

THE INTERACTION OF ATOMS WITH A SOLID SURFACE

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Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, Vol. 8, No. 4, pp. 113-117, 1967

Some results are given from a digital-computer investigation into the interaction of atoms with a solid surface at energies of about 10 eV. A method is described for the joint solution of a system of classical equations for the movement of atoms forming a solid and of a bombarding particle for a given law of pair interaction. In the majority of the calculations the Lennard-Jones 6-12 potential is used for this law.

A system of dimensionless parameters defining the processes concerned has been obtained, and typical results of the interaction have also been demonstrated, viz.: reflection, capture by the surface (adsorption), and absorption of the incident particle by the lattice. The interaction of an atom with the surface of an ideal crystal forming an Einstein lattice has been considered for various parameters and lattice types, and the effect of the form and parameters of the potential on the statistically averaged interaction characteristics (energy accommodation coefficient) has been determined. A method of averaging the interaction characteristics is described, from which it is possible to construct a model of the collision of atoms with an atomically smooth polycrystalline surface.

1. METHOD. SYSTEM OF CONTROLLING PARAMETERS

The experimental difficulties in producing strong atomic beams with energies of about 10 eV and also the complexity of the identification of the conditions at the interaction surface in various experimental setups lead to large discrepancies in the values of the characteristics of the interaction of atomic beams with a solid surface.

Papers devoted to the theoretical consideration of this process are based mainly on the simplification of the lattice model, which is replaced by a one-dimensional chain or by a two-dimensional network of atoms. In addition, a simplified law of pair interaction is often adopted. As a result of all this, these investigations must be regarded as being qualitative rather than quantitative in character. Only in [1, 2] is an attempt made to treat the problem more rigorously (space lattice, an interaction potential close to the actual one) and with a minimum number of simplifying assumptions. By such an approach it is possible to obtain data suitable for orientation in the results of the experimental studies and also to determine the extent of the effect of the various controlling parameters. No less important is the possibility of constructing energy and direction distribution functions for the reflected particles.

With this object in view a group of atoms in a solid with a regular crystal structure of one of the following types is considered: simple cubic (sc), face-centered cubic (fcc), and body-centered cubic (bcc). It is assumed that at a bombarding energy of about 10 eV per particle the thermal vibrations of the atoms in the lattice may be neglected. It may also be assumed that for the actual current densities in the atomic beams the probability of two or more particles falling simultaneously in a particular region is negligibly small.

Let the interaction of an incident particle with each of the atoms of the group be determined by the potential $V(r)$ and let the atoms themselves form an Einstein crystal. The latter assumption is valid only if the interaction time is less than the period of natural vibration of the atoms in the lattice, or it is sufficient if the mean speed of the incident atom is greater than the rate of propagation of elastic vibrations in the solid.

After the crystal lattice and its orientation with respect to the free surface (in the present calculations the 100 face) have been chosen, the interaction process is determined by the following parameters: the initial energy E_0 of the incident particle; the mass m_1 of the incident particle; the mass m_2 of an atom in the lattice; the parameters (ϵ, σ) of the Lennard-Jones 6-12 potential; the crystal lattice spacing d ; the spring constant κ , by means of which an atom in the lattice is maintained in its equilibrium position; the angles φ and ψ with the azimuth

of the direction of the initial rate of the incident particle; the rectangular coordinates x_{pi}, y_{pi} of the point of impact (pi) at the crystal surface.

Thus the energy accommodation coefficient α will depend on the eight dimensionless parameters

$$\mu = \frac{m_1}{m_2}, \quad w = \left(\frac{2E_0}{\mu\sigma^2\kappa} \right)^{1/2}, \quad \varphi, \quad s = \frac{24\epsilon}{\sigma^2\kappa},$$

$$a = \frac{d}{\sigma}, \quad \xi = \frac{x_{pi}}{\sigma}, \quad \zeta = \frac{y_{pi}}{\sigma}, \quad \psi.$$

Obviously the accommodation coefficients averaged with respect to the last three parameters will be of practical interest.

