A Mathematical Description of Gas-Surface Interactions Based on Reciprocity

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The general problem of the interaction between a monatomic gas and a solid surface is investigated from a mathematical point of veiw by the use of a scattering kernel. Based upon the assumptions that any scattering kernel must be non-negative, normalized in half velocity space, and satisfy the reciprocity relation, a series of product solutions is obtained in each of three coordinate systems. The first solution in each series is obtained in closed mathematical form, while subsequent solutions can be evaluated numerically. It is shown that the first scattering kernel in rectangular coordinates adequately describe experimentally observed results of gas-surface interaction. This solution has two parameters which are shown to be related to a tangential and normal thermal accommodation coefficient. This scattering kernel is integrated with the appropriate weighting function in order to obtain mean reflected properties.

Nomenclature

A_x, A_y, etc.	=	constant ≥ 1 related to α_x, α_y by Eq. (27)
I	=	reflected relative molecular flux
$P(v',v), P$	=	scattering kernel
$P_x(v_x', v_x)$, $P_y(v_y', v_y)$, etc.	=	scattering kernel in corresponding coordinate direction
R	=	gas constant per unit mass
S, S_x', etc.	=	dimensionless velocity, $v/(2RT_w)^{1/2}$, $v_x'/(2RT_w)^{1/2}$, etc.
T_w	=	wall or surface temperature
v	=	reflected molecular velocity
v'	=	incident molecular velocity
v_x, v_y', etc.	=	velocity component in corresponding coordinate
α	=	thermal accommodation coefficient
α_x, α_y, etc.	=	accommodation coefficient in corresponding coordinate direction

Introduction

THE interaction between a gas and a solid surface is important for many reasons, e.g., to specify the boundary conditions for fluid flow, to determine temperature jump and slip at a surface, or to provide a boundary condition for the Boltzmann equation under rarefied flow conditions. Maxwell, in 1879, proposed that when a gas reflects from a surface a certain fraction of the molecules is reflected diffusely and the remainder reflected specularly. This model is still probably the most widely used to describe the gross gas-surface interaction.

Nocilla[1] has more recently proposed that reflected molecules be represented by a drifting Maxwellian velocity distribution. This model has the advantage that it can be made to fit the observed reflected flux distribution and, unlike Maxwell's model, is continuous in velocity space. However, the static temperature and drifting velocity of the reflected distribution are empirical functions of incident velocity and will not, in general, reproduce the equilibrium velocity distribution for the case of a gas in equilibrium with the surface.

Epstein[2] determined a scattering kernel that would satisfy the equilibrium reflected velocity distribution. His model contains an empirical function of incident speed which is determined from the experimental thermal accommodation coefficient. This kernel, like Maxwell's, is also discontinuous in velocity space and is therefore not useful for a detailed description of the gas-surface interaction.

Cercignani,[3] Kuscer et al.,[4] and Wenaas[5] have shown that any gas-surface interaction model, in addition to satisfying the obvious condition of maintaining the equilibium velocity distribution at the wall temperature, must satisfy detailed balancing or the reciprocity relation. It is easy to see that detailed balancing must be maintained at the gas-surface interface when the gas and surface are in equilibrium at the wall temperature. The introduction of a scattering kernel, which gives the reflected probability density as a function only of incident and reflected velocity vectors, implicitly assumes that a molecule interacts with the wall on an individual basis, independent of other molecules. In other words, a molecule with velocity v doesn't "know" whether it is in a monoenergetic molecular beam or part of a gas in equilibrium with the wall. This result permits the reciprocity condition on the scattering kernel, which was derived for equilibrium condition, to be applied for nonequilbrium conditions.

Basic Equations

The time-independent interactions between a gas and a surface may be expressed mathematically by means of a scattering kernel, $P(v,v)$, which relates the probability of a molecule with velocity v' being scattered by a surface into a velocity close to v. Using the scattering kernel, it can be shown[3] that the velocity distribution of reflected molecules, f^+, is related to the distribution of incident molecules, f^-, by

$$f^+(v) = -\frac{I}{v_y}\int_{-\infty}^{\infty}\int_{-\infty}^{0}\int_{-\infty}^{\infty} v_y' P(v',v) f^-(v')\,dv_x' dv_y' dv_z' \quad (1)$$

Equation (1) is the basic boundary condition of the time-independent Boltzmann equation for a gas in contact with a solid boundary.

