INTERACTION OF MOLECULES WITH THE SURFACE OF A SOLID

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The interaction of molecules and atoms with the surface of a solid is considered on the basis of classical mechanics. A two-dimensional square lattice with atoms arranged at the lattice points was taken as the model for describing a solid. It is assumed that only neighboring atoms interact in the solid, while the gas molecules interact with the atoms located in its surface layer.

As a result of "collisions" with the surface, a gas molecule loses a part of its kinetic energy, and this process is characterized by the energy accommodation coefficient. In addition, another coefficient is introduced which takes account of that part of the energy of translational motion converted into energy of internal motion of the molecule (vibration and rotation). The possibility of the occurrence of inelastic losses and some special features of this phenomenon are illustrated by the interaction of a diatomic molecule with an isolated atom.

The available experimental data on the interaction of particles of gas with the surface of a solid are essentially associated with the low-energy region (the temperature of the gas is less than or on the order of several hundreds of degrees). One of the objectives of this research was to find the distribution function of particles reflected from the surface; in particular, the hypothesis of diffuse-specular reflection is tested [1–3]. However, the few experimental results provide evidence of the effect of a large number of factors on the nature of the interaction, rather than make it possible to establish strict laws for the process.

The theoretical investigations were conducted along the line of improving simple models—instead of modelling a solid by a one-dimensional chain of atoms [4, 5], two and three-dimensional lattices are introduced [6–8]. It is noted in [6] that the interaction of gas particles with a one-dimensional chain differs from the interaction with a three-dimensional lattice, and this fact can lead to a considerable divergence in the values of the accommodation coefficient when the mass of the incident molecule is comparable with the mass of an atom of the solid. It also follows from [6] that if we describe the interaction between gas atoms and those of the solid by the Morse potential, then we can select the parameters of the potential so that the calculated data will agree with the experimental data. Moreover, good results are obtained if we make use of parameters of the potential determined on the basis of the combination rule [7].

The interaction of atoms of gas with a three-dimensional lattice of finite size is considered in [8]. Forces with the Lennard-Jones potential act between gas atoms and atoms of the solid. The classical equations of motion of all particles were solved numerically on electronic computers.

In these references, a gas particle (molecule or atom) is regarded as a whole; however, the problem of the influence of internal degrees of freedom on the coefficients of energy and momentum exchange between the gas particles and the solid is interesting. An attempt is made in this work to take this influence into account on the basis of classical mechanics.

1. Inelastic losses. First, let us consider the interaction of a molecule with an isolated atom. Figure 1 shows the scheme for such an interaction: a molecule with atoms of mass m strikes an atom of mass M; at a great distance from the atom, the axis of the molecule forms the angle φ_0 with the initial direction of the velocity vector. We shall assume that the motion of all particles in the system can be described by the equations of classical mechanics. The following were studied in a similar formulation in [9–12]: a) chemical reactions such as $P + CH_3 \rightarrow CH_3 = PI$, where P is an alkali metal atom [10, 11]; b) dissociation of O_3 and N_2O molecules [9]; c) the excitation of the energy of internal motion with collinear collisions between molecules and between molecules and atoms [12].

In [10, 11], the potential energy of the interacting particles does not have the form of a simple sum of the potential energies of paired interactions, but an additional term is introduced to reduce the binding energy of the molecule (CH_3I) as it approaches an atom (P). It is shown that the introduction of such additional terms can cause the results from calculations to approach the results from experiments [11].

We shall consider purely pair-particle interactions. We shall take as our example a nitrogen molecule (N_2) in the ground state and a heavy atom (M = 184). We write the potential energies of interaction in the form

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

Here D is the depth of the potential well, b is the distance between particles at which the potential energy is minimum.

