EXCHANGE OF ENERGY AND MOMENTUM BETWEEN GAS PARTICLES AND THE SURFACE OF A SOLID

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This problem involves solving the equations of motion for all interacting particles if it is treated from the viewpoint of classical mechanics. The problem can be simplified in certain instances [1-3], e.g., by considering the atoms of the solid as independent harmonic oscillators [2], which gives a correct picture if the collisions are not
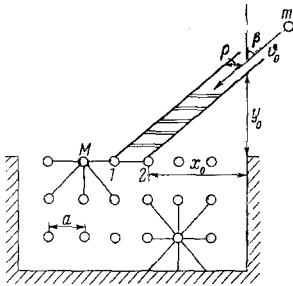

Fig. 1

prolonged. An attempt has been made [3] to take account of the effects of adjacent lattice atoms on the gas-solid interaction. In this case, the motion of not more than six atoms of the solid was discussed. The limits of application of these simplifications will not be examined here, but we note that it is necessary to take into account the bonds between atoms in the solid when the gas-solid collisions become prolonged. The exact number of bonds is dependent on the detailed conditions.

One method of simplification is to consider an equivalent planar model for the solid, which substantially reduces the volume of calculations. Here the gas-solid interaction is described via a model previously proposed [1], with revision of: 1) the choice of number of atoms needed in the description, 2) the definition of the parameters in the potential for interaction of the atoms in the solid, and 3) allowance for the effects on the gas atoms from atoms in the solid not located in the plane of motion.

§1. PLANAR MODEL

a) The basic parameter is the shortest distance a between atoms when a solid is represented as a planar square lattice, and this is dependent on the parameters of the actual spatial lattice. We shall consider the relation of the exchange coefficient to a.

b) The lattice atoms are assumed to have pair interaction via a Morse potential:

$$U(r) = D\left[e_2^{-2c(r-b)} - 2e^{-c(r-b)}\right],\qquad (1.1)$$

in which r is the distance between particles and b, c, and D are parameters. Each surface atom interacts with five neighbors, and each internal one with eight (Fig. 1). If we use parameters defined for the space lattice [4], characteristics such as the binding energy will differ greatly between the planar and spatial models. We therefore derive the parameters on the basis of equivalence of the parameters at the surface in the two cases, as follows:

1) A lattice atom is at its equilibrium position in the absence of interaction with a gas atom (sum of the forces on an atom equal to zero).

2) E_{s2} (binding energy of a surface atom in the planar lattice) should be equal to E_{s3} (that energy for the space lattice).

3) The period of vibration τ_{n2} of a surface atom in any direction (e.g., normal to the surface) should equal τ_{n3}, the same for the space lattice in the same direction.

These conditions correspond to the equations

$$e^{-2c(a\sqrt{2}-b)} - e^{-c(a\sqrt{2}-b)} + \tfrac{1}{2}\sqrt{2}\left[e^{-2c(a-b)} - e^{-c(a-b)}\right] = 0,$$

$$2c^2 D\left[2e^{-2c(a-b)}\left(1-\frac{1}{ac}\right) - e^{-c(a-b)}\left(1-\frac{2}{ac}\right) + \right.$$

$$+ e^{-2c(a\sqrt{2}-b)}\left(2-\frac{\sqrt{2}}{2ac}\right) -$$

$$\left. - e^{-c(a\sqrt{2}-b)}\left(1-\frac{\sqrt{2}}{2ac}\right)\right] = \frac{4\pi^2 M}{\tau_{3n}^2},$$

$$\left| 2D\left[e^{-2c(a\sqrt{2}-b)} - 2e^{-c(a\sqrt{2}-b)}\right] + \right.$$

$$\left. + 3D\left[e^{-2c(a-b)} - 2e^{-c(a-b)}\right]\right| = E_{s3},\qquad (1.2)$$

in which M is the mass of an atom in the body; this system is to be solved for b, c, and D.

c) We derive the parameters of the potential for interaction between the solid and gas atoms via the combination principle [5, 6], which may be formulated as follows for a Morse potential:

$$D_{ij}^2 = D_{ii}D_{jj}, \qquad 2c_{ij}^{-1} = c_{ii}^{-1} + c_{jj}^{-1}, \qquad 2b_{ij} = b_{ii} + b_{jj}. \qquad (1.3)$$

If the subscripts are the same, the interaction is that of atoms of the same kind.

