

Simple Model for the Energy Accommodation Coefficient

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Quantum mechanical expressions for the energy accommodation of a gas at a solid surface are developed using the general theory of inelastic surface scattering as developed by Manson and Celli. Calculations are presented for the accommodation of helium at a simplified model of a tungsten surface. The phonon spectrum at the surface is taken to be that of a semi-infinite isotropic continuum, and contributions to the accommodation are obtained from bulk, mixed, and Rayleigh phonon modes. For temperatures not too small the calculations agree qualitatively with experiment, and exhibit the property that the accommodation is nearly independent of surface temperature over a large range.

I. INTRODUCTION

The energy exchange at the interface between a surface and a gas can be characterized by the energy accommodation coefficient, α , originally defined by Knudsen¹ and usually expressed as

$$\alpha = (E - E_g) / (E_s - E_g), \quad (1)$$

where E_g is the average energy of a gas molecule before making a collision with the surface, E is the average energy of a gas molecule after making a collision, and E_s has the same meaning as E_g but is evaluated for a gas at the temperature of the surface. The denominator of Eq. (1) represents the maximum energy exchange at the surface and can be written as a simple function of the gas temperature, T_g , and the surface temperature, T_s . The numerator is the actual energy exchange upon collision, and cannot in general be represented by a simple function of temperature since the scattered particles will not necessarily be in an equilibrium distribution. For theoretical considerations, it is often convenient to define an accommodation coefficient which is a function of a single temperature²

$$\alpha(T) = \lim_{T_g \rightarrow T_s \rightarrow T} (E - E_g) / (E_s - E_g). \quad (2)$$

The most straightforward way to obtain the energy exchange at the surface is to consider the gas as composed of beams of particles spread over a range of energies and directed at all angles with respect to the surface. We then let $dR(\mathbf{k}_f, \mathbf{k}_i)/d\epsilon_f d\Omega_f$ be the probability that a particle is scattered from the unit incident beam of momentum \mathbf{k}_i into the small energy interval $d\epsilon_f$ centered at ϵ_f and into the small solid angle $d\Omega_f$. The energy of a particle of momentum \mathbf{k} is given by $\epsilon = \hbar^2 k^2 / 2m$, where m is the particle mass. The total energy exchanged at the surface by a unit beam of particles incident at momentum \mathbf{k}_i is then obtained by multiplying $dR/d\epsilon_f d\Omega_f$ by $(\epsilon_f - \epsilon_i)$ and summing over all possible final states into which the particle could be scattered, i.e.,

$$\int d\epsilon_f \int d\Omega_f (\epsilon_f - \epsilon_i) dR/d\epsilon_f d\Omega_f. \quad (3)$$

If Eq. (3) is multiplied by the probability, $P(\mathbf{k}_i)$, that the incident beam of momentum \mathbf{k}_i will strike the surface, and then summed over all angles and energies

of the incoming gas, we obtain the total energy exchanged at the surface

$$E - E_g = \int d\epsilon_i \int d\Omega_i \int d\epsilon_f \int d\Omega_f (\epsilon_f - \epsilon_i) P(\mathbf{k}_i) dR/d\epsilon_f d\Omega_f. \quad (4)$$

The accommodation coefficient follows directly from either Eq. (1) or (2).

A method for obtaining the differential reflection coefficient $dR/d\epsilon_f d\Omega_f$ is given by the general theory of surface scattering as developed by Cabrera, Celli, Goodman, and the author.³⁻⁵ We discuss only the essential features of the theory here. The starting point is the transition rate w_{fi} where f and i describe the quantum numbers of the final or initial state of the entire system (surface and particles),

$$w_{fi} = (2\pi/\hbar) |T_{fi}|^2 \delta(\epsilon_f - \epsilon_i), \quad (5)$$

where ϵ_f and ϵ_i are the total energies of the final and initial states, respectively, and T_{fi} is the transition matrix. To obtain the transition rate for the scattering of a single particle, Eq. (5) must be averaged over initial phonon states of the surface and summed over final states. The differential reflection coefficient is then obtained by dividing by the incident particle flux, $j_i = \hbar k_{zi}/m$ (where k_{zi} is the component of \mathbf{k}_i perpendicular to the surface) and multiplying by the density of final particle states.

$$dR/d\epsilon_f d\Omega_f = \{m(2m\epsilon_f)^{1/2} / [(2\pi\hbar)^3 j_i]\} \times \sum_{\{n_f\}} \sum_{\{n_i\}} \rho(\{n_i\}) w_{fi}, \quad (6)$$

where $\rho(\{n_i\})$ is the density of initial phonon states. The summations can be evaluated by standard field theoretical methods and $dR/d\epsilon_f d\Omega_f$ can be expressed as an ordered series, the first term describing elastic scattering, the next two terms describing single phonon emission or absorption, then two-phonon terms and so on. This result, together with Eqs. (4) and (1), shows that the accommodation coefficient can also be written in a similar type of ordered series.

