int\frac{d\omega'}{2\pi}C_{33}(\vec{p}_{||}-\vec{k}_{||},\omega-\omega'\,|\,00)\frac{\mathrm{Re}\alpha(\vec{p}_{||}\omega')}{\alpha^2(p_{||}\omega')}\left|\sum_{\kappa}W_{\kappa3}[\vec{0}\,|\,\alpha(k_{||}\omega),\alpha(p_{||}\omega')]\right|^2. \tag{5.12}$$

Furthermore, comparison of Eqs. (5.1b) and (3.16b) shows that

$$i\sum_{\kappa}W_{\kappa3}(\vec{0}\,|\,x_3)=\frac{d}{dx_3}\hat{V}(\vec{0}\,|\,x_3)\,, \tag{5.13}$$

so that

$$i\sum_{\kappa}W_{\kappa3}(\vec{0}\,|\,\alpha\alpha')=\int dx_3\chi^{+}(\alpha\,|\,x_3)^{*}\frac{d}{dx_3}\hat{V}(\vec{0}\,|\,x_3)\chi^{+}(\alpha'\,|\,x_3)\,. \tag{5.14}$$

Thus in this limit we recover the commonly made approximation that the effective inelastic potential is $u_3d\hat{V}(\vec{0}\,|\,x_3)/dx_3$.

For comparison with earlier results[1-6] we consider first the case when $\hat{V}(\vec{0}\,|\,x_3)$ can be approximated by a repulsive hard wall. Actually, it is computationally convenient to work with a finite-step potential

$$\hat{V}(\vec{0}\,|\,x_3)=H_0\Theta(-x_3)\,. \tag{5.15}$$

The results, somewhat surprisingly, are independent of H_0, as long as the height of the step is sufficient to prevent the atoms from penetrating into the surface. A hard-wall model for the average atom-surface potential implies a very short range for the atom-atom potential $U_{\kappa}(\vec{\rho})$, and is thus consistent with the assumptions made in deriving Eqs. (5.12)–(5.14) in the long-wavelength limit. It follows that we need only compute the matrix elements (5.14), which reduce to

$$-H_0\int dx_3\chi^{+}(\alpha\,|\,x_3)^{*}\delta(x_3)\chi^{+}(\alpha'\,|\,x_3)=-H_0\chi^{+}(\alpha\,|\,0)^{*}\chi^{+}(\alpha'\,|\,0)\,. \tag{5.16}$$

An easy calculation shows that for $H_0>\hbar^2\alpha^2/2m$ the potential (5.15) gives

$$|\,\chi^{+}(\alpha\,|\,0)\,|^2=\frac{2\hbar^2\alpha^2}{mH_0}\,. \tag{5.17}$$

Therefore,

$$\left|\sum_{\kappa}W_{\kappa3}[\vec{0}\,|\,\alpha(k_{||}\omega),\alpha(p_{||}\omega')]\right|=\frac{2\hbar^2}{m}\alpha(k_{||}\omega)\alpha(p_{||}\omega')\,, \tag{5.16'}$$

and

$$|D(\vec{k}_{||},\vec{k}_{||})|^2=1-4\alpha(k_{||}\omega)\int\frac{d^2p_{||}}{(2\pi)^2}\int\frac{d\omega'}{2\pi}C_{33}(\vec{p}_{||}-\vec{k}_{||},\omega-\omega'\,|\,00)\,\mathrm{Re}\alpha(p_{||}\omega')\,, \tag{5.18}$$

in agreement with the results of the vibrating hard-wall model,[5] if the integration over $\vec{p}_{||}$ is restricted to values of $\vec{p}_{||}-\vec{k}_{||}$ that lie in the first Brillouin zone. Such a restriction will appear naturally when $\hat{V}(\vec{0}\,|\,x_3)$ is derived from the interatomic potential, rather than being assumed to be a hard wall (see below).