d) A finite number of atoms in the solid is to be used because the number of equations increases with the number of atoms, and hence also does the computer time. On the other hand, the number of atoms must be large enough for $t > \tau$, in which t is the time taken for a perturbation generated at the surface to propagate through the atoms and be reflected at the far boundary to the surface, while τ is the duration of the interaction between solid and gas atoms. In that case, a gas atom reflected from the surface reaches the zone where the interaction with the surface is weak before the reflected perturbation reaches the surface. Obedience to $t > \tau$ is dependent on the ratio $\varkappa = m/M$, in which m is the mass of a gas atom, as well as on such factors as the angle of incidence β, the initial velocity v_0 of the gas atom, the interaction parameters, etc. Other conditions being the same, τ and $\varkappa$ increase together, and so high $\varkappa$ means that many lattice layers have to be considered. For instance, if $\varkappa \leq 0.5$ and $v_0 \approx 10^6$ cm/sec, three or four layers suffice to describe the interaction, while for $\varkappa = 0.5$ the energy should be such that a surface atom cannot escape from the lattice. We also have to choose the number of atoms in a layer. For an angle of incidence β (Fig. 1) and for an initial direction lying in the zone passing through the centers of atoms 1 and 2, we have the initial vertical coordinate $y_0 = x_0 \cot \beta$ in the worst case, where x_0 is the distance from atom 2 to the end of the upper layer. Here we must have $|U(y_0)| \ll E_0$, in which E_0 is the initial kinetic energy and $U(y_0)$ is the potential energy in the field of the solid. Then the number n of atoms in a layer is deduced from $n = 2x_0/a$, in which a is the parameter of the planar lattice. It is clear than n increases with β, but the interaction with the solid is weak when β is large, and so we can restrict consideration to fewer layers. In the present case, we have taken three layers of six atoms each for $\beta \leq 60°$, or one layer of 12 atoms for $60° \leq \beta \leq 80°$.

e) The gas atom is also influenced by atoms in the solid not lying in the plane of motion of the gas atom. The potential energy and force decrease very rapidly as the distances increase, so we need consider only a few layers in depth and a few layers laterally. We assume that these additional atoms do not move during τ. Here we consider two layers in depth and two layers to left and right.

§2. RESULTS AND DISCUSSION

Consider the accomodation coefficients for energy and momentum. That for the energy is

$$\alpha = 1 - \langle v^2 \rangle / v_0^2 , \qquad (2.1)$$

in which $\langle v^2 \rangle$ is the mean-square speed of a gas atom after collision, while v_0 is the speed before collision. The accommodation coefficients σ and σ' for the normal and tangential components of the momentum are

$$\sigma = \langle v_n \rangle / v_0, \qquad \sigma' = \langle v_\tau \rangle / v_0 , \qquad (2.2)$$

in which $\langle v_n \rangle$ and $\langle v_\tau \rangle$ are the mean normal and tangential components of the gas-particle velocity after collision. The averaging is performed with respect to parameter ρ (Fig. 1) via

$$\langle v \rangle = \left[\int_0^{1/2 a} v(\rho) \rho d\rho \right] \left[\int_0^{1/2 a} \rho d\rho \right]^{-1} . \qquad (2.3)$$

The sign of v_τ is dependent on the direction of escape relative to the original direction (positive if the direction is retained).

We now consider the interaction of a nitrogen molecule without allowance for the internal degrees of freedom, the solids being molybdenum and iron (M of 96 and 56). The parameters of the interaction potential for the atoms in the solid were derived via (1.2) for the following values of a, binding energy E_s of a surface atom, and period of vibration τ_n.

1) Model 1 (Mo), $E_s = 6.762$ eV [7], $\tau_n = 1.9 \cdot 10^{-13}$ sec, $a = 3.14$ Å, the last being the constant for the space lattice [8]. Solution of (1.2) gives $D_1 = 1.8886$ eV; $c_1 = 1.4153 \cdot 10^8$ cm^{-1}, $b_1 = 3.2583$ Å.

2) Model 2: $E_s = 6.762$ eV; $\tau_n = 1.9 \cdot 10^{-13}$ sec; $a = 2.85$ Å. Then $D_2 = 1.8344$ eV; $c_2 = 1.4032 \cdot 10^8$ cm^{-1}; $b_2 = 2.9845$ Å.