We will choose a rectangular system of coordinates with its origin at one of the surface atoms of the lattice in such a way that the plane $z = 0$ coincides with the free surface of the crystal and the z -axis lies in the direction of empty space. We will regard σ as the linear scale and $(m_2/\kappa)^{1/2}$ as the time scale. Then the system of equations which describes the movement of the incident atom and the atoms in the crystal will have the form

$$\frac{d^2\mathbf{R}_0}{d\tau^2} = -\frac{1}{\mu} s \sum_{l, m, n} f(|\mathbf{R}_0 - \mathbf{R}_{lmn}|) \frac{\mathbf{R}_0 - \mathbf{R}_{lmn}}{|\mathbf{R}_0 - \mathbf{R}_{lmn}|},$$

$$\frac{d^2\mathbf{R}_{lmn}}{d\tau^2} = sf(|\mathbf{R}_0 - \mathbf{R}_{lmn}|) \left[\frac{\mathbf{R}_0 - \mathbf{R}_{lmn}}{|\mathbf{R}_0 - \mathbf{R}_{lmn}|} + \mathbf{L}_{lmn} \right],$$

$$f(q) = q^{-7} - 2q^{-13}. \tag{1.1}$$

Here \mathbf{R}_0 is the radius vector of the incident particle; \mathbf{R}_{lmn} is the radius vector of an atom in the lattice with indices l, m, n ; \mathbf{L}_{lmn} is the force acting on the atom in the lattice with indices l, m, n from the direction of the crystal; τ is the time.

Because the interaction potential rapidly tends toward zero with increase in distance, not all of the atoms in the crystal take part in the interaction process, but only those which occur within a certain range of the target atom. For an Einstein crystal the number of atoms whose effect must be wholly taken into account is determined by the type of interaction potential. It will be shown below that for a Lennard-Jones 6-12 potential and not too large a value of φ , neglect of all the atoms situated at a distance greater than or equal to 3σ from the target atom does not lead to any significant errors in calculating the accommodation coefficient.

The initial conditions (when $\tau = 0$) for the solution of system (1.1) are given as follows:

$$R_{0x} = \xi - \eta_0 \operatorname{tg} \varphi \cos \psi,$$

$$R_{0y} = \zeta - \eta_0 \operatorname{tg} \varphi \sin \psi,$$

$$R_{0z} = \eta_0 = z_0 / \sigma,$$

$$dR_{0x}/d\tau = w \sin \varphi \cos \psi,$$

$$dR_{0y}/d\tau = w \sin \varphi \sin \psi,$$

$$dR_{0z}/d\tau = -w \cos \varphi,$$

$$d\mathbf{R}_{lmn}/d\tau = 0. \tag{1.2}$$

At the initial instant the values of the vectors \mathbf{R}_{lmn} correspond to the equilibrium positions in the chosen crystal type.

Based on the above, we put $\eta_0 = 3$. Control calculations for a greater value of η_0 showed this assumption to be justified.

Equations (1.1) for initial conditions (1.2) were integrated by the Runge-Kutta method on a BESM-2M computer with a variable integration step. A check on the accuracy was made by means of the energy integral.

2. POSSIBLE RESULTS OF THE INTERACTION PROCESS

The interaction process may lead to three fundamentally different results, each of which was found in the calculations made.

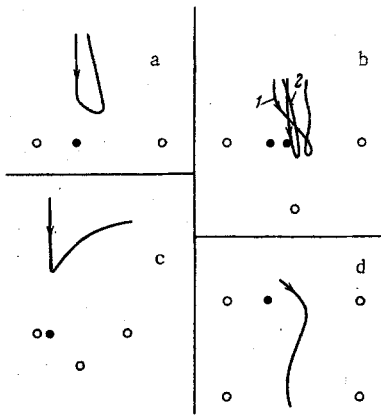


Fig. 1. Examples of typical trajectories (● is the point of impact, ○ are atoms in the lattice): a) reflection (sc, $a = 1$, $w = 1$, $s = 0.01$, $\mu = 0.5$, $\xi = \zeta = 0.33$, $\varphi = 0$); b) reflection (fcc, $a = 1.7$, $w = 1$, $s = 0.01$, $\mu = 0.5$, $\varphi = 0$, $\xi = 0$, $\xi = 0.56$ (1), $\xi = 0.79$ (2)); c) capture (bcc, $a = 0.8$, $w = 0.3$, $s = 0.01$, $\mu = 0.5$, $\varphi = 0$, $\xi = \zeta = 0.095$); d) absorption (sc, $a = 1.2$, $w = 1$, $s = 0.01$, $\mu = 0.5$, $\varphi = 0$, $\xi = \zeta = 0.40$).

