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# A DISCUSSION OF ENERGY AND MOMENTUM TRANSFER IN GAS-SURFACE INTERACTIONS

R. E. Stickney

ARO, Inc.

# February 1966

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# A DISCUSSION OF ENERGY AND MOMENTUM TRANSFER IN GAS-SURFACE INTERACTIONS

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#### FOREWORD

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This technical report has been reviewed and is approved.

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## ABSTRACT

The principal mechanisms of energy and momentum transfer between gas atoms and solid surfaces are considered for the range of impact energies encountered in high-speed flight (e.g., up to 10 ev). Included within are (1) introductory discussions of the nature of surfaces, intermolecular potentials, adsorption, and basic gas-surface interaction processes, (2) a critical survey of the definitions of energy and momentum accommodation coefficients, (3) summaries of existing theoretical and experimental results pertaining to the energy accommodation and directional distribution of atoms scattered from a surface, (4) an attempt to formulate the main parameters and regimes of gas-surface interactions, and (5) suggestions concerning future investigations.

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# NOMENCLATURE

a	Interaction parameter
D	Depth of the potential well
Ε	Translational energy
Ea	Heat of adsorption (approximately equivalent to D)
Ei	Translational energy of incident particles
Er	Translational energy of scattered particles
Ew	Translational energy of particles leaving the surface in a state of thermal equilibrium with the surface
h	Planck's constant
k	Boltzmann's constant
L	Characteristic length of the repulsive interaction
L'	Ratio of characteristic length for the attractive potential to the corresponding length for the repulsive potential
M, m	Mass of particle
'n	Rate of desorption of adatoms from a surface or number of incident particles striking the surface per unit area and unit time
$P_i$	Normal component of momentum for incident particle
$P_r$	Normal component of momentum for scattered particle
$P_W$	Normal component of momentum for complete accommodation
Q	Actual heat-transfer rate
Qo	Heat-transfer rate if gas particles attain state of thermal equilibrium with surface before leaving the surface

r	Distance between centers of the particles
r <sub>o</sub>	Separation distance for V = $D$
r <sub>i</sub>	Speed of particles
Т	Temperature
Ti	Temperature of impinging gas
Tr	Effective temperature of scattered particles
$T_w$	Temperature of the surface
V, v	Velocity of particles before collision
x, y, z	Coordinates used to describe the position of the particle relative to the surface
α	Energy accommodation coefficient
$\theta_{\mathrm{D}}$	Debye temperature of the solid
λ	de Broglie wavelength
$\mu$ $\equiv$	Ratio of the mass of the gas particles to the mass of the surface atoms
ν	Empirical factor (approximately equivalent to the vibrational frequency of the adatoms)
σ	Density of adatoms on a surface or coefficient of tangential momentum transfer
$\sigma^{1}$	Coefficient of normal momentum transfer
τ, τ*	Interaction time parameter
<sup>r</sup> i	Tangential component of momentum for incident particle
<sup>r</sup> r	Tangential component of momentum for scattered particle
ω	Vibrational frequency of surface atoms

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# SECTION I

At extremely low gas densities, the dominant processes which govern energy, momentum, and mass transfer between a gas and a solid are entirely different from those associated with continuum densities. From the viewpoint of fluid mechanics, this change in the dominant transport processes occurs in the transition regime between continuum flow and free molecule flow (Ref. 1). In continuum flow, the nature of the collisions between gas molecules in the immediate vicinity of the solid surface is the controlling factor (i.e., the transfer rates are limited by the transport properties of the gaseous boundary layer or buffer region which exists between the solid and the free stream). In free molecule flow, the transport processes depend entirely upon the collisions of gas molecules with the surface, the gas density being so low that collisions between gas molecules are insignificant (i.e., there is no buffer region in this case, and the free-stream molecules may impinge directly upon the surface). The latter case, the transport processes of gas-surface interactions or collisions, is the subject of this report.

In the free molecule and transition flow regimes associated with highaltitude flight, the aerodynamic drag and heat transfer depend upon the efficiencies (i. e., accommodation coefficients) of the momentum and energy transfer processes of gas-surface interactions. This presents a problem because at the present time the magnitudes of these efficiencies are not known for the interaction energies of high-speed flight. \* There are, however, experimental and theoretical data for lower energies (i. e., thermal energies). The purpose of this report is to review the existing information on momentum and energy transfer in gas-surface interactions and then attempt to formulate a qualitative description of the principal interaction regimes and parameters for the energy range of interest, 0 to 10 ev.

# SECTION II PRELIMINARY CONSIDERATIONS

The physical theories of processes occurring at a gas-solid interface are, at the present time, much less developed than those pertaining

<sup>\*</sup>The approximate range of these interaction or collision energies is 0 to 10 ev (electron volts). For example, the translational energy of a nitrogen atom at a speed of 20,000 ft/sec is 2.8 ev. Throughout this report it is assumed that the reference frame is fixed on the solid; therefore, the interaction energy is equivalent to the translational energy of the incident (impinging) gas molecule.

to processes occurring in either the bulk of a gas (Ref. 2) or the bulk of a solid (Ref. 3). This situation is obviously a result of the complexities that the interface introduces into the common two-fold problem of obtaining meaningful experimental data and formulating realistic theoretical models. Before considering this problem in detail, it is convenient to discuss the general aspects of gas-surface interactions.

### 2.1 SOLID SURFACES

First the nature of a solid surface which is perfectly clean (i.e., free of contaminants and impurities) will be considered. A surface is not a clearly defined region because an adequate description usually includes more than just the outermost layer of atoms. The properties of this thin boundary region between two homogeneous phases--solid and gas (or vacuum)--strongly affect all of the basic processes of mass, momentum, and energy transfer between the phases. The complex nature of surface properties results primarily from the fact that surfaces, unlike the interior of homogeneous gases or solids, are inherently asymmetric. The asymmetrical forces acting on surface atoms cause the lattice spacings and vibrational amplitudes to differ from corresponding values in the bulk of the solid (Refs. 4 and 5). Because of these complexities, it is extremely difficult to formulate a theoretical model of a surface which is both realistic and tractable (Refs. 5 through 7).

Experimental results indicate that surfaces are affected by various processes as the temperature increases. At a temperature which is approximately one third of the melting point, the outermost atoms acquire sufficient thermal energy to migrate quite freely over the surface (Ref. 8). At even higher temperatures, the solid will tend to minimize its free energy through structural changes, such as recrystallization and preferential grain growth (Ref. 9), surface faceting and reconstruction (Refs. 8 through 10), and alterations of the densities of dislocations and defects (Ref. 8).

# 2.2 INTERMOLECULAR POTENTIALS

The details of many gas-surface interactions depend strongly on the nature of the intermolecular forces between the gas atom (or particle\*) and the solid surface. Therefore, it is unfortunate that at the present

<sup>\*</sup>The terms particle and gas atom will be used interchangeably. The term molecule is avoided because the majority of the following considerations are limited to atoms.

time there is very little quantitative information, either theoretical or experimental, on the intermolecular potentials of gas-surface combinations. There are definite indications, however, that the desired experimental data may be obtained by newly developed techniques, such as low-energy electron diffraction (Ref. 11), field emission and field ion microscopy (Ref. 12), Mossbauer spectroscopy (Ref. 13), and improved molecular beam apparatus (Refs. 14 and 15).

The intermolecular potential of a gas-surface combination is extremely complex because each gas atom interacts simultaneously with several surface atoms and, in some cases, with other gas atoms which are adsorbed on the surface. This point is best illustrated by means of a simple hard-sphere model as shown in Fig. 1. In this highly idealized model, the surface is a regular array of "hills" and valleys," and it is obvious that the intermolecular potential depends on the position of the gas atom relative to the lattice structure. There have been few attempts to obtain a three-dimensional formulation of the intermolecular potential (Refs. 16 and 17).

In order to be consistent with the majority of publications pertaining to the present problem, it is assumed in this report that the intermolecular potential for the interaction of a single gas atom with a single surface atom may be represented by the Morse potential function (Ref. 18),

$$V(r) = D \left[ e^{-2a(r-r_{o})} - 2e^{-a(r-r_{o})} \right]$$
(1)

where r is the distance between the centers of the particles, D is the depth of the potential well (Fig. 2),  $r_0$  is the separation distance for V = D, and a is an interaction parameter. (The relationship of the Morse potential and the Lennard-Jones 6-12 potential is discussed in Ref. 19.) The general features of the potential are shown in Fig. 2; the intermolecular forces are attractive when  $r > r_0$  and repulsive when  $r < r_0$ .

Since a particle interacts simultaneously with a number of surface atoms, the total potential is equal to the sum of the individual potentials. The values of D and a will be the same for each term in the summation only if the surface is perfectly uniform. To simplify the discussions which follow, it is assumed that this summation may be represented by a more compact expression,

$$V(x, y, z) = D\left[e^{-2a(z-z_0)} - 2e^{-a(z-z_0)}\right]$$
(2)

where x, y, and z are the coordinates used to describe the position of the particle relative to the surface, x and y being in the plane of the surface with z directed along the normal (Fig. 1). In this expression

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the values of D and a are not identical to those in Eq. (1) because they are functions of x and y, as is  $z_0$ . This is best explained by referring to Fig. 3 where V (x, y, z) is drawn for two possible choices of x and y; note that the magnitude of D is greater for the case of a valley than it is for a hill because the particle is within the strong attraction region of several surface atoms. It is obvious that the valley is the most likely position for an adatom (i.e., an adsorbed gas atom) to reside, and such positions will be referred to as adsorption sites.\* The magnitude of D depends on the physical and chemical properties of the gas and solid (e.g., the polarizability, crystal structure, electron affinity, etc.), and it is generally assumed to be approximately equal to the heat of adsorption which may be measured experimentally. If the magnitude of D is of the same order as the energy of a chemical bond ( $\sim 0.5$  to more than 4 ev), the adatom is said to be chemisorbed (i.e., chemically adsorbed). If D is of the same order of magnitude as the heat of condensation of the gas  $(\sim 0 \text{ to } 0.5 \text{ ev})$ , the adatom is said to be physisorbed (i.e., physically adsorbed). There have been numerous publications on the general characteristics of both classes of adsorption; comprehensive reviews are presented in Refs. 8 and 20 through 23.

The rate of desorption (i.e., evaporation) of adatoms from a surface, n, is usually described quite accurately by the familiar exponential relation (Ref. 21),

$$\dot{n} = \sigma \nu \exp\left(-\frac{E_{a}}{k T_{w}}\right)$$
(3)

where  $\sigma$  is the density of adatoms on the surface,  $\nu$  is an empirical factor which is related to the vibrational frequency of the adatoms and the transmission coefficient,  $E_a$  is the heat of adsorption (approximately equivalent to D), k is Boltzmann's constant, and  $T_W$  is the surface temperature. From the form of this equation it is obvious that adatoms desorb rapidly when the magnitude of  $kT_W$  is comparable to  $E_a$ . Although it appears that a surface in a vacuum environment (i. e., one in which the partial pressures of adsorbable gases are extremely low) may be cleaned by heating it to an appropriate temperature, this technique is limited by the fact that the desorption temperatures of many chemisorbed substances exceed the melting temperatures of the solid substrate<sup>\*\*</sup>. It is, however,

<sup>\*</sup>This term may be misleading because adsorption actually occurs over the entire surface, i.e., on the hills as well as in the valleys (Ref. 20).