3) Model 3 (Fe): $E_s = 4.192$ eV [7]; $\tau_n = 1.6 \cdot 10^{-13}$ sec; $a = 2.85$ Å. The constant for the space lattice of Fe is 2.86 Å [8]. The parameters of the potential are $D_3 = 1.1889$ eV; $c_3 = 1.6552 \cdot 10^8$ cm^{-1}, $b_3 = 2.9434$ Å.

Formulas (1.3) are used with the parameters of the interaction potentials for identical atoms [4,9] in order to determine the parameters of the gas-solid interaction potential. We have

1) N_2-Mo interaction U: $D = 0.0964$ eV; $c = 1.5223 \cdot 10^8$ cm^{-1}; $b = 3.503$ Å.

2) N_2-Fe interaction U': $D' = 0.0692$ eV, $c' = 1.46 \cdot 10^8$ cm^{-1}; $b' = 3.437$ Å.

a) Normal incidence. Here we have considered the dependence of the exchange coefficients on the following: 1) mass ratio, 2) lattice parameter a, 3) characteristics of the solid, 4) gas-solid interaction-potential parameters, 5) incident energy. Results are given below for α and σ as functions of $\varkappa$ for models 1-3, with U taken as the gas-solid potential for models 1 and 2, and U' for 3. For $\varkappa$ of 0.15, 0.3,
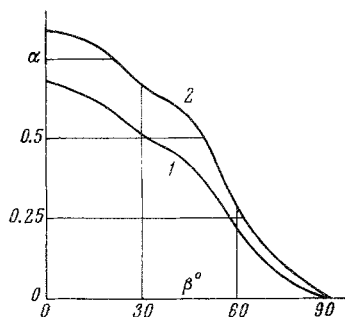
Fig. 2

and 0.4, E_0 was 14.5 eV, while the energy of the atom was $E_0/2$ for $\varkappa = 0.5$, because in that case the surface atom is detached for certain values of ρ if the energy is E_0, which affects the reflected gas atom.

$\varkappa =$	0.15	0.3	0.4	0.5	
$\alpha =$	0.437	0.682	0.791	0.837	(model 1)
$\sigma =$	0.686	0.516	0.422	0.370	
$\alpha =$	0.413	0.658	0.764	0.837	(model 2)
$\sigma =$	0.707	0.544	0.454	0.374	
$\alpha =$	0.448	0.699	0.803	0.838	(model 3)
$\sigma =$	0.691	0.514	0.417	0.379	

The results for models 1 and 2 show that α increases with a for a given gas-solid interaction potential. If $\eta = b/a$, in which b is the parameter of that potential, we can trace the variation in α with η. Mo-
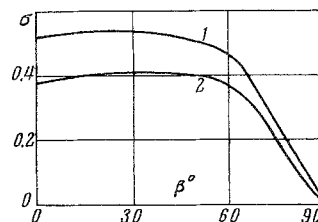
Fig. 3

del 1 gives $\eta_1 = 1.11$, while model 2 gives $\eta_2 = 1.23$. This 10% change in η involves a 6% change (at most) in α (for $\varkappa = 0.15$) and to a change of 7% (at most) in σ (for $\varkappa = 0.4$). Also, $d\alpha/d\eta$ is negative, whereas $d\sigma/d\eta$ is positive.

The following are results for α and σ for models 2 and 3, which differ in physical properties (binding energy, period of vibration) but which both have $a = 2.85$ Å. Potential U' has been used.

$\varkappa =$	0.3	0.4	0.5	
$\alpha =$	0.692	0.794	0.821	(model 2)
$\sigma =$	0.521	0.427	0.401	
$\alpha =$	0.699	0.803	0.838	(model 3)
$\sigma =$	0.514	0.417	0.379	

The changes in α and σ are 5% at the most. The results for model 2 with the two potentials are as follows:

$\varkappa =$	0.3	0.4	0.5	
$\alpha =$	0.658	0.764	0.837	(potential U)
$\sigma =$	0.544	0.454	0.374	
$\alpha =$	0.692	0.794	0.821	(potential U')
$\sigma =$	0.521	0.427	0.401	

The difference in α and σ arise here from the interaction potentials, since the η differ by only about 2.5% (1.23 for U, 1.20 for U'). The α for U' are higher than that for U for $\varkappa$ of 0.3 and 0.4 since the gas atom in the first case comes closer to the surface (D' < D), because the equipotentials for the gas-solid interaction have deeper wells for U', which increases the scope for multiple collisions. For $\varkappa = 0.5$ the main part is played by the fact that the perturbations in the lattice are large, the form of the equipotentials alters during the interaction, and the changes in α and σ arise because the reflected gas atom has to overcome a smaller potential barrier in the case of U'.