1. Reflection. After interaction the particle leaves the zone of influence of the crystal and continues in uniform motion in a straight line. In this case integration ended when the particle had left the solid by a distance η_0 . The accommodation coefficient was calculated from the formula

$$\alpha = 1 - E_f/E_0,$$

where E_f is the energy of the particle after interaction.

2. Capture. This is observed at a small initial energy of the incident particle. As a result of the interaction the particle loses the normal component of its velocity and, remaining within the solid, it is either trapped in the potential well of one of the atoms or it continues in motion along an equipotential surface without leaving the crystal. The accommodation coefficient for these trajectories was taken as unity.

Theoretical papers based on a one-dimensional model of the crystal give the ratio of the threshold capture energy to the depth of the potential well as a function of μ and the type of bond between the incident atom and the first atom in the lattice. In the notation adopted here, this ratio is $12\mu w^2/s$. Subsequently we shall show that in the

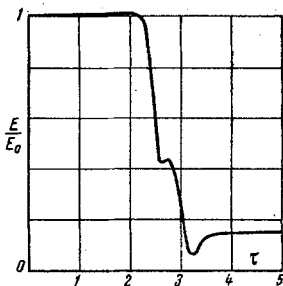


Fig. 2. Time dependence of the particle energy for the trajectory shown in Fig. 1a.

present calculations capture was observed at energies twenty times greater than those indicated in the papers cited. This discrepancy is obviously a result of the three-dimensional nature of the model we used.

3. Absorption. This is observed at large distances between the atoms in the crystal and great energies of the incident atom. As a result of the interaction the particle enters the solid and is either trapped in the chosen group of atoms or passes right through it, retaining the impulse directed into the solid. In this case also the accommodation coefficient was taken as unity. Examples of typical trajectories for the various cases of interaction are shown in Fig. 1a-d. It should be noted that in the interests of clear representation only plane trajectories are shown, for which the vector of the initial speed of the incident particle lies in the plane of symmetry of the crystal.

Figure 2 shows the time dependence of the energy E of the incident particle for the trajectory depicted in Fig. 1a. As can be seen from the graph, the interaction time for this case is approximately 2.5 and is less than the period of natural vibration of an atom in the crystal (2π in our variables). This confirms the validity of the assumption about the unimportance of the propagation of elastic waves in the crystal in calculating the accommodation coefficient (in our range of parameters).

3. ACCURACY

In estimating the error due to the finite nature of the chosen group of atoms, we calculated the accommodation coefficient for groups of various sizes. The effect of the size of the group on the results of the calculations for an individual trajectory and on the averaged parameters (for the method of averaging see below) was investigated for the following set of conditions: $w = 1$, $\mu = 0.5$, $\varphi = 0$, $s = 0.01$, $a = 1$. The results are given in Table 1.

Table 1

Effect of Size of Atomic Group on the Value of the Calculated Accommodation Coefficient

No. of atoms in group	α ($\xi = \zeta = 0$)			$\langle \alpha \rangle$
	bcc	simple cubic	fcc	
34			0.8876	
39	0.9016	0.8971		
50			0.8903	
51	0.9019	0.8972		0.7970
59	0.9022	0.8973	0.8909	0.7975

In all subsequent calculations a group consisting of 59 atoms was used. As can be seen from Table 1, the error in the value of α introduced by ignoring the remainder of the crystal always has a minus sign (i. e., it leads to a reduction in the value of α) and is about $5 \cdot 10^{-4}$. This choice of the group leads to the solution of a system of 360 first-order differential equations.