<sup>\*\*</sup>A discussion of techniques for obtaining clean surfaces appears in Ref. 24.

an effective method for removing physisorbed gases because the desorption temperatures are much lower in this case.

It is shown in Section 4.1 that the slope of the repulsive portion of the intermolecular potential has a strong influence on energy accommodation. For this reason, it is convenient to define a new parameter, L, which characterizes the slope:

$$L = \frac{1}{2a}$$
(4)

Note that L is simply the reciprocal of the coefficient appearing in the repulsive term of Eq. (2); since L has the dimensions of length, it will be referred to as the characteristic length of the repulsive interaction. As the magnitude of L increases, the slope decreases and the range of the repulsive force increases, the result being that the gas-surface interaction is less abrupt. The interaction becomes infinitely abrupt (i.e., impulsive) as L approaches zero.

# 2.3 INTERACTION PROCESSES

First, a general consideration of the various processes which may occur when a neutral atom impinges upon a surface will be discussed. One of the primary objectives of this section is to develop a well-defined set of descriptive terms which may be utilized throughout this report.

It is customary to describe the interaction of an atom with a surface in terms of the following two extreme cases:

- 1. <u>Adsorption</u>: This process is defined by the requirement that the mean adsorption lifetime (i. e., the time that the particle resides within the force field of the surface) be much greater than the characteristic vibrational period of the surface atoms. In this case the particles come to thermal equilibrium with the solid before evaporating or desorbing. (In many instances the adsorption lifetime is so great that evaporation does not occur within the time span of the experiment).
- 2. <u>Reflection</u>: This process is defined by the requirement that the particle rebounds immediately from the surface, the interaction time being too short to enable the particles to come to thermal equilibrium with the solid.

Although the definitions of adsorption and reflection given above have been widely used for many years, they are not sufficiently precise for the following consideration. For example, the dividing line between adsorption and reflection is arbitrary because it is impossible to define a unique value of the interaction time (e.g., the adsorption lifetime) which would be applicable to all atom-surface systems. Although it may be tempting to say that the logical choice for the dividing line is the interaction time which is exactly equal to the vibrational period, the validity of this choice is refuted by analytical results obtained by Goodman (Ref. 19), which indicate that a particle-surface interaction time is several times greater than the vibration period. Another fault of the above definitions is that they infer that energy transfer decreases as the interaction time approaches zero; theoretical and experimental results indicate that this is not a consistant criterion (Section 3.1).

Adsorption is actually a two-step process. The first step is a trapping\* process in which the particle transfers a sufficient fraction of its energy to the solid so that it cannot overcome the attractive forces associated with the intermolecular potential (i.e., the particle is trapped in the potential well). The second step is a relaxation process in which the trapped particles attain a state of thermal equilibrium with the solid (Ref. 20). This is analogous to the process of molecular recombination in gases; i.e., the collision of atoms results in the formation of molecules in excited states, and these molecules then come to equilibrium with the bulk of the gas through additional collisions unless dissociation occurs during the intervening period.

It is suggested here that the physical significance of the dividing line between adsorption (trapping) and reflection is best described in terms of the molecular dynamics of the particle-surface interaction. Specifically, a fundamental difference between reflection and trapping is that the velocity of the particle changes sign only once in the former process, whereas it changes more than once in the latter process (e.g., in the case of trapping, the particle oscillates at least once in the potential well before escaping). These modified definitions are highly theoretical as they stand, and an attempt will be made in Sections IV and V to relate them to experimental measurements of energy and momentum transfer.

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<sup>\*</sup>It is unfortunate that the term trapping is often used to represent two different processes: (1) the first step of the process of adsorption and (2) the capture of a noncondensable gas on a surface by a second gas which is condensable. Only the former definition will be used in this report.

The processes which may occur after a particle is trapped, or adsorbed, on a surface will now be considered. If the adsorption lifetime is sufficiently long, the adatom may migrate across the surface (Ref. 20) or diffuse into the bulk of the solid. Another possibility is that the adatom may experience a chemical reaction with the surface atoms (Ref. 25), with other adatoms of the same species (i.e., recombination, Ref. 23), or with adatoms of a second species (i.e., catalysis, Ref. 26), and then evaporate from the surface in the form of a molecule. There is also the probability that the atom may evaporate as an ion (Ref. 27).

Up to this point, the processes experienced by the gas atom without mentioning the accompanying processes experienced by the surface have been considered. The reason for this is that the changes of state of the surface are generally unimportant until the energy of the incident particle is increased above the thermal level. For energies near or above the binding energy of the solid, the situation may be reversed so that the changes of state of the surface now become more important than those of the gas particles. The principal surface process is the ejection of electrons (Ref. 27), atoms, and ions (i.e., sputtering, (Refs. 27 and 28). (Ejection processes may also occur at low kinetic energies if the incident atom is in an excited state (Ref. 27)). Lattice damage caused by particle bombardment may cause significant changes in the properties of the surface (Refs. 28 and 29).

Although it was assumed initially that all interactions of neutral atoms with solid surfaces may be classified into two general categories, adsorption and reflection, this assumption is not valid when the incident particle possesses sufficient energy to cause the ejection processes discussed above. In this case, the particle may penetrate into the lattice and become trapped below the surface (Refs. 28 through 30). These processes will not be considered here.

The preceding discussion has been restricted to the interaction of neutral atoms with surfaces because much of this information is needed in succeeding sections. The interaction processes associated with other types of incident particles are discussed in the following references: molecules (Ref. 23), ions (Ref. 27), and electrons (Ref. 31).

#### 2.4 INTERACTION VARIABLES

In the preceding discussion of possible interaction processes, no attempt was made to indicate the dependence of each process on the interaction variables (i.e., the experimental variables) or on the physical properties of the incident atom and the surface; this is done in Sections IV and V for energy and momentum accommodation. It suffices here to present a general list of the variables and properties which may influence the nature of particle-surface interactions.

Experimental Variables (for a particular gas-surface combination)

- 1. Energy of the incident particle
- 2. Angle of incidence
- 3. Surface temperature
- 4. Density of test particles adsorbed on the surface
- 5. Degree of surface cleanliness (i.e., fractional coverage of surface by adsorbable impurities)

# Properties of Incident Particle

- 1. Mass
- 2. Properties which influence the nature of the intermolecular potential of the particle and surface (e.g., charge, size, polarizability, ionization potential, electron affinity, etc.)

## Properties of Surface

- 1. Degree of surface smoothness
- 2. Uniformity of surface structure (i.e., grain size and orientation, dislocations, defects, etc.)
- 3. Crystallographic structure (i.e., lattice orientation and spacing)
- 4. Intermolecular potential between a surface atom and the neighboring solid atoms. (The anisotropic vibrations and intermolecular forces of the surface atoms depend on this potential; in some cases it may be sufficient to know the Debye temperature)
- 5. Intermolecular potential between atoms within the bulk of the solid, including the effects of impurities and defects
- 6. Properties which influence the nature of the intermolecular potential of the incident particle and surface (e.g., work function, polarizability, binding energy, etc.)

# Uncontrollable Variables

- 1. Point of impact of the particle on the surface lattice
- 2. Exact speeds and positions of the vibrating surface atoms

## SECTION III ENERGY AND MOMENTUM ACCOMMODATION COEFFICIENTS

In the field of rarefied gas dynamics it is customary to describe the energy and momentum transfer between gases and surfaces in terms of three macroscopic parameters (Ref. 1): the energy accommodation coefficient ( $\alpha$ ), the coefficient of tangential and momentum transfer ( $\sigma$ ), and the coefficient of normal momentum transfer ( $\sigma$ ). Since these coefficients may lead to confusion and error when used outside the limits of their original definitions, each will be discussed below in detail.

Before discussing the coefficients individually, it is informative to consider their dependence on the velocity distribution function of the scattered (reflected) particles. Since the distribution function specifies both the directions and speeds of the scattered particles, it provides a complete description\* of an interaction for a specific gas-surface combination if the temperature of the solid and the distribution function of the incident particles are given. Therefore, all of the pertinent coefficients may be calculated as integrals, or moments, of the distribution function according to the usual procedures of kinetic theory (Ref. 1).

It is obvious that the energy and momentum coefficients are not as descriptive or fundamental as the distribution function. Therefore, they should be used only when it is more convenient to do so or when the distribution function is unknown. As a general rule, an experimental or theoretical investigation will be more meaningful if it determines the distribution function rather than a specific coefficient. \*\*

### 3.1 ENERGY ACCOMMODATION COEFFICIENT

The energy accommodation coefficient,  $\alpha$ ,<sup>†</sup> may be considered from two viewpoints: near equilibrium and nonequilibrium. The advantages and limitations of these approaches will be discussed below.

\*This description is complete only if the interaction has not caused dissociation, ionization, excitation, etc.; otherwise, additional distribution functions are required to describe these various changes of state.

\*\*Although experimental determinations of scattered distribution functions were generally impractical in the past, they may now be obtained by means of improved molecular beam and detection techniques (Refs. 32 and 33).

<sup>†</sup>This parameter is usually referred to as the thermal accommodation coefficient, but the term energy is preferred here.

The majority of the experimental values of  $\alpha$  have been obtained at near equilibrium conditions in thermal conductivity cells (Refs. 27, 34, and 35). A typical thermal conductivity cell consists of a cylindrical tube which has a thin wire stretched along the axis and is filled with gas at low pressures. A small temperature difference is established between the wire and the gas, and the resulting heat-transfer rate is carefully measured. In this case, the energy accommodation coefficient is defined as the ratio of Q, the actual heat-transfer rate, to  $Q_0$ , the rate which would have occurred if the gas particles had attained a state of thermal equilibrium with the surface before leaving the surface (Ref. 34):

$$a = \frac{Q}{Q_0}$$
(5)

The value of Q is measured directly, and  $Q_0$  is calculated by kinetic theory using the measured gas pressure and temperature. (The methods of the calculating  $Q_0$  for free molecule and near free molecule conditions are described in Ref. 35.) From Eq. (5) it is seen that  $\alpha$  is essentially a measure of the efficiency of the energy transfer processes associated with gas-surface interactions.

