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SIMPLE CLASSICAL MODEL FOR THE SCATTERING OF GAS ATOMS FROM A SOLID SURFACE: III. ANALYSES FOR MONOENERGETIC BEAMS AND LOCK-IN DETECTOR SIGNALS*

R. E. Stickney, R. M. Logan, S. Yamamoto, and J. C. Keck

Department of Mechanical Engineering and
Research Laboratory of Electronics
Massachusetts Institute of Technology
Cambridge, Massachusetts

Various properties of the "hard-cube" model are considered. A closed-form analytical expression for the scattering of a monoenergetic molecular beam is examined and compared with the corresponding expression for a Maxwellian beam. The assumption that each incident molecule experiences only one collision with a single, independent lattice atom is studied, as is the assumption that the collision does not change the tangential velocity component of the gas molecule.

A recent analysis of lock-in detection of scattered molecular beams is employed to illustrate the dependence of the amplitude and phase of the output signal on the experimental parameters and on the collision model.

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Nomenclature

$\alpha_s = (2kT_s/m_s)^{1/2}$

$\alpha_i = (2kT_g/m_g)^{1/2}$

$B_1 = \frac{1+\mu}{2} \sin\theta_i \cot\theta_r - \frac{1-\mu}{2} \cos\theta_i$

$B_2 = \frac{dB_1}{d\theta_r} = \frac{1+\mu}{2} \sin\theta_i \csc^2\theta_r$

$B_3 = u_i/u_r = \sin\theta_r/\sin\theta_i$

ℓ_i = Distance from chopper to target

ℓ_r = Distance from target to detector

m_g = Mass of gas molecule

m_s = Mass of surface atom

μ = Mass ratio, m_g/m_s

T_g = Temperature of gas

T_s = Temperature of solid

θ_i = Incident angle, measured from surface normal

θ_r = Outgoing angle, measured from surface normal

u_i = Incident gas velocity (normal component = u_{ni})

u_r = Outgoing gas velocity (normal component = u_{nr})

v_i = Velocity (normal to surface) of surface atom before collision

ω = Modulation frequency, radians/sec

I. Introduction

Recently, we proposed and analyzed a simple classical model for the scattering of gas atoms from a solid surface (1,2). Since the theoretical results were shown to agree surprisingly well with the general, qualitative features of existing experimental data, we have suggested that this elementary model may provide a valid base for the development of a more exact scattering theory. The purpose of this paper is to consider (a) additional properties of the theoretical model that may be experimentally tested, (b) the limitations

of the present form of the model and analysis, and (c) the interpretation of scattering data obtained by lock-in detection techniques.

Many investigators are now attempting to reduce the velocity spread in the incident molecular beam because this spread tends to obliterate the details of the scattering data. In anticipation of their experimental results, the scattering characteristics of the "hard-cube" model are determined in Section II for a monoenergetic beam.

Several aspects of the basic assumptions and limitations of the hard-cube model are considered in Sections II and III. Existing experimental data for the scattering of ion beams from metal surfaces are discussed briefly to provide some insight into the nature of the appropriate collision model when the incident energy exceeds the thermal range.

In Section IV we consider the interpretation of signals associated with lock-in detection of scattered beams. The general expressions derived elsewhere (3) for the lock-in output signal are used to obtain numerical results illustrating the dependence of the signal amplitude and phase on the collision model and the experimental parameters.

II. Analysis of the Hard-Cube Model for a Monoenergetic Incident Beam

From previous analyses (1,2) of the hard-cube model it is simple to show that, for a monoenergetic beam, the flux scattered per unit angle at angle θ_r may be expressed as

$$\frac{1}{u_{ni}}\frac{dR}{d\theta_r} = \frac{B_2}{\sqrt{\pi}}\frac{u_i}{\alpha_s}(1+B_1\sec\theta_i)\exp\left(\frac{-B_1^2u_i^2}{\alpha_s^2}\right), \qquad (1)$$