If we restrict the gas particles to move perpendicularly to the surface the initial distribution probability is given by

$$P = (1/kT_g) \exp(-\epsilon_i/kT_g). \quad (7)$$

Using Eqs. (7), (4), and (1) the accommodation

coefficient becomes

$$\alpha(T_s, T_g) = [1/k^2 T_g (T_s - T_g)] \int d\epsilon_i \int d\epsilon_f (\epsilon_f - \epsilon_i) \times \exp(-\epsilon_i/kT_g) dR/d\epsilon_f, \quad (8)$$

where $dR/d\epsilon_f$ is the one dimensional form of (6) and we have used the relation $E_{s,g} = kT_{s,g}$.

If we make the further restriction that only a single phonon is transferred at the surface (this does not exclude the possibility of virtual phonon transfers) Eq. (8) can be cast into a somewhat simpler form through the use of detailed balancing. In this approximation the total energy absorbed by the gas is

$$(1/kT_g) \int d\epsilon_i \int d\epsilon_f (\epsilon_f - \epsilon_i) \exp(-\epsilon_i/kT_g) dR^{(a)}/d\epsilon_f, \quad (9)$$

where $dR^{(a)}/d\epsilon_f$ is the differential reflection coefficient for the absorption of a single phonon by a scattered particle. To calculate the energy given up to the surface we start with the inverse of the differential reflection coefficient. Let $dR^{(e)}/d\epsilon_i$ be the probability that a particle initially in the small energy range $d\epsilon_i$ centered at ϵ_i be scattered into the well defined beam of energy ϵ_f via a single phonon emission. Then the total energy given up to the surface in a single phonon process is

$$(kT_g)^{-1} \int d\epsilon_f \int d\epsilon_i (\epsilon_i - \epsilon_f) \exp(-\epsilon_i/kT_g) dR^{(e)}/d\epsilon_f. \quad (10)$$

Noting that $|\epsilon_f - \epsilon_i| = \hbar\omega$, the energy of the exchanged phonon, Eqs. (9) and (10) can be combined to obtain the total energy exchanged at the surface:

$$E - E_g = \frac{\hbar}{kT_g} \int_0^\infty d\epsilon_i \int_0^{\omega_D} d\omega \left(\frac{d\epsilon_f}{d\omega} \right) \omega \exp\left(-\frac{\epsilon_i}{kT_g}\right) \times \left[\frac{dR^{(a)}}{d\epsilon_f} - \frac{dR^{(e)}}{d\epsilon_f} \exp\left(-\frac{\hbar\omega}{kT_g}\right) \right], \quad (11)$$

where ω_D is the cutoff frequency corresponding to the minimum phonon wavelength. The principle of detailed balancing gives

$$dR^{(e)}/d\epsilon_f = \exp(\hbar\omega/kT_s) dR^{(a)}/d\epsilon_f d\Omega_f. \quad (12)$$

This can be seen directly from the results in I, where it is shown explicitly that the differential reflection coefficient for single phonon absorption is proportional to

$$n(\omega) = [\exp(\hbar\omega/kT_s) - 1]^{-1}, \quad (13)$$

the density of phonons at the unperturbed surface; while the differential reflection coefficient for single phonon emission is proportional to $[n(\omega) + 1]$.

Combining (12), (11), and (1) we obtain the accommodation coefficient in the form

$$\alpha(T_s, T_g) = \frac{\hbar}{k^2 T_g (T_s - T_g)} \times \int_0^\infty d\epsilon_i \int_0^{\omega_D} d\omega \left(\frac{d\epsilon_f}{d\omega} \right) \omega \exp\left(-\frac{\epsilon_i}{kT_g}\right) \times \frac{dR^{(a)}}{d\epsilon_f} \left\{ 1 - \exp\left[-\frac{\hbar\omega}{k} (T_g^{-1} - T_s^{-1})\right] \right\}. \quad (14)$$