More realistic model potentials can be constructed starting from a two-body potential of the Yukawa type:

$$U_\kappa(r)=U_0\frac{e^{-\beta r}}{r}\,. \tag{5.19}$$

For the interaction of He with a monatomic solid, β is approximately given by $\hbar^2\beta^2=8m_eE_I$, where E_I is the ionization energy of the atoms in the solid and m_e is the electron mass. The exponential behavior in Eq. (5.19) is dictated by the overlap repulsion between the outer electrons of the solid and those of the impinging atom. The preexponential factor $(1/r)$ is chosen for mathematical convenience and could be replaced by a more general slowly-varying factor $P(r)$ [for instance, $P(r)=1$] without altering the following results in an essential way. The two-dimensional Fourier transform of $U_\kappa(r)$, Eq. (5.19), is

$$\hat{U}_\kappa(\vec{q}_{||}\,|\,x_3)=U_0e^{-\beta(q_{||})|x_3|}/2\beta(q_{||})\,, \tag{5.20a}$$

$$\beta(q_{||})=(\beta^2+q_{||}^2)^{1/2}\,. \tag{5.20b}$$

It is convenient to define an effective thermally-averaged potential:

$$\begin{aligned}\hat{U}_\kappa^{\mathrm{eff}}(\vec{q}_{||}\,|\,x_3)&=\int\frac{dk_3}{2\pi}\hat{U}_\kappa(\vec{q}_{||}\,|\,k_3)e^{ik_3x_3}\\&\quad\times\exp[-\tfrac{1}{2}k_3^2\langle u_\perp^2(\kappa)\rangle]\\&=U_0\int_{-\infty}^{\infty}dx_3'\frac{\exp[-\beta(q_{||})\,|\,x_3-x_3'\,|\,]}{2\beta(q_{||})}\\&\quad\times\frac{\exp[-\frac{1}{2}x_3'^2/\langle u_\perp^2(\kappa)\rangle]}{[2\pi\langle u_\perp^2(\kappa)\rangle]^{1/2}}\,.\end{aligned} \tag{5.21}$$

It is legitimate to replace $|\,x_3-x_3'\,|$ by x_3-x_3' in the integrand, because in reality the distance between the gas atom and the top surface atom layer is always greater than the rms amplitude of surface vibrations, at least for a compact surface. We then obtain

$$\hat{U}_\kappa^{\mathrm{eff}}(\vec{q}_{||}\,|\,x_3)=\frac{U_0}{2\beta(q_{||})}e^{-\beta(q_{||})x_3}\exp\tfrac{1}{2}\beta^2(q_{||})\langle u_\perp^2(\kappa)\rangle\,. \tag{5.22}$$

Comparison of Eqs. (5.20a) and (5.22) shows that, in this case, the effect of thermal vibrations is simply to change the strength of the Fourier components of the potential, leaving unchanged the exponential dependence on x_3. By using the definition (5.21), Eq. (5.1) gives

$$\hat{V}(\vec{0}\,|\,x_3)=\frac{1}{a_c}\sum_\kappa\hat{U}_\kappa^{\mathrm{eff}}[\vec{0}\,|\,x_3-x_3(\kappa)]=V_0^{\mathrm{eff}}e^{-\beta x_3}\,, \tag{5.23a}$$

$$V_0^{\mathrm{eff}}=\frac{U_0}{2\beta a_c}\sum_\kappa e^{\beta x_3(\kappa)}\exp[\tfrac{1}{2}\beta^2\langle u_\perp^2(\kappa)\rangle]\,, \tag{5.23b}$$

and Eq. (3.16b) gives

$$\begin{aligned}iW_{\kappa\alpha}(\vec{q}_{||}\,|\,x_3)=&\left[iq_\alpha(1-\delta_{\alpha3})+\delta_{\alpha3}\frac{d}{dx_3}\right]\\&\times U_\kappa^{\mathrm{eff}}[\vec{q}_{||}\,|\,x_3-x_3(\kappa)]e^{-i\vec{q}_{||}\cdot\vec{x}_{||}(\kappa)}\\&\times\exp[-\tfrac{1}{2}q_{||}^2\langle u_{||}^2(\kappa)\rangle]\,.\end{aligned} \tag{5.24}$$