Kuscer et al.[4] pointed out the importance of reciprocity in connection with a mathematical description of gas-surface interaction. The reciprocity relation which must be satisfied by any scattering kernel is

$$-v_y' P(v',v)\exp(-v'^2/2RT_w) = v_y P(-v,-v')\exp(-v^2/2RT_w) \quad (2)$$

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In addition, $P(v'v)$ must satisfy the obvious condition of being non-negative and, for no mass exchange with the surface, normalized in half velocity space. In other words,

$$P(v',v) \geq 0 \quad \text{for} \quad \begin{matrix} v_y' \leq 0 \\ v_y \geq 0 \end{matrix} \tag{3}$$

and

$$\int_{-\infty}^{\infty}\int_{0}^{\infty}\int_{-\infty}^{\infty} P(v',v)\,dv_x dv_y dv_z = 1 \tag{4}$$

The problem addressed is to find expressions for $P(v',v)$ that satisfy the conditions expressed in Eqs. (2-4) also contain the experimentally observed characteristics of gas-surface interactions.

Mathematical Solution of $P(v',v)$

Borrowing from Maxwell the idea that each velocity component in a gas is independent, it is assumed that the interaction of each velocity component with the surface is independent. This is equivalent to assuming that $P(v',v)$ can be represented by a product of independent probability functions, one for each coordinate direction. The scattering kernel can therefore be written for rectangular coordinates as

$$P(v',v) = P_x(v_x',v_x)P_y(v_y',v_y)P_z(v_z',v_z) \tag{5}$$

Similar expressions can be written in cylindrical and spherical coordinates. See Fig. 1 for coordinate systems. The derivation of the coordinate kernel based upon Eqs. (2-4) will be given for only one coordinate. The derivation of P_y will be outlined with only important results given for the others since the mathematical processes are similar. In the following analysis the arguments of scattering kernels are omitted for simplicity unless needed for clarity.

From an inspection of Eqs. (3) and (5) it is obvious that each coordinate kernel must be non-negative. For P_y this condition can be written as

$$P_y \geq 0 \text{ for } v_y' \leq 0,\ v_y \geq 0 \tag{6}$$

In a like manner, Eq. (5) can be substituted into Eq. (2), and since the velocity components are independent, permits writing

$$-v_y' \exp(-S_y'^2)P_y(v_y',v_y) = v_y \exp(S_y^2)P_y(-v_y,-v_y') \tag{7}$$

where S is speed ratio. Equation (4) becomes for the y coordinate

$$\int_0^{\infty} P_y\,dv_y = 1 \tag{8}$$

Equations (6-8) are therefore the basic equations that must be satisfied by P_y.

To simplify Eq. (7), a new function, $g_y(v_y',v_y)$, is defined as

$$g_y = (P_y/v_y)\exp[(A_y^2-1)S_y'^2 + A_y^2 S_y^2] \tag{9}$$

where A_y is a constant equal to or greater than unity. Substituting Eq. (9) into Eq. (7) and (8) yields for the reciprocity relation

$$g_y(v_y',v_y) = g_y(-v_y,-v_y') \tag{10}$$

and for the normalization condition

$$\int_0^{\infty} v_y g_y \exp[-(A_y^2-1)S_y'^2 - A_y^2]\,dy_y = 1 \tag{11}$$

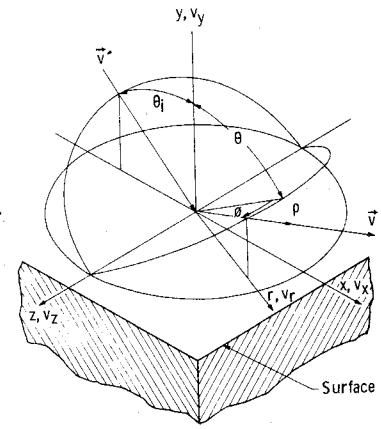

Fig. 1 Coordinate systems.

From Eq. (3) and (9) it can be seen that g_y must, like P_y, be non-negative.

Let g_y be represented by a double infinitive sum as follows

$$g_y = \sum_{j=0}^{\infty}\sum_{i=0}^{\infty} b_{ij} v_y'^i v_y^j \tag{12}$$

Reciprocity as expressed by Eq. (10) requires that

$$b_{ij} = (-1)^{i+j} b_{ji} \tag{13}$$

Taking advantage of the symmetry expressed by Eq. (13), the infinite sum can be rewritten as a double sum on the diagonals of the array of terms as follows

$$g_y = \sum_{n=0}^{\infty} B_n Y_n(v_y',v_y) \tag{14}$$

where

$$Y_n = \sum_{k=0}^{\infty} d_{n,k}(v_y'v_y)^k [v_y^n + (-v_y')^n] \tag{15}$$

Equation (15) automatically satisfies the reciprocity relation. The only restrictions upon Eq. (15) is that it be non-negative and normalized according to Eq. (11).