Since detailed summaries of the existing experimental data on energy accommodation coefficients may be found elsewhere (Refs. 27 and 35), it is not worthwhile to devote much space to this subject here. Suffice it to say that coefficients measured by different investigators using various techniques generally are not in good agreement. Results reported for noble gases on tungsten (Ref. 34) are more extensive and more reliable than those reported for other gases. As illustrated in Fig. 4, the energy accommodation coefficient,  $\alpha$ , depends markedly on the gaseous species and on temperature. Note the general tendency of  $\alpha$  to increase with the molecular weight of the species. In the case of helium, the extremely low value of  $\alpha \approx 0.02$  indicates that there is almost no energy transfer associated with this interaction. Other features of Fig. 4 will be discussed later.

It should be emphasized that the present considerations are restricted to interactions which affect only the translational (kinetic) energy of the gas particles. Very little is known about interactions which alter the rotational, vibrational, or electronic state of gas molecules (Ref. 35), and it may be advisable to define a separate accommodation coefficient for each of these processes. Present considerations of  $\alpha$  are further restricted to cases where both the composition and the mass flux of the scattered particles are equal to the corresponding values for the incident particles (i.e., no chemical reaction, dissociation, adsorption, or condensation). Without these restrictions, the relationship between  $\alpha$  and the change of translational energy of the gas particles is indefinite. With the above mentioned restrictions in mind, a second expression for  $\alpha$  may be derived. Let n represent the arrival rate (i.e., the number of incident particles striking the surface per unit area per unit time), and let  $E_i$  and  $E_r$  represent the mean translational energies of the incident and scattered particles, respectively. The energies  $E_i$  and  $E_r$  are measured relative to the surface, and it follows that their difference,  $E_i - E_r$ , represents the mean energy transfer associated with the particle-surface interaction. Since this discussion is restricted to the case where n is the same for both incident and reflected streams, the rate of energy transfer, Q, is simply equal to n ( $E_i - E_r$ ), and Eq. (5) may now be expressed as

$$\alpha = \frac{\dot{n}(E_i - E_r)}{\dot{n}(E_i - E_w)}$$
(6)

where  $E_W$  is the value which  $E_r$  would have if the particles were completely accommodated (i.e., if the particles leaving the surface are in a state of thermal equilibrium with the surface). The n in Eq. (6) may be canceled, and the following is obtained:

$$\alpha = \frac{E_i - E_r}{E_i - E_w}$$
(7)

The energy accommodation coefficient is often defined by means of an expression similar to Eq. (7) (Refs. 1 and 35). It is obvious that  $\alpha$  is a measure of the degree to which gas particles attain thermal equilibrium with the surface. Note that the value of  $\alpha$  is unity when  $E_r = E_W$  (i.e., complete accommodation) and is zero when  $E_r = E_i$  (i.e., specular reflection or zero energy transfer).

Historically, the definition of  $\alpha$  represented by Eq. (7) was preceded by an expression based on temperature (Ref. 36) which will be derived now. For the special case of an equilibrium gas at temperature T, the mean translational energy E of particles striking a fixed surface is given by (Ref. 36)

$$E = 2kT$$
(8)

where k is Boltzmann's constant. Therefore, Eq. (7) may be expressed as:

$$\alpha = \frac{T_i - T_r}{T_i - T_w}$$
(9)

where  $T_i$  and  $T_w$  are the temperatures of the impinging gas and the surface, respectively, and  $T_r$  is the effective temperature of the scattered particles. The presentation of  $E_r$  by a temperature  $T_r$  lacks theoretical justification because the scattered particles may have a non-Maxwellian distribution function. Similarly, the substitution of  $2kT_i$  for  $E_i$  is valid only if the incident gas is Maxwellian, as is generally the case in thermal conductivity cells and thermal molecular beams. Because of these inherent limitations of Eq. (9), the more general expression given by Eq. (7) is preferred.

An erroneous statement which often is found in discussions of energy accommodation is that all possible values of  $\alpha$  are contained in the interval from 0 to 1. This point has been considered in Refs. 37 and 38. From the Second Law of Thermodynamics, it is known that in a heat interaction between two systems which are in different equilibrium states initially, the net energy transfer is from the system of higher temperature to the system of lower temperature. From this it follows that  $\alpha$  cannot be negative if both of the interacting systems, the gas and the solid, are in equilibrium states when isolated from each other initially, i.e., before they are allowed to interact. \* This statement is not necessarily true, however, in the more general case where one of the systems is in a nonequilibrium state initially (the Second Law applies only to the interactions of systems which were initially in equilibrium states). Therefore, it can be seen that thermodynamics does not restrict the value of  $\alpha$  to the interval from 0 to 1 in nonequilibrium cases, such as the interaction of a non-Maxwellian stream of particles with a solid surface. \*\* Although it is tempting to justify this restriction by assuming it to be a consequence of the dynamics of particle-surface interactions, the analytical results obtained by Goodman (Ref. 37) seem to invalidate this assumption, at least for the simple interaction model which he employed.

An obvious difference between the thermal conductivity cell and molecular beam techniques is that the incidence angle of the impinging particles is random in the former case and directed in the latter. Since  $\alpha$  may depend on the angle of incidence, it follows that the value of  $\alpha$  measured for a single angle of incidence is not necessarily equal to that for random incidence. Hurlbut has suggested that measurements associated with a specific incidence angle be referred to as partial accommodation coefficients (Ref. 39).

The development of a complete theory of energy accommodation has not been possible to date because of the following features of the problem: (1) a large number of variables are involved (as listed in Section 2. 4), (2) a gas atom may interact with more than one surface atom simultaneously, and (3) the theories of lattice dynamics (Ref. 40) and atomic collisions (Ref. 41), both of which are also incomplete, must be employed.

<sup>\*</sup>The near equilibrium conditions maintained in thermal conductivity cells usually satisfy this requirement.

<sup>\*\*</sup>This point may be of no practical importance, however, because experimental values outside the interval from 0 to 1 have not been reported.

A brief survey of existing theoretical treatments of the problem is given below; more complete discussions may be found in the references which are included. (A qualitative discussion of the principal mechanisms of energy accommodation is presented in Section IV.)

The simplest model to be assumed for energy accommodation is suggested by the following form of Eq. (7):

$$\mathbf{E}_{\mathbf{r}} = (1 - \alpha) \mathbf{E}_{\mathbf{i}} + \alpha \mathbf{E}_{\mathbf{w}}$$

It is assumed that the scattered particles are divided into two classes, one consisting of the fraction  $\alpha$  of the particles which are completely accommodated, the other consisting of the remaining fraction,  $1 - \alpha$ , which experience no energy exchange. Since there does not seem to be a theoretical justification for assuming such a model, it should be discarded.

A classical treatment which assumes that both the gas particles and the surface atoms behave as hard spheres was presented by Baule in 1914 (Ref. 42). Using this hard-sphere model, the following expression is obtained for  $\alpha$  (see Appendix I):

$$\alpha = \frac{4\mu}{(1+\mu)^2} \tag{10}$$

where  $\mu$  is the ratio of the mass of the gas particles to the mass of the surface atom. In some cases, this expression agrees qualitatively with the general trends of experimental data (Ref. 34). Quantitative agreement is not expected because the model is far too simple (see Section 4.1). Goodman has employed a similar model recently in an interesting qualitative study of the dependence of  $\alpha$  on temperature and distribution function (Ref. 37).

Although it is expected that a complete theory of energy accommodation must be based on a quantum mechanical approach, classical mechanics has been employed in the majority of recent studies (Refs. 17, 19, 37, and 42 through 47). The reasons for favoring the classical approach have been stated by Zwanzig (Ref. 44): (1) the mathematical complexities associated with quantum mechanical treatments tend to obscure the essential features of the problem, and (2) existing quantum mechanical solutions cannot explain the large energy transfers which have been observed experimentally. The validity of the classical approach has been a subject of continuing discussion (e.g., Refs. 44, 48, and 49). A brief review of the quantum mechanical analyses by Lennard-Jones and his co-workers is presented in Ref. 35; the results of more recent analyses appear in Refs. 49 through 51.

At the present time, it appears that the most complete theory of energy accommodation is the classical treatment developed by Goodman (Ref. 45). The approach is similar to that introduced by Cabrera (Ref. 43) and Zwanzig (Ref. 44), but Goodman has made a significant improvement in representing the solid by a three-dimensional lattice instead of a onedimensional chain. The solid atoms are assumed to be interconnected by linear springs, and the spring constants are calculated from the Debye temperature of the solid. The intermolecular potential for a gas atom and surface atom is described by the Morse potential function Eq. (1). Unfortunately, a computer solution is required for each new set of initial conditions and system properties. By a trial-and-error procedure, Goodman has determined the values of the Morse parameters, a and D, which cause his theoretical predictions of  $\alpha$  to agree with experimental results. These values of a and D appear to be reasonable (Ref. 45), and this fact increases confidence in this theoretical approach. There are, however, a number of questionable assumptions underlying this theory:

- 1. The incident particles are directed along the surface normal. Because of this assumption, the validity of comparing the theoretical results to experimental values obtained for random angle of incidence is questionable.
- 2. All particle-surface interactions are considered to be head-on collisions. This assumption is valid only if it can be shown that the forces of attraction are such that the trajectories of the incident molecules are altered sufficiently to result in head-on collisions. It should also be noted that this model does not take into account the fact that the strongest adsorption sites on a surface are not these head-on positions but are those located in the valleys between adjacent surface atoms (Section 2. 2).
- 3. The effect of the temperature of the solid is negligible. In Goodman's model, the surface atoms are initially at rest, i.e., the temperature of the solid is essentially zero degrees absolute. Since there are experimental (Ref. 34) and analytical (Ref. 37) results which indicate that  $\alpha$  depends strongly on the temperature of the solid, it appears invalid to compare Goodman's results to the existing experimental measurements in the thermal energy range. It is expected, however, that the zero-temperature model may be valid in the case where  $E_i >> E_w$ .
- 4. The forces between solid atoms are linear. This approximation is not expected to be valid for energetic collisions which cause large displacements of the solid atoms. In addition, nonlinear terms may be needed to describe the anisotropic nature of the surfaces (Section 2.2).

Trilling has extended Goodman's treatment so that it may be used to study the dependence of energy accommodation on the angle of incidence (Ref. 47). The validity of the assumptions associated with this extension is questionable, however, and the numerical results are not yet sufficient to allow a complete assessment.

The analog computer is a convenient means for studying the properties of simple models of gas-surface interactions. The surface is usually represented by a single solid atom connected to a linear spring, although a variety of gas-surface intermolecular potentials has been employed. Parametric studies of this model have been conducted by Rodgers (Ref. 52). Berkman (Ref. 53) has shown that Goodman's three-dimensional lattice model may be represented by a simple mass-spring-damper system on the analog computer. The versatility of the analog computer approach to this problem has been demonstrated recently by Hurlbut's work (Ref. 54) which includes the features of variable angle of incidence and Lennard-Jones potentials between lattice atoms.