The following results give α as a function of E_0:

$\varkappa =$	0.292	0·4	0.5	
$\alpha =$	0.682	0.791	—	(E_0=14.5 eV)
$\alpha =$	0.649	0.761	0.837	(E_0= 7.25 eV)
$\alpha =$	—	—	0.830	(E_0= 4.83 eV)
$\alpha =$	0.653	0.790	—	(E_0= 3.625 eV)

The change in α in this range of E_0 does not exceed 5%.

b) Oblique incidence. Figures 2 and 3 show α and σ as functions of β as follows: 1) $\varkappa = 0.292$, potential U, $E_0 = 14.5$ eV, model 1; 2) $\varkappa = 0.5$, U', $E_0/2$, model 3. The results for σ' are as follows:

$\beta =$	15°	30°	45°	60°	70°	80°	
$\sigma' =$	0.100	0.340	0.510	0.739	0.886	0.972	($\varkappa$=0.292)
$\sigma' =$	0.129	0.342	0.508	0.762	0.881	0.962	($\varkappa$=0.5)

The differences from [10] are largest for $\beta > 60°$; in our case, α and σ are smaller by factors of 1.5–2, while our σ' is somewhat larger

[10]. The difference between the planar and spatial problems alone is insufficient to explain the differences, since closely similar results for the two problems are obtained in a model of close-packed hard spheres [10]. In the latter case, the radii of the atoms in the solid are inde-
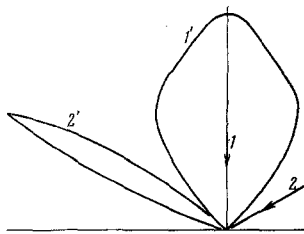

Fig. 4

pendent of β. In the model with potentials, a gas atom approaches the surface to a distance determined by E_0. The normal component of the velocity decreases as β increases, and so that distance increases. The equipotentials corresponding to low energies are smoother than those for high energies, so there is less energy and momentum exchange at large β in the potential model than in the hard-spheres model. This effect would correspond to variation of the radius with β in the hard-spheres model.

The following results are for α, σ, and σ' as functions of a (or η) for models 1 and 2 (potential U, E_0 = 14.5 eV, $\varkappa$ = 0.292 for model 1 and $\varkappa$ = 0.3 for model 2):

$\beta =$	15°	30°	45°	60°	70°	80°
			Model 1			
$\alpha =$	0.632	0.523	0.426	0.219	0.105	0.031
$\sigma =$	0.536	0.543	0.516	0.475	0.328	0.158
$\sigma'=$	0.100	0.340	0.510	0.730	0.886	0.972
			Model 2			
$\alpha =$	0.618	0.518	0.424	0.185	0.089	0.031
$\sigma =$	0.552	0.539	0.524	0.426	0.307	0.144
$\sigma' =$	0.160	0.390	0.526	0.793	0.903	0.974

This shows that reduction in a (increase in η) affects the accomodation coefficients as does increase in β. The differences are largest for σ' at small β (15 and 30°).

§3. INTERACTION OF MOLECULES WITH THE SURFACE

We now consider the effects of internal degrees of freedom on the accommodation coefficients. It has been shown [1, 11] that inelastic losses can occur when molecules collide with the surface.

a) We make the following assumption in order to determine the parameters for the interaction of the atoms in a molecule with some other atom: the potential U for that interaction is the sum of the potentials for the interaction of the atoms in the molecule with the third atom, the sum being averaged over the orientations of the molecule:

$$U = \langle 2\,U^* \rangle, \qquad (3.1)$$

in which $\langle \rangle$ denotes the averaging.

The form of U^* is that of (1.1), and we need three conditions in order to determine the three parameters of U^*:

1) $\langle 2\,U^* \rangle|_{r=b}$ = $-D$ when the distance r between the center of the molecule and the third atom is b;

2) The derivative of $\langle 2U^* \rangle$ with respect to r is zero for r = b;

3) $\langle 2U^* \rangle = 0$ for $r = b - c^{-1} \ln 2$.