It is now apparent that we can use the definition of Eq. (2) to obtain

$$\alpha(T) = \lim_{T_s \rightarrow T_g} \alpha(T_s, T_g) = \frac{\hbar^2}{k^3 T^3} \int_0^\infty d\epsilon_i \int_0^{\omega_D} d\omega \left(\frac{d\epsilon_f}{d\omega} \right) \omega^2 \times \exp\left(-\frac{\epsilon_i}{kT}\right) \frac{dR^{(a)}}{d\epsilon_f}. \quad (15)$$

Equations (14) and (15) with $d\epsilon_f/d\omega = \hbar$ are the expressions for the accommodation coefficient given in the fundamental paper of Devonshire.^{6,7}

II. THE DIFFERENTIAL REFLECTION COEFFICIENT

In order to proceed further with Eqs. (14) or (15) we must determine the differential reflection coefficient for single phonon absorption, $dR^{(a)}/d\epsilon_f$. In the work of Jackson⁸ and Devonshire,⁶ and many other treatments which have followed,⁹⁻¹¹ $dR^{(a)}/d\epsilon_f$ is calculated for the collision of the incoming molecule with a single surface atom, where the surface atom is treated as a quantum mechanical harmonic oscillator.

However, the true interaction must be a many body process, with the incident particles interacting with a large number of surface atoms. Thus such a restrictive model cannot account accurately for the interaction of the incident molecules with the phonon field of the surface, nor can it account for diffraction effects.

As a more realistic model for the differential reflection coefficient we choose

$$dR^{(a)}/d\epsilon_f = \int d\Omega_f dR^{(a)}/d\epsilon_f d\Omega_f, \quad (16)$$

where $dR^{(a)}/d\epsilon_f d\Omega_f$ is the term in (6) describing single phonon absorption, and is calculated for a perpendicularly incident beam using the general theory of inelastic surface scattering developed in I. This approximation assumes a perpendicularly incident gas, but allows the gas particles to scatter in accordance with the conservation of momentum and energy upon colliding with the surface.

The solid is approximated by a semi-infinite isotropic continuum whose surface can undergo perpendicular vibrations. Since the phonon spectrum is isotropic the particles will be scattered symmetrically about the incoming beam and (16) reduces to

$$dR^{(a)}/d\epsilon_f = 2\pi \int d\theta \sin\theta dR^{(a)}/d\epsilon_f d\Omega_f, \quad (17)$$

where θ is measured from the normal to the surface.

The interaction potential is taken as a step function

$$V = V_0 S(-z + u_z), \quad (18)$$

where V_0 is the strength of the interaction, u_z is the small displacement from equilibrium in the perpendicular direction, and

$$S(x) = 1, \quad x > 0 \\ = 0, \quad x < 0. \quad (19)$$

This model is very crude, most notably in that it neglects the discrete nature of the lattice, i.e., there are no diffraction effects, and does not account for the possibility of a bound or absorption state near the surface. Hence, we expect this model to reproduce only the qualitative features of the quantum mechanical accommodation coefficient.

Near the surface of an isotropic solid there are three types of phonon modes, surface or Rayleigh waves, mixed waves, and bulk waves. Each contributes independently to the scattering and the corresponding differential reflection coefficients are derived in I. For the case of Rayleigh modes the frequency is completely specified by the parallel component, Q , of the phonon wave vector; i.e., $\omega = \omega(Q) = \xi c_l |Q|$ where c_l is the velocity of transverse waves and ξ satisfies the Rayleigh condition¹²

$$\xi^6 - 8\xi^4 + 8\xi^2(3 - 2c_t^2/c_l^2) - 16(1 - c_t^2/c_l^2) = 0, \quad (20)$$

with c_l the velocity of longitudinal waves. Then the single phonon absorption term of Eq. (6) is

$$[dR^{(\omega)}/d\epsilon_f d\Omega_f](\hbar | \mathbf{k}_f | k_{zf}^2 k_{zi}/2\pi^2 \rho \omega) \times n(\omega) |e_z(Q)|^2 \delta(\epsilon_f - \epsilon_i - \hbar\omega), \quad (21)$$

where ρ is the mass density of the surface; $n(\omega)$ is given by (13); and $e_z(Q)$, the perpendicular component of the polarization vector, is given by

$$|e_z(Q)|^2 = (|Q| + \kappa_l b)^2 \times \left(\frac{\kappa_l^2 + Q^2}{2\kappa_l} + b^2 \frac{\kappa_l^2 + Q^2}{2\kappa_l} + 2b |Q| \right)^{-1}, \quad (22)$$