The interaction parameters for nitrogen atoms are known [13] ($D = 0.904$ eV, $c = 2.85 \cdot 10^8$ cm^{-1}, $b = 1.08 \cdot 10^{-8}$ cm), and the parameters of the N-M interaction were taken to be the following: $U_1 - D_1 = 5$ eV, $c_1 = 3 \cdot 10^8$ cm^{-1}, $b_1 = 1.5 \cdot 10^{-8}$ cm; $U_2 - D_2 = 0.5$ eV, $c_2 = 5.0 \cdot 10^8$ cm^{-1}, $b_2 = 1.5 \cdot 10^{-8}$ cm; $U_3 = D_3 e^{-c_3 r} - D_3 = 5.4 \cdot 10^3$ eV, $c_3 = 4.16 \cdot 10^8$ cm^{-1}.

The first of these potentials corresponds qualitatively to a strong chemical bond between the interacting particles; the third potential is close to the interaction potentials of inert gas atoms; the second potential occupies an intermediate position. Although the choice of parameters for the potential was arbitrary to a considerable extent, it does permit one to trace the differences in the nature of the interaction between a molecule and an atom in these cases. The difference between these potentials can be seen in Fig. 2.

The results of calculating the equations of motion of particles in the plane case show that a collision of a molecule with an atom leads to the following states of the system.

1) After collision, the molecule remains as an integral formation, but is excited (vibration and rotation). In this case, the exchange of translational energy and a part of the kinetic energy of the molecule is converted to energy of internal motion characterized by the coefficients α^* and α_+, which we define as follows:

$$\alpha^* = \frac{E^*}{E_0}, \quad \alpha_+ = \frac{E^\circ + U^* - U_0}{E_0}. \qquad (1.2)$$

Here, E^*, E_0 are the kinetic energy of the molecule before and after collision, E° is the kinetic energy of relative motion of the atoms of the molecule, U_0, U^* is the potential energy of the atoms in the molecule before and after collision.

2) As a result of collision the molecule dissociates. In this case

$$\alpha^* = \frac{E_1 + E_2}{E_0}, \qquad \alpha_d = \frac{D}{E_0}. \tag{1.3}$$

Here, E_1, E_2 is the kinetic energy of the dispersing atoms of the molecule, α_d is a coefficient which takes into consideration the part of the translational energy spent in dissociation.

3) The molecule dissociates, but one of its atoms forms a compound with atom M. Then

$$\alpha^* = \frac{E_i}{E_0}, \qquad \alpha_{d_i} = \frac{D - |U''|}{E_0}. \tag{1.4}$$

Here E_i is the kinetic energy of that atom which avoided capture, U" is the internal energy of relative motion and the potential energy of this system.

Thus, only in the first case is a part of the energy of translational motion converted into energy of internal motion of the molecule, for in the last two cases the molecule has ceased to exist as such. Further, we shall use α' to denote the coefficient characterizing that part of the energy of translational motion spent in exciting the molecule (up to disintegration).

All the enumerated cases took place with interaction with the potential U_1; as an example, Fig. 3 shows the results of calculating the coefficients α^* and α' as a function of the impact parameter ρ with $v_0 = 10^6$ cm/sec, $\varphi_0 = 45°$; in Fig. 3, zone 1 corresponds to case 3) (dissociation with capture of one atom of the molecule by atom M), and zone 2 with case 2) (dissociation of the molecule). Only the first two cases were observed with interaction with the potential U_2 and $v_0 = 10^6$ cm/sec. Finally, in the case of interaction with the potential U_3, inelastic losses were caused essentially by rotation of the molecule and strong vibrations (and dissociation) were possible with a greater initial velocity of the molecule, in excess of 10^6 cm/sec.

Figure 4 shows the results of calculating $\langle\alpha^*\rangle$ and $\langle\alpha'\rangle$ as functions of ρ for the potentials U_1 and U_2, and $v_0 = 10^6$ cm/sec. Here, $\langle\alpha^*\rangle$ and $\langle\alpha'\rangle$ are the values of α^* and α' averaged with respect ot the initial orientations (averaging $\langle\,\rangle$ was carried out over 12 values of the angle φ_0 ranging from 0 to 180° with a 15° interval).