where the symbols are defined in the nomenclature list and in Fig. 1. In this case, an interesting feature of the hard-cube model is that the molecules scattered at a given angle, θ_r, are monoenergetic, the expression for u_r being

$$u_r = \frac{\sin\theta_i}{\sin\theta_r}u_i = u_i/B_3. \qquad (2)$$

Since this predicts that u_r increases with decreasing θ_r, we see that the molecules scattered toward the surface normal

have higher speeds than those scattered toward the tangent. This characteristic, which results from the assumption that the tangential component of u_i is unchanged by the gas-solid collision, is a primary difference between the hard-cube model and the hard-sphere model which successfully describes experimental scattering data for incident energies of more than 500 eV. We shall return to this point in Section III.

In the following illustration we shall consider an Ar beam incident upon an Ag surface at angle $\theta_i = 50°$. Equation (1) has been plotted in Fig. 2 for two velocity ratios, $u_i/\alpha_s = 0.824$ and 9.64. For comparison, we have also plotted the corresponding curves for an incident beam having a Maxwellian distribution [Eq. (11) of Logan, Keck, and Stickney (2)]. The gas temperature in the Maxwellian case is chosen so that the average speed of the beam molecules, $1.33\alpha_i$, is equal to the speed of the monoenergetic beam.

An interesting feature of Fig. 2 is that the results for the monoenergetic case $u_i/\alpha_s = 9.64$ are almost identical to those for the Maxwellian case $T_s/T_g = 0.051$. This is surprising because our physical intuition leads us to expect that the distribution of velocities in the Maxwellian beam will cause its scattering pattern to be much broader than the corresponding pattern for the monoenergetic beam. As illustrated by the second comparison in Fig. 2, the agreement is not as close in the opposite extreme of a "cold" beam striking a "hot" target. Although the expected difference in breadth of the patterns is observed, the difference is not great.

Consider now the limiting case in which the speed of the monoenergetic beam is much larger than the mean speed of the solid atoms. In this limit, the solid atoms may be assumed to be at rest initially. Based on the hard-cube model, all of the gas molecules will be scattered at a single angle

$$\theta_r = \cot^{-1}\left(\frac{1-\mu}{1+\mu}\cot\theta_i\right) \tag{3}$$

with speed

$$u_r = u_i\left(1 - \frac{4\mu}{(1+\mu)^2}\cos^2\theta_i\right)^{1/2} \tag{4}$$

Notice that θ_r depends on μ but is independent of the incident speed, u_i. As discussed in Section III, the hard-cube

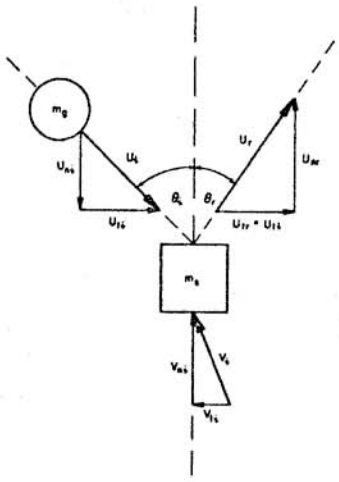

Fig. 1. The hard-cube model.

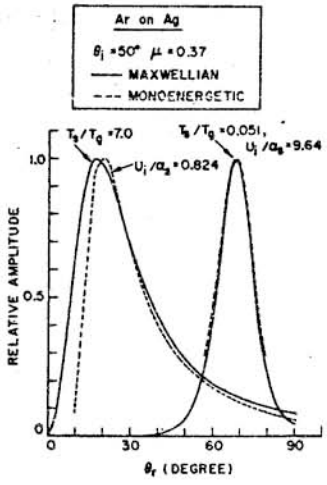

Fig. 2. Comparison of scattering patterns for monoenergetic and Maxwellian molecular beams. (Analysis based on the hard-cube model.)

model may not be valid at the high incident energies associated with this limit because the planar potential is no longer a realistic assumption. If, on the other hand, we attempt to achieve this limiting case by reducing the surface temperature to a very low value, we encounter the problem that the classical treatment of the surface atom velocity distribution is invalid when T_s is less than the Debye temperature of the solid.

