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Calculation of the Debye-Waller factor for atom-surface scattering: He on Ag(111)

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By a consistent application of the distorted-wave Born approximation, the Debye-Waller exponent for the scattering of He atoms from the Ag(111) surface is directly computed. When diffraction is negligible, as in this case, the decrease in specular intensity is simply obtained by summing the scattering due to all possible one-phonon processes. Using one-phonon computed intensities that agree with experiment along high-symmetry directions of the surface Brillouin zone, we find that the computed Debye-Waller exponent agrees with experiment and corresponds to an effective Debye temperature of 241 K. All corrections to the eikonal-type formula, $2W=4p_z^2\langle u_z^2\rangle$, are automatically included. In particular, the contribution of phonons with high parallel momentum is sharply cut off.

I. INTRODUCTION

Many papers have dealt with the theory of thermal attenuation of the diffracted beams in atom-surface scattering and on comparisons with experiment.[1-13] Empirically, it is found in many cases that the thermal attenuation is well described by a Debye-Waller factor, e^{-2W}, with

$$2W=\langle(\Delta\mathbf{p}\cdot\mathbf{u})^2\rangle\ , \tag{1.1}$$

where $\mathbf{u}$ is approximately the thermally induced displacement of a bulk atom (and not of a surface atom, as one would naively expect). Here $\Delta\mathbf{p}$ is the momentum change upon diffraction, with the z component modified by the effect of the attractive well (Beeby correction):[1]

$$p_z^2=k_z^2+2mD/\hbar^2\ , \tag{1.2}$$

where D is the depth of the attractive potential well, m is the mass of the atom, and k_z is the normal component of the wave vector at infinite distance from the surface. In the temperature range where the classical harmonic approximation is valid, $\langle u^2\rangle$ is proportional to the temperature T. Thus in practice, for specular reflection from a monatomic cubic solid, one can use[14]

$$2W=\frac{3T(\hbar^2\Delta k_z^2+8mD)}{Mk_BT_D^2} \tag{1.3}$$

for $T_D/20\leq T\leq T_D$, where T_D is roughly equal to the bulk Debye temperature. There are quantum corrections for $T<T_D/20$ and corrections due to anharmonic effects for $T>T_D$.

It is puzzling at first that the bulk Debye temperature should appear in Eq. (1.3), or the bulk displacements in Eq. (1.1). The following qualitative answer to this puzzle has been generally agreed upon. Equation (1.1) is obtained in the eikonal approximation to hard-wall scattering, where U is then the displacement of the hard wall that represents the repulsive part of the atom-surface potential.[2,3] There are several corrections to this simple result. To begin with, the eikonal approximation loses validity at low perpendicular momentum, and in particular the emission of energetic phonons cannot occur if the atom has insufficient energy.[3,5,6] Further, the true atom-surface collision is not impulsive, as assumed in the hard-wall model, and a soft potential gives less inelastic scattering than a hard wall.[2,15] Finally, the phonon-induced displacement of the effective hard wall is given by an appropriate average of the displacements of the underlying surface atoms, and thus its mean-square value is less than that of an individual surface atom.[4,11-13] Due to these three corrections, the effective $\langle u^2\rangle$ that appears in Eq. (1.1) is smaller than the $\langle u^2\rangle$ of a surface atom, typically by a factor of $\sqrt{2}$, and it is then (coincidentally) close to the $\langle u^2\rangle$ of a bulk atom.

The purpose of this paper is to quantitatively compute $2W$ and to test whether these qualitative arguments are in fact correct. We choose as a test case the scattering of He from Ag(111), because for this system the needed information is known: the dispersion relations and polarizations of bulk and surface phonons are given by slab calculations, with force constants adjusted to reproduce neutron and atom scattering data, while the atom-surface interaction potential has a theoretically determined shape, with parameters adjusted to give agreement with elastic and inelastic atom scattering data.[16-18] There are then no adjustable parameters in the calculations reported here, although we have varied the parameters to test that the predetermined parameters are indeed needed to reproduce the observed[19] value of $2W$ (within the experimental and theoretical uncertainties, of course).

