

Classical Theory for the Interaction of Gas Atoms with Solid Surfaces*

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A classical theory for the interaction of gas atoms with solid surfaces is presented. The principal assumptions of the model used are: (1) The surface atoms involved in the collisions can be represented as independent one-dimensional oscillators; (2) the gas atoms interact with the surface through a stationary square-well attractive potential and an exponential repulsive potential; (3) the surface is flat so that the tangential velocity component of the gas atom is unchanged; (4) the surface oscillators have an equilibrium energy distribution at the temperature of the solid. This model represents a logical successor to the "hard-cube" model introduced by Logan and Stickney and allows the important effects involving the collision time and the natural frequency of the surface atoms to be taken into account. An approximate closed-form expression is obtained for the angular distribution of particle flux for a monoenergetic atomic beam scattered from a surface. For physically reasonable values of the well depth and range of the exponential potential, good quantitative agreement is obtained with available experimental data for the angular position of the maximum of the scattering distribution. Satisfactory agreement with experiment is even obtained in a case where the gas atom is heavier than the surface atom (Xe on Ag); in a case such as this the hard-cube model would not give reasonable results. Values are also obtained for the fraction of incident gas atoms which are initially trapped on the surface.

I. INTRODUCTION

It has been shown^{1,2} that there is good qualitative agreement between many of the available experimental results for the scattering of atomic beams from solid surfaces and the theoretical results from a simple classical hard-cube model for this interaction. In two important respects, however, the hard-cube model cannot be regarded as satisfactory: (1) In some cases (e.g., the case of Ar scattered from Ag discussed below), it overestimates the magnitude of the energy transfer; (2) for large values of the gas-atom-to-surface-atom mass ratio, it breaks down due to the occurrence of multiple collisions with the surface atom.

In the hard-cube model it was assumed that the incident gas atom had an impulsive collision with a single surface atom isolated from the lattice. In reality the interaction potential is not impulsive, and there must be a finite collision time. In this paper we attempt to take account of such "soft" collisions by considering a model based on an exponential interaction between a gas atom and a single one-dimensional oscillator. Since we retain the assumption of a flat surface, it is convenient to regard the surface atom as a cube, and we refer to this new model as the soft-cube model (Fig. 1). With the use of physically realistic values for the well depth and range of the potential and the frequency of the oscillator, the soft-cube model gives good quantitative agreement with experimental data for the scattering of the rare gases from clean surfaces. Agreement is

even obtained for the case of Xe scattered from Ag; in this case, where the gas atom is heavier than the solid atom, the hard-cube model would break down completely.

One clue to the way in which the hard-cube model needs to be improved is given by Fig. 2. This shows a comparison between experimental results of Saltsburg and Smith,³ for the position of the maximum of the scattering pattern for Ar on Ag, and the corresponding results from the hard-cube model. It is seen that the hard-cube model tends to exaggerate the deviation of the pattern from the specular; since it has been shown² that effects of surface roughness probably have a small effect on the position of the maximum of the scattering pattern, these results imply that the hard-cube model tends to exaggerate the magnitude of the net energy exchange with the surface. We would expect the use of a soft potential to reduce these energy exchanges, thus giving better agreement in this case.

In the analysis to follow it will be necessary to introduce various unknown ("adjustable") parameters: notably, the well depth D , the interaction range b , and the oscillator frequency ω . At first this might appear to be a retrograde step from the hard-cube model which contains no adjustable parameters. It must be emphasized, however, that any complete theory of the gas-solid interaction must include the interaction potential, and at least two parameters are needed to describe this potential. Since there is at present no independent theoretical or experimental method of accurately obtaining these parameters (except for experimental values of the heat of adsorption), it is inevitable that our theory and others like it will contain such unknown parameters. Similarly, in any complete theory some of the elastic properties of the solid must be known; in this case it is usually possible to obtain

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¹ R. M. Logan and R. E. Stickney, *J. Chem. Phys.* **44**, 195 (1966).

² R. M. Logan, J. C. Keck, and R. E. Stickney in *Proc. Intern. Symp. Rarefied Gas Dyn.* 5th Oxford, 1966, **1**, 49 (1967).

³ H. Saltsburg and J. N. Smith, Jr., *J. Chem. Phys.* **45**, 2175 (1966).

suitable values, either indirectly from the Debye temperature or from direct experimental measurements.

II. SOFT-CUBE MODEL

The soft-cube model is a logical successor to the hard-cube model and is still basically very simple, as illustrated in Fig. 1. The basic assumptions involved are:

(1) The surface is effectively flat, so that the tangential component of velocity of the gas atom is unchanged.

(2) The gas atom interacts with the surface through a potential which has two parts: (a) a stationary attractive part which increases the normal component of velocity of the gas atom before the repulsive collision and decreases it again afterwards; (b) an exponential repulsive part which acts between the gas atom and the single surface atom involved in the collision.

(3) The surface atom involved in the collision is connected by a single spring to the remainder of the lattice, the latter being fixed.

(4) The ensemble of oscillators which comprises the surface has an equilibrium distribution of energies at the temperature of the solid.

Assumption (1) is partially justified by the reasonable agreement with experiment obtained in some cases with the hard-cube model. In Ref. 2, Sec. V, an analysis was developed by means of which a measure of the surface roughness could be deduced from the width of the scattering distribution in the out-of-plane direction. Unfortunately, there are very few available measurements of the out-of-plane distribution. In the data of Hinchin and Shepherd⁴ for the scattering of Ar from Ag, the pattern appears to have an angular half-width

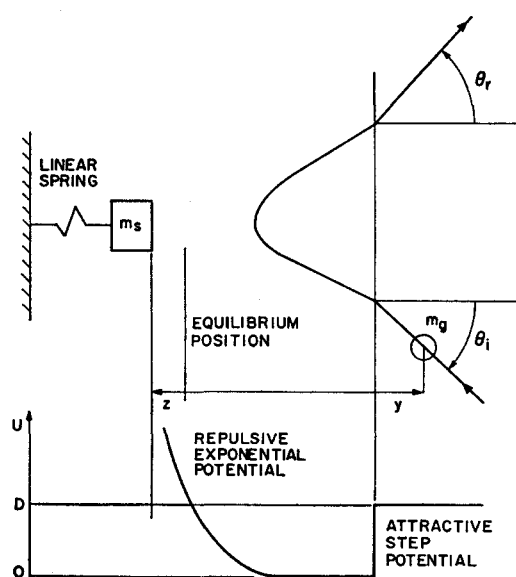


FIG. 1. Soft-cube model.

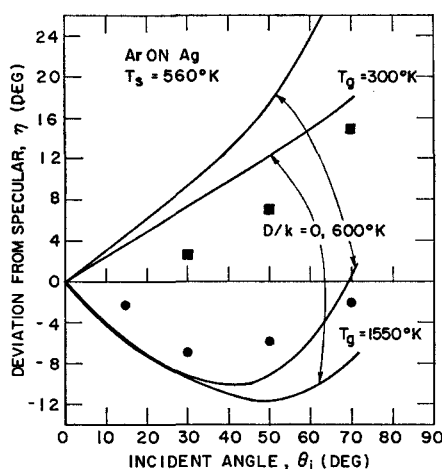


FIG. 2. Comparison between theoretical results from the hard-cube model and the corresponding experimental data for Ar/Ag from Ref. 3. Experimental points for $T_g = 300^\circ\text{K}$ (■) and $T_g = 1550^\circ\text{K}$ (●).

at the $1/e$ intensity point of about 13 deg. According to the analysis in Ref. 2, this corresponds to a value of the root-mean-square angular deviation of the actual surface from a flat surface of about 0.1 rad. The same analysis indicates that as far as its effect on the in-plane scattering pattern is concerned, this is a "small" roughness. There are also some recent direct experimental measurements of Moran⁵ for the system Ar on Pt which shows that at least in the region of the maximum of the scattering pattern, the outgoing tangential component of velocity is closely equal to the incident tangential component.

The justification for Assumption 2(a) comes from the fact that the attractive potential is due to a long-range interaction (primarily due to induced dipoles), and at any given position outside the solid probably has a significant contribution from several solid atoms. Assuming that the velocities of the solid atoms are uncorrelated, we would expect the net interaction to be reasonably stationary with respect to the center of mass of the solid. Since we assume the potential to be stationary, its shape does not affect the interaction—for convenience, therefore, we may think in terms of a square-well potential. Assumption 2(b) corresponds to the assumption widely used for gas-gas collisions that the repulsive potential has an exponential character (e.g., the Morse potential or Buckingham 6-exp potential).

In Assumption (2) it is also implied that the gas atom interacts with only a single surface atom. Since the impact points of the incident gas atoms tend to be distributed randomly over any unit cell of the surface, however, this may seem a questionable assumption. In Appendix A an analysis is given in which it is assumed that the potential energy of the gas atom at any point

⁴ J. J. Hinchin and E. F. Shepherd, in Proc. Intern. Symp. Rarefied Gas Dyn. 5th Oxford, 1966, 1, 239 (1967).

⁵ J. P. Moran, Ph.D. thesis, Massachusetts Institute of Technology, September 1967.

may be obtained by superposing the effects from all the solid atoms. Equipotential surfaces (Fig. 18) and fractional load contours (Fig. 17) are calculated, and from the latter it is seen that for impact points over a large fraction of the area of a unit cell, and hence for most collisions, most of the load is taken by a single surface atom. It must be emphasized that this conclusion depends on the assumption of the superposition of the potentials, which itself cannot be rigorously justified. We should also expect the interaction to affect more than one surface atom for grazing incident angles when the tangential velocity may be so high that the tangential distance traveled during the collision time is greater than a lattice spacing; we consider this point again in Sec. VI.

By means of Assumption (3) we introduce into the model the important parameter ωt_c , where ω is the natural frequency of the surface atom, and t_c is a measure of the collision time. In the hard-cube model this parameter was effectively set equal to zero, and since the magnitude of the energy exchange is sensitive to the value of ωt_c , this was probably a major shortcoming of the hard-cube model. We have still omitted lattice interactions, however. While omission of lattice interactions can only really be justified for high-energy collisions (i.e., small ωt_c), there is some evidence that this is a reasonable assumption for all values of ωt_c . Oman *et al.*⁶ have shown, by comparing a computer simulation of the interaction with a lattice of coupled oscillators to that with a lattice of independent oscillators (corresponding to our situation here), that the error in the energy change of the gas atom by neglecting the lattice is less than 10% of the incident energy in nearly all cases. As pointed out in Ref. 6, at large ωt_c when the lattice may play an important role, the energy exchange is such a small fraction of the incident energy that it is negligible for practical purposes anyway.

III. ANALYSIS

In Sec. III.A we derive an exact series solution for the force as a function of time acting between the gas atom and oscillator atom in the collision. In Sec. III.B we reduce this exact solution to an approximate form which depends on a parameter γ proportional to ωt_c ; using this approximate form we calculate the impulse given to the gas atom and hence relate γ to the outgoing angle θ_r . In Sec. III.C we use the condition of energy conservation during the collision to relate the initial velocity amplitude and phase of the oscillator to θ_r . In Sec. III.D we derive the probability distribution for the phase of the oscillator, and in Sec. III.E we use this, together with the known distribution for the velocity amplitude, to calculate the angular distribution of scattered flux corresponding to an incident monoenergetic gas beam.