For Ar striking Ag at an incident angle of $\theta_i = 50°$, Eq. (3) predicts that, in the limit $u_i/\alpha_s \to \infty$, all of the molecules will be scattered at the angle $\theta_r \simeq 69°$. We see in Fig. 2 that a speed ratio of $u_i/\alpha_s = 9.64$ is sufficiently high to cause the maximum of the scattering pattern to appear approximately at this angle, although the width of the pattern is still substantial.

As shown in Fig. 2, a small fraction of the gas molecules is scattered at angles below the tangent to the surface (i.e., $\theta_r > 90°$). This characteristic results from the fact that, as discussed previously (2), the closed-form expression for the hard-cube scattering pattern does not permit a given gas molecule to have more than one collision with the surface. Hence, the model should not be applied to cases in which μ is sufficiently large that a significant fraction of the gas molecules is scattered at angles greater than 90°. Although the "exact" analysis presented originally (1) provides for multiple collisions so that none of the molecules are scattered at $\theta_r > 90°$, we do not believe so simple a model can give a realistic treatment of multiple collisions. It follows, therefore, that the hard-cube analysis is limited, at present, to small μ.

III. Discussion of the Hard-Cube Model in the Light of Experimental Results for Fast Ion Scattering

The existing experimental and theoretical results for the scattering of thermal beams from solid surfaces are not sufficiently exact to establish a general collision model. Hence, it may be useful to consider also the scattering results for beams of higher energy, since these data provide a description of the nature of the collision model in one limiting case.

The results of experimental investigations of the scattering of fast (i.e., energies greater than ~1000 eV) ions from metal surfaces indicate that a fraction of the

collisions may be considered as an elastic two-body interaction of the primary ion with a single atom in the solid. (See, for example, the recent reviews by Snoek and Kistemaker (4) and by Kaminsky (5).) By elastic we mean that the translational energy of the system, ion plus solid atom, is conserved (e.g., no electronic excitation). This does not necessarily mean, however, that the ion is scattered specularly with no energy loss. It appears that the solid atom behaves as a free particle when the collision time is small relative to the period of lattice vibrations. The validity of this collision model is clearly demonstrated by the experimental results of Datz and Snoek (6) which show that the energy distribution of Ar^+ scattered from Cu contains separate peaks for the common isotopes of Cu.

Because of the difficulties of conducting scattering experiments with low-energy ion beams, we do not have sufficient results to determine how low the incident energy may be before the two-body collision model must be replaced by one that accounts for the effect of the lattice on the interaction. Smith (7) has recently reported that the two-body model is still valid at incident energies as low as 500 eV for He^+, Ne^+, and Ar^+ on Mo and Ni surfaces. Although several experiments (8)-(12) have been conducted at energies below 100 eV, the results are not in good agreement and the majority are unreliable because, as discussed by Kaminsky (5), it is suspected that the surfaces were contaminated. Among these experiments, the most recent are the energy distribution measurements of Veksler (8) for 10-250 eV Cs^+ and Rb^+ scattered from Mo. The results led Veksler to assume that more than a single lattice atom is involved in the elastic collision of a low-energy ion with the surface. Based on this assumption, he estimates that at an incident energy of 20 eV the ion interacts elastically with a group of lattice atoms having an effective mass that is approximately three times that of a single atom. The problem may be complicated, however, by the fact that the probability of multiple collisions is high in Veksler's experiments because the mass ratio is of the order of unity (e.g., μ equals 0.9 and 1.4 for Rb^+ and Cs^+ on Mo, respectively).

