least 3 bands. For frequencies ω and 2ω not very near the absorption edges for the interband transitions, the residual parts may always be neglected. However, for frequencies near the absorption edges it is better, at this stage, to determine the residual parts experimentally by comparing the experimental values with the phenomenological expressions obtained for the reflected intensities in Sec. V. Since there is no bilinear surface current for the incident light wave polarized perpendicular to the plane of incidence ($\phi=90°$), the experimental value for α may be obtained directly by doing experiments with $\phi=90°$. One could then find β by measuring the intensity and polarization of the second-harmonic reflected wave for $\phi=0°$.

ACKNOWLEDGMENTS

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Single-Phonon Energy Transfer between Molecular Beams and Solid Surfaces*

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The quantum-mechanical lattice theory in thermal-accommodation-coefficient theory is approached from the same point of view as the lattice theory of neutron scattering and Mössbauer effects. Treating the surface atoms from a displacement-field-theoretic point of view, rather than from the customary single-particle point of view, is more consistent with other solid-state theories. Virtual-phonon processes occurring in the field formulation give rise to a nontrivial modification in existing single-phonon accommodation-coefficient theories. This modification takes the form of a pseudo–Debye-Waller factor. When the existing theoretical accommodation coefficients are modified by the pseudo–Debye-Waller factor, it is found that the resulting accommodation coefficient, obtained herein, displays trends similar to experimental data for helium accommodation on tungsten.

I. INTRODUCTION

SEVERAL quantum-mechanical theories for describing the energy-transfer process in a collision of an inert-gas atom with a solid surface have been presented.[1–5] In most of these treatments, explicit results are obtained for a collision process in which a single phonon is created or destroyed in the solid. The objective in these theories is an expression for the thermal accommodation coefficient (denoted here as AC). The philosophy of the accommodation coefficient has been discussed in quantum-mechanical papers[1–5] and in the series of papers by Goodman.[6]

The author has been impressed by the possible formal similarity in mathematical structure between single-phonon AC theory and the lattice-dynamic aspects of neutron-scattering theory[7] and Mössbauer effect theory.[8] In these three cases an external probe, the inert-gas atom, the neutron, or the recoiling nucleus, interacts with the phonon field of the lattice, usually through assumed single-phonon transitions. Calculations are usually done through time-dependent perturbation theory or Born approximations. The relevant quantities calculated, AC's, transition probabilities, or cross sections, are expressed in terms of the square of a matrix element of a lattice displacement field operator taken between initial and final states of the lattice differing by some stated number of phonons multiplied by a matrix element describing the change of state of the external probe. From the point of view of the lattice, the neutron and Mössbauer theories are identical. In both cases, lattice effects are represented principally through a Debye-Waller factor. It seems reasonable to

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believe that if the inert-gas scattering problem is formulated along the same lines as the other theories, some factor playing a role similar to the Debye-Waller factor should appear. Furthermore, approaching the problem from a boson-field point of view is a sufficiently general method, so that, in principle, a simple theory can be readily extended to include complicated real and virtual multiphonon processes.

We shall show that presently existing quantum-mechanical AC theory can be adapted to the point of view presented herein.

II. THEORY

The energy accommodation coefficient for an incident flux of molecules upon a surface is given by

$$\alpha=\frac{\epsilon-\epsilon_2}{\epsilon_1-\epsilon_2}$$

in which ϵ_2 is the incident energy flux in the molecular beam, ϵ_1 is the energy flux of the outgoing beam if thermal equilibrium between the beam and the surface were attained, and ϵ is the true energy flux of the outgoing beam.