A. Exact Series Solution

The equations of motion of the gas and surface atoms are

$$\ddot{y} = F/m_g \quad (1)$$

$$\ddot{z} = F/m_s - \omega^2 z, \quad (2)$$

where y and z are the displacements from the equilibrium position shown in Fig. 1, m_g and m_s are the masses of gas and surface atoms, F is the force, and ω is the natural frequency of the surface oscillator. We assume an interaction potential of the form

$$U = B \exp[-(y+z)/b] = U_0 \exp[-(y+z-y_0-z_0)/b], \quad (3)$$

where b and B are constants and subscript (0) indicates quantities evaluated at the turning point. Using Eq. (3) we may rewrite Eqs. (1) and (2) in the following dimensionless form

$$Z'' = [2\mu/(1+\mu)]e^{-R} - \chi^2 Z \quad (4)$$

$$R'' = 2e^{-R} - \chi^2 Z, \quad (5)$$

where

$$Z = z/b,$$

$$R = [(y+z) - (y_0+z_0)]/b,$$

$$\tau = (t-t_0)/t_c,$$

$$\mu = m_g/m_s,$$

$$\chi = \omega t_c,$$

$$t_c = (2m_g b^2/U_0)^{1/2},$$

$$m_r = m_g m_s / (m_g + m_s),$$

and a prime (') denotes differentiation with respect to τ . It follows from Eqs. (4) and (5) that the dependence of Z and R on τ is controlled by the values of the two parameters μ and χ .

We now assume that the relative coordinate R may be expanded around the turning point ($\tau=0$) in a Taylor series; i.e.,

$$R = (2!)^{-1} R_0'' \tau^2 + (3!0^{-1} R_0''' \tau^3 + (4!)^{-1} R_0'''' \tau^4 + \dots + \quad (6)$$

Noting that $e^{-R} = 1$ at $\tau=0$, it immediately follows from Eq. (5) that

$$R_0'' = 2 - \chi^2 Z_0. \quad (7)$$

Similarly by differentiating Eq. (5) and using $R_0' = 0$,

$$R_0''' = -\chi^2 Z_0'. \quad (8)$$

Differentiating Eq. (5) again and eliminating Z'' from Eq. (4) gives

$$R_0'''' = -2(2 - \chi^2 Z_0) - \chi^2 \{ [2\mu/(1+\mu)] - \chi^2 Z_0 \}. \quad (9)$$

⁶ R. A. Oman, A. Bogan, and C. H. Li, in Proc. Intern. Symp. Rarefied Gas Dyn, 4th Toronto, 1964, 2, 396 (1965).

Substituting Eqs. (7)–(9) into Eq. (6), we obtain

$$R = (2!)^{-1}(2 - \chi^2 Z_0) \tau^2 - (3!)^{-1} \chi^2 Z_0' \tau^3 - (4!)^{-1} \{2(2 - \chi^2 Z_0) + \chi^2 [2\mu/(1 + \mu) - \chi^2 Z_0]\} \tau^4 + \dots + \quad (10)$$

The coefficients of all higher powers of τ can similarly be expressed in terms of the quantities μ , χ , Z_0 , and Z_0' .

For a collision between two free particles ($\omega=0$), we can obtain an exact closed-form solution for R . In this case Eq. (5) for the relative coordinate becomes

$$R'' = 2e^{-R}. \quad (11)$$

Multiplying through by $2R'$, integrating with respect to τ , and using the condition $R_0' = 0$,

$$R' = 2(1 - e^{-R})^{1/2}. \quad (12)$$

The next integration may be simply carried out by transforming to a new variable x such that $e^{-R} = \text{sech}^2 x$. As a result of this integration, we obtain

$$e^{-R} = \text{sech}^2 \tau. \quad (13)$$

Setting $\omega=0$ ($\chi=0$) in Eq. (10) and comparing with Eq. (13), it follows that

$$\exp[-(2!)^{-1} 2\tau^2 + (4!)^{-1} 4\tau^4 - \dots] = \text{sech}^2 \tau. \quad (14)$$

Using Eq. (14) in Eq. (10), the force pulse acting during the collision is given by

$$F = U_0 e^{-R}/b = (2m_r b \omega^2 / \chi^2) (\text{sech}^2 \tau) \times \exp[(2!)^{-1} \chi^2 Z_0 \tau^2 + (3!)^{-1} \chi^2 Z_0' \tau^3 + \dots +]. \quad (15)$$

There are four unknowns in this expression for the force pulse: the displacement Z_0 of the surface at the turning point; the velocity Z_0' of the surface at the turning point; the potential energy U_0 at the turning point (this latter quantity having been absorbed in the definition of χ); and the time instant t_0 of the turning point itself. In principle it is possible to obtain the four equations required for an exact solution: Z_0 and Z_0' are given in terms of the force pulse and the initial motion by using Eq. (22) in Sec. III.B; U_0 may be found in terms of Z_0 , Z_0' , and the initial conditions by applying the condition of conservation of energy at the turning point; and t_0 may be related to the force pulse and the initial conditions by means of a procedure given in Sec. III.D. In general, however, these equations would have to be solved numerically, and in the next section we give instead an approximate method based on Eq. (15) which leads to a convenient closed-form solution.

B. Approximate Force Pulse

Under a wide range of conditions to be specified below, the coefficients $(2!)^{-1} \chi^2 Z_0$, etc., in the exponential term in Eq. (15) are small compared to unity and

steadily decrease with increasing power of τ . Under these conditions we can expand the exponential term in Eq. (15) and keep just the leading term; i.e.,

$$F \cong (\pi^2 m_r b \omega^2 / 2 \gamma^2) (\text{sech}^2 \tau) [1 + (2/\pi^2) \gamma^2 Z_0 \tau^2], \quad (16)$$

where the parameter $\gamma \equiv \pi \chi / 2$ has been introduced for convenience later on. We shall require integrals of the general form

$$Q_n(\tau_1) = \int_{-\infty}^{\tau_1} e^{i2\gamma\tau/\pi} \text{sech}^2 \tau d\tau.$$

Integral $Q_0(\infty)$ is given below, and this result may be derived by straightforward contour integration

$$Q_0(\infty) = \int_{-\infty}^{\infty} e^{i2\gamma\tau/\pi} \text{sech}^2 \tau d\tau = 2\gamma \text{csch} \gamma \quad (17)$$

$$= 2 \quad \lim_{\gamma \rightarrow 0}. \quad (17')$$

For higher values of n , we use the general relation $Q_{n+1}(\tau_1) = (\pi/2i) dQ_n(\tau_1)/d\gamma$; for $n=2$, for example, we obtain

$$Q_2(\infty) = \int_{-\infty}^{\infty} e^{i2\gamma\tau/\pi} \tau^2 \text{sech}^2 \tau d\tau = \pi^2 \text{csch} \gamma (\coth \gamma - \gamma \text{csch}^2 \gamma - \frac{1}{2} \gamma) \quad (18)$$

$$= \pi^2/6 \quad \lim_{\gamma \rightarrow 0}. \quad (18')$$

Using contour integration we can also show that

$$\begin{aligned} \text{Im} Q_0(0) &= \int_{-\infty}^0 \sin(2\gamma\tau/\pi) \text{sech}^2 \tau d\tau \\ &= -(2/\pi) (\gamma \text{csch} \gamma) \int_0^{\pi/2} \cot \eta \sinh(2\gamma\eta/\pi) d\eta \\ &= -(4.340/\pi^2) (\gamma^2 \text{csch} \gamma) G(\gamma), \end{aligned} \quad (19)$$

where

$$G(\gamma) = 1.0 + 0.0346\gamma^2 + 0.00076\gamma^4 + \dots + \quad (20)$$

and this last result has been obtained by expanding the $\sinh$ term in the integral on the right-hand side. In the analysis to follow we restrict ourselves to values of γ of order unity, and hence only need the leading terms in the series for $G(\gamma)$. We also need an approximate value for $\text{Im} Q_2(0)$, and this may be obtained by keeping the leading term in Eq. (19) and using the relation $Q_2(0) = -(\pi^2/4) d^2 Q_0(0)/d\gamma^2$:

$$\begin{aligned} \text{Im} Q_2(0) &= \int_{-\infty}^0 \sin(2\gamma\tau/\pi) \tau^2 \text{sech}^2 \tau d\tau \\ &\cong 2.170 \text{csch} \gamma [(1 - \gamma \coth \gamma)^2 - \frac{1}{2} \gamma^2]. \end{aligned} \quad (21)$$

The velocity and position of the oscillator at the turning point are given by the following standard expression

$$\begin{aligned} \dot{z}_0 - i\omega z_0 &= (1/m_s) \int_{-\infty}^{t_0} \exp[i\omega(t_1 - t_0)] F(t_1) dt_1 \\ &\quad + v \exp(-i\omega t_0). \end{aligned} \quad (22)$$

TABLE I. Approximate lattice stiffness.

Species	At. mass M_s	θ_D (°K)	$K_s^{\dagger}$ (gram ^{1/2} sec ⁻¹)
Be	9.0	1160	585
Si	28.1	640	571
Ni	58.7	440	571
Cu	63.5	344	459
Mo	95.9	440	730
Ag	107.9	225	402
W	183.8	405	925
Pt	195.1	240	565
Au	197.0	165	390

By substituting Eq. (16) into Eq. (22) and using the integrals in Eqs. (19) and (21), it can be shown that

$$Z_0 = \frac{N(\gamma \operatorname{csch} \gamma) G(\gamma) + (v/\omega b) \sin \omega t_0}{1 + N\gamma \operatorname{csch} \gamma [(1 - \gamma \coth \gamma)^2 - \frac{1}{2}\gamma^2]}, \quad (23)$$

where $N \equiv (4.340/\pi) [\mu/(1+\mu)]$ and $(v/\omega) \sin \omega t_0$ is the undisturbed position of the surface at the turning point.

The quantity $v/\omega b$ is the ratio of the initial amplitude of the oscillator to the range of the force, and the order of magnitude of this term is given by

$$v/\omega b \sim (2kT_s/m_s)^{1/2} (\hbar/k\Theta_D) (1/b), \quad (24)$$

where Θ_D is the Debye temperature of the solid. For making general estimates from Eq. (24), it is convenient to define a lattice stiffness K_s such that $K_s^{1/2} = m_s^{1/2} k\Theta_D/\hbar$. Values for $K_s^{1/2}$ are shown in Table I, and it is seen that $K_s^{1/2}$ varies relatively much less than Θ_D or the atomic mass M_s . Equation (24) then becomes

$$v/\omega b \sim 3T_s^{1/2} K_s^{-1/2} a_0 b^{-1}. \quad (25)$$

From Table I we may choose $K_s^{1/2} = 500$ for a typical numerical value and from Table III of Sec. IV, we may choose $b/a_0 = 0.50$ as a typical value; for $T_s = 600^\circ\text{K}$ we then obtain $v/\omega b \sim 0.3$.