It is now assumed that each Y_n individually satisfies Eq. (11), in other words, for arbitrary B_n's, subject to

$$\sum_{n=0}^{\infty} B_n = 1$$

Substituting Eq. (15) into Eq. (11), integrating, and equating coefficients of like power of v_y', recurrence relations are obtained for $d_{n,k}$ in terms of n, k, and A_y. These relations are presented in detail in Ref. 6.

Similar expressions can be obtained for the coefficients in the other coordinate directions and in each of the other coordinate systems. These results are also given in Ref. 6.

For $n=0$, the scattering kernel in each coordinate system can be obtained in closed mathematical form from the infinite series. The analytic solutions for these scattering kernels in rectangular, cylindrical, and spherical coordinate systems, respectively, are

$$P(v',v) = \frac{2A_y^2 A_x A_z}{(2RT_w)^{3/2}} S_y I_0(-2A_y\sqrt{A_y^2-1}\,S_y'S_y)$$
$$\times \exp[-(\sqrt{A_x^2-1}S_x' - A_x S_x)^2 - (A_y^2-1)S_y'^2$$
$$-A_y^2 S_y^2 - (\sqrt{A_z^2-1}S_z' - A_z S_z)^2] \tag{16}$$

$$P(v',v) = \frac{2A_y^2 A_r^2}{\pi(2RT_w)^{3/2}} S_y I_0(-2A_y\sqrt{A_y^2-1}S_y'S_y)$$
$$\times \exp[-(A_y^2-1)S_y'^2 - A_y^2 S_y^2]$$
$$\times I_0(2A_r\sqrt{A_r^2-1}S_r'S_r)$$
$$\times \exp[-(A_r^2-1)S_r'^2 - A_r{}^r S_r^2] \quad (17)$$

$$P(v',v) = \frac{2A_\rho^3 S_y}{\pi(2RT_w)^{3/2}} \frac{I_1(2A_\rho\sqrt{A_\rho^2-1}S'S)}{\sqrt{A_\rho-1}S'S}$$
$$\times \exp[-(A_\rho{}^2-1)S'^2 - A_\rho{}^2 S^2)] \quad (18)$$

For the special case of $A_x=A_y=A_z=A_r=A_\rho=1$, each of the previous equations reduces to

$$P(v',v) = (2/\pi)(2RT_w)^{-2} v_y \exp(-v/2RT_w) \quad (19)$$

which is the scattering kernel for complete accommodation of a gas to a surface. At the other extreme, for $A_x=A_y=A_z\to\infty$, Eq. (16) reduces to

$$P(v',v) = \delta(v_x'-v_x)\delta(v_y'+v_y)\delta(v_z'-v_z) \quad (20)$$

which is specular reflection. Likewise, for $A_y=A_r=A\to\infty$, Eqs. (17) and (18) reduce to

$$P(v',v) = \frac{\delta(v_y'+v_y)\delta(v_r'+v_r)}{2\pi v_r} \quad (21)$$

and

$$P(v',v) = v_y\delta(v'+v)/(\pi v^3) \quad (22)$$

Equation (22) is the scattering kernel for Diffuse Elastic or Lambert scattering.

For the special case of a gas with a Maxwellian velocity distribution incident upon a surface, the reflected distribution can be determined. Assuming

$$f^- = (2\pi RT^-)^{-3/2}\exp(-v'^2/2RT^-) \quad (23)$$

and for simplicity that $A_x=A_y=Z_z=A_r=A_p=A$, Eq. (23) and each scattering kernel given by Eqs. (16), (17), or (18) can, in turn, be substituted into Eq. (1) to obtain the reflected velocity distribution. The result in each case is identical and is equal to

$$f^+ = (2\pi RT^+)^{-3/2}(T^-/T^+)^{1/2}\exp(-v^2/2RT^+) \quad (24)$$

where

$$T^+ = T^-(A^2-1+T_w/T^-)/A^2$$

or rearranging, yields

$$A^{-2} = \frac{T^+-T^-}{T_w-T^-} \quad (25)$$

which is the definition of the thermal accommodation coefficient, α. Thus

$$A^{-2} = \alpha \quad (26)$$

or, generalizing for the case where the A's are not necessarily equal, we let

$$A_x^{-2} = \alpha_x,\ A_y^{-2} = \alpha_y,\ \text{etc.} \quad (27)$$

The term $(T^-/T^+)^{1/2}$ in Eq. (24) comes about from the conservation of molecules at the surface. Thus, the density of reflected molecules is $(T^-/T^+)^{1/2}$ times that of the incident density.