For a monatomic, unreconstructed surface, we can choose $\vec{x}_{||}(\kappa)=0$. We then see that Eqs. (5.12) and (5.13) are obtained if $q_{||}^2\ll\beta^2$ for all the values of $q_{||}$ of interest. (This approximation is reexamined later on.) The factor $\exp[-\frac{1}{2}\beta^2\langle u_\perp^2(\kappa)\rangle]$ that appears both in $\hat{V}(\vec{0}\,|\,x_3)$ and in $W_{\kappa\alpha}(\vec{q}_{||}\,|\,x_3)$ has no effect, because it corresponds to a shift of the origin of x_3. The factor

$$\exp[\tfrac{1}{2}q_{||}^2[\langle u_\perp^2(\kappa)\rangle-\langle u_{||}^2(\kappa)\rangle]]$$

in $W_{\kappa\alpha}(\vec{q}_{||}\,|\,x_3)$ should be set equal to unity in the present calculation of the Debye-Waller effect for the specular intensity, because only terms of order u^2 are consistently kept.

The explicit result for the matrix elements (5.14), with $\hat{V}(\vec{0}\,|\,x_3)$ given by Eq. (5.23a), was given long ago by Jackson and Mott.[11] For ease of comparison with the hard-wall result (5.16b), it can be rewritten

$$\left|\sum_\kappa W_{\kappa3}(\vec{0}\,|\,\alpha\alpha')\right|=\frac{2\hbar^2}{m}\alpha\alpha'S(\pi\alpha/\beta,\pi\alpha'/\beta)\,, \tag{5.25}$$

where the function $S(p,q)$ is defined by

$$\begin{aligned}S(p,q)=&\frac{(p-q)/2}{\sinh[(p-q)/2]}\frac{(p+q)/2}{\sinh[(p+q)/2]}\\&\times\left[\frac{\sinh p\sinh q}{pq}\right]^{1/2}.\end{aligned} \tag{5.26}$$

Therefore, in this approximation the final result for $D^2(\vec{k}_{||},\vec{k}_{||})$ differs from the vibrating hard-wall result (5.18) only because of the presence of a "softness cutoff factor"

$$S^2[\pi\alpha(k_{||})/\beta,\pi\alpha(p_{||})/\beta] \tag{5.27}$$

under the integral sign. [For a graph of this fact, see Ref. 12.]

Improvements on these formulas will now be discussed. First, we note that in Eq. (5.11) it is not necessary to replace $C_{33}(\vec{p}_{||}-\vec{k}_{||},\omega-\omega' \mid \kappa\kappa')$ with its value for $\kappa=\kappa'=0$, because the sums over κ and κ' can be factored out of the computation of the matrix elements. The net effect is that, in Eq. (5.18), $C_{33}(\vec{p}_{||}-\vec{k}_{||},\omega-\omega' \mid 00)$ should be replaced by

$$\bar{C}_{33}(\vec{p}_{||}-\vec{k}_{||},\omega-\omega')=\frac{\sum_{\kappa\kappa'} C_{33}(\vec{p}_{||}-\vec{k}_{||},\omega-\omega' \mid \kappa\kappa') f_\kappa(\vec{k}_{||}-\vec{p}_{||}) f^*_{\kappa'}(\vec{k}_{||}-\vec{p}_{||})}{\sum_\kappa f_\kappa(\vec{k}_{||}-\vec{p}_{||}) \sum_{\kappa'} f^*_{\kappa'}(\vec{k}_{||}-\vec{p}_{||})} \tag{5.28a}$$

with

$$f_\kappa(\vec{q}_{||})=e^{\beta x_3(\kappa)} \exp[\tfrac{1}{2}\beta^2\langle u_1^2(\kappa)\rangle] e^{-i\vec{q}_{||}\cdot\vec{x}_{||}(\kappa)} . \tag{5.28b}$$

This correction may be called a "perpendicular correlation factor." For typical values of β and of the interplanar spacing, over 90% of the contribution to the sums in (5.28a) comes from $\kappa=\kappa'=0$, for a compact monatomic surface (for an open surface, the assumption that specular reflection is dominant breaks down). Thus we shall neglect this correction in the rest of the discussion.