The theoretical studies by Oman et al. (Ref. 17) appear to be the only extensive attempt to determine the effect of both the angle of incidence and the point of impact on energy and momentum transfer. The surface is represented by a layer of harmonic oscillators, and a Lennard-Jones 6-12 potential is used to describe the interaction between a gas atom and the individual surface atoms. Using classical mechanics exclusively, the trajectory of a gas particle is determined by numerical computation. The major disadvantages of this approach are (1) the essential features of the interaction are obscured by the numerical techniques; (2) calculations require a considerable amount of computer time; (3) many calculations must be performed because there are a large number of variables; (4) intermolecular forces between surface atoms are assumed to be linear and identical to those in the bulk of the solid (Section 2.1); and (5) the surface model is not valid for collisions having long interaction times. Oman et al. have taken many steps to minimize these disadvantages, and it appears that the results of these computer experiments will be very useful in the determination of the principal parameters and the formulation of improved models.

In summary, both the experimental results and the theories of energy accommodation are insufficient at present to provide accurate values of  $\alpha$  for a wide range of test conditions. The existing data are, in general, incomplete and unreliable. Much additional work is required to improve present understanding of the physical details of this interaction.

## 3.2 MOMENTUM COEFFICIENTS

The momentum transfer between a stream of gas atoms and a solid surface may cause the surface to experience forces both in the normal and tangential directions. In order to describe these forces, two parameters have been introduced:  $\sigma$ , the coefficient of tangential momentum transfer, and  $\sigma'$ , the coefficient of normal momentum transfer (Ref. 1).

$$\sigma = \frac{\tau_i - \tau_r}{\tau_i}$$
(11)

$$\sigma' = \frac{P_i - P_r}{P_i - P_w}$$
(12)

 $r_i$  and  $r_r$  are the mean tangential components of momentum for the incident and scattered particles, respectively;  $P_i$  and  $P_r$  are similarly defined for the normal components of momentum. The term  $P_W$  represents the normal momentum component corresponding to complete accommodation. (r is equal to zero in the case of complete accommodation; therefore,  $r_W$  does not appear in Eq. (11).)

Both  $\sigma$  and  $\sigma'$  are equal to zero for specular reflection and equal to unity for complete accommodation. These relationships are not unique, however, because both  $\sigma$  and  $\sigma'$  depend on the directions of the scattered particles as well as on the speeds. For instance,  $\sigma$  is equal to unity as long as the scattering directions are diffuse, regardless of the degree of energy accommodation. An undesirable feature of  $\sigma'$  is that its value is not restricted to the interval from 0 to 1; this point is discussed in Refs. 37 and 38.

It is expected that the value of  $\sigma$  for a specific gas-surface combination does not depend on the tangential component of the incident momentum alone; most likely, the magnitude of  $\sigma$  is affected by changes in the speed and angle of incidence even when  $\tau_i$  is maintained constant. An analogous statement could be made with respect to  $\sigma'$ . As stated in Section III, the energy and momentum coefficients are not independent parameters because all three depend on the distribution functions of the incident and scattered particles.

Direct experimental measurements of momentum transfer have been accomplished by means of the rotating cylinder (Ref. 55) and torsion balance techniques (Ref. 38); in all cases the surfaces were contaminated to an unknown degree. Indirect measurements are provided by the results of the scattering studies which will be discussed in Section V. As for theoretical calculations of momentum transfer, it suffices here to say that the approaches are similar to those for energy accommodation (Section 3. 1).

## SECTION IV ENERGY ACCOMMODATION: INTERACTION REGIMES AND PARAMETERS\*

Although it would be advantageous to know the velocity distribution function of the particles scattered from a surface, this is not possible at present because of insufficient experimental and theoretical results. There is, however, a considerable amount of experimental data on two features of the distribution function: the mean speed (energy accommodation) and the directional distribution (scattering pattern). These features are considered separately below; however, it is emphasized that they are not truly independent processes, since energy accommodation is not completely independent of the direction of the scattered particles.

The primary purpose of Sections 4.1 and 4.2 is to attempt to describe, qualitatively, the general characteristics of energy accommodation for incident energies of 0 to 10 ev. The description is qualitative rather than quantitative because experimental data are not available above  $\sim 0.1$  ev. An attempt is made to point out the existence of different interaction regimes and to determine the principal parameters of each.

In order to simplify these discussions, the following assumptions are made unless specified otherwise: (1) the incident particles are directed along the surface normal, (2) the incident particles are monoenergetic, and (3) the particle-surface interaction is represented by the effective intermolecular potential defined by Eq. (2). Although these assumptions are not entirely realistic or representative of the usual experimental conditions, they give a clear observation of the qualitative dependence of  $\alpha$  on three variables: the incident energy E<sub>i</sub>, and the Morse potential parameters, a and D. A fourth variable, the angle of incidence, is considered in Section V.

### 4.1 INTERACTION OF INERT GASES WITH SOLID SURFACES

It is logical to consider the energy accommodation coefficient of inert gases (i.e., helium, neon, argon, krypton, and xenon) first because this is the simplest case, and the existing experimental data are more reliable than for other gases. The qualitative dependence of  $\alpha$  on  $E_i$ , the energy of the incident particles, is postulated in Fig. 5; this postulation is based on available experimental data (e.g., Fig. 4) and theoretical predictions (Ref. 45). In addition, it is postulated that the interaction may be divided into several distinct regimes. The curve

<sup>\*</sup>Much of the material in this section appears in Ref. 56.

shown in Fig. 5 may be considered to be a composite of the characteristic curves of the different regimes. The major features of each regime are discussed below.

#### 4.1.1 Condensation (Physisorption)

For a gas atom to be trapped\* by a surface, the energy transfer of the particle-surface collision must be such that the particle no longer has sufficient energy to overcome the intermolecular forces of attraction. In most cases, this condition of complete accommodation is possible only if the interaction time is sufficiently long to allow energy to propagate into the lattice from the point of impact. Since the interaction time increases with decreasing incident velocity (as will be discussed shortly), it is concluded that condensation will occur only when  $E_i$  is below a certain critical value,  $E_i^*$ , which is discussed in Section 4.1.2.

There is a second condition which must be satisfied if condensation is to occur: the surface temperature must be low enough to effect a long adsorption lifetime. (The adsorption lifetime is inversely proportional to the evaporation rate defined by Eq. (3).) In the case of inert gases, condensation usually begins only after the surface temperature is reduced below the critical temperature of the gas (Refs. 34 and 57).

#### 4.1.2 Partial Trapping

If the energy of the incident particle exceeds a certain critical value,  $E_i$ \*, the accommodation coefficient decreases rather sharply (Fig. 5). Two possible reasons for this decrease are (1) the energy transfer of the particle-surface collision may no longer be sufficient to cause trapping, and (2) the trapped particles may be in highly excited vibrational states during the initial oscillations, thereby causing the desorption probability to be large. It is expected that the magnitude of  $\alpha$  is affected much more by the first point than by the second, especially in the case of inert gases.

The obvious parameter for describing this partial trapping regime is the ratio  $E_i/E_i^*$ . The usefulness of this parameter is limited by the fact that a general expression of  $E_i^*$  has not been found; however, qualitative expressions of  $E_i^*$  have been derived using simple theoretical models (Refs. 44 through 46). There is an increasing amount of experimental data on the trapping probabilities of various particle-surface combinations (Refs. 58 and 59). An excellent survey of trapping is presented in Ref. 23.

<sup>\*</sup>As defined in Section 2.3, a particle is said to be trapped by a surface if it oscillates at least once before escaping.

#### 4.1.3 Nonadiabatic Regime

As stated above, the probability of trapping tends toward zero when the energy of the incident particles exceeds a certain critical value,  $E_i$ \*. As  $E_i$  becomes large compared to  $E_i^*$ , the particle-surface interaction passes into another regime. It is appropriate to call this the nonadiabatic regime since it is characterized primarily by the transition from the adiabatic limit to the hard-sphere limit. The term adiabatic is used in the theory of molecular collisions (Refs. 41 and 60) to represent interactions which occur so slowly that the particles pass through a series of quasi-static equilibrium states, the result being a reversible process with no net energy exchange.<sup>†</sup> If the interaction is not sufficiently slow (i.e., nonadiabatic), the inertia of the system causes the two particles to be out-of-phase, and this departure from a quasi-static process results in a transfer of energy. For example, consider the action of a vertical force on a mass which is suspended at one end of a spring. If the force is applied and then removed slowly, the final state of the mass-spring system will be identical to its initial state, and it is concluded that the net energy transfer is zero. If, on the other hand, the force is applied and then removed suddenly, the mass-spring system will be left in a state of oscillatory motion, and it is concluded that the net energy transfer is not zero because the final state is unequal to the initial state of the system.

It is postulated that the nonadiabatic regime is best characterized by means of a parameter that compares the vibrational period of the surface atoms (i.e.,  $\frac{2\pi}{\omega}$ ) to the interaction time. The ratio of these two characteristic times is a measure of the speed of the interaction. Since the exact value of the interaction time is unknown unless a complete solution of the problem exists beforehand, it is customary to approximate it by the time required for a particle of speed,  $\dot{r}_i$ , to travel a distance equal to the characteristic length,  $L = (2a)^{-1}$ , which appears in the repulsive term of the Morse potential (Section 2.2). The ratio of these times will be used to define an interaction parameter,  $\tau$ , for the nonadiabatic regime:

$$\tau = \frac{2\pi/\omega}{L/\dot{r}_{i}} = \frac{2\pi\dot{r}_{i}}{\omega L}$$
(13)

<sup>&</sup>lt;sup>†</sup>An adiabatic limit such as this does not actually exist for gassurface interactions because (1) there will be a net energy transfer caused by the propagation of energy through the crystal lattice and (2) trapping generally occurs long before the limiting conditions are attained.

An alternate form of this expression is

$$\tau = \frac{h}{k \theta_{\rm D} L} \left(\frac{2 E_{\rm i}}{M}\right)^{1/2}$$
(14)

where  $(2E_i/M)^{1/2}$  has been substituted for  $\dot{r}_i$ , and it has been assumed that  $\omega$ , the vibrational frequency of the surface atoms, is related to the Debye temperature of the solid,  $\theta_D$ , by (Ref. 45)

$$\omega = \frac{2\pi k \theta_{\rm D}}{\rm h}$$
(15)

where k is the Boltzmann constant and h is Planck's constant.

#### 4.1.4 Hard-Sphere Limit

From Eq. (14), it is apparent that the interaction parameter,  $\tau$ , approaches infinity as  $E_i$  increases. Therefore, the interaction force may be considered as an impulse in the limit, and it becomes a simple matter to calculate the energy transfer based on the assumption that the gas and surface atoms are perfectly elastic spheres (i.e., hard spheres). In this case,  $\alpha$  depends only on  $\mu$ , the ratio of the mass of the gas atom to the mass of the surface atom (see Appendix I):

$$\alpha = \frac{4\mu}{(1+\mu)^2}$$
(16)

The validity of this expression depends upon the following assumptions, some of which were discussed previously:

- 1. All collisions are head-on encounters between the gas and surface molecules. As stated in Section 3.1, the validity of this assumption is questionable.
- 2. The initial velocities of the surface atoms are negligible. This appears to be a very good assumption in the present case since the kinetic energy of the surface atoms  $(kT_w)$  is negligible compared to that of the gas atoms,  $E_i$ .
- 3. The collision is perfectly elastic. In some cases it may be that the value of  $E_i$  associated with the hard-sphere limit will be large enough to result in inelastic processes such as electronic excitation of the atoms.