For γ of order unity or less and $\mu < 1$, the denominator in Eq. (23) is approximately unity. Using the above estimate for $v/\omega b$, the contribution to the coefficient $(2/\pi^2)\gamma^2 Z_0$ in Eq. (16) from the initial motion is, therefore, $\lesssim 0.06\gamma^2$ under a wide range of conditions. For this range of γ the integrals $Q_2(\infty)$ and $Q_0(\infty)$ are of the same order; thus this initial motion term makes only a small contribution to integrals of the form

$$\int_{-\infty}^{\infty} F dt$$

and

$$\int_{-\infty}^{\infty} \exp(i\omega t) F dt,$$

and for γ of order unity or less, we shall neglect it in our expression for the approximate force pulse.

For γ of order unity or smaller, the contribution to the coefficient $(2/\pi^2)\gamma^2 Z_0$ from the first term in Eq.

(23) (the recoil) is approximately $(2N/\pi^2)\gamma^2$, where we have once again assumed that the denominator in Eq. (23) is approximately unity. For small values of the mass ratio μ , this term is negligible along with the initial motion term discussed above; but for $\mu = 1$, for example, it has a value of approximately $0.25\gamma^2$ for $\gamma \sim 1$. We conclude that when $\gamma \sim 1$ and $\mu \sim 1$, the contribution to the $(2/\pi^2)\gamma^2 Z_0$ term in the integrals

$$\int_{-\infty}^{\infty} F dt \quad \text{and} \quad \int_{-\infty}^{\infty} \exp(i\omega t) F dt$$

should not be neglected, and thus we retain this recoil contribution in our expression for the force pulse. We also notice that under conditions of large μ the denominator in Eq. (23) becomes somewhat less than unity, but under these conditions the recoil term tends to dominate the initial motion term.

Our assumed form for the force pulse [Eq. (16)] may now be written

$$F = (\pi^2 m_r b \omega^2 / 2\gamma^2) (\operatorname{sech}^2 \tau) [1 + (2/\pi^2)\gamma^2 Z_{0R} \tau^2], \quad (26)$$

where Z_{0R} is the recoil displacement of the surface atom at the turning point $t = t_0$. We note that the above analysis represents an attempt to justify the form of Eq. (26) rather than a rigorous derivation of it. So that we may from now on work consistently with this force pulse, we now use Eq. (26) in Eq. (22) to recalculate Z_0 , giving

$$\begin{aligned} Z_0 &= N(\gamma \operatorname{csch} \gamma) G(\gamma) / \{1 + N(\gamma \operatorname{csch} \gamma) [(1 - \gamma \coth \gamma)^2 \\ &\quad - \frac{1}{2}\gamma^2]\} + [(v \sin \omega t_0) / \omega b] \\ &\equiv Z_{0R} + [(v \sin \omega t_0) / \omega b]. \end{aligned} \quad (27)$$

The parameter $\gamma (= \pi\chi/2)$ was originally defined in terms of the "collision time" t_c which itself depended on the potential energy at the turning point. Rather than attempt to solve for the potential energy at the turning point, we choose the value of γ such that the impulse applied to the gas atom leads to the correct outgoing angle; i.e., we find γ as a function of the outgoing angle θ_r . We define a dimensionless impulse as follows:

$$I = (m_g u)^{-1} \int_{-\infty}^{\infty} F dt.$$

Substituting for F from Eq. (26) and using Eqs. (17') and (18'), this becomes

$$I = [2\pi/(1+\mu)] (\sigma/\gamma) (1 + \frac{1}{6}\gamma^2 Z_{0R}), \quad (28)$$

where $\sigma \equiv \omega b/u$ and u is the incident normal component of the gas-atom velocity inside the potential well. The incident normal velocity outside the well will be denoted u_∞ , and the corresponding outgoing velocities inside and outside the well u' and u'_∞ .

By using the assumption that the tangential component of velocity of the gas atom is unchanged, the impulse I can also be related to the outgoing angle

θ_r of the gas atom:

$$I = 1 + (u'/u) = 1 + \{[(\cot^2\theta_r/\cot^2\theta_i) + W]/(1+W)\}^{1/2}, \quad (29)$$

where

$$W = 2D/m_g u_\infty^2.$$

From Eqs. (28) and (29) we can obtain γ as a function of θ_r and the parameters μ , σ , W , and θ_i .

In summary, we have developed an approximate expression for the force pulse acting between the gas and surface atoms, as given by Eq. (26). The pulse has basically a $\text{sech}^2\tau$ form and is exactly correct (for the assumed exponential potential) in both the impulsive and free-particle limits. The pulse also includes a correction term which has the effect of broadening the pulse due to the recoil of the surface atom. The parameter γ is determined in terms of the outgoing angle θ_r by using Eqs. (28) and (29), such that the impulse given to the gas atom is correct. This assumed form should be most valid under conditions where γ ($\sim \omega\tau$ collision time) is of order unity or less and the quantity $v/\omega b$ is $\ll 1$. It is under these same conditions that the coefficients of the higher powers of τ in Eq. (15) will be successively smaller than the leading term. We note that while our assumed force pulse has a symmetric form, we should, in general, expect the actual pulse to have an antisymmetric component; such a component arises if we retain the term $(3!)^{-1}\chi^2 Z_0' \tau^3$ in Eq. (15). For the conditions specified above, however, the complications arising from the introduction of this term do not seem warranted at this stage.

C. Energy Conservation

In the previous section we found an approximate expression for the force pulse acting during the collision as a function of the outgoing angle θ_r . We now consider the determination of θ_r for given initial conditions. This may be done by applying the condition of energy conservation; that is, the net energy lost by the gas atom in the collision must equal the net energy gained by the surface oscillator.

The energy transferred to the oscillator in the collision is given by the standard expression

$$\Delta E_s = \mu(m_g u^2/2) \{ |J|^2 + (v/\mu u) [J \exp(-i\omega t_0) + J^* \exp(i\omega t_0)] \}, \quad (30)$$

where

$$J = (m_g u)^{-1} \int_{-\infty}^{\infty} \exp[i\omega(t-t_0)] F(t) dt \quad (31)$$

and J^* is its complex conjugate.

By substituting Eq. (26) into Eq. (31) and using Eqs. (17) and (18), we obtain

$$J = fI, \quad (32)$$

where I is given by Eq. (28) and the adiabaticity f is

given by

$$f = (\gamma \csc \gamma) \times [1 + Z_{0R}(\gamma \coth \gamma - \gamma^2 \text{csch}^2 \gamma - \frac{1}{2}\gamma^2)] / (1 + \frac{1}{6}Z_{0R}\gamma^2). \quad (33)$$

Since J is real in this case, Eq. (30) becomes

$$\Delta E_s = \mu(m_g u^2/2) \{ J^2 + [(2J/\mu)(v \cos \omega t_0)/u] \}. \quad (34)$$

Once again using the assumption that the tangential component of velocity of the gas atom is unchanged, the energy loss of the gas atom may be written

$$\Delta E_g = (m_g u_\infty^2/2) [1 - (\cot^2\theta_r/\cot^2\theta_i)]. \quad (35)$$

Equating the right-hand sides of Eqs. (34) and (35) and solving for $(v \cos \omega t_0)/u$:

$$v_c \equiv (v \cos \omega t_0)/u = (1/2J) \{ (u_\infty/u)^2 [1 - (\cot^2\theta_r/\cot^2\theta_i)] - \mu J^2 \}. \quad (36)$$

Since J may be written as a function of γ , and γ is a function of θ_r , v_c is a function of θ_r .

We note that in the limit $\gamma=0$, $f=1$, and the result corresponds to the impulsive collision between two free particles, as in the hard-cube model. In the limit $\gamma \rightarrow \infty$, $f \rightarrow 0$, and the collision is elastic with $\theta_r = \theta_i$.

D. Phase Probability

In the previous section it was shown that within the limits of our approximations, there is a one-to-one relation between the undisturbed velocity of the oscillator at the turning point $v \cos \omega t_0$ and θ_r . To find the angular distribution of the outgoing gas atoms, we therefore need to know the probability distribution for $v \cos \omega t_0$. The velocity amplitude v is simply related to the energy of the oscillator, and the distribution of energies is known as a function of the equilibrium temperature of the solid.

To find the distribution of phase angles ωt_0 at the turning point, or phase probability, we proceed as follows. Integrating the equation of motion of the gas atom [Eq. (1)] twice gives

$$y - y_0 = -u(t - t_0) - (1/m_g) \int_{t_1}^{t_0} \int_{-\infty}^{t_1} F(t_2) dt_2 dt_1, \quad (37)$$

where t_1 and t_2 are dummy variables of integration. Since F has a sech^2 form and cuts off rapidly for $|t_0 - t| > t_c$, we may extend the lower limit of the t_1 -integral to $-\infty$ for cases where $t \ll t_0 - t_c$. Then Eq. (37) becomes

$$y = (y_0 - y_f) - u(t - t_0); \quad t \ll t_0 - t_c, \quad (38)$$

where

$$y_f \equiv (m_g)^{-1} \int_{-\infty}^{t_0} \int_{-\infty}^{t_1} F(t_2) dt_2 dt_1. \quad (39)$$

The physical interpretation of Eq. (38) is shown in

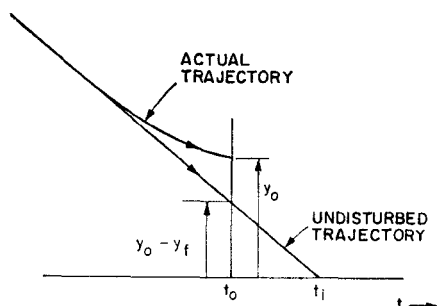


FIG. 3. Trajectory of incident gas atom.

Fig. 3; this shows that if the gas atom had proceeded on its undisturbed trajectory, it would have been at a position $(y_0 - y_f)$ at time t_0 . It is clearly a reasonable assumption, however, that there is a uniform distribution of undisturbed trajectories; i.e., the time instants t_i at which the undisturbed trajectories would cross the line $y=0$ are uniformly distributed. From Fig. 3 it is seen that t_i is given by

$$t_i = t_0 + [(y_0 - y_f)/u].$$

Hence the probability that in a collision the phase angle will be in the range ωt_0 to $\omega t_0 + d(\omega t_0)$ is

$$\begin{aligned} P(\omega t_0) d\omega t_0 &= (1/2\pi) (d\omega t_i/d\omega t_0) d\omega t_0 \\ &= (1/2\pi) \{1 + \sigma(d/d\omega t_0) [(y_0 - y_f)/b]\} d\omega t_0. \end{aligned} \quad (40)$$

Since our approximate form for the force pulse [Eq. (26)] is a function of the time difference $(t - t_0)$, it can be shown that the definite integral for y_f [Eq. (39)] is explicitly independent of t_0 but is a function of γ and hence θ_r . Using Eq. (3) the quantity y_0/b may be written

$$y_0/b = [(y_0 + z_0)/b] - z_0/b = \ln B - (\ln U_0) - Z_0.$$

U_0 , the potential energy at the turning point, is related through our assumed form for the force pulse to the parameter γ and hence θ_r ; i.e., we can in principle find $U_0 = U_0(\theta_r)$. Z_0 , given by Eq. (27), consists of a recoil term Z_{0R} which is a function of γ and hence of θ_r , together with the initial position $(v/\omega b) \sin \omega_0 t$. Using these facts in Eq. (40), we obtain

$$P(\omega t_0) = (1/2\pi) [1 - v_c + \sigma v_s (d\theta_r/dv_c) (d\Gamma/d\theta_r)], \quad (41)$$

where $v_c \equiv (v \cos \omega t_0)/u$, $v_s \equiv (v \sin \omega t_0)/u$, and Γ is some function of θ_r . By using Eq. (36) we can in principle write $d\theta_r/dv_s$ as a function of θ_r .