More important is the fact that, even if $q_{||}^2 \ll \beta^2$, it is not legitimate to approximate $\exp[-\beta(q_{||})x_3]$ with $\exp(-\beta x_3)$, unless $[\beta(q_{||})-\beta]x_3 \ll 1$ for the relevant values of x_3. To leading order

$$\beta(q_{||})-\beta=\tfrac{1}{2}q_{||}^2/\beta , \tag{5.29}$$

and the relevant values of x_3 are around the classical turning point z_t. Typical values of the parameters, for metal surfaces, are $z_t=4.25$, 4.23, and 4.28 Å, and $\beta=2.00$, 2.17, and 2.10 Å^{-1}, for Cu, Ag, and Au, respectively (see Ref. 13 for a table of calculated values and values referred from inelastic scattering experiments). Thus the typical value of the "cutoff parallel momentum," $(\beta/z_t)^{1/2}$, is 0.7 Å^{-1}, which is not large compared to typical values of $q_{||}$ [the Brillouin-zone boundary, for Ag(111), is at $q_{||}=2.51$ Å^{-1}]. A rough approximation is to set

$$e^{-\beta(q_{||})x_3} \cong \exp(-\tfrac{1}{2}q_{||}^2 z_t/\beta) e^{-\beta x_3} . \tag{5.30}$$

With this correction included in Eq. (5.18), along with the "softness cutoff" correction (5.26), the final result for the Debye-Waller factor for specular scattering becomes

$$|D(\vec{k}_{||},\vec{k}_{||})|^2=1-4\alpha(k_{||}\omega)\int\frac{d^2p_{||}}{(2\pi)^2}\int\frac{d\omega'}{2\pi}\bar{C}(\vec{p}_{||}-\vec{k}_{||},\omega-\omega')\frac{\beta^2}{\beta^2+(\vec{k}_{||}-\vec{p}_{||})^2} \times \mathrm{Re}\alpha(p_{||}\omega')S^2\left[\frac{\pi\alpha(k_{||}\omega)}{\beta},\frac{\pi\alpha(p_{||}\omega')}{\beta}\right] e^{-(\vec{k}_{||}-\vec{p}_{||})^2 z_t/\beta} , \tag{5.31a}$$

with

$$\bar{C}(\vec{q}_{||},\Omega)=\frac{1}{\beta^2+q_{||}^2}\left[(\beta^2+q_{||}^2)\bar{C}_{33}(\vec{q}_{||},\Omega)+\sum_{\alpha\beta} q_\alpha \bar{C}_{\alpha\beta}(\vec{q}_{||},\Omega) q_\beta\right] , \tag{5.31b}$$

where $\bar{C}_{33}(\vec{q}_{||},\Omega)$ is defined by Eq. (5.28a), and $\bar{C}_{\alpha\beta}(\vec{q}_{||}\Omega)$ for $\alpha=1,2$ and $\beta=1,2$ is similarly defined. In practice, as was pointed out in the discussion of Eq. (5.28a), it is a good approximation to replace $\bar{C}(\vec{q}_{||},\Omega)$ by $\bar{C}_{33}(\vec{q}_{||},\Omega \mid 00)$.