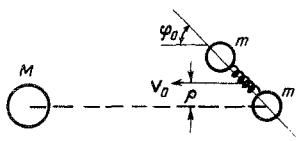

Fig. 1

2. Collision between a molecule and the surface. Figure 5 shows the scheme of a model adopted for studying the interaction between gas particles (atoms and molecules) and the surface of a solid. Four M atoms located at lattice points of a two-dimensional square lattice simulate the surface of the body. It is assumed with regard to all other atoms of the body that they remain motionless during the interaction, thus the interaction of the four chosen atoms with the remaining ones is replaced by interaction with fixed centers located at the lattice points. The validity of this assumption can be substantiated with the aid of the Frenkel criteria [14], but since these criteria are of an orientational nature, the assumption made here was verified for each actual form of the potential of interaction of a molecule with the "surface" of the body. It was also assumed that: a) only nearest neighbors interact in the solid; b) at the initial instant of time, all atoms in the solid are motionless and in the equilibrium position; c) the atoms of the molecule interact with each of the selected atoms located on the surface.

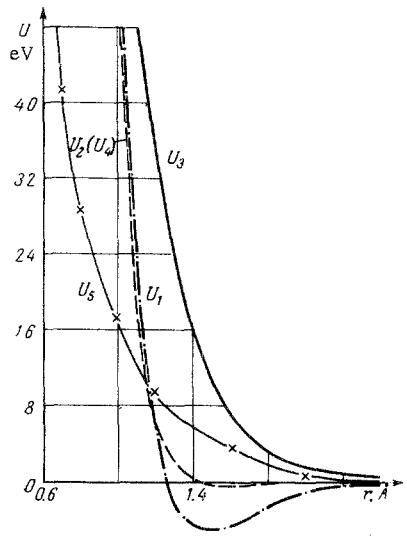

Fig. 2

The Morse function (1.1) was taken as the potential interaction function.

Let us consider the interaction of a nitrogen molecule in the ground state at the initial instant of time with the "surface" of tungsten. The parameters of the interaction potential of nitrogen atoms were given above and the parameters of the potential of the N-W interaction were chosen to be of two types: U_4—D_4 = = 0.5 eV, $b_4 = 1.5 \cdot 10^{-8}$ cm, $c_4 = 5 \cdot 10^8$ cm^{-1}; U_5—D_5 = = 0.0535 eV, $b_5 = 3.0 \cdot 10^{-8}$ cm, $c_5 = 1.47 \cdot 10^8$ cm^{-1} (Fig. 2). The parameters of the potential U_5 were determined with the aid of the combination principle (refer, for example, to [15]), making use of data on W-W and N_2-N_2 interactions [16, 17]. The parameters for the W-W interaction (U_6) were chosen to be different from those of reference [16] since the plane case is considered. Since only the interaction of nearest neighbors was taken into consideration, $D_6 = H/3 = 2.9$ eV; here, the value of the sublimation energy of a tungsten atom from the surface was taken as the quantity H in accordance with the data of [18] (H = 8.741 eV).

The quantity $b_6 = (M/\rho_1)^{1/3} = 2.5 \cdot 10^{-8}$ cm was taken as the lattice parameter; the value $c_6 = 3 \cdot 10^8$ cm^{-1} was selected so that the periods of vibrations of atoms in the direction normal to the surface differed little for the two-dimensional and three-dimensional lattices.

After the parameters of the interaction potentials were selected, it was necessary to solve a system consisting of 12 second-order ordinary differential equations. The system of equations was solved on an electronic computer by the Runge-Kutta method. The integration step was chosen constant and equal to $h = k(a_0/v_0)$, where

$a_0 = 10^{-8}$ cm and v_0 the initial velocity of the molecule. The coefficient k was selected so that a given degree of accuracy of the solution of the system was achieved. Usually, k = 0.02 to 0.05, and in this case the error in the law of conservation of energy amounted to 0.1 to 0.01%. The impact parameter ρ (Fig. 5) varied by 0.1Å. The initial distance between the molecule and the surface was chosen so that the potential energy of interaction of the molecule with atoms of the solid body was far less than its kinetic energy.