The expressions for the energy-transfer process in the paper of Allen and Feuer[5] serve as a suitable starting point for the present theory. They state previous results for which the AC for an inert-gas atom upon a harmonic oscillator of frequency ν and in an eigenstate m is given by an expression of the form

$$\alpha(\nu)=\sum_n \gamma(\nu)|B_{n,m}|^2, \tag{1}$$

where the sum is over possible final states, $\gamma(\nu)$ contains constants, density of states, and statistical factors, and $B_{n,m}$ is the matrix element for the process

$$B_{n,m}=\int\int d^3r d^3u\,\phi^*(\mathbf{r})\psi_n^*(\mathbf{u})[V(\mathbf{r}-\mathbf{u})-V(\mathbf{r})]\times\psi_m(\mathbf{u})\phi'(\mathbf{r}). \tag{2}$$

In Eq. (2), $\psi_i(\mathbf{u})$ is an assumed harmonic-oscillator wave function representing the surface atom, $\phi'(\mathbf{r})$ and $\phi(\mathbf{r})$ are eigenfunctions of the external atom before and after collision, and the interaction term is the difference between the true interaction and the interaction when the surface atom is at its equilibrium point. If one wishes to consider the interaction of the inert gas with the normal modes of the lattice, as is the experimentally meaningful situation, Eq. (1) must be integrated over all normal-mode frequencies with a suitable distribution function inserted. That is,

$$\alpha=\int \alpha(\nu)f(\nu)d\nu. \tag{3}$$

This is the expression that ultimately can be compared with experimental data. Allen and Feuer[5] and earlier workers[1–3] have done very detailed calculations in evaluating Eqs. (1)–(3), which will be used henceforth.

In the present work it is assumed that the displacement field of surface atoms can be given by the same expression as that used for the bulk of the solid. The work of Wallis and others[9–11] suggests that the displacement of surface atoms as compared with bulk atoms is not drastically different. Thus it will be assumed that the results of normal-mode analysis of the lattice can be used to describe surface events.

If one does the usual normal-mode analysis of the harmonic lattice, as, for example, in Pines,[12] and then second quantizes the normal modes, one obtains a Boson field in which the number of phonons in a given mode is an eigenvalue of the lattice Hamiltonian operating upon a basis vector in the occupation-number representation. The lattice Hamiltonian is given as

$$H_{\mathrm{LAT}}=\sum_{q,j}\hbar\omega_{q,j}(a_{q,j}^\dagger a_{q,j}+\tfrac{1}{2}).$$

The sum is over all normal modes q and polarizations j. The operators $a_{q,j}^\dagger$ and $a_{q,j}$ are phonon creation and annihilation operators satisfying the usual Boson commutation relations. The number operator $N_{q,j}$ is defined through the following eigenvalue equation:

$$a_{q,j}^\dagger a_{q,j}|s\rangle=N_{q,j}|s\rangle=n_{q,j}|s\rangle,$$

where $n_{q,j}$ is the number of phonons of frequency q and polarization j present in the arbitrary eigenstate $|s\rangle$. If the lattice is in thermal equilibrium, the number of phonons in the qth mode is given by

$$n_{q,j}=[e^{\hbar\omega_{q,j}/kT}-1]^{-1}. \tag{4}$$

Typical matrix elements of the a operators in the occupation number representation are

$$\begin{aligned}\langle n_q+1|a_q^\dagger|n_q\rangle&=(n_q+1)^{1/2},\\ \langle n_q-1|a_q|n_q\rangle&=(n_q)^{1/2},\\ \langle m|n\rangle&=\delta_{m,n}.\end{aligned} \tag{5}$$

In the normal-mode analysis it is shown that the coordinates of a lattice atom become operators, defined at each point of the lattice,

$$u_l=\sum_{q,j}(h/2MN\omega_{q,j})^{1/2}(\hat{e}_{q,j}a_{q,j}e^{i\mathbf{q}\cdot\mathbf{R}_l}+\hat{e}_{-q,j}a_{q,j}^\dagger e^{-i\mathbf{q}\cdot\mathbf{R}_l}). \tag{6}$$

In this Fourier expansion, $\hat{e}$ is the polarization vector, M the mass of the lattice atom, N the number of atoms in the crystal, and R_l the distance of the lth atom from an arbitrary origin. In the present paper, scattering from the atom at the origin with $R_l=0$ will be considered.