We compute the thermal attenuation to second order in the atom-phonon interaction, i.e., we include only one-phonon processes; the specular intensity then is of the form $1-2AT$. Obviously this formula is valid only for

$T \ll A^{-1}$. We assume then that for all temperatures the specular intensity is given approximately by e^{-2AT}. This expression has been found by Armand and Manson[9,10] to be a good approximation up to second order in T, by explicitly summing all the two-phonon interactions. If only on-shell processes are kept in this model, one obtains $[(1-0.5AT)/(1+0.5AT)]^2$, which agrees with e^{-2AT} to second order in AT.[9] The exponential form can also be justified by using cumulants and assuming that only the one-phonon cumulant average is important. It must be recognized, however, that there is no rigorous justification of the extension of the second order result, and that we rely on the fact that the Debye-Waller exponential form gives a good fit of the experimental data for Ag(111).[19]

The results obtained here are valid even though they are based on a theory of the He-surface interaction that may need to be refined, as discussed after Eq. (2.12). Since the parametrized interaction of Refs. 17 and 18 accurately reproduces the experimental inelastic intensities for phonons along the high-symmetry directions, it can be used to interpolate the experimental inelastic intensities for phonons throughout the surface Brillouin zone, which are all that is needed for the comparison of the present calculation with experiment. However, the possibility of changing the parameters in a physically motivated interaction also enables us to make comparisons with several simple models that are obtained as limiting cases, as discussed in Sec. III.

II. FORMALISM

The thermal attenuation of the specular intensity is given by $|S_{00}|^2$, where S_{00} is the specular element of the S matrix. $|S_{00}|^2$ can be found either by computing S_{00} directly or by using the unitarity of the S matrix to write

$$|S_{00}|^2 = 1 - \sum_p |S_{p0}|^2 , \tag{2.1}$$

where the sum is over all inelastic processes (in the absence of diffraction). Elaborate derivations of this result and explicit formulas for the one-phonon processes have been given by Armand and Manson[9,10] and by Celli and Maradudin;[11,12] we will use the final expression of Ref. 11, Eq. (5.31), for our numerical calculations. The connection with the formalism of Manson *et al.*[10] is established by writing $S = 1 - 2\pi i T$, so that

$$\begin{aligned} |S_{00}|^2 &= |1 + 2\pi \operatorname{Im} T_{00}|^2 + 4\pi^2 |\operatorname{Re} T_{00}|^2 \\ &= 1 + 4\pi \operatorname{Im} T_{00} + 4\pi^2 |T_{00}|^2 . \end{aligned} \tag{2.2}$$

Using the optical theorem for the T matrix, it can be seen that Eq. (2.2) is exactly equivalent to (2.1), with $S_{p0} = -2\pi i T_{p0}$. The two equations also correspond order by order, although one must go one order higher in the calculation of T_{00}. We compute S_{p0} to first order and use Eq. (2.1), which is equivalent to computing $\operatorname{Im} T_{00}$ to second order ($T_{00}=0$ to first order) and neglecting $|T_{00}|^2$ (which is of the fourth order) in Eq. (2.2). The starting formula, using the distorted-wave Born approximation[20] to compute S_{p0}, is then

$$\begin{aligned} 2W = \frac{m^2}{2\hbar^3 N M k_{iz}} \sum_{\mathbf{Q}\nu} \frac{\operatorname{Re} k_{fz}}{|k_{fz}|^2 \omega_\nu(\mathbf{Q})} n(\omega_\nu(\mathbf{Q})) \\ \times \left| \int dz\, \chi(k_{fz};z) \nabla\cdot\mathbf{U}_{\mathbf{Q}}(z) \chi(k_{iz};z) \right|^2 , \end{aligned} \tag{2.3}$$

where m is the He mass, M the Ag mass, N is the number of Ag atoms on the surface of area L^2, $(\mathbf{K}_i, k_{iz})$ and $(\mathbf{K}_f, k_{fz})$ are the initial and final momentum of the He atom, $\mathbf{Q}$ and $\omega_\nu(\mathbf{Q})$ are the parallel momentum and the frequency of a phonon belonging to the branch ν, $n(\omega)$ is the Bose function: $n(\omega) = [\exp(\hbar\omega/k_B T) - 1]^{-1}$, $\chi(k_{iz};z)$ and $\chi(k_{fz};z)$ are the wave functions of the He atom in the static potential of the surface, normalized to the asymptotic behavior $\chi(k_z;z) \to 2\sin(k_z z + \delta)$, and the dynamic interaction $\nabla\cdot\mathbf{U}_{\mathbf{Q}}(z)$ is defined in Eq. (2.9) below. The final momentum $(\mathbf{K}_f, k_{fz})$ is determined by the conservation laws