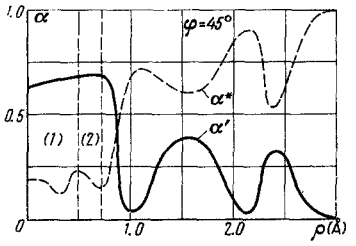

Fig. 3

The exchange of coefficient of translational energy between the molecule and the surface α^* and the coefficients which take into account the part of the energy of translational motion converted into internal energy and spent on dissociation, α_+, α_d determined by formulas (1.2)-(1.4) were calculated for two values of the parameters of the potentials (U_4, U_5). In this case, the atoms of the solid were either bound by the potential U_6 or the bond between them was broken ($D_6 = 0$)—this is the case of an isolated atom. The table gives values of the coefficients $\langle\alpha\rangle$ averaged over angles φ_0 and over ρ. Averaging over the angles was performed for the case in which φ_0 ranged from 0 to 180° with an interval of 30° (changing to an interval of 15° doubles the computation time while the average values $\langle\alpha\rangle$ for $\Delta\varphi_0 = 15°$ are close to the average values for $\Delta\varphi_0 = 30°$, which is illustrated in Fig. 6 for the case $v_0 = 10^6$ cm/sec, $D_6 \neq 0$, U_4).

Calculations show that the average values $\langle\alpha\rangle$ with the N-W interaction described by the potential U_4 do not differ greatly for the case $D_6 \neq 0$ and $D_6 = 0$ when $v_0 = 10^6$ cm/sec; more noticeable differences occur for the potential U_5. However, the effect of a change in the potential of the N-W interaction is considerably stronger on $\langle\alpha\rangle$ than the presence or disruption of bonding of atoms in the lattice. Thus, when considering the interaction of molecules with the surface in cases in which the Frenkel conditions are either satisfied or almost satisfied, the requirements with respect to the form of the interaction potential of atoms in the lattice can be reduced. The details of interaction for potentials U_4 and U_5 differ as in the case of the interaction of a molecule with an isolated atom.

The change in $\langle\alpha\rangle$ when the velocity v_0 is decreased is not the same for the two potentials U_4 and U_5. A possible explanation of this fact can be found in changes in the relationships between the characteristic time of collision t and the characteristic times of the processes of exciting rotation τ' and vibration τ'' of a molecule. We shall call a collision an impulsive collision when $t \ll \tau$ as opposed to adiabatic collision ($t \ll \tau$). If a collision is implusive in nature relative to any degree of freedom, it can be excited; when the conditions of impulsive impact are violated, the probability of excitation is decreased (collisions with a relative velocity $v > 10^4$ cm/sec are impulsive relative to rotations, thus rotations are easily excited; potential U_4, a collision is an impulsive collision relative to vibrations when $v_0 = 10^6$ cm/sec, and the condition of impulsive impact is violated when $v_0 = 5 \cdot 10^5$ cm/sec, then the decrease in that part of the energy going into internal degrees of freedom becomes understandable.