#### 4.2 INTERACTION OF CHEMISORABLE GASES WITH SOLID SURFACES

In the preceding section the discussion was restricted to gases having such weak forces of attraction with solid surfaces that adsorption (trapping) occurs only at temperatures that are near or below the critical temperature of the gas. The more general case, chemisorption, will now be considered. The attractive forces are strong enough to produce heats of adsorption that are the same order of magnitude as chemical bonds (Section 2.2). It is of interest to obtain information on the accommodation coefficients of such gases since the majority of the species found in the atmosphere are capable of chemisorbing on the surfaces of common engineering materials.

The present problem is far more complex than the preceding one because chemisorption involves many processes that vary with temperature and pressure. There have been a great number of experimental studies of the chemisorption properties of various gas-surface systems (Refs. 20 through 23), and the most informative data are currently being obtained by the well-developed techniques of low-energy electron diffraction. Recent results obtained by this technique indicate that the chemisorption of certain gases on metallic surfaces may completely change the lattice structure of the surface (Ref. 11). At present, no comprehensive theoretical treatments of chemisorption have been found, but many of the important concepts can be explained semiquantitatively (Ref. 22).

It appears that the only reliable experimental values of  $\alpha$  for chemisorbable gases are those obtained by Wachman (Ref. 61). As for theoretical studies of the effect of surface impurities (adatoms) on energy accommodation, Goodman (Ref. 62) and McCarroll (Ref. 63) have obtained qualitative results. The surface model employed in both of these studies assumes that energy transfer depends primarily on the fact that the adatom is part of a linear chain of substrate atoms. It is thought that this model is not realistic when the size of the adatom is comparable to the substrate atom; in this case the adatom sits between a group of substrate atoms, and the energy transfer depends primarily on the geometry and forces associated with this group.

The following considerations of energy accommodation will generally be restricted to the steady-state conditions existing after the surface has been exposed to a specific flux of particles for a time sufficiently long to establish constant surface conditions. It is expected that  $\alpha$  will depend on the arrival rate of the gas molecules if the coverage (i.e., the density of the adsorbed layer) varies with this rate.

The dependence of  $\alpha$  on  $E_i$  is postulated in Fig. 6 for the special case of a gas which has a single chemisorption state. Although this case is unrealistic because of oversimplification, it is thought that it is best for illustrating the principal characteristics of gas-surface interactions involving chemisorbable species. The behavior of a more realistic model would be extremely complex because  $\alpha$  would change with each transition of the adsorption state (Ref. 60). It is also assumed that the gas particles are atoms rather than molecules.

Although a chemisorbed layer exists on the surface, the first three regimes shown in Fig. 6 are essentially the same as those discussed in the preceding section. The same parameters may be used except that the Debye temperature appearing in Eq. (14) now depends on the combined vibrational characteristics of the adatoms and the solid substrate. In the first partial trapping regime, a portion of the incident particles are physisorbed upon the chemisorbed surface layer. The hardsphere limit of  $\alpha$  in the first nonadiabatic regime is unity because the mass of the adatoms is the same as that of the incident atoms (i. e.,  $\mu = 1$ ). However, this limit is probably never achieved because of the onset of the regimes described below.

When the magnitude of  $E_i$  is comparable with the heat of adsorption of the monolayer, E<sub>a</sub>, it is expected that the coverage will be incomplete because of a reduced trapping probability. Thus, there is a second partial trapping regime in which a fraction of the incident particles will now impinge upon the bare solid surface while the remainder collide with adatoms. The former will be accommodated quite effectively because the strong attractive forces between the gas atoms and the bare surface are capable of producing partial trapping; the latter will be partially accommodated as in the previous regime where the monolayer was complete. The net result is that  $\alpha$  may increase during the first stages of partial trapping and then decrease as  $E_i$  increases to the extent that the trapping probability goes to zero. The magnitude and position of this transition "bump" (Fig. 6) depend on the arrival rate in addition to the heat of adsorption of the gas atom on the bare surface, and it may be an insignificant effect unless the value of  $\alpha$  for the preceding regime is much less than unity. This feature of Fig. 6 is purely speculative, since the appropriate experimental data do not exist at present.

Note that two different nonadiabatic regimes are shown in Fig. 6, the first for a surface partially covered by chemisorbed atoms, and the second for a bare surface. The necessary condition for attaining the second case is

$$E_i >> E_a \tag{17}$$

since this ensures that the trapping probability is negligible. As discussed in Section 4.1.3, the magnitude of  $\alpha$  in the nonadiabatic regime depends on the interaction parameter,  $\tau$ . Since the characteristic time of the repulsive part of the interaction has the greatest effect on accommodation, it is appropriate to define the interaction time in terms of the speed that the gas molecule possesses when it enters the repulsive region.

In the present case of chemisorbable gases, this speed may exceed the initial value,  $\dot{r}_i$ , because of acceleration during the attractive region of the interaction. From qualitative considerations (Ref. 56), it appears that the following interaction parameter may be appropriate:

$$\tau^* = \tau \left[ 1 + \frac{D}{E_i} \left( \frac{\tau}{L' + \tau} \right) \right]^{\prime_2}$$
(18)

where r is defined by Eq. (14) and L' is equal to the ratio of the characteristic length for the attractive potential to the corresponding length for the repulsive potential. (L' is equal to two for a Morse potential.) It can be concluded from Eq. (18) that r\* will be approximately equal to r throughout most of the nonadiabatic regime because  $E_i > D$ . Since the exact magnitude of D is an unknown in most cases, it is necessary to assume that it is approximately equal to the corresponding experimental value of Ea, the heat of adsorption.

The discussion of the hard-sphere limit in Section 4.1.4 applies equally well to the case of chemisorbable gases except that the necessary condition is now expressed as  $r^* >> 1$ . As stated above, it is likely that  $r^*$  will be approximately equal to r for the values of  $E_i$  associated with attaining the hard-sphere limit. The actual existence of this limit is questionable as stated before.

It is expected that  $\alpha$  will depend on the history of the test specimen. This point may be illustrated by considering the following two experimental procedures:

- 1. Point-by-point procedure. The surface is cleaned by an appropriate technique (e.g., by flashing it at a high temperature) before each measurement of the steady-state value of  $\alpha$  at different values of  $E_i$ . The advantage of this method is that the history associated with a measurement at a particular value of  $E_i$  is well defined since the surface has been exposed only to particles of that energy.
- 2. Continuous procedure. This method differs from the preceding one in that the surface is not cleaned between measurements at different values of  $E_i$ . After an initial cleaning of the surface, the energy of the incident particles is varied, and the steady-state value of  $\alpha$  is recorded. In this case it is difficult to define the exact history of the surface (that is, the past exposure of the surface to particles of varying energy).

The preceding considerations of the dependence of  $\alpha$  on E<sub>i</sub> have been based on the point-by-point procedure in order to simplify the problem. It is also worthwhile to consider the continuous procedure because it illustrates the history effects which may be relevant to high-altitude flight. The dependence of  $\alpha$  on  $E_i$  is postulated in Fig. 7 for the continuous procedure. The dashed line represents  $\alpha$  for increasing  $E_i$ ; the solid line is for decreasing  $E_i$ , and it should generally give the same results as obtained by the point-by-point procedure. The hysteresis results from the fact that the adsorbed monolayer exists until  $E_i$  becomes large enough to remove it by sputtering.\* (The surface temperature is assumed to be insufficient to produce thermal desorption.) Since the energy required for sputtering may be much larger than the energies encountered in high-speed flight are not sufficient to remove strongly adsorbed gases such as oxygen. Therefore, it is of practical interest to study the effect of adsorbed monolayers on energy accommodation (Ref. 55).

#### SECTION V

#### SCATTERING PATTERNS OF GAS-SURFACE INTERACTIONS

# 5.1 GENERAL

Investigations of momentum and energy transfer in gas-surface interactions generally employ either the thermal conductivity cell technique described in Section 3.1 or the molecular beam scattering technique which is considered in the present section. \*\* It suffices here to say that the problem of surface contamination due to residual gases causes experimental results obtained with molecular beams to be less reliable in general than those obtained with conductivity cells.

The results of a number of gas-surface scattering experiments are summarized below. The basic mechanisms which influence the directional distribution of scattering particles are almost completely unknown, but an attempt will be made to evaluate several models, qualitatively, after the existing data have been studied.

<sup>\*</sup>The word sputtering is used here to represent the removal of the adsorbed monolayer by the bombardment of the surface by the incident atoms.

<sup>\*\*</sup>Other techniques, such as the rotating cylinder or torsion balance (Section 3.2), are of minor importance at the present time because of the difficulty of obtaining clean surfaces in these apparatus.

#### 5.2 DIFFRACTION

The first significant investigations of the scattering of atomic and molecular beams from solid surfaces were initiated around 1930 for the purpose of confirming the diffraction effects predicted by the newly developed quantum theory. (A more complete review of these studies may be found in Ref. 64.) According to this theory, material particles may be treated as wave packets characterized by the de Broglie equation,

$$\lambda = h/mr \tag{19}$$

where  $\lambda$  is the de Broglie wavelength, h is Planck's constant, m is the mass of the particle, and  $\dot{\mathbf{r}}$  is its velocity. Therefore, diffraction should occur when a beam of particles impinges upon a ruled grating (in practice, a crystal surface) having a spacing which is comparable to  $\lambda$ .

Definite diffraction effects have been observed experimentally for helium and hydrogen scattered from crystal surfaces which are clean, smooth, and of uniform structure (Refs. 65 and 66). These results are in complete accordance with quantum theory; the de Broglie wavelengths of helium and hydrogen at normal temperatures are of the same order of magnitude as the lattice spacing of common crystalline materials. Since the de Broglie wavelength decreases with increasing mass and velocity, diffraction is neither expected nor observed for gases of high molecular weight or high temperature (Refs. 67 through 69).

From the preceding considerations, it may be concluded that gassurface interactions associated with upper atmospheric and space environments will generally not be influenced by diffraction effects because: (1) the magnitudes of the masses and/or velocities of the gas molecules are such that the de Broglie wavelengths are much smaller than the lattice spacings; (2) the solid surfaces are usually nonuniform (i.e., polycrystalline) and are often contaminated with oxides and adsorbed impurities. The effects of the above conditions on scattering will now be considered in detail, first for interactions involving single-crystal surfaces and then for the case of engineering surfaces.