$$\mathbf{K}_f = \mathbf{K}_i + \mathbf{Q} , \tag{2.4}$$

$$\hbar^2(\mathbf{K}_f^2 + k_{fz}^2) = \hbar^2(\mathbf{K}_i^2 + k_{iz}^2) + 2m\hbar\omega_\nu(\mathbf{Q}) . \tag{2.5}$$

It is understood that both positive and negative values of $\omega_\nu(\mathbf{Q})$ must be included in Eq. (2.3), with positive $\omega_\nu(\mathbf{Q})$ corresponding to phonon annihilation. The dynamic interaction $\nabla\cdot\mathbf{U}_{\mathbf{Q}}(z)$ is derived from a He-Ag repulsive potential $v(\mathbf{r})$, taken to be proportional to the surface charge density $\rho(\mathbf{r})$ of Ag

$$v(\mathbf{r}) = A\rho(\mathbf{r}) \tag{2.6}$$

with $A = 375$ eV. The same pairwise interactions, plus the van der Waals attraction, give the static He-surface potential. As in previous calculations,[17,18] the static potential is approximated by

$$V_0(z) = U_0 e^{-\beta z} - \frac{C_3}{(z-z_0)^3} f_3(k_c(z-z_0)) \tag{2.7}$$

with $U_0 = 296$ eV, $C_3 = 0.44$ eV Å^3, $z_0 = 1.38$ Å and β adjusted at each incident energy to give the correct logarithmic derivative at the classical turning point z_t of the potential (2.7). The damping function f_3 is given by

$$f_3(x) = 1 - [2x(1+x) + 1]e^{-2x} \tag{2.8}$$

with $x = K_c(z - z_0)$, where K_c is a parameter of the order of an inverse atomic radius. $K_c = 1.1$ Å^{-1} reproduces the bound states of He/Ag(111) and the depth of the well. In a consistent way, the dynamic interaction is well approximated by

$$\nabla\cdot\mathbf{U}_{\mathbf{Q}}(z) = \frac{N U_0}{L^2} \left[i\mathbf{e}\left(0\middle|\begin{matrix}\mathbf{Q}\\ \nu\end{matrix}\right)\cdot\mathbf{Q} - e_z\left(0\middle|\begin{matrix}\mathbf{Q}\\ \nu\end{matrix}\right)\beta \right] e^{-\beta z} e^{-Q^2 z_t/2\beta} \tag{2.9}$$

where

$$\mathbf{e}\left(0\middle|\begin{matrix}\mathbf{Q}\\ \nu\end{matrix}\right)$$

is the polarization vector of the $(\mathbf{Q},\nu)$ mode normalized to

$$\sum_l \left| e\left(l\middle|\begin{matrix}\mathbf{Q}\\ \nu\end{matrix}\right) \right|^2 = 1 \tag{2.10}$$

and evaluated for the surface atom ($l=0$). The lateral cutoff factor $\exp(-Q^2/2Q_c^2)$, with $Q_c^2=\beta/z_t$, naturally arises from a pairwise sum of Born-Mayer potentials and quantitatively describes the "Armand effect"[4] for this type of interaction.[11,12,17] The effect of the attractive potential has been simulated by the Beeby correction, i.e., k_z is replaced by p_z given by Eq. (1.2), because the exact calculation was reproduced to within 10% by the Beeby correction. The relevant matrix elements are then

$$\int dz\, \chi(k_{fz};z) U_0 e^{-\beta z} \chi(k_{iz};z) = \frac{2\hbar^2 p_{iz} p_{fz}}{m} S\left[\frac{\pi p_{iz}}{\beta}, \frac{\pi p_{fz}}{\beta}\right] \tag{2.11}$$

with

$$S(x,y) = \frac{\frac{x-y}{2}}{\sinh\frac{x-y}{2}} \frac{\frac{x+y}{2}}{\sinh\frac{x+y}{2}} \left[\frac{\sinh x \sinh y}{xy}\right]^{1/2} . \tag{2.12}$$

Inserting these expressions in Eq. (2.3), we obtain a formula equivalent to Eq. (5.31) of Ref. 11.