An expression for the Debye-Waller factor that more closely resembles the temperature factor appearing in theories of the scattering of x rays, neutrons, or electrons from atomic vibrations can be obtained by regarding the result given by Eqs. (5.31) as the first two terms in the expansion of an exponential. The exponentiation of Eq. (5.31a) can be done directly, and justified by cumulant methods,[5] with the result that

$$|D(\vec{k}_{||},\vec{k}_{||})|^2 \cong \exp\left[-4\alpha(k_{||}\omega)\int\frac{d^2p_{||}}{(2\pi)^2}\int\frac{d\omega'}{2\pi}\bar{C}(\vec{p}_{||}-\vec{k}_{||},\omega-\omega')\frac{\beta^2}{\beta^2+(\vec{k}_{||}-\vec{p}_{||})^2} \times \mathrm{Re}\alpha(p_{||}\omega')S^2\left[\frac{\pi\alpha(k_{||}\omega)}{\beta},\frac{\pi\alpha(p_{||}\omega')}{\beta}\right] e^{-(\vec{k}_{||}-\vec{p}_{||})^2 z_t/\beta}\right] . \tag{5.32}$$

Further discussion of the results given by Eqs. (5.31) or (5.32) is postponed to the next section.

In concluding this section we note that had we restricted our treatment to a pairwise sum of Yukawa potentials from the start, we could have made simplifications and avoided certain approximations. For instance, in Eq. (3.14) the factor

$$[\exp\langle -\vec{k}\cdot\vec{u}(l\kappa;t)\vec{k}'\cdot\vec{u}(l'\kappa';t')\rangle - 1]$$

can be kept exactly by expanding the exponential to all or-

ders and replacing powers of k_3 with powers of id/dx_3, acting on $U_\kappa^{\rm eff}(\vec{k}_{||}|x_3)$ given by Eq. (5.21). For Yukawa potentials, the explicit result (5.22) shows that d/dx_3 can be replaced by $-\beta(k_{||})$. If only the 33 components of the correlation functions are kept, the expansion can be resummed, with the result that, in Eq. (3.18) and in the following, $C_{33}(\vec{p}_{11}-\vec{k}_{||},\omega-\omega'|\kappa\kappa')$ should be replaced by

$$\sum_l \int dt \exp\{-i(\vec{p}_{||}-\vec{k}_{||})\cdot[\vec{x}_{||}(l\kappa)-\vec{x}_{||}(0\kappa')]\} \times e^{i(\omega-\omega')t}\frac{1}{\beta(p_{||})\beta(k_{||})} \times\{\exp[\beta(p_{||})\beta(k_{||})\langle u_3(l\kappa;t)u_3(0\kappa';0)\rangle]-1\}. \quad (5.33)$$

VI. DISCUSSION AND SUMMARY

The main results of this paper include: the formal developments leading to Eqs. (2.40), the general second-order formulas for the optical potential, Eqs. (3.17a) and (3.18), and the corresponding formula for the temperature effect on the diffracted intensities, Eq. (4.32).

Accurate numerical calculations of diffracted intensities can now be performed by constructing the Fourier coefficients of the optical potential $\hat{M}_\omega(\vec{k}_{||}+\vec{G}_{||}, \vec{k}_{||}+\vec{G}'_{||}|x_3x'_3)$, Eq. (3.18), and then applying the coupled-channel method or other numerical techniques. It is hoped that such accurate, but difficult, calculations will be carried out in the near future. Approximate evaluations of the temperature effects on diffraction, however, are best obtained from Eq. (4.33). As a first application we have explicitly derived the Debye-Waller factor for specular reflection from a monatomic surface, in the limit where diffraction is negligible, under the assumption that the surface atom-gas atom potential is of the Yukawa type, Eq. (5.19). The final formula for this Debye-Waller factor, Eq. (5.31) or (5.32), is the other major result of this paper. It should be applicable to the scattering of He from compact metal surfaces, because it is also approximately valid in the presence of attractive Van der Waals forces, provided that the incoming perpendicular energy is larger than the surface well depth and that surface resonances are avoided. The usual Beeby correction to the perpendicular energy may be applied to improve the result.