#### 5.2.1 Single-Crystal Alkali Halide Surfaces

The majority of the single-crystal studies have employed alkali halide crystals because of their availability. Other advantages of using alkali halides are (1) a fresh surface may be obtained when desired by cleaving the crystal, and (2) relatively clean surface conditions may be obtained by heating the crystal in vacuum, since most of the common residual gases and vapors physisorb (rather than chemisorb) on these materials.\* The primary disadvantages of using alkali halides are (1) it is difficult to formulate an accurate theoretical model of the lattice and surface structures because alkali halides are composed of two chemical elements rather than one; (2) since alkali halides are ionic crystals it is possible that the nature of the intermolecular forces between the gas and surface atoms may be quite different from the case which is of primary interest in this report (i. e., the interaction of gas atoms with metallic surfaces).

A logical extension of the experimental studies of the diffraction of helium, hydrogen, and neon from alkali halide crystals was to use the same apparatus to investigate the scattering pattern of heavier atoms (i.e., shorter de Broglie wavelengths) such as argon, nitrogen, and mercury. The results of these experiments are summarized below although their validity is questionable because the test surfaces may have been covered partially with adsorbed impurities. (Water vapor may be the most detrimental adsorbate, Refs. 66 and 67.)

The scattering of mercury atoms from alkali halide crystals is an interesting case because the mass of mercury is large compared to the mass of the crystal atoms and to the mass of those gaseous species which exhibit strong diffraction effects (e.g., helium and hydrogen). As a result, the average momentum of mercury atoms impinging with thermal energy is unusually large, and their de Broglie wavelength is much smaller than the lattice spacing. From these points, together with the fact that at thermal temperatures mercury condenses readily on a large number of substances, it would be expected that the energy transfer in this particle-surface interaction should be large and the scattering pattern should be diffuse. It is surprising, therefore, that Hancox (Ref. 67), Josephy (Ref. 68), and Zahl and Ellett (Ref. 69) have observed pseudospecular patterns for mercury scattered from various alkali halide crystals (Fig. 8). The results of these experiments may be summarized as follows:

1. A pseudospecular lobe appears in the scattering pattern when a significant fraction of the adsorbed impurities have been removed by thermal desorption.

<sup>\*</sup>That the adsorption of gases and vapors on alkali halide crystals is generally weak has been established in a number of studies (Refs. 70 and 71)
- 2. The direction of this lobe deviates from the direction of specular reflection; the deviation generally increases with increasing angle of incidence\*.
- 3. Although the lobe is usually located between the surface normal and the specular direction, it may lie below the specular direction when the incidence angle is small (< 30 deg).
- 4. The angular position of the lobe increases with increasing gas temperature and decreasing surface temperature.
- 5. As the surface temperature is reduced, the width of the lobe decreases although its intensity falls off because a greater fraction of the atoms is scattered diffusely; it is believed that the first effect results from reduced thermal motion of the surface atoms, whereas the second is attributed to the adsorption of impurities (Ref. 67).
- 6. There are no significant changes in the scattering pattern when the crystal is rotated about its normal, indicating that, contrary to the case of diffraction, there is no strong dependence on the spacing of the rows of surface atoms.

The different attempts to explain these features of the scattering pattern by means of simple theoretical models will be discussed in Section 5.4. It suffices here to emphasize the fact that these results clearly show that in this specific particle-surface interaction there are preferred directions for momentum transfer which are functions of the angle of incidence and the temperatures of the gas and the surface. Although the measurement technique\*\* employed in these studies does not provide a direct means for determining the degree of energy accommodation, it is expected to be incomplete because momentum accommodation is incomplete.

An experimental program conducted at Carnegie Institute of Technology was designed to determine the velocity distribution of atoms

<sup>\*</sup>The reader is reminded here that the angle of incidence is measured from the surface normal.

<sup>\*\*</sup>The scattering patterns were measured with an ionization gage which revolved about the crystal. This technique provides direct measurements of the intensity of the scattered atoms versus angular position; it does not provide a direct measurement of either the momentum or energy of the scattered atoms.

scattered from solid surfaces (Ref. 32). In order to reduce the problem of detecting the small signals of the scattered atoms, potassium was selected as the molecular beam vapor because it permits use of the surface ionization gage technique. At an incidence angle of 45 deg and with the detector positioned along the specular direction, the measured velocity distribution of potassium scattered from lithium fluoride deviated significantly from Maxwellian, the deviation being greatest in the low-speed portion of the distribution. The energy accommodation coefficient computed from these results is  $0.7 \pm 0.1$  for surface temperatures between 600 and 900°K and incident beam temperatures from 550 to 750°K. That the distribution was not Maxwellian and the accommodation coefficient was not unity is somewhat a surprise because: (1) at thermal temperatures potassium condenses readily on many substances, (2) the attractive forces between potassium and a large number of substances are quite strong because of the loosely bound valence electron of alkali metal atoms, (3) the same researchers found that energy accommodation was complete for potassium scattered from Cu, W, Au, and MgO, and (4) similar experiments performed earlier in other laboratories indicated complete accommodation (Refs. 72 and 73).

It is unfortunate that in the above-mentioned investigation the measurements were restricted to the specular direction and a single angle of incidence (45 deg). Measurements of the speed distribution at all possible combinations of incidence and scattering angles certainly provide the most complete description of a gas-surface interaction.

From these results obtained for mercury and potassium, the pseudospecular pattern might be expected to be even more pronounced in the case of inert gases scattered from alkali halide crystals. This expectation is substantiated by the scattering patterns reported recently by Crews (Ref. 65) for argon on a lithium fluoride crystal. \* With both the surface and gas temperatures at 24°C and an incidence angle of 68.5 deg from the normal, the pattern exhibits a broad pseudospecular lobe having maximum intensity in a direction that is 11.5 deg above the specular direction. This angular deviation was found to be independent of the azimuthal orientation of the crystal about its normal; there were indications, however, that the width of the lobe did vary slightly as the crystal was rotated

<sup>\*</sup>References to other investigations related to this subject may be found in Crews' paper (Ref. 65).

about its normal. If the anomalous argon data are compared with the welldefined diffraction patterns obtained for helium in the same apparatus, the conclusion is that argon is not diffracted by the crystal to an extent that is detectable in the present experiment (Ref. 65). Crews also concludes that the argon pattern is not a simple superposition of a diffuse and a specular pattern.

#### 5.2.2 Single-Crystal Gold Surfaces

The recent work of Smith and Saltsburg (Ref. 74) appears to be the first investigation of the scattering of gases from metallic single-crystals. They have successfully solved the problem of obtaining a clean surface of known orientation by employing epitaxially grown gold films which may be deposited continuously during an experimental run. The films had a shiny appearance, and their structure was that of a twinned single-crystal with the (111) plane parallel to the surface.

The scattering patterns of helium, neon, argon, and xenon are shown in Fig. 9 for a gas temperature of 300°K, a surface temperature of about 600°K, and an incidence angle of 50 deg. Although the helium pattern appears to be highly specular, the patterns for the other gases are pseudospecular because the angular positions of their intensity maxima deviate from the specular direction. The main feature of these results is that the deviation and dispersion\* of the pseudospecular patterns increase with the molecular weight of the test gas.

When the temperature of the incident gas is increased from 300 to 2550°K with all other conditions remaining the same, the helium pattern is unchanged, whereas the patterns for neon and argon become specular and less disperse (see Fig. 10). In the case of xenon, the intensity maximum also shifts to the specular direction, the the presence of a large diffuse component led Smith and Saltsburg to hypothesize that the pattern consisted of a superposition of diffuse and specular components. The xenon pattern is almost identical to those for the other noble gases if the diffuse component is subtracted from the data.

Smith and Saltsburg also investigated the effects of surface contamination. Additions of water vapor and carbon monoxide to the background gas resulted in increased dispersion of the patterns of all test gases; additions of nitrogen, oxygen, and acetylene had little effect. Contamination also caused the intensity maxima to be displaced toward the surface normal.

<sup>\*</sup>As used here, the term dispersion refers to the broadening of the pseudospecular lobe.

It is possible to degrade the structural perfection of gold films by maintaining the substrate at sufficiently low temperatures during deposition. The rough, polycrystallinc films obtained by this technique produced diffuse scattering patterns.

Saltsburg and Smith have extended this investigation recently to include silver surfaces (Ref. 75). The results are essentially the same as those obtained with gold surfaces.

## 5.3 SCATTERING FROM ENGINEERING SURFACES

Since the surfaces of satellites and flight vehicles are neither clean nor single-crystal in general, it is of practical importance to study the scattering of particles from the common engineering materials in their most natural form. These engineering surfaces usually have rough, polycrystalline structures which are covered with oxides, organic substances, and adsorbed gases. As would be expected, the scattering patterns are generally diffuse for this class of surfaces.\* It should be emphasized, however, that diffuse scattering is not always indicative of complete energy and momentum accommodation (Ref. 38).

The first indication that the scattering from metallic engineering surfaces could deviate significantly from a diffuse pattern was reported in 1962 (Refs. 25 and 78). This change was the result of several improvements in experimental technique: (1) the degree of surface contamination was reduced by the development of better diffusion pumps and refrigerated baffles, (2) through proper selection of the test specimen material, it is possible to obtain a surface which is capable of being cleaned to a large extent by heating it to high temperatures in vacuum or in either a reducing or oxidizing atmosphere, (3) recontamination of the surface is reduced by maintaining the specimen at moderate temperature levels throughout the experimental run, and (4) modulated atomic beam techniques enable the detection of smaller signals.

Smith and Fite (Ref. 25) have investigated the scattering of hydrogen and argon from polycrystalline nickel. \*\* The results of the first stage of this study indicated that scattering was diffuse for all surface temperatures in the experimental range (20 to 1200°C). It was known that the

<sup>\*</sup>Hurlbut has observed diffuse patterns for nitrogen scattered from steel and aluminum specimens (Ref. 76); pseudospecular patterns were observed for nitrogen, argon, air on glass, and Teflon<sup>®</sup> (Ref. 77).

<sup>\*\*</sup>Tungsten was investigated to a lesser extent in this study.

surface was not clean during these initial runs because a temperature of 1200°C is not sufficient to desorb oxygen from nickel, and the residual gas pressure of approximately  $10^{-7}$  mm Hg was too high to maintain clean surface conditions during measurements. The next step was to heat the specimen in a hydrogen atmosphere in order to remove oxides. Following this treatment, the scattering patterns for hydrogen and argon were pseudospecular for surface temperatures in the range from 200 to 800°C, although diffuse patterns were observed for surface temperatures above and below this range. This temperature dependence of the scattering pattern was thought to result from the following processes: (1) diffuse scattering occurs at low surface temperatures because of the adsorption of residual gases upon the specimen increases, (2) for surface temperatures between 200 and 800°C, most of the residual gas contaminants desorb but the presence of carbon impurities modifies the surface structure so as to produce pseudospecular reflection, and (3) above 800°C the carbonnickel surface undergoes a structural change\* which results in diffuse scattering. Smith and Fite established the importance of carbon impurities by showing that the pattern changed from diffuse to pseudospecular when an ultrapure nickel specimen was deliberately carbonized. They also illustrated the effect of oxygen: pseudospecular scattering was degraded to diffuse scattering by heating the specimen in an increased background pressure of oxygen.