Although the possible final states of elastic binary collisions may be determined from the conditions of energy and momentum conservation, the probability of these states depends, of course, on the form of the interaction potential. The potential form depends strongly on the incident

energy, varying from Coulombic repulsion of the nuclei at extremely high energies to impulsive repulsion (hard sphere) at energies low enough to prevent significant penetration of the electron clouds (5). The hard-sphere approximation is valid, for example, for incident energies below 1×10^4 eV for He^+ on Ag, and below 1.4×10^5 eV for Ar^+ on Ag. The hard-sphere collision diameter increases with decreasing energy, and this, together with the smoothing effect of the conduction electrons (13), lends support to the assumption that the interaction potential is approximately planar at very low incident energies. This assumption is also supported by the fact that the hard-sphere scattering distributions computed by Goodman (14) are much broader than the experimental distributions, unless the collision diameter is assumed to be considerably larger than the lattice spacing.

From these considerations we conclude: (a) There is no definite experimental evidence to discourage the use of the elastic two-body collision model at low incident energies, as long as μ is sufficiently small to cause multiple collisions to be negligible and the intermolecular potential is strongly repulsive so that the interaction time is not large relative to the period of lattice vibrations. Since, however, the time required for molecules having thermal energies to travel one angstrom is of the same order of magnitude as the characteristic vibrational period (i.e., $\sim 10^{-12}$ sec), it would be of interest to modify the hard-cube model to include the effect of lattice coupling on the motion of the solid atoms. (b) It appears reasonable to assume that the interaction potential changes from spherical to planar as the incident energy approaches zero. Both conclusions serve as partial justification for employing the hard-cube model within the appropriate ranges of the mass ratio, incident energy, and interaction potential. A stronger justification is, that within the appropriate range, the major characteristics of existing experimental scattering data may be described qualitatively by means of the model.

In its present elementary form, the hard-cube model does not provide a satisfactory description of the scattering patterns in cases in which the magnitude of μ approaches, or even exceeds, unity (e.g., Hg on LiF). The last problem is especially interesting, as discussed in detail elsewhere (15), the scattering characteristics for $\mu > 1$ appear to be quite similar to those for $\mu < 1$. This

may be an indication that, instead of considering multiple two-body collisions when $\mu > 1$, it may be more profitable to investigate the influence of the lattice on the effective mass of the surface.

IV. Analysis of Lock-In Detection of Scattered Beams

In most experimental studies of the scattering of modulated molecular beams from solid surfaces, the detector signal, $S_n(t)$, is proportional either to the instantaneous density or flux of the scattered beam molecules. By means of the lock-in amplifier (i.e., narrow-band amplification and phase-sensitive detection), this ac signal is converted to a dc output signal that is proportional to A_n, the average value of the fundamental Fourier component of $S_n(t)$. In practice, A_n is maximized by adjusting Φ_n, the phase angle of the fundamental component of $S_n(t)$ relative to the reference signal from the chopper. (A more detailed description of lock-in detection of molecular beams is given elsewhere (3).)

It is usual to assume, for the sake of simplicity, that the magnitude of A_n measured in scattering experiments is directly proportional to the density (or flux, dependent on the detector design) of the scattered molecules. Also, it is tempting to assume that the measured change of the phase angle may be expressed as a simple function of the "temperature" or mean speed of scattered molecules (16). Our purpose here is to consider briefly the validity of these assumptions.

Recently, we have derived general expressions for A_n and Φ_n as functions of the modulation frequency, the molecular velocity distribution, and the pertinent dimensions for molecular beams scattered from solid surfaces (3). The analysis is essentially an extension of the work of Harrison, Hummer, and Fite (17) and of Fite, Hummer, and Wilkins (18). These methods are applied here to determine the dependence of A_n and Φ_n on the nature of the gas-solid collision model. Three different collision models are considered:

1) Hard-Cube Model (1,2)
2) Correlated Maxwellian Model: It is assumed that, for all gas molecules u_r is correlated with u_i by the relation $u_r = u_i(T_r/T_g)^{1/2}$. Hence, a Maxwellian beam is scattered with a Maxwellian distribution having a temperature T_r that is not

necessarily equal to T_s or T_g.

3) Uncorrelated Maxwellian Model: It is assumed that the values of u_i and u_r of any molecule are uncorrelated, but the scattered distribution is Maxwellian with temperature T_r that is not necessarily equal to T_s or T_g.