We have already compared Eq. (5.31) to the result of the vibrating hard-wall model, Eq. (5.18). We can also identify in Eq. (5.31a) the various corrections to the simple result

$$D^2(\vec{k}_{||},\vec{k}_{||})=1-4\alpha^2(k_{||}\omega)\langle u_3(0)^2\rangle \quad (6.1)$$

that are discussed, for instance, by Meyer.[1] Basically, the "closed-channel correction" is due to the fact that the factor $\mathrm{Re}\alpha(p_{||}\omega)$, which appears instead of one of the factors of $\alpha(k_{||}\omega)$, restricts the integration to the "open" final channels (more generally, we are dealing here with a multiple-scattering effect, as pointed out in Ref. 5); the softness cutoff factor $S^2[\pi\alpha(k_{||}\omega)/\beta, \pi\alpha(p_{||},\omega)/\beta]$ corresponds to the Levi correction; and the parallel momentum cutoff factor, given by $\exp[-(k_{||}-p_{||})^2z_t/\beta]$ for small momentum transfer, introduces the Armand correction. To see the last point more clearly, let us assume that all other factors are slowly varying compared to the correlation function and to the parallel momentum cutoff factor, which are peaked at $\vec{p}_{||}=\vec{k}_{||}$, $\omega=\omega'$. We obtain then

$$D^2(\vec{k}_{||},\vec{k}_{||})=1-4\alpha^2(k_{||}\omega)S^2\left[\frac{\pi\alpha(k_{||}\omega)}{\beta},\frac{\pi\alpha(k_{||}\omega)}{\beta}\right] \times\int\frac{d^2q_{||}}{(2\pi)^2}C_{33}(\vec{q}_{||})e^{-q_{||}^2z_t/\beta}, \quad (6.2)$$

where

$$C_{33}(\vec{q}_{||})=\int\frac{d\Omega}{2\pi}\bar{C}_{33}(\vec{q}_{||}\Omega) \quad (6.3)$$

is an equal time correlation function. In the approximation where the topmost layer ($\kappa=0$) makes the dominant contribution to the atom-surface potential, we have simply

$$\int_{\rm BZ}\frac{d^2q_{||}}{(2\pi)^2}C_{33}(\vec{q}_{||})e^{i\vec{q}_{||}\cdot\vec{x}_{||}(l)}=\langle u_3(l0)u_3(00)\rangle \quad (6.4)$$

[recall the definitions (3.15) and (5.28)]. The integral in Eq. (6.2) is formally extended to all values of $\vec{q}_{||}$, although the approximation scheme is consistent only if the major contribution comes from the first Brillouin zone: Indeed, the parallel momentum cutoff factor effectively restricts the integration to a fraction of the Brillouin zone. This is the Armand effect in momentum space; it can also be displayed in coordinate space through the identity

$$\int\frac{d^2q_{||}}{(2\pi)^2}\bar{C}_{33}(\vec{q}_{||})e^{-q_{||}^2z_t/\beta} =\frac{\pi\beta a_c}{4z_t}\sum_l\langle u_3(l0)u_3(00)\rangle \times\exp\{-\beta[\vec{x}_{||}(l)-\vec{x}_{||}(0)]^2/4z_t\}. \quad (6.5)$$

We can also show the the equivalence of either side of Eq. (6.5) to an expression that has recently been used by Lapujoulade[14] to justify the original intuitive derivation of the Armand effect. The essential idea is to use what may be called the "vibrating turning-point approximation" to express the Debye-Waller factor in terms of the correlation function of the turning point. If the closed-channel correction is neglected (to be treated separately), Eq. (10) of Ref. 14 can be written in the form (6.1), but with $\langle u_3(0)^2\rangle$ replaced by the average over the unit cell of the mean-square vibration amplitude of the turning point, which, in our notation is given by

$$\frac{1}{a_c}\int_{\rm uc}d^2x_{||}[V'_{\rm st}(\vec{x}_{||}|z_t)]^{-2}\sum_{ll'}\langle u_3(l0)u_3(l'0)\rangle \times U'_\kappa[\vec{x}_{||}-\vec{x}_{||}(l0)|z_t] \times U'_\kappa[\vec{x}_{||}-\vec{x}_{||}(l'0)|z_t], \quad (6.6)$$