The averaging of the accommodation coefficient with respect to the points of impact and ψ was carried out by means of Gauss' squaring formulas. The nature of the dependence of α on the point of impact and the azimuth varies for different angles of incidence of the particles: at normal incidence there is no dependence on the azimuth and the dependence on the point of impact is most marked; on the other hand, at large angles of incidence the dependence on the point of impact falls off, while the dependence on the azimuth becomes very complex. Hence the choice of the methods of averaging with respect to the points of impact and the estimation of the errors caused by this averaging were made for $\varphi = 0$. A comparison of the results of calculating the mean accommodation coefficient for 6 ($\langle \alpha \rangle_6$) and for 10 ($\langle \alpha \rangle_{10}$) trajectories for all types of crystal lattice showed that $\langle \alpha \rangle_6 > \langle \alpha \rangle_{10}$. This difference is 0.3–1.5% for various sets of conditions and depends mainly on the type and spacing of the crystal lattice. Errors of 1% or more occurred only for the simple cubic lattice, where the dependence of α on the point of impact is most marked. For this reason averaging with respect to the points of impact was as a rule carried out for six trajectories.

In calculating inclined trajectories ($\varphi \neq 0$), averaging of the accommodation coefficient with respect to the azimuth was carried out

for each point of impact. The accuracy of this averaging depends on the point of impact and the angle φ and is on the average about 1.5% for $\varphi = 45^\circ$.

Thus, with the chosen method of calculation, it is possible to obtain values of the parameters of individual trajectories with an accuracy of about 0.1% and values of the averaged parameters with an accuracy of 1.5-2.0%.

4. SOME RESULTS

Using the methods set out above, the dependence of the averaged accommodation coefficient on the energy of the incident particle has been obtained for the set of conditions bcc, $\varphi = 0$, $\mu = 0.5$, $s = 0.01$, $a = 0.8$.

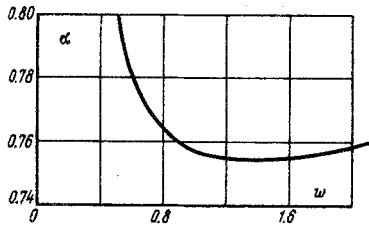


Fig. 3. Dependence of accommodation coefficient on particle energy.

The results are presented in Fig. 3. At small values of w the accommodation coefficient α should be equal to unity (adsorption). It is difficult to determine accurately the threshold capture energy w_* from the numerical experiments. For this set of conditions, with $w = 0.3$, the majority of the trajectories were "trapped" (one of them is shown in Fig. 1). Thus, if we put $w_* = 0.3$, the criterion of capture $12 \mu w_*^2 / s = 54$, which is many times greater than the value predicted from one-dimensional calculations. According to such calculations w_* for our conditions is about 0.06. The dependence of α on the type of crystal and lattice spacing was investigated by the same method for the conditions

$$w = 1, \mu = 0.5, s = 0.01, \varphi = 0.$$

The results are given in Table 2. For the case marked by an asterisk in the table, averaging was carried out with respect to ten trajectories, while in the remaining cases it was done with respect to six trajectories. On bombarding a simple cubic lattice having $a = 1.2$ three of the six trajectories situated close to the center of the face were "absorbed," the particles passing through the whole group of atoms. One of these trajectories is shown in Fig. 1d. For comparison of the lattices among themselves, Fig. 4 shows the results in relation

Table 2

Effect of Crystal Type and Lattice Spacing				
a	Lennard-Jones 6-12 potential			Morse potential $a\sigma = 7.4$
	simple cubic	fcc	bcc	bcc
0.65	0.7147			
0.8	0.7554	0.6692	0.7576	0.7450
1.0	0.8009	0.7422	0.7975	0.7844
1.2	0.7954	0.7706	0.8266	0.8170
1.5		0.8099*	0.8841	

to one parameter—the specific volume of the lattice γ , i.e., the volume occupied by one atom of the crystal. As is well known, this quantity is

$$a^3 \text{ — for simple cubic, } \frac{1}{2} a^3 \text{ — for bcc, and } \frac{1}{4} a^3 \text{ — for fcc lattices}$$

A series of calculations was performed to determine the effect of the type of interaction potential and its parameters on the accommodation coefficient obtained.