A word of caution about this formula is in order. A completely consistent theory of the He-Ag interaction on the basis of a pairwise sum of repulsions is not possible: either the static corrugation comes out too large, or the attractive well is too shallow.[21,22] Here we have chosen a dynamic interaction that is consistent with the well depth, and have disregarded the (very small) static corrugation altogether. One reason for doing so is that the theory of the laterally averaged potential (2.8) is thought to be in better shape than the theory of the static corrugation.[23] A more practical reason is that we need the wave functions of the potential (2.8) to compute the matrix elements of (2.9), but can neglect the corrugation.

Most of the calculations reported here were carried out for a slab of 24 atom layers and the sum over the lateral momentum **Q** in Eq. (2.4) was performed by using 18 special (Baldereschi) points in the irreducible part of the surface Brillouin zone.[24] This procedure yields results that are accurate to better than 5%; convergence was tested by performing some calculations with a variable number of atom layers (6 to 42) and of Baldereschi points (up to 45) as discussed in the next section. The phonon frequencies and polarizations have been computed by the slab method within a force constant parametrization scheme, by adjusting the force constants in the surface region[16,17] to obtain agreement with the phonon frequencies measured by inelastic He scattering.[25]

III. NUMERICAL RESULTS

Figure 1 shows the effective surface-projected momentum-selected phonon density of states, i.e., the contribution for different **Q** vectors to the effective mean-square surface displacement, $2W/4p_{iz}^2$, where $2W$ is given by Eq. (2.3) and p_{iz} contains the Beeby correction according to Eq. (1.2). The vibrating-soft-atom (VSA) results were obtained using the He-surface interaction parameters determined by previous work[17,18] and thus represent our best theoretical prediction; the results of the vibrating-soft-wall (VSW) model and those of the intermediate VSA (IVSA) model are also shown for comparison, as discussed more fully below. The dotted curves have been interpolated through the values calculated for a slab of 12 atom layers at the 18 Baldereschi points (7,1), (8,2), (9,1), (6,2), (6,4), (7,5), (8,4), (9,5), (7,7), (8,8), (9,7), (5,1), (4,2), (4,4), (5,5), (3,1), (1,1), and (2,2) in units of $(\sqrt{3}/54,\sqrt{2}/27)(2\pi/a_0)$. The small deviations of the computed points from a smooth curve show that **Q** values in different directions give contributions that depend approximately on $\mathbf{Q}^2$ only. All three curves in Fig. 1 diverge as $\mathbf{Q}^{-1}$ for small **Q** in the limit of infinite slab thickness. For a slab of N layers, however, the curves diverge as $\mathbf{Q}^{-3}$ for $\mathbf{Q}<2\pi/\mathrm{N}a_0$, because the frequencies of the slab bending modes are proportional to $\mathrm{N}a_0\mathbf{Q}^2$, and not to **Q**. This divergence creates numerical integration problems that are avoided in practice by using a number of Baldereschi points N_B smaller than $N/6+N^2/12$, so that the first Baldereschi point is not too close to the origin. In order to display the behavior near $\mathbf{Q}=0$, the data of Fig. 1 have been multiplied by **Q** and replotted in Fig. 2 with **Q** as abscissa; several points computed with