Smith extended the above-mentioned study to include helium, neon, and krypton in addition to hydrogen and argon (Ref. 79). As before, the nickel specimen was intentionally carbonized in order to obtain the pseudospecular behavior. The surface was polycrystalline with an average grain size of  $\sim 0.1$  mm after heating in vacuum. It was not expected that the surface was completely free of adsorbed contaminants such as oxygen, but supplementary tests proved that the scattering patterns are not sensitive to substantial increases in the pressures of various residual gases. Only room temperature molecular beams were employed, and the angle of incidence was limited to the range from 50 to 60 deg. The main features of the experimental results are similar to those associated with scattering from alkali halide and gold crystals. That is, the angular position of the intensity maxima of the scattering patterns deviates more from the specular direction as either the surface temperature\*\* or mass of the incident molecules is increased.

<sup>\*</sup>Detailed studies of the effects of carbon and oxygen on the structure of nickel surfaces have been conducted using the low-energy electron diffraction technique (Ref. 11).

<sup>\*\*</sup>This statement is valid only for temperatures within the range which causes pseudospecular scattering (i.e., from 150 to 900°C).

The detector employed by Smith enabled him to determine approximately the dependence of energy accommodation on the angular direction of the scattered particles (Ref. 79). As would be expected, these results show that the degree of energy accommodation is lower in the direction of the pseudospecular maximum than the direction of the surface normal. Results of a supplementary experiment indicate that the probability of a molecule being scattered diffusely increases as its initial (i.e., incident) speed decreases. These points led Smith to postulate the following qualitative model. The scattering patterns consist of a superposition of two components: (1) a diffuse component which is formed primarily from the slower particles of the incident beam (although this component is diffuse, its energy is not necessarily accommodated completely to the surface), and (2) a pseudospecular component resulting from faster particles which are accommodated to a lesser degree (this accommodation is not necessarily zero, and the direction of maximum intensity is not required to correspond to the specular direction). This model will be discussed further in Section 5.4.

Pseudospecular scattering patterns have also been reported for platinum surfaces. Datz, Moore, and Taylor (Ref. 78) studied the scattering on helium and deuterium from a polycrystalline platinum ribbon having large grains (~1 mm) which were extremely smooth. A systematic study of helium, neon, argon, and krypton on platinum has been conducted by Hinchen and Foley (Ref. 80). The results of these investigations will not be discussed in detail here because their main characteristics are similar to those of the results for nickel and gold which were described above. The following points are particularly noteworthy: (1) contrary to the case of nickel, the patterns observed for platinum do not exhibit the degradation to diffuse scattering at high surface temperatures (Ref. 78), (2) background pressures of oxygen above a certain critical level ( $\sim 5 \times 10^{-6}$  mm Hg) caused the pattern to change from pseudospecular to diffuse, and (3) energy accommodation coefficients measured in the direction of maximum intensity of the pseudospecular lobe appeared to be rather insensitive to surface temperature (Ref. 80).

In these platinum studies the degree and nature of surface contamination was unknown. Recently, however, Moore, Datz, and Taylor (Ref. 81) have investigated the effects of various surface treatments on the scattering characteristics. The results indicate that carbon impurities generally exist on the platinum specimens, a situation which is identical to that for impure nickel specimens as reported earlier by Smith and Fite (Ref. 25). The following treatment was employed to reduce the carbon impurities: the platinum was cycled for several minutes between 900 and 1600°K in a relatively high pressure of oxygen (~ $10^{-3}$  mm Hg) and then maintained at 1300°K in oxygen at ~ $10^{-6}$  mm Hg throughout the scattering measurements. This treatment produced the peculiar pattern for helium shown in Fig. 11. The outstanding feature here is the double-lobe nature of Curves I and III which suggests that diffraction processes may be influential. Moore, Datz, and Taylor (Ref. 81) stated that these results were unexplainable at the present time and that they plan to continue the investigation after replacing the polycrystalline speciment with a single crystal.

#### 5.4 THEORETICAL MODELS OF PARTICLE-SURFACE SCATTERING PROCESSES

The experimental results discussed in Sections 5.2 and 5.3 indicate that there are many definite similarities between the scattering patterns of a number of different surfaces. It is truly remarkable that these similarities should exist for several gases (e.g., the inert gases, hydrogen, and mercury) on a wide variety of solids (e.g., ionic and metallic, monocrystalline and polycrystalline, with different lattice structure, surface preparations, impurities, and atomic masses). The main characteristics which are common to the majority of these scattering patterns are summarized below:\*

#### Characteristic 1:

A pseudospecular lobe often appears in the scattering pattern when the surface is either clean or contaminated in a special manner (e.g., with carbon).

#### Characteristic 2:

Energy accommodation is less complete for the particles in the pseudospecular lobe than for those scattered in the direction of the surface normal.

#### Characteristic 3:

Other conditions being the same, the deviation of the preferential direction\*\* from the specular direction increases with the mass of the gas particles.

<sup>\*</sup>These characteristics apply specifically to the inert gases; although the experimental data are lacking, it is believed that all of these characteristics apply to hydrogen and mercury also.

<sup>\*\*</sup>The preferential direction is the direction of maximum intensity of the pseudospecular lobe.

## Characteristic 4:

The angular position of preferential direction increases with the energy of the incident particles.

## Characteristic 5:

The angular position of the preferential direction increases with decreasing surface temperature as long as this temperature remains sufficiently high to inhibit contamination caused by adsorption of residual gases.

## Characteristic 6:

The dispersion (e.g., the width of the pseudospecular lobe) decreases with surface temperature as long as this temperature remains sufficiently high to inhibit contamination.

## Characteristic 7:

The deviation of the preferential direction from specular increases with the angle of incidence (i.e., the deviation is greatest for grazing angles).

The existence of a pseudospecular pattern (Characteristic 1) indicates that the gas particles are not completely accommodated to the surface and the surface is sufficiently smooth that the probability of a particle experiencing more than a single collision with the surface before escaping is negligible. In addition, the existence of a narrow lobe indicates that the structure and composition of the surface are very uniform.

A valid theoretical model of gas-surface interactions must be compatible with all seven of the characteristics listed above. In this section, the qualitative features of a number of simple, classical models will be considered. The choice of classical mechanics rather than quantum mechanics is not clearly justified, as was mentioned previously in Section 3.1.

An attempt will be made to apply the ideas developed in Section 4.1 to this problem. On the basis of experimental data obtained by Thomas et al. (e.g., see Fig. 4), it was postulated that as the energy of incidence of a given gas increases, the particle-surface interaction changes from the partial trapping regime to the nonadiabatic regime. Assuming this model to be valid, it is seen in Fig. 4 that, at room temperature, helium and neon are in the nonadiabatic regime, whereas argon, krypton, and xenon are still in the partial trapping regime. Thus, at slightly higher gas temperatures (i.e., higher incident energies), the accommodation coefficients of helium and neon remain essentially constant, whereas those of argon, krypton, and xenon decrease significantly. If the interaction of these inert gases with other metals is similar to that shown in Fig. 4 for tungsten, a possible explanation of Characteristics 3 and 4 has been found. For example, the following points should be considered:

- 1. The scattering patterns for helium and neon are nearly specular at room temperature and above (Figs. 9 and 10) because they are already in the nonadiabatic regime where their accommodation coefficients are very small as a result of their low molecular weights and weak adsorption energies.
- 2. The temperature of transition from the partial trapping regime to the nonadiabatic regime increases with the mass of the inert gas atom because both the degree of polariz-ability and the temperature of the critical point increase. This is in accordance with Characteristic 3.
- 3. Since argon, krypton, and xenon are in the partial trapping regime at room temperature, the high-speed atoms in the velocity distribution will be accommodated less than the low-speed atoms.\* In addition, the degree of accommodation will decrease as the gas temperature increases and, therefore, the preferential direction will increase\*\* in agreement with Characteristic 4.

As it now stands, the model proposed in Section 4.1 is not applicable to Characteristics 5 and 6 because it was based on the assumption that surface temperature remains constant at a low level. Therefore, further additions to the model are required. It seems reasonable to expect that the decrease in dispersion with surface temperature (Characteristic 6) results from the reduction of the noise or randomness associated with the thermal motion of the surface atoms. An explanation of the dependence of the preferential direction on surface temperature (Characteristic 5) is much less obvious. One possible approach is the following. It is assumed that the assymmetric nature of the solid surface causes the momentum transfer processes of gas-surface interactions to be anisotropic (e.g., the coefficient of normal momentum transfer is not equal to the coefficient of tangential momentum transfer). If momentum

<sup>\*</sup>This point agrees with Smith's experimental results for nickel (Ref. 79).

<sup>\*\*</sup>On the basis of the optical analog and Characteristic 2, it is assumed here that as the energy accommodation coefficient decreases, the preferential direction approaches the specular direction. It is not possible at the present time to justify this assumption completely; it would certainly be valid if the surface were a perfectly smooth plane. This question will be discussed later.

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accommodation is greater for components normal to the surface than it is for tangential components, \* the preferential direction of the scattered particles will increase with increasing gas temperature and decreasing surface temperature, just as required by Characteristics 4 and 5, respectively. Furthermore, as the gas temperature is increased above the surface temperature, the preferential direction will increase to the extent that it may be located below the specular direction; this is in agreement with the results of several different experiments (Refs. 67, 75, 81, and 82). Following this line of reasoning, Logan and Stickney (Ref. 83) have proposed a simple classical model for describing, qualitatively, some of the main features of gas-surface scattering patterns.

The problem has been oversimplified in the preceding discussion because the fact has been neglected that the interaction may depend strongly on the point of impact of the gas atom on the solid lattice. As mentioned in Section 2.2, the intermolecular potential of the gas-surface interaction varies with the point of impact because the surface is not a perfectly smooth plane on the atomic scale. Since the most probable position of the point of impact depends on the angle of incidence, the azimuthal angle (that is, the orientation of the principal axes of the surface lattice with respect to the direction of the incident gas atoms)\*\*, the lattice spacing, the surface uniformity, and the magnitude of the intermolecular potential, it follows that this problem is extremely complex. In addition, it is impossible to determine the point of impact by direct experimental observation. Therefore, the position of the impact point must be deduced from the characteristics of the scattering patterns, and the validity of these deductions is suspect.