E. Scattering Distribution

We now consider the scattering distribution obtained from the scattering of a monoenergetic beam from the surface. The use of a monoenergetic beam allows a closed-form expression for the scattering distribution to

be obtained, and there is some evidence⁷ that the scattering patterns for Maxwellian and monoenergetic beams are closely similar; we should expect this to be especially true when the well depth D/k is large compared to the temperature of the incident beam.

For unit beam density the differential rate at which collisions occur between incident gas atoms and surface atoms is given by

$$d^2R = u P_1(\omega t_0) P_2(v) d\omega t_0 dv, \quad (42)$$

where $P_1(\omega t_0)$ is the phase probability given by Eq. (41) and $P_2(v)$ is the probability distribution for the velocity amplitude of the oscillators given by

$$P_2(v) dv = (m_s v/kT_s) \exp[-(m_s v^2/2kT_s)] dv. \quad (43)$$

By substituting Eq. (43) into Eq. (42) and transforming to the variables v_c and v_s , we obtain

$$\begin{aligned} d^2R &= u (m_s u^2/kT_s) P_1(v_c, v_s) \\ &\quad \times \exp\{-[m_s u^2(v_c^2 + v_s^2)/2kT_s]\} dv_c dv_s. \end{aligned} \quad (44)$$

The probability for scattering into the angular range θ_r to $\theta_r + d\theta_r$ is then given by

$$\begin{aligned} u^{-1} \frac{dR}{d\theta_r} &= \frac{m_s u^2}{kT_s} \int_{-\infty}^{\infty} P_1(v_c, v_s) \\ &\quad \times \exp\left[-\frac{m_s u^2}{2kT_s} (v_c^2 + v_s^2)\right] \left|\frac{\partial v_c}{\partial \theta_r}\right|_{v_s} dv_s. \end{aligned} \quad (45)$$

In Eq. (36), however, we have shown that v_c is a function of θ_r and not v_s . Hence terms involving v_c and $|\partial v_c/\partial \theta_r|_{v_s} (= dv_c/d\theta_r)$ may be brought outside the integral in Eq. (45). We also note that the antisymmetric v_s term in the phase probability [Eq. (41)] will give zero contribution when integrated over the range $-\infty \rightarrow \infty$. The integral over v_s then becomes a standard definite integral, and the scattering distribution is

$$\begin{aligned} (1/u) dR/d\theta_r &= (m_s u^2/2\pi kT_s)^{1/2} (1 - v_c) \left| dv_c/d\theta_r \right| \\ &\quad \times \exp(-m_s u^2 v_c^2/2kT_s). \end{aligned} \quad (46)$$

The above scattering distribution is expressed in terms of the variable v_c ; but we know v_c as a function of γ [Eq. (36)], and we know θ_r as a function of γ [Eqs. (28) and (29)]. Hence, using γ as the working variable, we may calculate the scattering distribution as a function of θ_r . The derivative $dv_c/d\theta_r$ may be written in terms of θ_r and γ explicitly, and the result is given in Appendix B.

In the original analysis¹ of the hard-cube model an ideally flat surface was considered, giving rise to a purely two-dimensional scattering pattern. In Ref. 2 an approximate method was presented for taking into account surface roughness, and it was shown that

⁷ R. E. Stickney, R. M. Logan, S. Yamamoto, and J. C. Keck, in *Fundamentals of Gas-Surface Interactions*, H. Saltsburg, J. N. Smith, Jr., and M. Rogers, Eds. (Academic Press Inc., New York, 1967), p. 422.

when we consider the scattering distribution for flux per unit solid angle, the expression for the in-plane distribution should include a factor $|(\partial\alpha_2/\partial\phi)_{\theta_r}|$, where the angles α_2 and ϕ are as illustrated in Fig. 4. An expression for this factor is derived in Appendix C, and to lowest order in α_1 and α_2 , has the following form:

$$(\partial\alpha_2/\partial\phi)_{\theta_r} = \tan\theta_i \csc\theta_r \{[(\cot^2\theta_r/\cot^2\theta_i) + W]^{1/2} + (1+W)^{1/2}\}^{-1}. \quad (47)$$

Including this factor in Eq. (46) the modified expression for the in-plane ($\phi=0$) scattering distribution for flux per unit solid angle is

$$u^{-1} \frac{dR}{d\Omega} \Big|_{\phi=0} = (\pi^{1/2}\langle\alpha\rangle)^{-1} \left(\frac{m_s u^2}{2\pi k T_s} \right)^{1/2} \times \left| \left(\frac{\partial\alpha_2}{\partial\phi} \right)_{\theta_r} \right| (1-v_c) \left| \frac{dv_c}{d\theta_r} \right| \exp \left(-\frac{m_s u^2 v_c^2}{2k T_s} \right). \quad (48)$$

The normalization factor $1/\pi^{1/2}\langle\alpha\rangle$ in the above equation arises from an assumed Gaussian distribution $(1/\pi^{1/2}\langle\alpha\rangle) \exp(-\alpha_2^2/\langle\alpha\rangle^2)$ for α_2 . The actual shape, and hence the position of the maximum, of the distribution in Eq. (48) is independent of the assumed distribution for α_2 in the limit of small roughness.

In summary, Eq. (48) should be valid in cases where the surface roughness $\langle\alpha\rangle$ is considerably smaller than the thermal angular half-width of the in-plane scattering pattern, but the angular width of the scattering pattern in the out-of-plane direction ($\sim 2\langle\alpha\rangle$) is considerably greater than the angle subtended by the detector. This probably corresponds to the usual experimental arrangement. In cases where the detector subtends an angle of order $2\langle\alpha\rangle$ or greater, and hence integrates over the angle ϕ , Eq. (46) should be used.

IV. COMPARISONS WITH EXPERIMENTS

For specified experimental conditions, the results from the soft-cube model are governed by the values of the quantities ω , b , and D . It may be seen from the above analysis [Eq. (28)], however, that the first two of these occur only in the combination $\sigma = \omega b/u$. It is therefore convenient to define a quantity n such that

$$n(k\Theta_D/\hbar)a_0 \equiv \omega b, \quad (49)$$

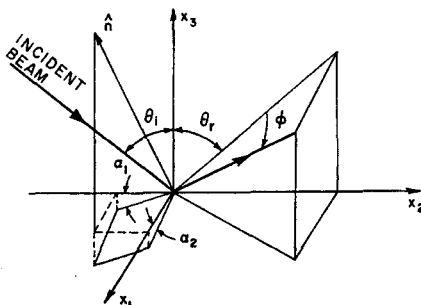


FIG. 4. Coordinate system for rough surface. The x_1x_2 plane represents the ideal flat surface, and $\hat{n}$ represents the normal to the actual surface at the origin.

TABLE II. Comparison of experimental results of Smith and Saltsburg⁹ and results from the soft-cube model. Deviation from specular, η (degree), $\theta_i = 50^\circ$, and $T_s = 600^\circ\text{K}$.

System	$T_s = 300^\circ\text{K}$		$T_s = 2550^\circ\text{K}$	
	Experiment	Soft-cube	Experiment	Soft-cube
He/Au	0 ± 1	0.9	0 ± 1	-0.6
Ne/Au	4 ± 1	3.7	-2 ± 1	-3.0
Ar/Au	8 ± 1	7.8	-3 ± 1	-3.4
Xe/Au	$24^a(21) \pm 2$	19.2	$-4^a(-7) \pm 2$	-6.5

^a Significant cosine component implied in these cases, correction for which gives approximately the value in parentheses. (See Fig. 14.)

where Θ_D is the Debye temperature of the solid, and a_0 is the Bohr radius. There is evidence⁸ that the surface layer of a solid has a slightly lower Debye temperature (i.e., a lower maximum frequency) than the bulk of the solid. Assuming that the correct frequency to use for our single oscillator in the soft-cube model is given approximately by the Debye temperature, we expect that the quantity n has the value $n \sim b/a_0$; by comparison with values for the range found in gas-gas collisions, we expect this quantity to have a value of about 0.5. Below we find values for the quantities n and D by matching with experimental data for the scattering of atomic beams from surfaces.

For the purpose of obtaining a "best fit" between theory and experiment, it is convenient to have a single quantity for describing the scattering distribution. A suitable quantity is the angular position of the maximum of the distribution. As already mentioned in Sec. III, the position of the maximum is not very sensitive to the presence of a velocity distribution in the incident beam or to surface roughness. The velocity distribution and the roughness would, however, be expected to broaden the scattering distribution; thus the scattering distributions given by Eq. (48) should appear somewhat narrower than the corresponding experimental ones. This is shown below to be the case.

To obtain a suitable criterion for judging the quality of the agreement between theory and experiment, we define the quantity

$$\Lambda \equiv \sum_j |\Delta\theta_{\max(j)}| / \sum_j 1,$$

where the subscript j identifies the conditions applying for a particular experiment, and the sum is over a set of experiments pertaining to a given gas-surface system. $\Delta\theta_{\max(j)}$ is the difference between the experimental and theoretical results for the position of the maximum of the scattering pattern for the j th set of conditions.

To illustrate the method used for making comparisons with experiments, we consider the system Ar/Au using experimental results of Smith and Saltsburg.⁹ The experimental conditions and the deviations of the

⁸ A. U. Macrae, Surface Sci. 2, 522 (1964).

⁹ J. N. Smith, Jr., and H. Saltsburg, in Proc. Intern. Symp. Rarefied Gas Dyn. 4th Toronto, 1964, 2, 491 (1965).

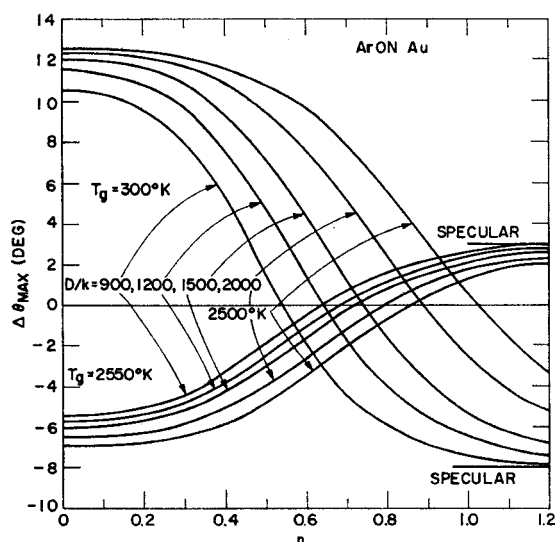


FIG. 5. Comparison between theory and experiment; $\Delta\theta_{\max}$ as a function of n for various values of D/k . This comparison based on experimental data for Ar/Au (shown in Table II) from Ref. 9.

maxima of the scattering patterns are given in Table II. These experiments used a Maxwellian incident beam, and we have used the relation $u_{\infty}^2 = 4kT_g \cos^2\theta_i/m_g$ to define the incident normal velocity of an equivalent monoenergetic beam. Using the soft-cube model [Eq. (48)], we have calculated $\Delta\theta_{\max}$ as a function of n for various values of D/k as shown in Fig. 5; from the results in Fig. 5, we have calculated Λ as a function of n for the same values of D/k , as shown in Fig. 6. Using Fig. 6 we have constructed contours of constant Λ , and these are shown in Fig. 7(A) as a function of n and D/k . From this latter figure we see that for the system Ar/Au there is a limited region over which Λ is acceptably small, and this region covers values of the well depth D corresponding to the existing estimates and experimentally measured values of the heat of adsorption ΔH for argon on a metal surface, as given in Table III. In view of the assumptions and approximations in the analysis and the inaccuracies involved in estimating the position of the maximum from the experimental scattering distributions, $\Lambda \sim 1.0^\circ$ can be considered as acceptably small. Values of n and D selected from Fig. 7(A) to give optimum agreement with experiment are shown in Table III.