In the case of the potential U_5, we assume that the condition of impulsive collision relative to vibrations of a molecule is not satisfied for either value of the velocity v_0 and vibrations are weakly excited (as we noted in §2). The transition of energy in internal degrees of freedom is connected essentially with rotation. Figure 7 shows the dependence of the coefficient α_+, averaged over angles φ_0, with $v_0 = 10^6$ cm/sec (curve 1) and $v_0 = 5 \cdot 10^5$ cm/sec (curve 2) on the impact parameter. It can be seen that the values of $\langle\alpha_+\rangle$ differ slightly in these two cases, but when $v_0 = 5 \cdot 10^5$ cm/sec, the maximum values of $\langle\alpha_+\rangle$ are shifted toward large impact parameters, which was the cause for increasing $\langle\alpha_+\rangle$ when averaging over the impact parameters. Averaging over ρ was carried out in the following way:

$$\langle\alpha\rangle = \left[\int_0^{\rho_{max}} \alpha(\rho)\,\rho d\rho\right]\left[\int_0^{\rho_{max}} \rho d\rho\right]^{-1}.$$

However, the change in $\langle\alpha_1\rangle$ when $v_0 = 5 \cdot 10^5$ cm/sec in the transition from the potential U_4 to U_5 is apparently connected with violation of the Frenkel conditions.

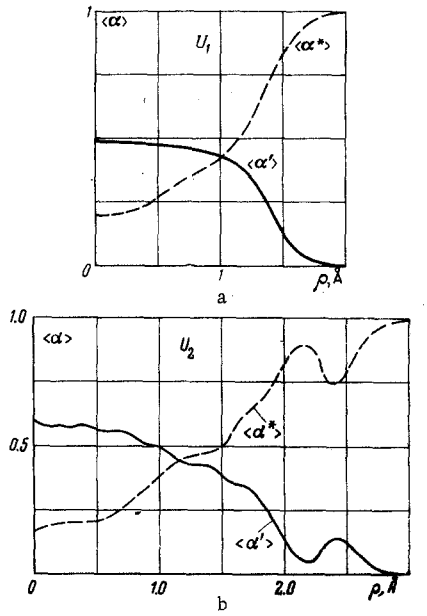

Fig. 4

3. Collision of a molecule regarded as a whole with a surface. Now, let us consider the collision of N_2 molecule with the surface of a body, assuming that the molecule is an integral entity and not a group consisting of two atoms. The model of interaction with the surface remains as before, and we shall take the Morse potentials as the potentials of the N_2-W interaction: 1) with parameters determined on the

basis of the combination principle, making use of the data of [16, 17], $D_7 = 0.107$ eV, $b_7 = 3.53 \cdot 10^{-8}$ cm, $c_7 = 1.47 \cdot 10^8$ cm^{-1}; and 2) with parameters of the potential U_4. If we take the potential U_6 as the interaction potential in the solid, then we obtain the following values for the case $v_0 = 10^6$ cm/sec for the coefficients $\langle\alpha\rangle$: U_7, $\langle\alpha*\rangle = 0.654$, $\langle\alpha_1\rangle = 0.346$; U_4, $\langle\alpha*\rangle = 0.529$, $\langle\alpha_1\rangle = 0.471$. These results can be compared with the tabulated results associated with the potentials U_5 and U_4, respectively, for although the total interaction of the atoms in the solid with the atoms of the molecule is not equal to the interaction with the molecule as a whole, the nature of the interaction is similar for comparable potentials. It can be seen that in the case of the potential U_4, the difference is considerably larger than in the case of potentials U_5 and U_7; here, the different nature of the interaction, which was noted previously in Sections 2 and 3, is also noticeable.

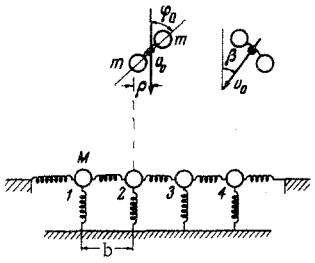

Fig. 5

Now, we shall change the W-W interaction,

$$D_8 = 2.9\,\text{eV},\ b_8 = 3.0 \cdot 10^{-8}\,\text{cm},\ c_8 = 1.41 \cdot 10^8\,\text{cm}^{-1};$$

the parameters b and c of this potential are taken in accordance with [16], and the depth of the potential well is, as before, $D_8 = H/3$. The introduction of such a potential makes it possible to trace the dependence of $\langle\alpha\rangle$ on the distance between atoms in the lattice since the distances between atoms in the lattice vary for different directions. (For example, in the tungsten lattice, the smallest distance between atoms is $2.73 \cdot 10^{-8}$ cm and the lattice constant is $3.16 \cdot 10^{-8}$ cm.) We shall describe the interaction between a nitrogen molecule and a tungsten atom by the potential U_7. Increasing the distance between the atoms in the body leads to a decrease in the influence of the remote atoms in the body (remote relative to the given initial impact parameter) on the interaction process, that is, the nature of individual collision is more pronounced.