It may well be that this classical concept of a point of impact is unrealistic and should be abandoned in favor of a region of interaction, since both the range of the intermolecular forces and the wave-mechanical nature of the particles suggest that a gas atom interacts simultaneously with a number of solid atoms. This question was discussed in Section 3.1, and it was stated that the mathematical complexities associated with wavemechanical approaches have caused the majority of researchers to resort to classical approaches. However, these researchers have tried to employ models which include classical analogs of the most influential quantum effects (e.g., the nature of lattice vibrations).

\*Datz, Moore, and Taylor (Ref. 78) have proposed that this may result from the fact that the probability for the gas atom receiving an impulse from the surface atom is greatest in the direction of the surface normal.

\*\*This is some evidence that the azimuthal angle is not important except in the special case of diffraction (Refs. 65 and 67).

The theoretical analyses of Oman et al. (Ref. 17) and Trilling (Ref. 47) were described briefly in Section 3.1, and the principal assumptions associated with their models were examined. These analyses will not be considered in greater detail here because the results are still quite limited and the validity of the models is questionable. It suffices to say that both are capable of yielding results which agree qualitatively with experimental data (i.e., pseudospecular scattering with partial accommodation of energy). A more rigorous evaluation of these theoretical treatments will be possible after both are employed in attempts to interpret the experimental results which are now being obtained for single-crystal specimens (Refs. 74 and 75).

# SECTION VI SUGGESTIONS AND CONCLUSIONS

From the preceding considerations it is quite obvious that the study of gas-surface interactions is not a well-established science. It is believed, however, that significant advances may be obtained in the near future through the use of the improved experimental and analytical techniques which will be discussed below.

#### 6.1 EXPERIMENTAL STUDIES

Detailed experimental investigations of gas-surface interactions require an apparatus having the following features:

- Variable Beam Energy. In order to simulate high-speed flight conditions, the energy of the incident particles must be variable from essentially zero to several electron volts. It should be noted also that data over a range of energies are necessary to establish the general parameters and trends which aid in formulating a physical model of the interaction. A thorough discussion of supersonic molecular beams has been presented recently by Knuth (Ref. 84); this report also includes references on ion beams.
- 2. Variable Surface Temperature. Since the majority of the existing theoretical models are based on the assumption that the initial motions of the surface atoms may be neglected (see Section 3.1), it is of interest to obtain data for low surface temperatures so that a valid comparison of theory with experiment may be made. In addition, data for variable temperature are required in order to ascertain the effects on energy and momentum transfer.

- 3. Variable Angle of Incidence. Much additional information on the nature of gas-surface interactions is provided by varying the incidence angle (Section V).
- 4. Controllable Surface Cleanliness. In order to study the effects of surface impurities on energy and momentum transfer, the level of surface contamination must be determined and controlled. A detailed discussion of the production of clean surfaces has been presented by Roberts (Ref. 24). Recent investigations by means of the low-energy electron diffraction technique have shown that it is often difficult to remove certain impurities, such as carbon, from surfaces (Refs. 11 and 85). The maintenance of controlled surface conditions generally requires an ultrahigh vacuum system.
- 5. Well-Defined Crystallographic Structure. The surface structure of a test specimen must be uniform and well defined if the experimental results are to be of maximum usefulness in formulating a theoretical model of the interaction. It is fortunate that high-purity single-crystals are now available commercially.
- 6. Intensity and Velocity Detectors. As discussed in Section III, the ideal detector would be capable of measuring the distribution function (i.e., intesnity, speed, and direction) of the scattered gas atoms. Various designs of velocity detectors are described in Refs. 33 and 86. If the beam intensity is below the useful limit of these velocity detectors, the narrow-band amplification and phase-sensitive detection technique which is capable of measuring relative intensities and average speeds may be employed (Ref. 25).

Two types of experimental studies are needed: (1) exploratory studies of the general features of gas-surface interactions for a variety of gases and solids over a wide range of temperature, angle of incidence, and surface conditions, and (2) detailed studies of interactions occurring at well-defined surfaces.

The exploratory studies are needed in order to determine the gross properties of various gas-surface interactions. In addition to providing necessary engineering data, the results of these experiments would establish general relationships between interaction properties and the principal variables or parameters. It would be desirable to be able to determine the dependence of the scattering pattern, energy accommodation coefficient, and capture or sticking coefficient on the variables listed in Section 2.4.

Following the completion of exploratory studies, it would be desirable to perform detailed investigations of the interaction of particles with well-defined surfaces. The primary purpose of these experiments would be to obtain the data which are needed in order to test and improve the existing theoretical models.

### 6.2 THEORETICAL STUDIES

There are a number of basic questions which must be answered before it is possible to establish a valid theoretical treatment of gassurface interactions. When is it appropriate to use classical mechanics in place of quantum mechanics? What are the detailed characteristics of the intermolecular potential for a gas atom at a solid surface? Is the asymmetric nature of a surface of principal importance? Under what conditions does the phonon or frequency spectra of the solid influence gas-surface interactions? What are the effects of surface roughness, imperfections, and crystallographic structure? When is it permissible to neglect the initial motion of the surface atoms (i.e., neglect the effect of surface temperature)?

There is little hope of finding a single theoretical model which will be valid over the entire range of interaction energy. More likely, there are many interaction regimes, and it would be best to develop a specific model for each case (Section IV). This situation is similar to that existing in fluid mechanics where it has been found that, in general, each regime is described best by adopting different physical models and analytical methods. Hence, a rational program would be to identify the various interaction regimes and then concentrate on each separately rather than attempting to discover a universal solution.

## 6.3 CONCLUSIONS

In addition to governing heat transfer and drag in rarefied gases, the energy and momentum transfer characteristics of gas-surface interactions affect the behavior of substances in space environments, the pumping speeds of cryopumps and getters, the deposition rate of thin films, and the efficiene cies of catalysts. It is expected that potential applications such as these will cause the general field of gas-surface interactions to grow at an exceptional rate during the present decade. This growth would be a logical extension of that experienced by solid-state physics in recent years.

The basic mechanisms of energy and momentum transfer in gassurface interactions will not be understood in sufficient detail until additional experimental and analytical investigations have been conducted. There is a good possibility these investigations also will provide unique information on the nature of surfaces and intermolecular potentials and the use of impurities to construct surfaces possessing exceptional properties (Ref. 56).

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# APPENDIX I DERIVATION OF THE ENERGY ACCOMMODATION COEFFICIENT FOR THE HARD-SPHERE MODEL

Consider the energy transfer associated with the collision of two spheres which are unbound and perfectly elastic. The case of head-on collisions may be treated as a one-dimensional problem because only the velocity components along the line connecting the centers at the time of impact are affected. In this case, let v and V represent the velocity components of the spheres of mass m and M, respectively. The momentum and energy equations are:

$$mv + MV = mv_o + MV_o \qquad (I-1)$$

$$1/2 \text{ mv}^2 + 1/2 \text{ MV}^2 = 1/2 \text{ mv}_0^2 + 1/2 \text{ MV}_0^2$$
 (I-2)

where  $v_0$  and  $V_0$  are the velocities before the collision. Equation (I-1) may be expressed as

э,

$$m(v_o - v) = -M(V_o - V)$$
(I-3)

and Eq. (I-2) as

$$m(v_{o} - v)(v_{o} + v) = -M(V_{o} - V)(V_{o} + V)$$
(I-4)

Dividing (I-4) by (I-3) gives

$$(v_0 + v) = (V_0 + V)$$
 (I-5)

This may be used to eliminate v from Eq. (I-1), thereby obtaining the following expression after rearrangement:

$$V = \frac{2 m v_{o} + (M - m) V_{o}}{M + m}$$
 (I-6)

With the above relation an expression may be derived for the energy transfer from M to m:

$$1/2 M (V_o^2 - V_o^2) = \frac{2 m M}{(M + m)^2} (V_o - v_o) (MV_o + mv_o)$$
(I-7)

If the sphere of mass m is initially at rest ( $v_0 = 0$ ), this reduces to

$$1/2 M (V_0^2 - V^2) = \frac{2\mu}{(\mu + 1)^2} M V_0^2$$
 (I-8)

where  $\mu = M/m$ .

As discussed in Section 3.1, the energy accommodation coefficient may be defined as

$$a = \frac{\mathbf{E}_{i} - \mathbf{E}_{r}}{\mathbf{E}_{i} - \mathbf{E}_{w}}$$
(I-9)

Assuming that the surface temperature is essentially zero (i.e.,  $E_W = 0$ ) and that m and M represent the surface atom and the gas atom, respectively, Eq. (I-8) may be substituted for the numerator of Eq. (I-9) and  $E_i = 1/2 \text{ MV}_0^2$  for the denominator:

$$a = \frac{4\,\mu}{(\mu+1)^2} \tag{I-10}$$

This result predicts that  $\alpha$  depends only on  $\mu$ , the ratio of the molecular weights of the gas and the surface atoms.

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Fig. 1 Simple Surface Model



Fig. 2 Intermolecular Potential between a Gas Atom and a Surface Atom





Fig. 3 Dependence of Intermolecular Potential on Position



Fig. 4 Temperature Dependence of the Energy Accommodation Coefficient of Inert Gases on Tungsten (Ref. 34)







Fig. 6 Postulated Regimes of the Energy Accommodation Coefficient of Chemisorbable Gases





	Crystal	Beam
<u>Curve</u>	Temperature, <sup>o</sup> C	<u>Temperature, <sup>o</sup>C</u>
А	50	170
В	350	170
С	50	500
D	350	500





Fig. 8 Angular Distribution of Mercury Atoms Scattered from NaCl as a Function of the Crystal Temperature and the Temperature of the Incident Beam (Ref. 69)



Fig. 9 Angular Distributions of He, Ne, Ar, and Xe Scattered from Clean Gold Film (Ref. 74)

Note: Beam temperature  $\approx 2550^{\circ}$ K; target temperature  $\approx 600^{\circ}$ K. The symbols for the various gasses are the same as those in Fig. 9; angle of incidence is 50 deg, measured from surface normal.







Note: In order to remove carbon impurities from the platinum surface, the specimen was cycled for several minutes between 900 and  $1600^{\circ}$ K in a relatively high pressure of oxygen (~10<sup>-3</sup> torr) and then maintained in an oxygen atmosphere (~10<sup>-6</sup> torr) at high temperature (~900°K) before and during measurement.

Fig. 11 Angular Distribution of Helium Scattered from Platinum (Ref. 81)

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The principal mechanisms of energy and momentum transfer between gas atoms and solid surfaces are considered for the range of impact energies encountered in high-speed flight (e.g., up to 10 ev). In- cluded within are (1) introductory discussions of the nature of sur- faces, intermolecular potentials, adsorption, and basic gas-surface interaction processes, (2) a critical survey of the definitions of energy and momentum accommodation coefficients, (3) summaries of existing theoretical and experimental results pertaining to the energy accommodation and directional distribution of atoms scattered from a surface, (4) an attempt to formulate the main parameters and regimes of gas-surface interactions, and (5) suggestions con- cerning future investigations.									

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