with

$$\kappa_{l,i} = (Q^2 - \omega^2/c_{l,i}^2)^{1/2}, \quad (23)$$

and

$$b = 2(1 - \xi^2)^{1/2}/(2 - \xi^2). \quad (24)$$

For bulk and mixed phonons, there are three independent components of the wave vector and

$$dR^{(\omega)}/d\epsilon_f d\Omega_f = (| \mathbf{k}_f | k_{zf}^2 k_{zi}/2\pi^2 \rho \omega) \times (dq_z/d\omega) |e_z|^2 n(\omega), \quad (25)$$

where energy conservation implies $\epsilon_f - \epsilon_i = \hbar\omega$ and $dq/d\omega$ is the density of phonon states for perpendicular motion. For the bulk modes we can write

$$\frac{dq}{d\omega} |e_z|^2 = \frac{c_t^2 \cos\theta_t (c_l \sin 2\theta_l \sin 2\theta_t \sin\theta_t - c_l \cos^2 2\theta_t \sin\theta_t)}{\sin\theta_l (c_t^4 \sin^2 2\theta_l \sin^2 2\theta_t - c_t^4 \cos^4 2\theta_t)}, \quad (26)$$

where θ_t and θ_l are, respectively, the angles at which the transverse and longitudinal parts of the waves are incident on the surface.

For mixed modes this becomes

$$\frac{dq}{d\omega} |e_z|^2 = (c_l \cos\theta_t)^{-1} \times \frac{2 \sin 2\theta_t (\sin^2 \theta_t - c_t^2/c_l^2)}{\cos^4 2\theta_t + 4 \sin^2 2\theta_t \sin^2 \theta_t (\sin^2 \theta_t - c_t^2/c_l^2)}. \quad (27)$$

Finally we need the density of states $d\epsilon_f/d\omega$ appearing in (14) and (15). This is simply \hbar for bulk and mixed modes where there are three independent components of the wave vector, but for surface modes it is given by $2\epsilon_f/\omega$.

In obtaining the results (21) and (25) we have made use of the distorted wave Born approximation for the transition rate of Eq. (6). In I it is shown that in this case the transition matrix for single phonon processes becomes the matrix element of the first derivative of the thermal average of the total interaction potential, V , taken between wavefunctions of this thermally averaged potential. In the limit of small surface vibrations the thermal average of (18) is a step function, the one-phonon interaction is proportional to a δ function, and the matrix elements become independent of the strength V_0 of the interaction.

The extension of this process to the exchange of two or more phonons is straightforward. If $\langle V \rangle$ is the thermal average of V then the interaction potential for the exchange of n phonons is proportional to $d^n \langle V \rangle / dz^n$ and the matrix element is again taken with the wavefunctions of $\langle V \rangle$.

It is also shown in I that a much better approximation to this one phonon transition matrix is obtained by replacing $d\langle V \rangle/dz$ with

$$(d\langle V \rangle/dz)/(1 + R_i/4), \quad (28)$$

and taking matrix elements with states of $\langle V \rangle$. Here R_i is the total probability in the Born approximation that a particle in the incoming beam of momentum \mathbf{k}_i will be scattered out of the specular beam, and is equal to the integral of the one-phonon Born approximation differential reflection coefficient (both for absorption and emission) over all final energies and angles. In this approximation the total number of particles is conserved during the scattering process, i.e., the property of unitarity is obeyed. Thus we see that the one-phonon Born approximation is valid only if R_i is small compared to unity and this gives a very good test for the validity of the approximation.

III. CALCULATIONS AND DISCUSSION OF RESULTS

Figure 1 shows the results of a numerical calculation of the accommodation, $\alpha(T)$, of helium at a tungsten surface, using Eqs. (15) and (17) together with (21) and (25). Values of c_l , c_t , and ρ are taken from the American Institute of Physics Handbook.¹³ The cutoff frequency was determined by assigning the same