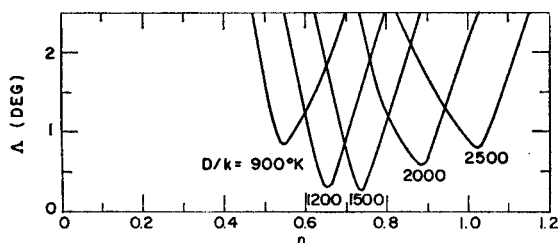


FIG. 6. Λ as a function of n for same conditions as in Fig. 5.

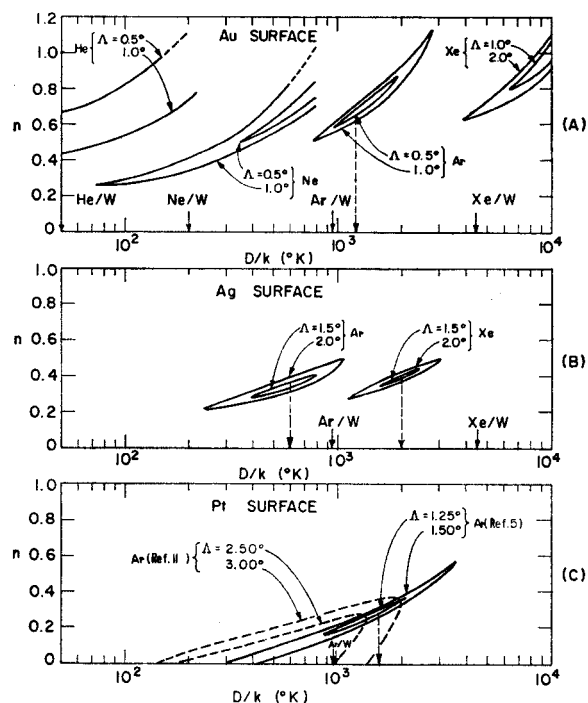


FIG. 7. Comparison between theory and experiment; contours of constant Λ as a function of n and D/k for the following systems: (A) He, Ne, Ar, and Xe/Au using experimental data from Ref. 9; (B) Ar and Xe/Ag using experimental data from Ref. 3; (C) Ar/Pt using experimental data from Ref. 5 and 11.

TABLE III. Comparison of values used in the soft-cube model with literature values.

System	n	Values for the gas-surface interaction obtained by comparison between experiment and the soft-cube model (Fig. 7)		Literature values for the gas-gas interaction range for He, Ne, Ar, and Xe and the heat of adsorption ΔH for these gases on W	
		b (Å) ^a	D/k (°K)	b (Å)	$\Delta H/k$ (°K)
He/Au	0.50 ^b	0.26	50 ^b	0.26 ^d	~50 ^f
Ne/Au	0.46	0.24	300 ^c	0.27 ^e	200 ^f
Ar/Au	0.65	0.34	1200	0.34 ^e	950 ^g
Xe/Au	0.76	0.40	6000 ^c	0.40 ^e	4500 ^g
Ar/Ag	0.35	0.18	600	0.34 ^e	950 ^g
Xe/Ag	0.39	0.21	2000	0.40 ^e	4500 ^g
Ar/Pt	0.30	0.16	1600	0.34 ^e	950 ^g

^a Values for the interaction range obtained from the values of n by assuming $\omega = k\theta_D/\hbar$ in Eq. (49).

^b Obtained by comparison with literature values. In this case a wide range of values of n and D yields good agreement with experiment (Fig. 7A).

^c Values selected as a compromise between the literature values and the somewhat higher values suggested by Fig. 7(A).

^d Derived from value estimated by Goodman (Ref. 17) for the range of a Morse potential in the gas-gas collision. For comparison with a Morse potential of the form $\phi = D[\exp(-2\alpha(r-r_m)) - 2\exp(-\alpha(r-r_m))]$, we have assumed the relation $b = 1/(2\alpha)$.

^e Derived from values for the range of a Morse potential for the gas-gas collision, determined [D. D. Konowalow and J. O. Hirschfelder, Phys. Fluids 4, 629 (1961)] by comparison with experiments.

^f Values estimated by Trilling (see Ref. 13).

^g Experimental values on tungsten given by G. Ehrlich, in *Molecular Processes at the Gas-Solid Interface. Structure and Properties of Thin Films* (John Wiley & Sons, Inc., New York, 1959), p. 433.

Using experimental results from Table II, we have also calculated Λ contours for the systems He/Au, Ne/Au, and Xe/Au, as shown in Fig. 7(A). Once again only certain combinations of n and D/k give acceptably small values of Λ , but the regions are not as restricted as in the case Ar/Au. In particular, for the system He/Au good agreement with experiment is obtainable for a very wide range of values of n and D . Guided by the existing estimates of D , we have selected from Fig. 7(A) combinations of n and D which provide good agreement with experiment; these values are shown in Table III, and the corresponding values for the position of the maximum are shown in Table II. In Table III values are given for b obtained from the value of n by using the assumption that $\omega = k\theta_D/\hbar$. It

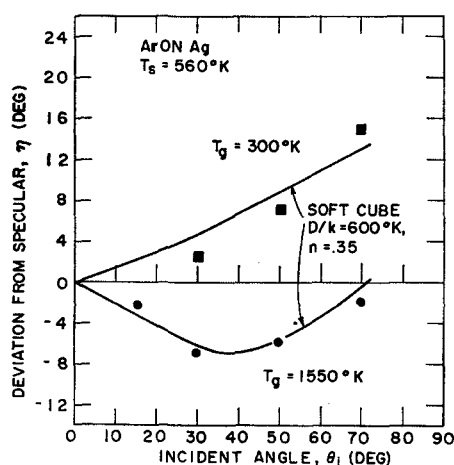


FIG. 8. Comparison between theoretical results from the soft-cube model and the corresponding experimental data for Ar/Ag from Ref. 3. Experimental points for $T_g = 300^\circ\text{K}$ (■) and $T_g = 1550^\circ\text{K}$ (●).

is seen that these values for b are of the same order as the literature values for the range of the repulsive exponential potential in the corresponding gas-gas collision.

Using experimental results of Saltsburg and Smith,³ we have also calculated Λ contours for the systems Ar and Xe/Ag, shown in Fig. 7(B). In each of these cases the comparison is based on six experimental points (namely, those at $\theta_i = 30^\circ, 50^\circ$, and 70° in Figs. 8 and 9), and there is a quite limited range of n and D over which Λ is acceptably small. Values selected from Fig. 7(B) are given in Table III; once again the values of D/k are reasonable, and the values of b obtained by assuming $\omega = k\theta_D/\hbar$ are of the same order as the gas-gas values. In Fig. 8 a comparison is shown between the experimental results for Ar/Ag and the results from the soft-cube model using the values for n and D in Table III. It is seen that the soft-cube model yields good agreement with the experimental results and gives significantly better agreement than is obtainable with

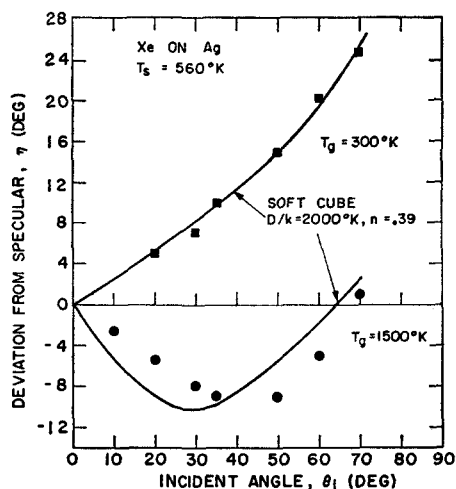


FIG. 9. Comparison between theoretical results from the soft-cube model and the corresponding experimental data for Xe/Ag from Ref. 3. Experimental points for $T_g = 300^\circ\text{K}$ (■) and $T_g = 1500^\circ\text{K}$ (●).

the hard-cube model, even when a reasonable well depth (600°K in this case) is incorporated in the hard-cube model [Fig. (2)]. In Fig. 9 a similar plot is shown for the system Xe/Ag. Once again the soft-cube model gives good agreement with experiment; in this case, however, we note that the mass ratio $\mu = 1.215$, and the hard-cube model could not sensibly be applied for such a high mass ratio.

We have also made comparison with some recent experimental results of Moran⁵ for the system Ar/Pt. These results are notable in that an approximately monoenergetic gas beam was used, a fact which helps the validity of application of Eq. (48). Using the seven experimental points shown in Fig. 10, we have con-

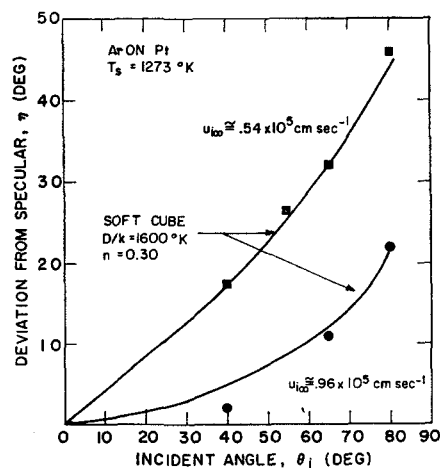


FIG. 10. Comparison between theoretical results from the soft-cube model and the corresponding experimental data for Ar/Pt from Ref. 5. Experimental points for incident gas-atom velocity (outside potential well) $u_{i\infty} \approx 0.54 \times 10^5 \text{ cm sec}^{-1}$ (■) and $u_{i\infty} \approx 0.96 \times 10^5 \text{ cm sec}^{-1}$ (●).

TABLE IV. Values for the deviation from the specular η for the system Ar/Pt obtained from experimental results of Hinchin and Malloy.¹¹

θ_i (degree)	T_s (°K)	T_g (°K)	η (degree)
45.0	300	870	-16 ± 1
45.0	1025	1020	0 ± 1
67.5	300	300	15.5 ± 1
67.5	300	620	1.5 ± 1
67.5	300	870	-1.5 ± 1
67.5	300	1100	-2.5 ± 1
80.0	300	870	8 ± 1

structed Λ contours as shown in Fig. 7(C) and again there is a fairly restricted region of n and D over which Λ is acceptably small. A selected combination of n and D which gives optimum agreement with experiment is shown in Table III. While the value for n is still of the correct order, it is noticeably smaller than the value found for the system Ar/Au; this point will be discussed further in Sec. VI. The actual theoretical results obtained using these values of n and D are shown for comparison with the experimental results in Fig. 10.