A comparison was made of the two most widely used potentials: Lennard-Jones 6-12

$$V(r) = 4\epsilon [r^{-12} - r^{-6}]$$

and Morse

$$V(r) = 4\epsilon [e^{-2a\sigma(r-1)} - e^{-a\sigma(r-1)}].$$

The depth of the potential well was taken as s for both potentials. The choice of the parameter $a\sigma$ requires an additional condition.

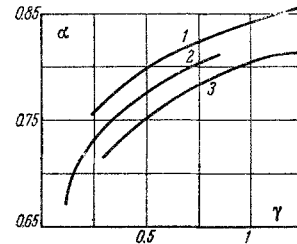


Fig. 4. 1) bcc, 2) fcc, simple cubic.

For this parameter a value 55/12 is usually assumed, which ensures the identity of

$$\int_1^\infty V(r) dr$$

for both potentials. This requirement has no physical significance, but it leads to good agreement between the results at small particle energies, when the range $r > 1$ plays the principal part. In the present calculations the energy of the incident particle was 50-1000 times greater than the depth of the potential well, and no agreement was observed between the results obtained by the use of the two potentials

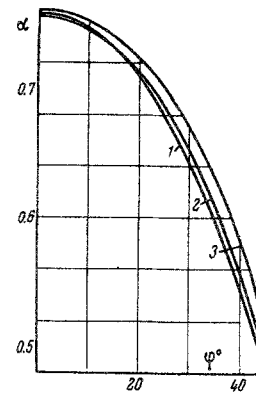


Fig. 5. Dependence of the accommodation coefficient on the angle of incidence. 1) $w = 1.0$, 2) $w = 1.4$, 3) $w = 2.0$.

at $a\sigma = 55/12$. For such large energies (compared with ϵ) the identity of the repulsive part of the potential ($r < 1$) will be more important; this is achieved if identity of the distance of maximum approach of particles with energy E_0 is required. In this case

$$a\sigma = \left(\ln \frac{1 + \sqrt{1 + E_0/\epsilon}}{2} \right) \left[1 - \left(\frac{2}{1 + \sqrt{1 + E_0/\epsilon}} \right)^{1/6} \right]^{-1}.$$

The dependence of $a\sigma$ on E_0/ϵ is slight:

$$a\sigma = 6 \text{ at } E_0/\epsilon = 0, \quad a\sigma = 7.4 \text{ at } E_0/\epsilon = 600$$

(as already noted, $E_0/\epsilon = \mu w^2/s$).

The results of calculating α with this choice of $a\sigma$ are given in the last column of Table 2 (the values of the dimensionless parameters being the same as for the rest of the table). The calculated values of the accommodation coefficient are close to the corresponding values

obtained by using the Lennard-Jones 6-12 potential. Thus, in our range of parameters and with a suitable choice of $a\sigma$, the two potentials should be equivalent. The Lennard-Jones potential was used in all the other calculations.

The effect of the depth of the potential well on the accommodation coefficient was examined for the conditions bcc, $w = 1$, $\mu = 0.5$, $\varphi = 0$, $a = 0.8$. The following results were obtained:

$$\begin{array}{ccc} s = 0.01 & 0.02 & 0.04 \\ \langle \alpha \rangle = 0.7576 & 0.7733 & 0.8077. \end{array}$$

An increase in the depth of the potential well leads to a certain increase in α .

All the results given above relate to normal incidence of the atom on the crystal surface ($\varphi = 0$). Figure 5 gives the results of calculating the accommodation coefficient (averaged with respect to the azimuth and the points of contact) as a function of the angle φ and the energy

of the incident particle for the bcc conditions, $\mu = 0.5$, $s = 0.01$. On increasing the angle φ , the minimum on the $\alpha(w)$ curve is shifted in the direction of lower energies, the reflection approximates to mirror reflection, and the dependence of α on the point of impact falls off.

REFERENCES

1. R. A. Oman, A. Bogan, C. H. Weiser, and C. H. Li, "Interactions of gas molecules with an ideal crystal surface," Amer. Inst. Aeronaut. and Astron. J. vol. 2, no. 10, p. 1722, 1964.
2. Yu. A. Ryzhov and D. S. Strizhenov, "Energy exchange in the interaction of atoms with the surface of an ideal crystal," Dokl. AN SSSR, vol. 172, no. 6, p. 1309, 1967.

1 December 1966

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