The relation of U to $\langle 2U^* \rangle$ has been formulated for the case of r reasonably large, where the short-range forces are not decisive. These conditions give us the following:

1) N — M_0 (U_1^*):

$D_1^* = 0.0593$ eV; $c_1^* = 1.5356 \cdot 10^8$ cm^{-1}; $b_1^* = 3.3226$ Å,

2) N — Fe (U_2^*):

$D_2^* = 0.0419$ eV; $c_2^* = 1.4734 \cdot 10^8$ cm^{-1}; $b_2^* = 3.2642$ Å.

The potentials U and U' have been determined in §2 for the interaction of N_2 (taken as a whole) with Mo and Fe.

b) Let α' be the ratio of E', the translational energy of the center of mass of the molecule after collision, to E_0:

$$\alpha' = E' / E_0. \qquad (3.2)$$

Let α^* be the fraction of E_0 that is converted to energy of internal motion:

$$\alpha^* = \frac{T + U^+ - U_0}{E_0}, \qquad (3.3)$$

in which T is the kinetic energy of the relative motion of the atoms in the molecule, while U_0 and U^+ are the potential energies of those atoms before and after collision.

Then σ and σ' are defined as for an atom,

$$\sigma = \frac{v_n}{v_0}, \qquad \sigma' = \frac{v_\tau}{v_0}, \qquad (3.4)$$

in which v_n and v_τ are the normal and tangential components of the velocity of the center of mass of the molecule after collision, while v_0 is the velocity of the molecule before collision. The definitions of (3.2) and (3.3) are correct only when the molecule after collision still exists as a single entity; if dissociation or adsorption occurs, the definitions must be altered [1]. The fraction of the energy converted to heat is

$$\alpha = 1 - \alpha' - \alpha^*. \qquad (3.5)$$

The coefficients are calculated by averaging over the initial orientations of the molecule (angle φ_0) and with respect to ρ; φ_0 was varied from 0 to 180° by steps of 30°, with steps $\Delta\rho$ of 0.15 Å (the square in model 1 has a_1 = 3.14 Å, while model 2 has a_2 = 2.85 Å). Formula (2.3) is used for the averaging with respect to ρ, with integration replaced by summation in view of the discrete steps in ρ. The averaged results are denoted by $\langle\alpha\rangle$, $\langle\sigma\rangle$, $\langle\sigma'\rangle$.

Interaction of N_2 with Mo (model 1) for E_0 = 14.5 eV ($\varkappa$ = 0.292) gives

$$\beta = 0° - \langle\alpha'\rangle = 0.270, \quad \langle\alpha^*\rangle = 0.091,$$
$$\langle\alpha\rangle = 0.639, \quad \langle\sigma\rangle = 0.468,$$
$$\beta = 30° - \langle\alpha'\rangle = 0.396, \quad \langle\alpha^*\rangle = 0.138, \quad \langle\alpha\rangle = 0.466,$$
$$\langle\sigma\rangle = 0.503, \quad \langle\sigma'\rangle = 0.307,$$
$$\beta = 60° - \langle\alpha'\rangle = 0.763, \quad \langle\alpha^*\rangle = 0.056, \quad \langle\alpha\rangle = 0.181,$$
$$\langle\sigma\rangle = 0.422, \quad \langle\sigma'\rangle = 0.758$$

Similarly, N_2 with model 3 (E_0 = 7.25 eV, $\varkappa$ = 0.5) gives

$$\beta = 0°; \quad \langle\alpha'\rangle = 0.155; \quad \langle\alpha^*\rangle = 0.059; \quad \langle\alpha\rangle = 0.786;$$
$$\langle\sigma\rangle = 0.336.$$

In both cases the molecule before collision is in the ground state. In the case of interaction of the molecule with model 1, the energy conservation law is obeyed very precisely; model 3 involves large perturbations, so the conservation law is obeyed only to ~2%.

The results for molecules and atoms give not more than 12% change in $\langle\sigma\rangle$ and $\langle\sigma'\rangle$, while the maximum difference (20%) in $\langle\alpha\rangle$ occurs for β = 60°. For model 3 (N_2-Fe), the differences in $\langle\alpha\rangle$ and $\langle\sigma\rangle$ for normal incidence are 6.5 and 3.5%, respectively.

Figure 4 shows the scattering indicatrices for molecules for: 1) β = 0, 2) β = 60° constructed by reference to 132 loci for each angle (model 1, E_0 = 14.5 eV).

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