Extensive experimental results for the scattering distributions and the angular position of the maximum for various gases on various metals have been given by

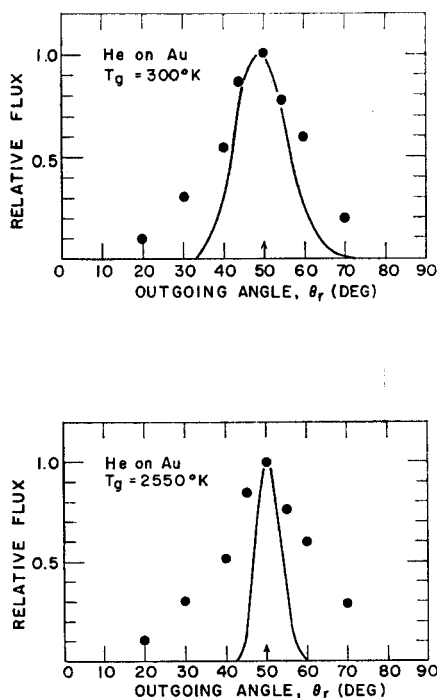


FIG. 11. In-plane scattering distributions for He/Au; comparison between results from soft-cube model [Eq. (48)] using values for n and D given in Table III and experimental data from Ref. 9 (●). $T_s = 600^\circ\text{K}$ and $\theta_i = 50^\circ$.

Hinchin and Shepherd,⁴ Hinchin and Foley,¹⁰ and Hinchin and Malloy.¹¹ In these experiments the density (rather than flux) distributions of the outgoing atoms were measured, and thus Eq. (48) cannot be applied directly. Using our assumptions of a monoenergetic incident beam and unchanged tangential velocity component, it follows that the outgoing velocity at any angle θ_r is proportional to $\csc\theta_r$. Hence for making approximate comparisons with these data, we can convert Eq. (48) into a density distribution by dividing by $\csc\theta_r$. There appear to be some internal inconsistencies in the plotting of the data in Refs. 4 and 10, and, therefore, we have only used the results for

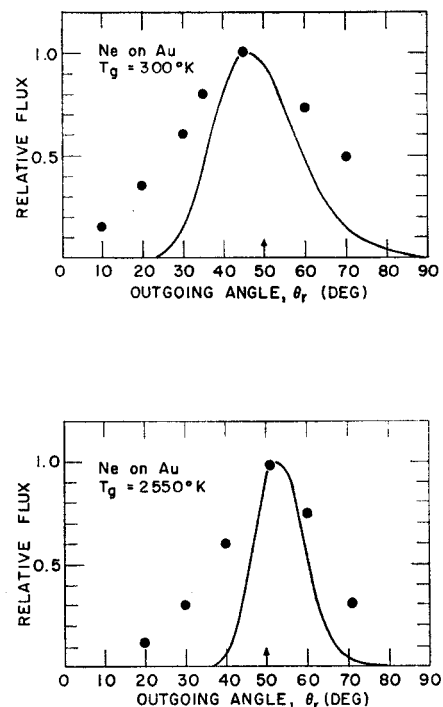


FIG. 12. In-plane scattering distribution for Ne/Au; other details as for Fig. 11.

the system Ar/Pt in Ref. 11 (as shown in Table IV) for making quantitative comparisons; the corresponding Λ contours are shown in Fig. 7(C). While the agreement between theory and experiment is not as good in this case as in the other cases considered above, it is seen that the region of best agreement coincides approximately with that obtained from the independent results for the system Ar/Pt in Ref. 5. Due to the uncertainties involved in transforming to a density distribution, our values for n and D in Table III are based only on the comparison with the results in Ref. 5.

¹⁰ J. J. Hinchin and W. M. Foley, in Proc. Intern. Symp. Rarefied Gas Dyn. 4th Toronto, 1964, 2, 505 (1965).

¹¹ J. J. Hinchin and E. S. Malloy, in *Fundamentals of Gas-Surface Interactions*, H. Saltsburg, J. N. Smith, Jr., and M. Rogers, Eds. (Academic Press Inc., New York, 1967), p. 448.

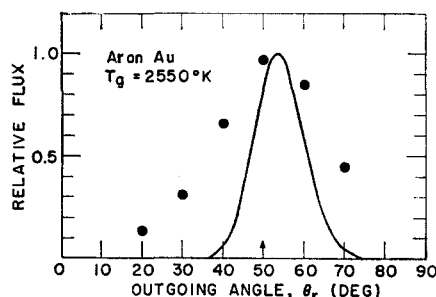
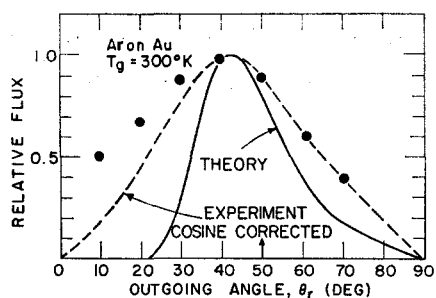


FIG. 13. In-plane scattering distributions for Ar/Au; comparison between results from soft-cube model [Eq. (48)] using values for n and D given in Table III, experimental data from Ref. 9 (●) and same experimental data after correction for an assumed cosine component (---). $T_s = 600^\circ\text{K}$ and $\theta_i = 50^\circ$.

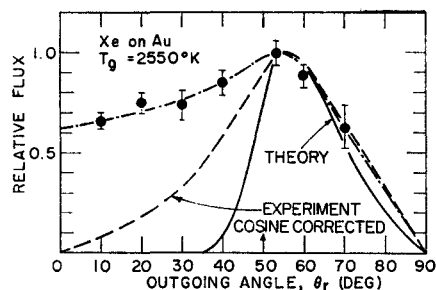
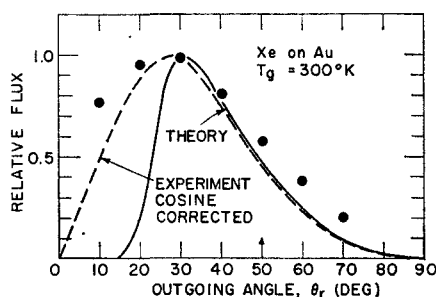


FIG. 14. In-plane scattering distributions for Xe/Au; other details as for Fig. 13.

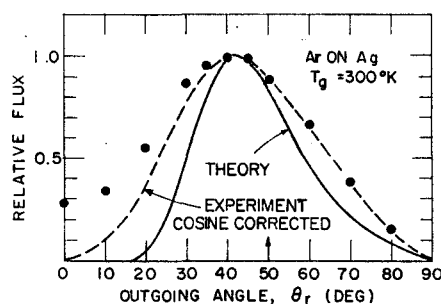


FIG. 15. In-plane scattering distributions for Ar/Ag; comparison between results from soft-cube model [Eq. (48)] using values for n and D given in Table III, experimental data from Ref. 3 (●), and same experimental data after correction for assumed cosine component (---). $T_s = 560^\circ\text{K}$ and $\theta_i = 50^\circ$.

Using the values of n and D given in Table III, we have used Eq. (48) to calculate the full in-plane distributions corresponding to some of the cases considered above, as shown in Figs. 11–16. It is seen that in all these cases the theoretical distributions from the soft-cube model are narrower than the corresponding experimental ones. There are several reasons why a discrepancy of this type is to be expected: (1) The experimental measurements include gas atoms which are adsorbed on the surface and then re-emitted. In Figs. 13–16 we have corrected the experimental results for the presence of these re-emitted atoms by assuming that the flux along the normal ($\theta_r = 0$) is due entirely to re-emitted atoms, and these atoms have a diffuse distribution such that the re-emitted flux at any angle θ_r is proportional to $\cos\theta_r$. Subtracting this component from the experimental results and renormalizing leads to the distributions shown by a broken line in Figs. 13–16; (2) the experimental results in Figs. 11–16 were obtained with incident Maxwellian beams, whereas Eq. (48) applies for a monoenergetic beam. By comparison with the results for the hard-cube model in Ref. 7, we should expect the use of a Maxwellian beam in the soft-cube model to give a somewhat broader distribution, especially at angles towards the normal, while having only a small effect on the position of the maximum; (3) in deriving Eq. (48) the broadening of

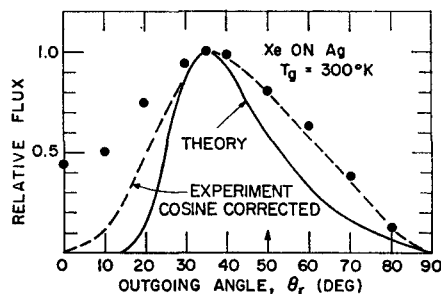


FIG. 16. In-plane scattering distributions for Xe/Ag; other details as for Fig. 15.

the in-plane scattering pattern due to surface roughness was neglected.

From consideration of the Λ contours in Fig. 7, it is apparent that in these cases there is a range of values of n and D which yield almost constant theoretical results. This connection between n and D arises through the strong dependence of the model on the parameter $\sigma = \omega b/u$ [Eq. (28)]. We note that increasing n increases the value of σ , but increasing D increases u and hence decreases σ . Thus for a given set of experimental conditions, we may find n as a function of D for a constant value of σ . Fortunately, this relation between n and D will be different for different values of u_∞ , and the model also depends on D independently through the ratio u_∞/u which occurs in Eq. (36). In principle, therefore, it should be possible to obtain unique optimum values of n and D by comparison with experimental results.

V. FRACTION INITIALLY TRAPPED

Using the soft-cube model we may calculate the fraction of the incident gas atoms which are initially trapped, i.e., the fraction which has insufficient energy to escape from the potential well after collision with the oscillator. For a solid at a nonzero temperature, a trapped atom will, in fact, oscillate in the potential well, and its energy will change due to further interaction with the solid until it has enough energy to escape. To this part of the process one may ascribe an adsorption time, which is the average time a trapped atom stays on the surface. Since the adsorbed atom has a random type of motion up and down the energy levels of the potential well, the adsorption time will, in general, be somewhat greater than the period of oscillation of the adsorbed atom in its well; a calculation of the adsorption time will not be attempted here.

To find the number of atoms scattered into all directions above the surface, we integrate the scattering distribution [Eq. (48)] over the inplane angle θ_r and the out-of-plane angle ϕ . Integration over ϕ simply eliminates the factor $(1/\pi^{1/2}\langle\alpha\rangle)(\partial\alpha_2/\partial\phi)_\theta$ in Eq. (48), and hence the fraction which leaves at angles above the surface (and therefore is not trapped) is given by

$$f_r = (m_s u^2 / 2\pi k T_s)^{1/2} \int_{-\infty}^{v_c^*} (1 - v_c) \times \exp(-m_s u^2 v_c^2 / 2k T_s) dv_c$$

$$= \frac{1}{2} \left\{ 1 + \operatorname{erf} \left[\left(\frac{m_s u^2 v_c^{*2}}{2k T_s} \right)^{1/2} \right] + \pi^{-1/2} \left(\frac{2k T_s}{m_s u^2} \right)^{1/2} \times \exp \left(-\frac{m_s u^2 v_c^{*2}}{2k T_s} \right) \right\}, \quad (50)$$

where v_c^* is the surface velocity corresponding to an

outgoing angle $\theta_r = \pi/2$. From Eq. (36) v_c^* is given by

$$v_c^* = \left(\frac{1}{2} J^* \right) [(u_\infty/u)^2 - \mu J^{*2}],$$

where J^* is the value of J corresponding to $\theta_r = \pi/2$. To calculate J^* from Eq. (33) we must use $\gamma = \gamma^*$, found by using Eqs. (28) and (29) with the condition $\theta_r = \pi/2$.