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The interaction between the incident atom and the surface atom is a function of their relative separation. The unspecified, arbitrary interaction is expanded and only linear terms retained. Thus

$$V_a(\mathbf{r}-\mathbf{u})-V_a(\mathbf{r})\simeq-\mathbf{u}_l\cdot\nabla V_a(\mathbf{r}). \quad (7)$$

Looking at the matrix elements of Eq. (5) and the form of the second quantized displacement field Eq. (6), it is seen that the interaction of Eq. (7) couples orthogonal states differing by one phonon only. These matrix elements would take the form

$$\mathfrak{M}=\langle n\pm1|-\mathbf{u}_l|n\rangle\cdot\mathbf{a}f(\mathbf{r})$$

with $f(\mathbf{r})=(1/|\mathbf{a}|)\nabla V_a(\mathbf{r})$. Since the lattice states are orthogonal, $0=\langle n\pm1|1|n\rangle f(\mathbf{r})$; consequently,

$$\mathfrak{M}=\langle n\pm1|1-\mathbf{u}_l\cdot\mathbf{a}|n\rangle f(\mathbf{r}).$$

The scaling parameter a is such that $\mathbf{u}_1\cdot\mathbf{a}\ll1$. Consequently,

$$1-\mathbf{u}_l\cdot\mathbf{a}\simeq1-\mathbf{u}_l\cdot\mathbf{a}+(\tfrac{1}{2})(\mathbf{u}_l\cdot\mathbf{a})^2+\cdots=e^{-\mathbf{u}_l\cdot\mathbf{a}},$$

and thus

$$\mathfrak{M}=\langle n\pm1|e^{-\mathbf{a}\cdot\mathbf{u}_l}|n\rangle(1/|\mathbf{a}|)\nabla V_a(\mathbf{r}).$$

Comparing this with the original expression for $\mathfrak{M}$ allows Eq. (7) to take the useful form

$$V_a(\mathbf{r}-\mathbf{u})-V_a(\mathbf{r})\simeq e^{-\mathbf{a}\cdot\mathbf{u}_l}(1/|\mathbf{a}|)\nabla V_a(\mathbf{r}). \quad (8)$$

This result is independent of the form of the interaction. Treating interactions in a similar manner has been done previously by Lipkin[13] in order that the displacement field operator might appear in an exponential function.

The interaction has been brought to the form of Eq. (8) so that a result previously derived by Glauber[14] can be used in the present context. His result states that if there exists an operator of the form e^U, where U is a sum of creation and annihilation operators for all normal modes of the field, then when the field is in thermal equilibrium at a temperature T, that operator deriving from e^U which induces n quantum transitions is given by

$$\langle e^U\rangle_T{}^{(n)}=(U^n/n!)e^{1/2\langle U^2\rangle_T}. \quad (9)$$

In the present case $U=-\mathbf{a}\cdot\mathbf{u}$. $\langle U^2\rangle_T$ is the expectation value of the square of the operator with respect to the thermally excited state. The factor that resembles but is not a Debye-Waller factor takes into consideration the higher order terms in the Taylor series expansion of the interaction which give rise to n phonon transitions. For example, if $n=1$, the cubic term included in the expansion of Eq. (7) would give rise to single-phonon transitions in the qth mode from operators of the form $a_{q'}a_q{}^\dagger a_{q'}{}^\dagger$ in which a phonon is virtually emitted in the q'th mode before the phonon in the qth mode is emitted. These virtual processes which result in the emission or absorption of one real phonon are satisfactorily taken into consideration by using Glauber's result.

We are now in a position to carry on with the theory of the collision process. If the interaction of Eq. (8) is used with Eq. (9), the new matrix element describing a collision in which a single phonon is created is given by

$$B'_{n,n-1}=\frac{\mathbf{a}}{|a|}\cdot\langle n|\mathbf{u}|n-1\rangle e^{\frac{1}{2}\langle U^2\rangle_T}\int d^3r\phi^*(\mathbf{r})\times\nabla V_a(\mathbf{r})\phi'(\mathbf{r}), \quad (10)$$

which resembles the original matrix element Eq. (2). If the energy transfer is only to longitudinal modes of the lattice, a result which is required through conservation of k vector, and if it is realized that $\mathbf{a}=|a|\hat{\imath}_z$, then the result