Although the two Maxwellian models may be unrealistic, they have been selected because of their behavior in the following limiting cases. As $T_r \to T_g$, the correlated Maxwellian model predicts specular reflection. As $T_r \to T_s$, the uncorrelated Maxwellian model predicts complete accommodation (i.e., the state of the scattered molecules is independent of the incident state because the molecules come to equilibrium with the surface before being re-emitted).

Since Hinchen and Foley (16) have conducted the most detailed experimental measurements of the phase shift of scattered beams, we have chosen to consider their apparatus in our investigation of the dependence of Φ on the collision model. Numerical results for one specific case are shown in Fig. 3. The curve labeled "Correlated Maxwellian" was computed from the numerical data of Harrison et al. (17) by the procedure devised by Hinchen and Foley (15); this procedure gives results that equal those computed on the basis of the correlated Maxwellian model. The phase angle for the hard-cube model was computed at the maximum of the scattering distribution, and the effective temperature T_r was defined by the relation $U_d^*(\theta_r) = (2kT_r/m_g)^{1/2}$, where $U_d^*(\theta_r)$ is the most probable speed of molecules scattered into angle θ_r. (See Eq. (20) of Logan, Keck, and Stickney (2).) From the results shown in Fig. 3, we conclude that the interpretation of Φ in terms of a mean speed or an effective temperature depends on the nature of the assumed collision model.

Consider the question of whether or not the lock-in signal amplitude, A_n, is always directly proportional to the flux (or density) of the scattered beam. Using the hard-cube model and the analysis of lock-in detection (3), we may compute scattering patterns, A_n vs θ_r, for various modulation frequencies. The results for a particular example are shown in Fig. 4. For comparison we have included the flux distribution, which is computed for a steady (i.e., unmodulated) beam. Although A_n appears to be directly proportional to the flux when the modulation frequency is 100 cps, we notice a deviation from this relationship at 3600 cps. In a second example, which is presented in Fig.5,

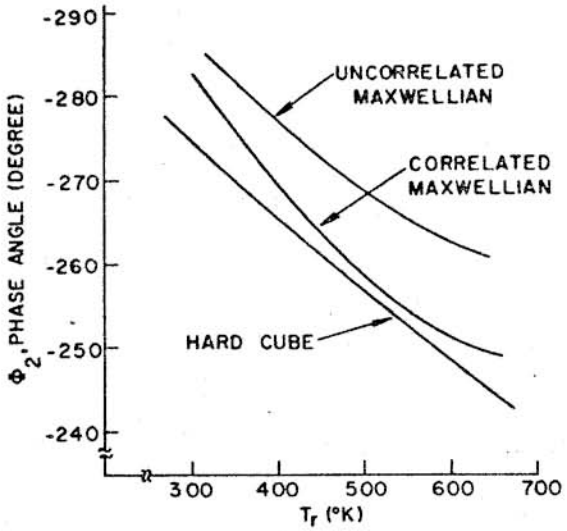

Fig. 3. Dependence of phase angle on the effective temperature of the scattered molecules for three collision models. Conditions: Ar on Pt, $\mu = 0.2$, $T_g = 300^{o}K$, $\theta_i = 50^{o}$, $\ell_i = 5.16$ cm, $\ell_r = 5.32$ cm $\omega = 22{,}600$ radians/sec (3600 cps).

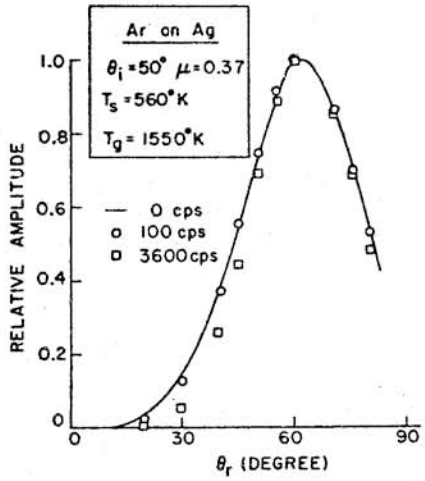

Fig. 4. Dependence of normalized scattering pattern on modulation frequency. (Analysis based on the hard-cube model.)