Values for the fraction of gas atoms initially trapped $f_T (= 1 - f_r)$ calculated from Eq. (50) are shown in Table V. The values given are for the same experimental conditions as some of the cases considered in Sec. IV, and the values of the parameters n and D given in Table III have been used here. The qualitative behavior of f_T for the various cases listed seems to be reasonable. For He and Ne there is virtually no trapping at either low (300°K) or high (2550°K) gas temperatures. For Xe at 300°K, on the other hand, approximately one half of the incident gas atoms are initially trapped on the surface. The qualitative behavior shown here also seems to be consistent with the nature of the corresponding experimental scattering distributions (Figs. 11–16) in which there appears to be a diffuse component which is most marked for Xe and very small for He.

McCarroll and Ehrlich¹² have experimentally determined the sticking coefficient for Xe at 300°K on a W surface at 80°K. They found a value of about 0.42, although this result varied somewhat with the surface coverage; this value may also include re-evaporation effects. This experimental result is somewhat lower than our value in Table V for the system Xe/Au, but

TABLE V. Fraction initially trapped f_T . Values from soft-cube model using n and D values from Table III $\theta_i = 50^\circ$.

T_g (°K)	System	T_s (°K)	f_T
300	He/Au	600	0.00
2550	He/Au	600	0.00
300	Ne/Au	600	0.02
2550	Ne/Au	600	0.02
2550	Ne/Au	600	0.00
300	Ar/Au	600	0.15
2550	Ar/Au	600	0.00
300	Xe/Au	600	0.66
2550	Xe/Au	600	0.25
300	Ar/Ag	560	0.11
1550	Ar/Ag	560	0.01
300	Xe/Ag	560	0.40
1500	Xe/Ag	560	0.17

¹² B. McCarroll and G. Ehrlich, J. Chem. Phys. **38**, 523 (1963).

about the same as our value for Xe/Ag. To our knowledge there are no other experimental results for the sticking coefficients of the rare gases on metal surfaces in the temperature range of present interest.

VI. DISCUSSION AND CONCLUSIONS

In Sec. IV we have shown that for reasonable values of the range b and well depth D of the potential (Table III), the soft-cube model yields good quantitative agreement with experimental data for the position of the maximum of the scattering pattern for the rare gases on various metals. With the available experimental data we have not been able to determine with precision unique values for n and D for each gas-surface system, but the fact that in several cases the Λ contours (Fig. 7) tend to restrict our choice to a small and reasonable range of n and D is encouraging, and it is to be hoped that further comparisons with more extensive experimental data will enable "optimum" values of n and D to be determined accurately.

Other attempts to determine the range and well depth for the gas-surface interaction have been made, notably those of Trilling¹³ and Goodman.¹⁴ Using classical models which include lattice interactions, and making comparisons with experimental data for the energy accommodation coefficient, these authors have also arrived at reasonable values (similar to those found in this paper) for parameters corresponding to b and D . It should be noted, however, that both these authors assume a lattice at 0°K in their analysis and make comparison with experiments in which the surface was at a higher temperature than the gas; this procedure can be justified if it is assumed that the energy-accommodation coefficient is independent of the surface temperature, and there is some experimental and theoretical evidence^{15,16} that this may be the case.

The literature values for b and D given in Table III do not strictly apply for the systems we have considered and are intended for an order of magnitude comparison only. In cases where the range of the potential for the metal-metal interaction is known, in addition to the value for the gas-gas interaction, we could obtain a better estimate for b by using a combination rule given by Goodman¹⁷; the necessary values do not seem to be available, however, for Au, Ag, or Pt. From Fig. 7 it is seen that our model indicates that a significantly lower value of n should apply for the system Ar/Pt than for the system A/Au, unless we use an unrealis-

tically high value of D for the first system. The fact that there is apparently a difference between these systems is perhaps not surprising if we notice from Table I that while Au and Pt have similar masses, the Pt lattice is about twice as stiff as the Au lattice. It is possible that a stiffer lattice would arise from a steeper repulsive potential between the atoms, associated with a smaller value of b . Until our theory has been tested by more extensive comparisons with data, we are not in a position to draw any conclusions about the reasons for this difference between Au and Pt.

As mentioned in Sec. II, the assumption that the gas atom interacts with a single surface atom cannot be justified in cases where the gas atom travels a tangential distance as great as a lattice spacing during the collision time. From the $\text{sech}^2\tau$ form of our approximate force pulse [Eq. (26)] and the relation $\tau \equiv t/t_c$, we see that the force pulse has a width of approximately $2t_c$. Using the parameter $\gamma \equiv (\pi/2)\omega t_c$, the tangential distance travelled by the gas atom during the time $2t_c$ may be written

$$l = (4\gamma\hbar/\pi k\theta_D) u_{i\infty} \sin\theta_i, \quad (51)$$

where we have assumed $\omega = k\theta_D/\hbar$. Of the cases considered in Sec. IV, the one leading to about the largest value for l is that for the system A/Au with $\theta_i = 50^\circ$ and $T_g = 2550^\circ\text{K}$. Using these values in Eq. (51) together with the value $\gamma = 1.89$ corresponding to the maximum of the scattering pattern yields the result $l = 1.25 \text{ \AA}$. This distance is equal to about half a lattice spacing, and, therefore, we expect that tangential velocity effects would not be too important in this case. In the other cases considered in this paper, l was of this order of magnitude or less.

We believe that the soft-cube model represents a considerable advance on the hard-cube model since it includes the important ωt_c factor and can handle cases with higher mass ratio μ . When suitable values for n and D have been determined by comparison with experimental data, the soft-cube model should provide much more accurate predictions than would be possible using the hard-cube model. There are several obvious limitations to the validity of the soft-cube model which should be borne in mind in any attempt to apply the model or improve it:

(1) The analysis uses classical mechanics and, therefore, would not apply to light slow atoms (whose wavelength is of the order of the lattice spacing) or for cases where the gas or surface temperatures are below the Debye temperature of the solid.

(2) The effects of surface roughness have been assumed small compared to the thermal width of the in-plane scattering pattern, so that the analysis presented here cannot apply to the scattering of very high-energy particles. The surface roughness "seen" by an incident gas atom is clearly a function of its energy (Fig. 18).

¹³ L. Trilling, in Proc. Intern. Symp. Rarefied Gas Dyn. 5th Oxford, 1966, 1, 139 (1967).

¹⁴ F. O. Goodman, in Proc. Intern. Symp. Rarefied Gas Dyn. 4th Toronto, 1964, 2, 366 (1965).

¹⁵ F. O. Goodman and H. Y. Wachman, J. Chem. Phys. 46, 2376 (1967).

¹⁶ R. M. Logan, Research Laboratory of Electronics Quarterly Progress Rept. No. 80, p. 43, M.I.T., 1966 (unpublished).

¹⁷ F. O. Goodman, J. Phys. Chem. Solids 24, 1451 (1963).

(3) With respect to the neglect of lattice interactions and the approximations made in Sec. III.B, the validity of the model should increase as the incident energy increases. (Note that for the heavier atoms, such as Xe, the presence of a large potential well helps to make the repulsive collision faster.) While it might be possible to extend the present analysis to include the initial motion contribution to the correction term $(2/\pi^2)\gamma^2 Z_0$ in Eq. (26) and the antisymmetric τ^3 term in Eq. (15), thus making the analysis valid for larger values of γ , it is debatable whether this is worthwhile unless some account is taken of lattice interactions. When the thermal motion is incorporated into the lattice models,¹⁸ they apparently become too complicated for comparison with experiments to be practical. At present, therefore, one is faced with the choice of including either lattice effects or surface temperature effects, but not both. From the point of view of making comparisons with most of the existing experimental data, we believe that the surface temperature effects are more important.

(4) The analysis presented here applies for a monoenergetic incident beam; for detailed comparisons with experimental scattering patterns obtained using a Maxwellian beam, straightforward numerical integration of Eq. (48) [or Eq. (46)] could be employed.

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Numerical calculations were performed at the MIT Computation Center.

APPENDIX A: EQUIPOTENTIAL SURFACES AND FRACTIONAL LOAD CONTOURS

In order to calculate approximate equipotential surfaces, we consider an idealized surface consisting of a square lattice with each surface atom fixed at its equilibrium position (Fig. 17). We focus attention on the atom at 0, with coordinates (0, 0, 0); we specify the coordinates of the i th surface atom to be $(x_{1i}, x_{2i}, 0)$.

We assume that the potential energy of interaction between the gas atom and any surface atom has the form $U = B \exp(-r/b)$, where B is a constant and r the separation, and also assume that the total potential energy of the system is given by a linear superposition of the effects due to each surface atom. Then for the gas atom at a position (x_1, x_2, y) , the potential energy of the system is

$$U = B \sum_i \exp\{-[(x_1 - x_{1i})^2 + (x_2 - x_{2i})^2 + y^2]^{1/2}/b\} + \text{constant.} \quad (\text{A1})$$

In most metals the lattice spacing is about 3 Å, and hence for our idealized lattice, we choose $2a = 3$ Å. From Table III we see that the range b is typically about 0.3 Å, and hence for the ratio a/b , we use the value 5.0. Using this value in Eq. (A1), we have calculated cross-sections of equipotential surfaces along the x_1 (or x_2) axis and along the diagonal in the $x_1 x_2$ plane, as shown in Fig. 18.

For an atom incident normally on the atom 0 with thermal energy, we would expect the distance of closest approach to be of the same order as the lattice spacing. Thus the equipotential sections passing through the point (0, 0, $2a$) may be taken as representative for the interaction of thermal beams with surfaces. From Fig. 18 it is seen that this equipotential surface has a maximum slope of about 10° along the x axis and about 15° along the diagonal. In Fig. 18 we also show the circular sections which correspond to the potential due to atom 0 alone. The equipotentials for $y/a = 2.0$ follow the circular sections quite closely out to about $x/a = 1$, and this suggests that over much of the unit cell most of the load is taken by the atom 0 alone. This point may be illustrated more clearly as follows.

The line-of-centers force acting between the gas atom and the i th surface atom is $(B/b) \exp\{-[(x_1 - x_{1i})^2 + (x_2 - x_{2i})^2 + y^2]^{1/2}/b\}$. The fraction of the normal component of the force acting between the gas atom at (x_1, x_2, y) and the surface which is taken by atom 0 is then given by

$$f_L = \frac{[y/(x_1^2 + x_2^2 + y^2)^{1/2}] \exp[-(x_1^2 + x_2^2 + y^2)^{1/2}/b]}{\sum_i \{y/[(x_1 - x_{1i})^2 + (x_2 - x_{2i})^2 + y^2]^{1/2}\} \exp\{-[(x_1 - x_{1i})^2 + (x_2 - x_{2i})^2 + y^2]^{1/2}/b\}}. \quad (\text{A2})$$

Using Eq. (A2) we have calculated f_L for cases where the gas atom lies on the equipotential surface which passes through the point (0, 0, $2a$) in Fig. 18, and contours of constant f_L (fractional load contours) are shown in Fig. 17. This figure indicates that over a large fraction of the area of the unit cell, most of the load is taken by the central atom at 0.