where a prime denotes differentiation with respect to x_3, at $x_3=z_t$. We have kept only the contribution of the topmost atoms ($\kappa=0$) to the 33 component of the correlation function, in order to make a direct comparison with Eq. (6.5); a more general correspondence with Lapujoulade's results can also be established. Using Eqs. (5.1a) and (5.20a), we find

$$U'_\kappa(\vec{x}_{||}\,|\,z_t)=\frac{U_0}{2}\int\frac{d^2q_{||}}{(2\pi)^2}e^{i\vec{q}_{||}\cdot\vec{x}_{||}}e^{-\beta(q_{||})z_t}\,, \tag{6.7}$$

$$V'_{\rm st}(\vec{x}_{||}\,|\,z_t)=\frac{U_0}{2a_c}e^{-\beta z_t}\,, \tag{6.8}$$

and therefore the expression (6.6) becomes

$$\int\frac{d^2q_{||}}{(2\pi)^2}\bar{C}_{33}(\vec{q}_{||})e^{-2[\beta(q_{||})-\beta]z_t}\,, \tag{6.9}$$

which is identical to the left-hand side of Eq. (6.5) when $\beta(q_{||})$ is expanded to lowest order in $q_{||}$. It should be noted that the same expansion of $\beta(q_{||})$ was used in obtaining Eq. (5.31a) [compare Eq. (5.30)], which in fact hinges on the same turning-point approximation that has been used by Lapujoulade.

It can then be said that the "quick calculation" of Ref. 14 omits the softness factor S^2. It is comforting to see that the calculated value is larger than the experimental value by a factor of $0.329/0.251=1.31$.

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APPENDIX: QUANTUM TREATMENT

Let $H_{\rm osc}$ (where osc denotes oscillation) be the Hamiltonian of the crystal in the harmonic approximation. It is a function of the atomic displacements, $\{\vec{u}_S(l\kappa)\}$, and their conjugate momenta. The subscript S, on $\vec{u}_S(l\kappa)$ and on other operators in what follows, denotes a Schrödinger operator. Thus, $\vec{r}_S$ and $\vec{p}_S$ are the position and momentum operators of the scattering atom.

The total Hamiltonian is then

$$H=p_S^2/2m+\sum_{l\kappa}U_\kappa[\vec{r}_S-\vec{x}(l\kappa)-\vec{u}_S(l\kappa)]+H_{\rm osc}\,, \tag{A1}$$

and we want to solve the Schrödinger equation

$$i\hbar\frac{\partial\,|\,\Psi(t)\rangle}{\partial t}=H\,|\,\Psi(t)\rangle \tag{A2}$$

with the initial condition $|\,\Psi(t_0)\rangle=|\,\Phi\rangle$, where $|\,\Phi\rangle$ is the direct product of a free-particle eigenstate for the incident atom, $|\,\phi_{\rm inc}\rangle$, and an eigenstate of $H_{\rm osc}$, $|\,\Phi_{\rm osc}\rangle$.

By the transformation

$$|\,\Psi(t)\rangle=e^{-iH_{\rm osc}t/\hbar}\psi(t)\,|\,\Phi\rangle\,, \tag{A3}$$

we reduce (A2) to a form similar to Eq. (2.6), with the only difference that $\psi(t)$ is still an operator over the space spanned by $\vec{r}_S$ and $\vec{u}_S(l\kappa)$:

$$i\hbar\frac{\partial\psi(t)}{\partial t}=\left[\frac{p_S^2}{2m}+V(\vec{r}_S,t)\right]\psi(t) \tag{A4}$$

where, in analogy to Eq. (2.5),

$$V(\vec{r}_S,t)=\sum_{l\kappa}U_\kappa[\vec{r}_S-\vec{x}(l\kappa)-\vec{u}_H(l\kappa;t)]\,, \tag{A5}$$

and $\vec{u}_H(l,\kappa;t)$ is the Heisenberg displacement operator

$$\vec{u}_H(l,\kappa,t)=e^{iH_{\rm osc}t/\hbar}\vec{u}_S(l,\kappa)e^{-iH_{\rm osc}t/\hbar}\,. \tag{A6}$$