$$\frac{\mathbf{a}}{|a|}\cdot\langle n|\mathbf{u}|n-1\rangle=\left(\frac{\hbar}{2MN\omega}\right)^{1/2}$$

is readily obtained by using Eqs. (5) and (6). This result is exactly equivalent to the harmonic-oscillator results which would be obtained if Eq. (2) were evaluated. Consequently, $B_{n,m'}$ of Eq. (10) is expressed in terms of Eq. (2) as

$$B_{n,m'}=e^{1/2\langle(\mathbf{a}\cdot\mathbf{u})^2\rangle_T}B_{n,m},$$

which, when combined with Eqs. (1) and (3), allows a new AC to be defined in terms of previous derived ones. The new result is simply

$$\alpha_n=e^{\langle(\mathbf{a}\cdot\mathbf{u})^2\rangle_T}\alpha_0, \quad (11)$$

where α_0 is the AC obtained from the original matrix element $B_{n,m}$ as in Allen and Feuer's work. The only problem is to evaluate the mean-square exponent. This is standard fare,[12] so only a rudimentary sketch is given here. We write

$$\langle(\mathbf{a}\cdot\mathbf{u})^2\rangle_T=\sum_{\substack{q,j\\q',j'}}(\mathbf{a}\cdot\hat{e}_{qj})(\mathbf{a}\cdot\hat{e}_{q'j'})\left(\frac{\hbar}{2MN}\right)\frac{1}{\omega_q{}^{1/2}\omega_{q'}{}^{1/2}}\times\langle n|(a_q+a_q{}^\dagger)(a_{q'}+a_{q'}{}^\dagger)|n\rangle$$

which with the aid of Eqs. (5) reduces to

$$\langle(\mathbf{a}\cdot\mathbf{u})^2\rangle_T=\sum_{q,j}(\mathbf{a}\cdot\hat{e}_{qj})^2\left(\frac{\hbar}{2MN}\right)\frac{2}{\omega_q}(n_{q,j}+\tfrac{1}{2}). \quad (12)$$

Assuming longitudinal mode transfer only, a nondispersive medium with $\omega=cq$, using Eq. (4) and straightforward techniques, gives

$$\langle(\mathbf{a}\cdot\mathbf{u})^2\rangle_T=\frac{\hbar a^2}{M}\frac{3}{4\omega_D{}^3}\int_0^{\omega_D}\omega\coth\left(\frac{\hbar\omega}{KT}\right)d\omega\int_0^{\pi}\cos^2\theta\sin\theta d\theta$$

$$=\frac{\hbar^2a^2}{2m}\frac{1}{\hbar\omega_D}\left\{\frac{1}{\omega_D{}^2}\int_0^{\omega_D}\omega\coth\left(\frac{\hbar\omega}{KT}\right)d\omega\right\}. \quad (13)$$

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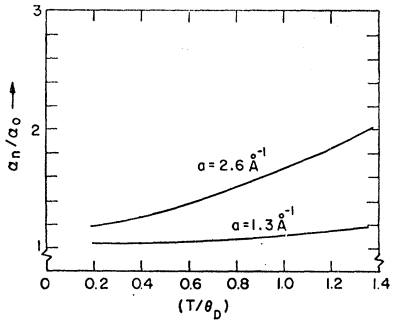

FIG. 1. Pseudo–Debye-Waller correction factor for existing single-quantum accommodation coefficient theories.

In Eq. (13) the substitution $N/L^3=\omega_D{}^3/6\pi^2c^3$ has been made. This result closely resembles the structural form of the exponential lattice factor appearing in neutron and Mössbauer theory. The result becomes more transparent if we work with Eq. (12), however. It may readily be shown that Eq. (12) when done as an integral becomes

$$\langle(\mathbf{a}\cdot\mathbf{u})^2\rangle_T=\frac{\hbar^2a^2}{Mk\Theta_D}\left[\frac{1}{4}+\left(\frac{T}{\Theta_D}\right)^2\int_0^{\theta_D/T}\frac{xdx}{e^x-1}\right] \quad (14)$$

in which $x=\hbar\omega/kT$. Equation (14) may be evaluated by performing a numerical integration. The exact expressions for the mean-square displacement given by Eq. (13) or (14) can be used in Eq. (11) to give the improved accommodation coefficient.