¹⁸ F. O. Goodman, Surface Sci. 3, 386 (1965).

APPENDIX B: EXPRESSION FOR $dv_c/d\theta_r$

From Eq. (29)

$$v_c \equiv (v \cos \omega t_0)/u = (1/2J) \{ (u_\infty/u)^2 \times [1 - (\cot^2 \theta_r / \cot^2 \theta_i)] - \mu J^2 \}.$$

By straightforward differentiation and rearranging, it

can be shown that

$$\frac{dv_e}{d\theta_r} = J^{-1} \left(\frac{u_\infty}{u} \right)^2 \frac{\csc^2 \theta_r \cot \theta_r}{\cot^2 \theta_i} \times \left[1 + (I-1)^{-1} \left(f + I \frac{df}{d\gamma} \frac{d\gamma}{dI} \right) (v_e + \mu J) \right], \quad (B1)$$

where

$$\frac{df}{d\gamma} = \frac{f}{Q} \frac{dQ}{d\gamma} + \frac{Q}{(1 + \frac{1}{6} Z_{0R} \gamma^2)} \left(\frac{dZ_{0R}}{d\gamma} H + Z_{0R} \frac{dH}{d\gamma} \right) - \frac{f}{(1 + \frac{1}{6} Z_{0R} \gamma^2)} \left(\frac{\gamma^2}{\frac{1}{6}} \frac{dZ_{0R}}{d\gamma} + \frac{1}{3} \gamma Z_{0R} \right), \quad (B2)$$

$$Q \equiv \gamma \operatorname{csch} \gamma,$$

$$dQ/d\gamma = Q[(1/\gamma) - \coth \gamma],$$

$$H \equiv \gamma \coth \gamma - \gamma^2 \operatorname{csch}^2 \gamma - \frac{1}{2} \gamma^2,$$

$$dH/d\gamma = \coth \gamma (1 - \gamma \coth \gamma) - 2Q(dQ/d\gamma),$$

$$\frac{dZ_{0R}}{d\gamma} = Z_{0R} \left[Q^{-1} \frac{dQ}{d\gamma} (1 + NQS)^{-1} - \frac{NQ}{(1 + NQS)} \frac{dS}{d\gamma} + G^{-1} \frac{dG}{d\gamma} \right],$$

$$G \equiv 1.0 + 0.0346\gamma^2 + 0.00076\gamma^4 + \dots,$$

$$dG/d\gamma = 0.0692\gamma (1.0 + 0.0439\gamma^2 + 0.00091\gamma^4 + \dots),$$

$$S \equiv (1 - \gamma \coth \gamma)^2 - \frac{1}{2} \gamma^2,$$

$$dS/d\gamma = 2(-\coth \gamma + \gamma \operatorname{csch}^2 \gamma)(1 - \gamma \coth \gamma) - \gamma, \quad (B3)$$

and from Eq. (28)

$$\frac{dI}{d\gamma} = I \left[-\gamma^{-1} + \frac{\frac{1}{6} [\gamma^2 (dZ_{0R}/d\gamma) + 2\gamma Z_{0R}]}{(1 + \frac{1}{6} Z_{0R} \gamma^2)} \right]. \quad (B4)$$

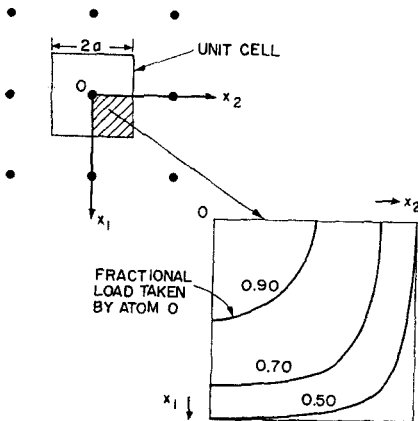


Fig. 17. Surface lattice and fractional load contours, showing fraction of normal load taken by atom at 0 for gas atom at various points on the equipotential surface passing through (0, 0, 2a); $a/b = 5.0$.

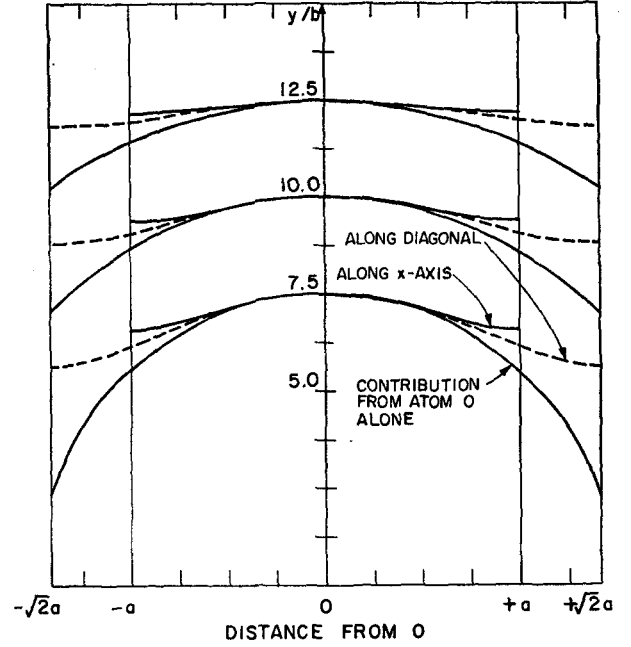


Fig. 18. Sections of equipotential surfaces calculated from Eq. (A1) using $a/b = 5.0$.

The quantities N and Z_{0R} are as specified in Sec. III.B and the adiabaticity f is given by Eq. (33).

APPENDIX C: SOLID ANGLE FACTOR

Consider the coordinate system shown in Fig. 4. Within the attractive potential well, the incident velocity of the gas atom may be written

$$\mathbf{u}_i = \begin{pmatrix} 0 \\ u_{i2} \\ u_{i3} \end{pmatrix}. \quad (C1)$$

Keeping terms to first order in α_1 and α_2 and transforming to an $x_1^* x_2^* x_3^*$ coordinate system such that the new $x_1^* x_2^*$ plane is parallel to the local surface, the incident velocity becomes

$$\mathbf{u}_i^* = \begin{pmatrix} 1 & 0 & -\alpha_2 \\ 0 & 1 & -\alpha_1 \\ \alpha_2 & \alpha_1 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ u_{i2} \\ u_{i3} \end{pmatrix} = \begin{pmatrix} -\alpha_2 u_{i3} \\ u_{i2} - \alpha_1 u_{i3} \\ u_{i3} + \alpha_1 u_{i2} \end{pmatrix}. \quad (C2)$$

The x_1^* and x_2^* components are unchanged by the collision (because the surface is now locally flat), but the outgoing x_3^* component becomes u_{r3} , the actual value of which will depend on the collision model used. Transforming back to the $x_1 x_2 x_3$ coordinate system, the

outgoing velocity within the potential well is

$$\mathbf{u}_r = \begin{pmatrix} \alpha_2(u_{r3} - u_{i3}) \\ u_{i2} + \alpha_1(\dots) \\ u_{r3} + \alpha_1(\dots) \end{pmatrix}. \quad (\text{C3})$$

Outside the potential well the x_3 component is reduced while the other two components are unchanged. Hence the outgoing velocity of the gas atom outside the potential well is

$$\mathbf{u}_{r\infty} = \begin{pmatrix} \alpha_2(u_{r3} - u_{i3}) \\ u_{i2} + \alpha_1(\dots) \\ (u_{r3}^2 - 2D/m_g)^{1/2} + \alpha_1(\dots) \end{pmatrix} = \begin{pmatrix} u_{r\infty 1} \\ u_{r\infty 2} \\ u_{r\infty 3} \end{pmatrix}. \quad (\text{C4})$$

From Fig. 4 it is seen that

$$\tan\phi = u_{r1}/u_r, \quad (\text{C5})$$

and

$$\cot\theta_r = u_{r3}/u_{r2}. \quad (\text{C6})$$

By using Eqs. (C4)–(C6) and assuming that ϕ is small so that $\tan\phi \cong \phi$, we obtain

$$\alpha_2 = \phi \tan\theta_i \csc\theta_r \{ [(\cot^2\theta_r/\cot^2\theta_i) + W]^{1/2} + (1+W)^{1/2} \}^{-1} + \phi O(\alpha). \quad (\text{C7})$$

Hence to lowest order in α_1 and α_2 we have

$$(\partial\alpha_2/\partial\phi)_{\theta_r} = \tan\theta_i \csc\theta_r \{ [(\cot^2\theta_r/\cot^2\theta_i) + W]^{1/2} + (1+W)^{1/2} \}^{-1}. \quad (\text{C8})$$

We note that this result is independent of the interaction model assumed.

Dissociation Behavior of Uranium Monocarbide

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Uranium monocarbide was found to lose uranium preferentially in the temperature range 2250°–2525°K until a constant vaporizing, nonstoichiometric composition approaching $\text{UC}_{1.1}$ was formed. Rates of evaporation of this composition, measured from 2190° to 2525°K by the Langmuir method, are described by $\log_{10} m(\text{UC}_{1.1(g)}) = 9.148 - 3.574 \times 10^4 T^{-1} (\text{g cm}^{-2} \cdot \text{sec}^{-1})$. Based on the decomposition process, $\text{UC}_{1.1(g)} \rightarrow \text{U}_{(g)} + n_1 \text{C}_{1(g)} + n_2 \text{C}_{2(g)} + n_3 \text{C}_{3(g)}$, the partial pressure of uranium is given by $\log_{10} P_{\text{U}_{(g)}} (\text{atm}) = 8.191 - 3.624 \times 10^4 T^{-1}$. The partial pressure of carbon, expressed as effective monatomic pressure, is $\log_{10} P_c = 8.341 - 3.608 \times 10^4 T^{-1}$. These data yield a heat of vaporization at 298°K of 235.1 ± 2.7 kcal/mole for the above vaporization process. The resultant standard heat of formation of $\text{UC}_{1.1(g)}$ at 298°K is -21.2 ± 4.1 kcal/mole if 125 ± 3 kcal/mole is taken as the heat of sublimation of uranium.

I. INTRODUCTION

High-temperature thermochemical data are necessary to the understanding of the behavior of the class of materials often called the interstitial refractory compounds. Uranium carbide, which is of practical interest to the nuclear industry, exhibits the general properties of this class, hence this study of its thermochemical properties is of interest in the more general sense.

It was the purpose of this investigation to study the vaporization behavior of uranium monocarbide in

vacuum using the Langmuir evaporation technique. Vaporization rates were measured over the temperature range 2190°–2525°K and the partial pressures of the gaseous species calculated. The heats of vaporization and formation at 298°K were calculated. Uranium monocarbide vaporization data have been previously reported by this laboratory¹ but uncertainties in the temperature measurements prompted repeating the investigation.

The dissociation pressure of uranium dicarbide has been investigated by Leitnaker and Witteman,²

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² J. M. Leitnaker and W. G. Witteman, J. Chem. Phys. **36**, 1445 (1962).