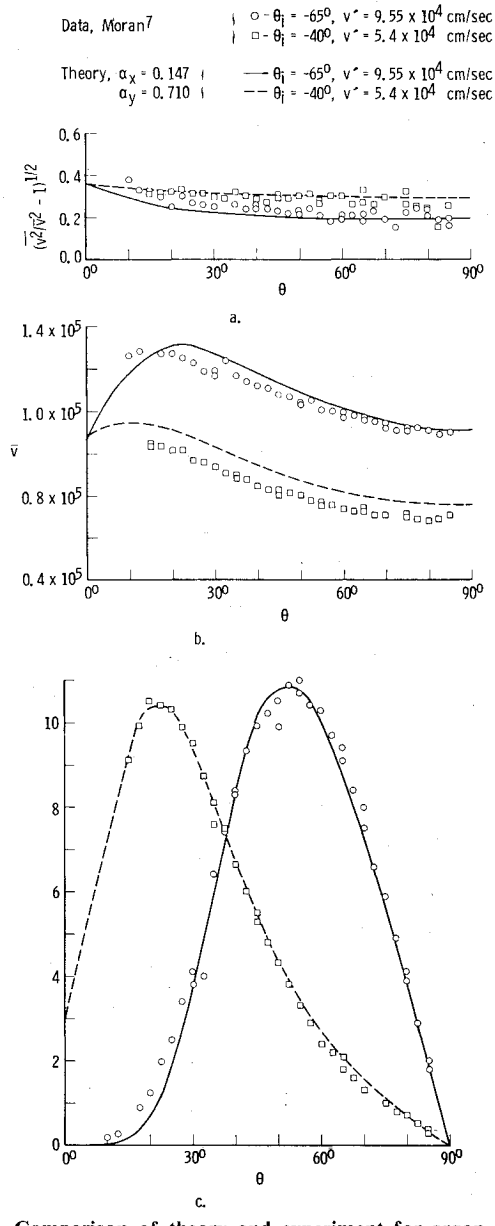

Fig. 2 Comparison of theory and experiment for argon scattered from 1273° K platimum: a) $(\bar{v}^2/\bar{v}^2-1)^{1/2}$ vs θ; b) mean speed, $\bar{v}$ (cm/sec), vs θ; c) relative flux, I vs θ.

Comparison of Theory with Experiment

To adequately check the theoretical results, it is desirable to have experimental measurements on several reflected molecular properties from a given surface for various incident angles and velocities. One of the most complete experimental investigations of the interaction between a monatomic gas and an isotropic surface is that done by Moran[7] for argon on platinum. He measured the reflected time-of-flight signal as a function of reflected angle for two incident energies at several incident angles from which several reflected properties are determined. These include reflected relative flux, I, mean speed, $\bar{v}$, and mean squared velocity, $\overline{v^2}$, as a function of direction. The solution for $n=0$ in rectangular coordinates (Eq. 16) is adequate to describe these experimental results.

Equation (16) must be integrated with the appropriate weighting function in order to obtain mean reflected properties. It was not possible to obtain these properties in closed mathematics form, therefore numerical integration was

required. Values of α_x, α_y, and α_z were determined such that the reflected molecular flux distributions obtained from Eq. (16) best fit the experimental results in a least-squares sense. All the data presented by Moran for a given target was used in this curve fit where $20° \leq \theta_\theta \leq 80°$ and $v' = 5.4 \times 10^4$ cm/sec and 9.55×10^4 cm/sec. Values of α determined were: $\alpha_x = -\alpha_z = 0.147$ and $\alpha_y = 0.710$. After the α's were determined, $\bar{v}$ and $\bar{v^2}$ were calculated. Figure 2 shows the results of this calculation compared to the experimental results for two representative conditions. The comparisons with the remaining results is included in Ref. 6. Notice that not only is there agreement between theory and experiment for the reflected flux distribution, but there is also fairly close agreement for the reflected mean speed and $(\bar{v^2}/\bar{v}^2 - 1)^{1/2}$. The only consistent disagreement is in the mean speed in Fig. 2 where the theory is higher than the expermental results by approximately 10% and 5%, for the two conditions.

Miller and Subbarao[8] have presented an experimental verification of the reciprocity relation. They measured the ratio of scattering kernels for two different conditions and for the inverse conditions and found, for six sets of conditions, that reciprocity (Eq. 2) does indeed hold under nonequilibrium conditions.

Conclusions

The gas-surface interaction model developed in this paper accurately describes the actual scattering of a monatomic gas from an isotropic surface. The reciprocity relation dictates the effect of incident gas velocity and directions on the scattered properties. Thus, based upon the present results, directional thermal accommodation coefficients can be determined for a surface over a limited range of parameters, and the theory then used to calculate scattering characteristics over more extreme ranges of parameters. This has been confirmed experimentally by Miller and Subbarao.[8]

For other, more general, surfaces it may be necessary to construct a scattering kernel which is a linear combination of kernels such as given by Eqs. (16-18) or an arbitrary number of each with varying values of α_x, α_y, etc. This is possible since Eqs. (2-4) are linear in the scattering kernel.

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