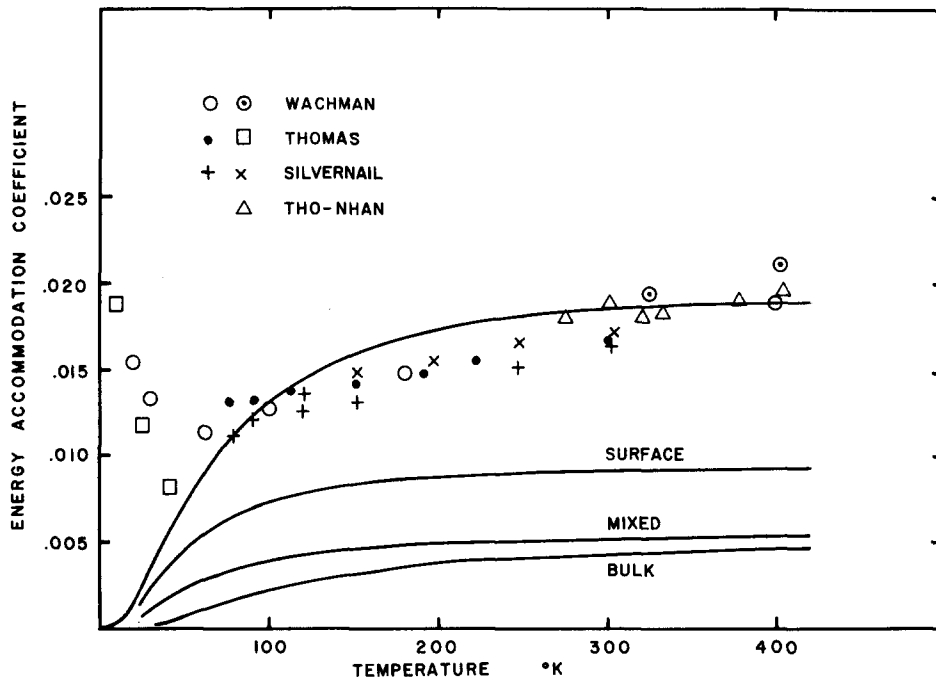


FIG. 1. The accommodation coefficient $\alpha(T)$ as a function of temperature for the scattering of helium at a tungsten surface. The experimental data are that of Thomas *et al.*¹⁴ The total accommodation coefficient is the sum of the surface, mixed, and bulk mode contributions.

minimum wavelength to each of the three phonon modes which contributed to the scattering. The cutoff was adjusted to match the experimental data of Thomas *et al.*¹⁴ at $T=100^\circ\text{K}$, and corresponds to a Debye temperature of 325°K for bulk longitudinal modes. A temperature of 100°K was chosen because it is well within the range of validity of the one-phonon Born approximation, as seen by evaluating R_i for the highest energy incoming particles which contribute significantly to the accommodation. Specifically, in the integration over ϵ_i in Eq. (15) the factor $\exp(-\epsilon_i/kT)$ insures that only those energies for which $\epsilon_i < 5kT \lesssim 5\hbar\omega_D$ contribute significantly to the accommodation, while a closer investigation shows that the largest contributions come from the region $\epsilon_i \sim 2\hbar\omega_D$. The value of R_i for $\epsilon_i = 5\hbar\omega_D$ and $T=100^\circ$ is 0.35 (i.e., 35% of the incident beam of momentum \mathbf{k}_i is scattered out of the specular beam) while for $\epsilon_i = 2\hbar\omega_D$ we obtain $R_i = 0.14$. These values together with Eq. (28) show that the error incurred by the neglect of unitarity is less than 5% for temperature around 100° .

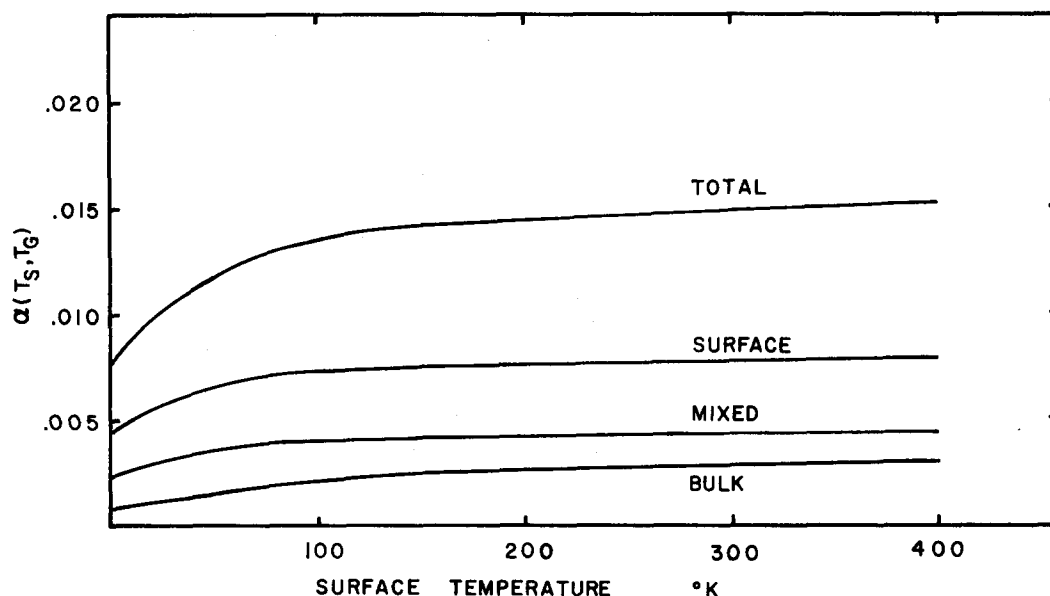
Each of the three types of phonons contributes separately to the accommodation, with the contribution due to the surface modes being considerably larger than that of the bulk or mixed modes. The agreement with the experimental data is qualitatively good for temperatures greater than 50°K , while for lower temperatures the agreement seems rather poor. The tabulated values for the Debye temperature of tungsten range from 270°K ¹³ to 379°K ¹⁵ so the chosen value of 325° lies well within this range. (One would expect that the Debye temperature would be lower in the surface region due to the change in periodicity of the lattice and this result has been confirmed by low energy elec-