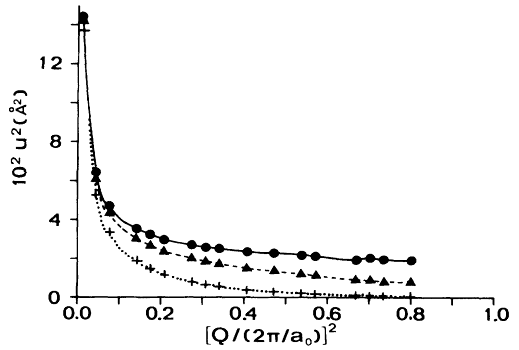

FIG. 1. Effective mean-square surface displacement of a 12-layer Ag(111) slab vs Q^2 [Q summand in Eq. (2.3), normalized to $4P_{iz}^2$ when summed over the surface Brillouin zone] at $T=600$ K, $E_i=63$ meV, $\theta_i=50°$, $\beta=2.14$ Å^{-1}, $D=6$ meV. a_0 is the lattice constant of Ag. ○, $Q_c^{-1}=0$, vibrating soft wall (VSW). △, $Q_c^{-1}=0.685$ Å, intermediate vibrating-soft-atom (IVSA) model. +, $Q_c^{-1}=1.37$ Å, vibrating-soft-atom (VSA) model (predetermined parameters).

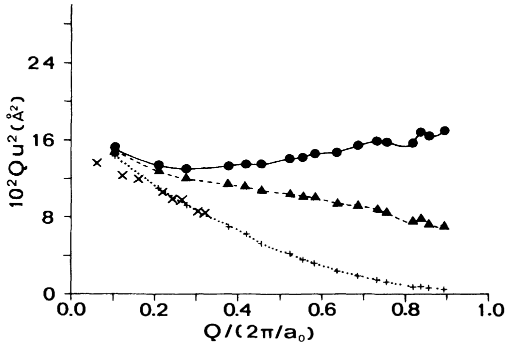

FIG. 2. Same as Fig. 1, multiplied by Q, vs Q. To illustrate convergence few points computed for a 24 layers slab in the VSA model are shown as ×.

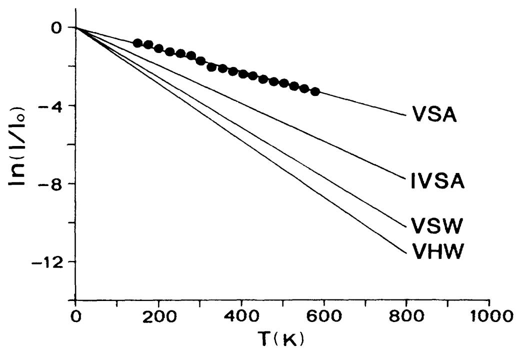

FIG. 3. Comparison of computed thermal attenuation with experimental data, ●, for Ag(111) (Ref. 19). The effect of the lateral cutoff is seen by comparing the curves labeled VSA ($Q_c^{-1}=1.37$ Å), IVSA ($Q_c^{-1}=0.685$ Å), and VSW ($Q_c^{-1}=0$). The effect of the softness correction is seen by comparing VSW with VHW (vibrating hard wall, $\beta=\infty$ and $Q_c^{-1}=0$).

$N=24$ have also been added. The behavior for $N\rightarrow\infty$ and the error made using a finite N_B are easily inferred from these plots. The small **Q** contribution to $2W$ is accurately given by the area under the curves in Fig. 2, because $\sum_Q f(Q)$ is well approximated by $2\pi\int Qf(Q)dQ$ when $Qf(Q)$ is nearly constant and independent of the direction of **Q**.

The results obtained with the help of Fig. 2 are shown in Fig. 3 in comparison with the experimental specular reflectivity obtained by Horne, Yerkes, and Miller[19] for He/Ag(111). As explained in the Introduction, we have extended the validity of our calculation by replacing $1-2W$ with e^{-2W} and we compare e^{-2W} to the experimental specular intensity normalized to unity at $T=0$. The predetermined values of the "softness parameter" β and of the "cutoff parameter" Q_c have been obtained as explained in Sec. II and correspond to the full vibrating-soft-atom model. We also use a depth $D=6$ meV as in Ref. 15, rather than the value of $D=8.2$ meV chosen by Horne *et al.*[19] on the basis of a fit to other data at lower incident energy and high incident angles (which we have not tried to reproduce because they do not behave exponentially with T over a wide range). It can be seen that the computed Debye-Waller factor agrees with the data for these values of the parameters.