We can in fact make Eq. (A4) formally identical to Eq. (2.6) by taking the matrix element between $\langle\vec{r}\,|$ and $|\,\phi_{\rm inc}\rangle$, and defining

$$\psi(\vec{r},t)=\langle\vec{r}\,|\,\psi(t)\,|\,\phi_{\rm inc}\rangle \tag{A7}$$

and also, consistently with (A4),

$$\psi_{\rm inc}(\vec{r},t)=\langle\vec{r}\,|\,e^{-ip_S^2(t-t_0)/2m}\,|\,\phi_{\rm inc}\rangle\,. \tag{A8}$$

It should be noted, however, that $\psi(\vec{r},t)$ is still an operator acting on the space spanned by $\vec{u}_S(l\kappa)$. Finally, $\langle\psi(\vec{r},t)\rangle$ is now the statistical average of $\langle\Phi_{\rm osc}\,|\,\psi(\vec{r},t)\,|\,\Phi_{\rm osc}\rangle$ over the occupation numbers of the various states $|\,\Phi_{\rm osc}\rangle$.

All the formal developments presented in this paper remain true when $\psi(\vec{r},t)$ is an operator, provided that the correct order of operator products is preserved, as we have done. In practice, the only difference of the full quantum treatment is in the values of the harmonic correlation functions $C_{\alpha\beta}(\vec{q}_{||}\Omega\,|\,\kappa\kappa')$.

We note that, formally, the recoil of the lattice is contained in Eq. (2.18) through the self-consistent use of $\langle G\rangle$ and $\langle M\rangle$.

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[1]H. D. Meyer, Surf. Sci. **104**, 117 (1981).
[2]J. L. Beeby, J. Phys. C **5**, 3438 (1972); **5**, 3457 (1972); **6**, 1229 (1973).
[3]G. Armand and J. R. Manson, Surf. Sci. **80**, 532 (1979).
[4]A. C. Levi and H. G. Suhl, Surf. Sci. **88**, 133 (1979).
[5]N. Carcia, A. A. Maradudin, and V. Celli, Philos. Mag. A **45**, 287 (1982).
[6]N. Garcia and A. A. Maradudin, Surf. Sci. **119**, 384 (1982).
[7]V. Bortolani, A. Franchini, F. Nizzoli, G. Santoro, G. Benedek, and V. Celli, Surf. Sci. **128**, 249 (1983).
[8]V. Celli, G. Benedek, U. Harten, J. P. Toennies, R. B. Doak, and V. Bortolani, Surf. Sci. **143**, L376 (1984).

[9]M. Manson and V. Celli, Surf. Sci. **24**, 495 (1971); N. Cabrera, V. Celli, and R. Manson, Phys. Rev. Lett. **22**, 346 (1969).
[10]See Y. Hamauzu, J. Phys. Soc. Jpn. **42**, 961 (1977).
[11]J. M. Jackson and N. F. Mott, Proc. R. Soc. London, Series A **137**, 703 (1932). For a more recent reference, see G. Armand and J. R. Manson, Phys. Rev. B **20** 5020 (1979); G. Armand, J. Phys. (Paris) **41**, 1975 (1980), or Ref. 12.
[12]V. Celli and D. Evans, in *Dynamics of Gas-Surface Interaction,* edited by G. Benedek and U. Valbusa (Springer, Berlin, 1982), p. 2.
[13]V. Bortolani, A. Franchini, N. Garcia, F. Nizzoli, and G. Santoro, Phys. Rev. B **28**, 7358 (1983).
[14]J. Lapujoulade, Surf. Sci. **134**, L139 (1983).