tron diffraction experiments.^{16,17}) At low temperatures the accommodation coefficient falls to zero and it can be readily shown that it follows a T^3 dependence as $T \rightarrow 0$ if $\hbar\omega_D \ll 2mc_l^2$. For the parameters used in Fig. 1, $\hbar\omega_D/2mc_l^2 \sim 0.1$ and the low temperature behavior goes very nearly as T^3 .

The fact that the accommodation falls to zero as $T \rightarrow 0$ is in agreement with other quantum mechanical calculations.⁶⁻¹¹ However, this behavior is in disagreement both with the experimental data shown in Fig. 1, and also with classical calculations, which generally show the accommodation rising to a finite value at $T=0$.¹⁸⁻²¹ The quantum mechanical results of Gilbey⁹ using the Devonshire theory seem to indicate that the accommodation coefficient could rise sharply before falling to zero, but in order to obtain this "hump" at low temperatures, rather unrealistic values of the parameters describing the surface must be used. No such behavior appears in the present calculations, but one might suspect that, as in the case of Gilbey's calculations, this "hump" is due to the effects of the attractive adsorption well which has been neglected here. However, calculations have been carried out for the square well and Morse potentials and the results are quite similar to those shown in Fig. 1, with no rises in $\alpha(T)$ at low temperatures.²²

Measurements have shown that the accommodation coefficient is virtually independent of the temperature of the surface.¹⁴ To test this aspect of the present theoretical model we have carried out calculations of the double temperature accommodation coefficient using Eq. (14). It is readily shown using Eqs. (14), (17), (21), and (25) that $\alpha(T_s, T_g)$ with T_g fixed approaches nonzero finite limits both for $T_s \rightarrow 0$ and $T_s \rightarrow \infty$. A

FIG. 2. The double temperature accommodation coefficient, $\alpha(T_s, T_g)$, for helium on tungsten plotted as a function of surface temperature with the gas temperature fixed at 100°K.



typical result of these calculations is given in Fig. 2 which shows the accommodation coefficient as a function of surface temperature with the gas temperature fixed at 100°K, all other parameters being the same as for Fig. 1. For surface temperatures above 100° it is seen that the accommodation is very nearly constant in agreement with experiment. However, this model seems to indicate that for low temperatures the accommodation does vary rather strongly with surface temperature. These calculations have also been carried out with the square well and Morse potentials for the surface interaction and the results are again similar to those in Fig. 2.²²

For light gas atoms and low temperatures one would expect the interactions between gas particles and the surface to be definitely quantum mechanical in nature. This can be verified in the present model by calculating the total number of particles scattered by single phonon events, and as discussed above this is quite small at low temperatures. Thus the discrepancy between theory and experiment may be a result of some rather severe limitations in the theory. The most obvious deficiency in the present model is the lack of an attractive adsorption well near the surface, and the possibility of interacting with the bound states. As mentioned above, the simple inclusion of an attractive well without considering the bound states does not seem to significantly alter the low temperature behavior. However, if the gas particles can interact with the bound states there is the possibility of adsorption which could lead to larger transfers of energy. Perhaps equally important is the fact that this model does not allow diffraction of particles at the surface. If diffraction is allowed then it is possible for a gas particle to interact resonantly with a bound state (i.e., a particle can enter a bound state while still conserving energy). Such processes generally lead to enhanced scattering probabilities and could possibly

contribute significantly to adsorption and energy transfer.

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