III. RESULTS AND DISCUSSION

The results of Eq. (14) are used to obtain numerical results for a typical system of experimental interest, helium on tungsten. In general, the interaction potential used in theories in which α_0 is derived is either taken to be a Morse potential or exponential repulsive potential. The value of the parameter a in Eq. (8) is closely related to the range parameter in the Morse potential. Since the repulsive portion of the Morse potential varies as e^{-2a_1r}, we take $a_1\leq a\leq 2a_1$ in Eq. (8) and thus in subsequent equations. For the He-W system, $a_1=1.3$ Å^{-1} is acceptable.[6] For Θ_D we take 300°K. Consequently,

$$\langle(\mathbf{a}\cdot\mathbf{u})^2\rangle_T=0.5[\tfrac{1}{4}+I(T/\Theta_D)],$$

in which $I(T/\Theta_D)$ is the integral of Eq. (14) which is evaluated numerically. The dimensionless quantity $\alpha_n/\alpha_0=e^{\langle(\mathbf{a}\cdot\mathbf{u})^2\rangle_T}$ is drawn as a function of temperature in Fig. 1 with parametric values of a. It is seen that an extremely nontrivial correction results when the pseudo–Debye-Waller factor is included as it must be. It is not likely quantitative significance can be given to the present result for temperatures much above the Debye temperature for at these temperatures the validity of the single-phonon approximation and normal-mode analysis becomes dubious.

The present result can be compared with previous quantum-mechanical AC's, and the unpublished experimental data from Thomas's group which appeared in Goodman's work.[15] In Gilbey's paper[4] are drawn graphs of Devonshire's AC as a function of temperature. These curves are drawn to approach the hard-sphere asymptotes $\alpha=m/M$. Three curves are drawn for various well depths in the Morse potential. In particular, we are interested in the curve for $D=0.10$ kcal/mole, where D is the Morse potential well depth. In reality, $D\simeq 0.10$ kcal/mole for He-W. Although the Gilbey-Devonshire (GD) result is obtained for a hypothetical system in which the gas-atom–to–surface-atom mass ratio is 4/100, this fact principally affects the absolute magnitude of the asymptotic AC, and not the shape of the curve. Since the absolute values of the GD expressions are somewhat arbitrary, we adjust the scale on the Gilbey graph so that at $T=300$°K, the value of $\alpha_n=e^{\langle(\mathbf{a}\cdot\mathbf{u})^2\rangle_T}\alpha_0$ agrees with the experimental data of Thomas and co-workers. Using the Gilbey $D=0.10$ kcal/mole curve for values of α_0 as a function of temperature, we have drawn curves of α_0, α_n, and α_{expt} in Fig. 2 for He-W with $a=2a_1$.

It is clear from Fig. 2 that the modified AC of Eq. (11) does not indicate trends that contradict existing experimental data. Since the values of α_0 have been obtained only in an approximate manner, too much quantitative significance should not be attached to the values of α_n; however, the approximations used to obtain α_0 have affected the position of the asymptotic α_0 and not the shape of the α_0 curve in the temperature range under 300°K.

A very important correction to the single-phonon AC has been provided in the new AC. As can be seen in Fig. 2, the original AC rises rapidly from a low value at low temperature and approaches the so-called hard-sphere asymptote from above as the temperature is increased. This is in disagreement with experiment for the case of light gases such as helium or neon. By correctly including the exponential Debye-Waller–type factor, the theoretical AC takes on the correct temperature dependence and approaches the high-temperature limit from the same direction as the experimental data. We should also remark that the constant AC hard-sphere asymptote has yet to be observed experimentally. Instead, a monotonically increasing AC with temperature is observed in accord with the present theoretical predictions.