the parameter X is defined as the ratio of the characteristic "molecular flight time," ℓ_i/α_i, to the modulation period, $1/\omega$, which gives

$$X = \frac{\omega \ell_i}{\alpha_i}, \tag{5}$$

where ω is the modulation frequency (radians/sec), and ℓ_i is the distance from chopper to target. When $X \ll 1$, the amplitude of $S_n(t)$ equals that of the unmodulated beam. When $X \gg 0$, the amplitude of $S_n(t)$ deviates from that of the unmodulated beam because the finite molecular speed results in dispersion of the signal pulses. (This topic is considered in more detail by Yamamoto and Stickney (3).) Hence, the agreement of the scattering patterns for modulated and unmodulated beams will decrease with increasing X as shown in Fig. 5.

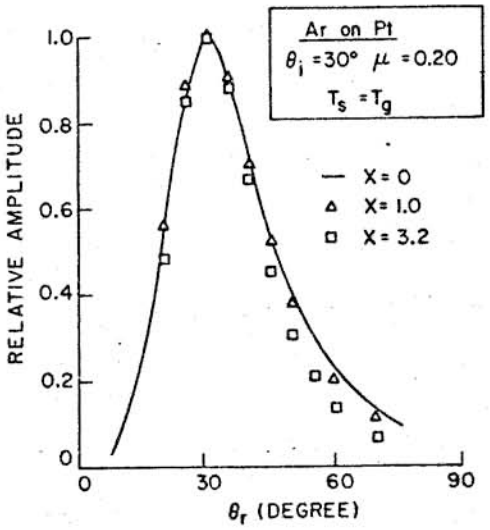

Fig. 5. Dependence of normalized scattering pattern on the parameter $X = \omega \ell_i/\alpha_i$. (Analysis based on the hard-cube model.)

References

1. Logan, R. M. and Stickney, R. E., J. Chem. Phys. 44, 195 (1966).
2. Logan, R. M., Keck, J. C., and Stickney, R. E., In Rarefied Gas Dynamics, Proc. 5th Intern. Symp., Oxford, England (1966), Academic Press, New York (to be published).
3. Yamamoto, S. and Stickney, R. E., (to be published).
4. Snoek, C. and Kistemaker, J., In Advances in Electronics and Electron Physics, 21, 67 (L. Marton, ed.) Academic Press, New York (1965).
5. Kaminsky, M., Atomic and Ionic Impact Phenomena on Metal Surfaces, Academic Press, New York (1965).
6. Datz, S. and Snoek, C., Phys. Rev. 134, A347 (1964).
7. Smith, D. P., Bull. Am. Phys. Soc. 11, 770 (1966).
8. Veksler, V. I., Soviet Physics JETP 15, 222 (1962); and Soviet Physics Solid State 4, 1043 (1962).
9. Gurney, R. W., Phys. Rev. 32, 467 (1928).
10. Read, G. E., Phys. Rev. 31, 629 (1928).
11. Sawyer, R. B., Phys. Rev. 35, 1090 (1930).
12. Longacre, A., Phys. Rev. 46, 407 (1934).
13. Harrison, W. A., Phys. Rev. 136, A1107 (1964).
14. Goodman, F. O., In Rarefied Gas Dynamics, Proc. 5th Intern. Symp., Oxford, England (1966), Academic Press, New York (to be published).
15. Stickney, R. E., In Advances in Atomic and Molecular Physics, Vol. III, (D. R. Bates and I. Estermann, editors), Academic Press, New York (to be published).
16. Hinchen, J. J. and Foley, W. M., Report D910245-7, United Aircraft Research Labs, 1965. these Proceedings, pg. 448.
17. Harrison, H., Hummer, D. G., and Fite, W. L., J. Chem. Phys. 41, 2567 (1964).
18. Fite, W. L., Hummer, D. G., and Wilkins, J. E., General Atomic Report GA-3832, June 19, 1963.