The other lines drawn in Fig. 3 display the effect of the lateral cutoff and of the wall softness. From the slopes of the plots in Fig. 3 and other calculations, we obtain, according to Eqs. (1.1) and (1.2), effective Debye temperatures T_D that are reported in Table I. From this table it is seen that our computed "bulk" value of T_D is in good agreement with the experimental bulk value ($T_{DB}=225$ K). The experimental value of T_D for He scattering, $T_{D\mathrm{He}}$, is 247 K (this differs slightly from the value given in Ref. 19 because we use a different D for the Beeby correction) and is in good agreement with the VSA value. As remarked by Horne *et al.*,[19] $T_{D\mathrm{He}}$ is higher than the bulk Debye temperature, $T_{DB}=225$ K, and much higher than the surface Debye temperature as determined by electron scattering, $T_{DS}=155$ K, which is about equal to $T_{DB}/\sqrt{2}$, as expected for a (111) surface. The apparent increase of the Debye temperature, or the apparent decrease of $\langle u^2\rangle$, is due to the corrections discussed in the Introduction, all of which are automatically included in the VSA calculation through the "softness factor" S^2 [Eq. (2.12)] and the lateral cutoff factor $e^{-Q^2/2Q_c^2}$ (which gives the "Armand effect"[4]). The separate effects of the various corrections are shown in Table I; in particular, the Debye-Waller factor computed for a hard wall corresponds to a Debye temperature of 151 K, in agreement with the surface Debye temperature $T_{DS}=155$ K measured by electron scattering. T_D is practically unchanged

TABLE I. Computed values of $2A=2W/T$ and of the effective Debye temperature T_D for a 24 layer slab of Ag(111), using the model of Ref. 15 (modified surface force constants), or, for comparison, a model with surface force constants equal to those in the bulk. He beam parameters and well depth D as in Fig. 1. Bulk: computed from $2W=4k_{iz}^2\langle u_z^2\rangle$ for the 12th layer. Eikonal: computed from $2W=4p_{iz}^2\langle u_z^2\rangle$ for the surface layer. VHW: From Eq. (2.4) with $\beta=100$ Å^{-1}, $Q_c^{-1}=0$ (vibrating hard wall). VSW: $\beta=2.14$ Å^{-1} and $Q_c^{-1}=0$ (vibrating soft wall). VHA: $\beta=100$ Å^{-1}, $Q_c^{-1}=1.37$ Å (vibrating hard atoms). IVHA: $\beta=100$ Å^{-1}, $Q_c^{-1}=0.685$ Å (intermediate VHA). VSA: $\beta=2.14$ Å^{-1}, $Q_c^{-1}=1.37$ Å (vibrating soft atoms). IVSA: $\beta=2.14$ Å^{-1}, $Q_c^{-1}=0.685$ Å (intermediate VSA). (MA) indicates that p_f is computed for $Q=0$ (Manson-Armand simplification).

	Bulk force constants		Modified surface force constants	
Models	$2A$ (K^{-1})	T_D (K)	$2A$ (K^{-1})	T_D (K)
Bulk	0.007 08	216	0.007 09	216
Bulk (MA)	0.007 10	216	0.007 11	216
Eikonal	0.014 47	151	0.014 64	150
VHW	0.014 37	152	0.014 55	151
VHW (MA)	0.014 45	151	0.014 62	150
VSW	0.012 15	165	0.012 86	160
VHA	0.006 12	232	0.006 23	230
IVHA	0.010 79	175	0.010 94	174
VSA	0.005 47	246	0.005 69	241
IVSA	0.009 29	189	0.009 78	184
VSA (MA)	0.005 79	239	0.006 01	235

by taking $p_{iz}=p_{fz}$ in Eq. (2.4), showing that the "closed channel effect"[3,5,6] is not important in this energy range, or in other words that the hard-wall potential could be treated in the eikonal approximation. The main correction, as discussed already, is due to the lateral cutoff Q_c. If this cutoff is included, it is not a bad approximation to make the "Manson"-Armand simplification,[10] i.e., to ignore the lateral momentum transfer in computing the rest of the matrix element (which depends only on p_f). A simplification of this type can be very useful for a realistic theory of many phonon effects, including higher-order corrections to the elastic Debye-Waller factor, thermal attenuation of one-phonon processes, and possible multiphonon structure in inelastic scattering.

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