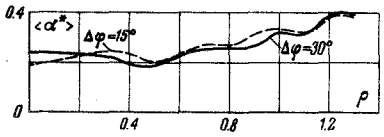

Fig. 6

Thus, $\langle\alpha^*\rangle$ should be decreased. We present the results from computations of the accommodation coefficients for different values of the angle of incidence for the same case:

β =	0°	15°	30°	45°	60°,
$\langle\alpha^*\rangle$ =	0.586	0.620	0.690	0.748	0.901
$\langle\alpha_1\rangle$ =	0.414	0.380	0.310	0.252	0.099

These data agree qualitatively with the results obtained for a solid sphere model [20, 21]. We note that the effect of the boundary of the chosen zone of a solid body begins to be noticeable with large angles of incidence β. Thus, $\alpha^* = 0.875$ when $\beta = 60°$, when the direction of the initial motion of the molecule passes through the center of atom 2, and $\alpha^* = 0.834$, when the direction of the initial motion passes through the center of atom 3 (see Fig. 5).

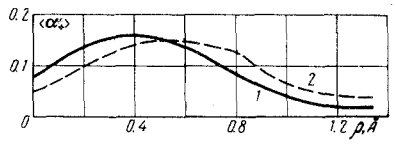

Fig. 7

In conclusion, we note that in this article we have investigated a case in which the Frenkel conditions are satisfied or almost satisfied, which is ensured by the high speed of the incident particle and the small ratio of the mass of the molecules to the mass of an atom in the body ($\varkappa = 28/184 = 0.152$). Therefore, the solid body is simulated by just its surface layer. It is necessary to comment in regard to inelastic losses that the obtained results are qualitative in nature; this is connected, on one hand, with the fact that the phenomenon was considered from a purely classical standpoint whose identity with quantum reasoning is indicated only in the case of small excitations of internal degrees of freedom [22, 23]; on the other hand, it was necessary to choose the interaction potentials of the particles, and the information

v_0 cm/sec	U_{N-W}	U_{W-W}	$\langle\alpha^*\rangle$	$\langle\alpha_+\rangle$	$\langle\alpha_d\rangle$	$\langle\alpha_1\rangle$
10^6	U_4	$D_6 \neq 0$	0.278	0.315	0.045	0.362
		$D_6 = 0$	0.246	0.299	0.041	0.414
	U_5	$D_6 \neq 0$	0.576	0.076	—	0.348
		$D_6 = 0$	0.490	0.079	—	0.431
$5 \cdot 10^5$	U_4	$D_6 \neq 0$	0.328	0.236	—	0.436
	U_5	$D_6 \neq 0$	0.652	0.095	—	0.253

The quantity $\langle\alpha_1\rangle = 1 - \langle\alpha^*\rangle - \langle\alpha_+\rangle - \langle\alpha_d\rangle$ characterizes that part of the energy transmitted to the solid body.

available in this field is far from complete. Nevertheless, in spite of these gaps, we may hope that the results from solving this type of problem on the basis of classical mechanics with suitable choice of the parameters of the interaction potentials will yield qualitative agreement with the experimental data, as noted in §§1 and 2.

We also note that the energy accommodation coefficient did not exceed 0.5 in any of the problems under consideration; moreover, the share of the energy transferred to internal degrees of freedom can reach a substantial value (from 0.1 to 0.35, depending on the interaction potential).

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