In summary, it has been shown that existing single-phonon accommodation coefficient theories can easily be modified so that they are consistent both with experimental data and similar theories of other lattice perturbations, neutrons and recoiling Mössbauer nuclei. No attempt is made to justify the quantum-mechanical

[15] F. O. Goodman and H. Y. Wachman, MIT Fluid Dynamics Research Laboratory Report No. 66-1, 1966 (unpublished); also U. S. Air Force Office of Scientific Research Report No. AFOSR 66-0295 (unpublished).

theories, but if the quantum-mechanical theories are in essence correct, they must be modified as has been done herein. Most likely, it is more beneficial to approach the lattice from a field-theoretic point of view than from a particle point of view.

At this point we might also inquire into the real meaning and region of validity of the present model. In the original quantum-mechanical theories, the essence of the calculation is to obtain a matrix element of a temperature-independent operator given by Eq. (7) between temperature-dependent states. Thus $\mathfrak{M}_0 = \langle n_1(T)| \mathcal{O} |n_0(T)\rangle$. The temperature-independent operator of Eq. (7) gives rise to real single-phonon processes only. The temperature dependences for this sort of process are contained in the state vectors only.

If, on the other hand, we retain the higher order terms, which induce virtual as well as real processes, a new temperature dependence comes into existence. For example, the previously mentioned operator $a_{q'}a_q^\dagger a_{q'}^\dagger = a_q^\dagger(1+N_{q'}) = a_q^\dagger(1+\langle n_{q'}(T)\rangle)$, by virtue of the usual Boson commutators and Eq. (4). Thus the true single-phonon operator is seen to have a temperature dependence also. Consequently, the corrected single-phonon matrix elements are written as $\mathfrak{M}_n = \langle n_1(T)| \mathcal{O}(T) |n_0(T)\rangle$. The pseudo–Debye-Waller factor is the manifestation of this new temperature dependence. It must be remembered that the precise functional form of the new temperature correction, the exponential, is accurate only as long as the linearization and approximation scheme leading to Eq. (8) is valid. At temperatures above the Debye temperature, these approximations may not provide the most accurate description. That is, the lattice operator will, of course, remain temperature-dependent but most likely will have a functional form different from that of an exponential.

The corrections to the original α_0 are much more substantial than would be suspected. We imagine that if the existing quantum-mechanical theories are extended to the case in which impurities are on the surface in a manner similar to that of Allen and Feuer,[16] then the pseudo–Debye-Waller corrections could be suitably adapted. It seems that in the case of a light impurity, such as hydrogen or even oxygen, the correction would be quite significant. If the results of Eq. (14) could be directly transposed to the case of an impurity mode, then because the impurity mass is such a small fraction of the substrate atom mass, the expectation value of Eq. (14) would be greater than it is for the pure surface. Of course, the Debye temperature would have to be changed to the effective temperature of the localized mode. In any event, the exponential correction factor would be likely to play an even more significant role in the light-impurity collision process.

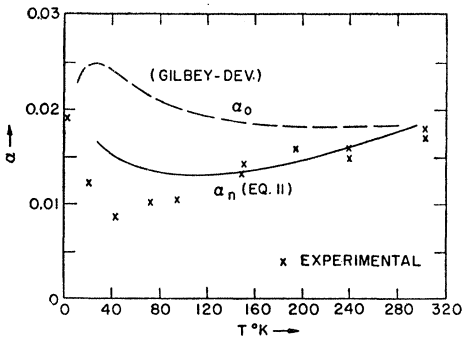

FIG. 2. Curves of accommodation coefficients as a function of temperature for He-W. The points denoted by x are experimentally measured values. The curve labeled α_0 is from the paper of Gilbey. The solid curve is the theoretical curve obtained in the present work.

A final word of caution: It has been shown that reasonable quantitative agreement between quantum-mechanical AC's and experimental data can be obtained. It must be realized, however, that basically the existing quantum-mechanical theories are low-temperature theories and thus should not be extended to temperatures much in excess of the Debye temperature of the lattice. Furthermore, the correction factor derived here is most valid in the low-temperature regime, as it may produce unphysical divergences when overextended. A rigorous cutoff procedure could be built into the theory, but this would have influence only in the temperature region in which the existing quantum-mechanical theories are invalid.

ACKNOWLEDGMENTS

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