INTERACTION OF A MONOENERGETIC BEAM OF GAS ATOMS WITH A THREE-DIMENSIONAL CRYSTAL

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There has been a rapidly increasing number of theoretical studies of the interaction of gas atoms (and molecules) with solid surfaces. Of particular interest are the so-called numerical experiments carried out on high-speed computers, which permit a study of a process with various sets of interaction parameters, permit a qualitative estimate of their effect on the process, and permit selection of results with parameters corresponding to the physical experiments.

The calculation time required depends primarily on the dimensionality and size of the solid unit containing the atoms participating in the collision with the gas atoms. For this reason, there is some interest in rather crude models, e.g., the one-dimensional models [1, 2], two-dimensional models [3], binary-interaction models [4, 5], three-dimensional models with a normal interaction [6, 7], and three-dimensional models with oblique, nonnormal interactions, but with a bounded solid unit [7, 8]. In particular, studies of these models have clarified the effect of various parameters on the interaction; these results have been used in studies involving a nearly exact formulation of the problem [8-10]. Nevertheless, the harmonic approximation was used to take into account lattice dynamics in nearly all these studies, and in only a few of them were the first lattice atom [1, 7] or all the atoms [3] (in the two-dimensional case) related to their neighbors by either a Lennard–Jones or Morse potential.

In the numerical experiments reported here, we attempted, along with a specific calculation of the accomodation coefficient as functions of the interaction parameter, study of the effect of the atomic binding in the lattice on the interaction. As a binding potential in the lattice we adopted a Morse potential with parameters chosen according to the actual lattice property of various materials (FE, Mo, W). A nitrogen molecule (N_2) interacts with a lattice according to a Morse or a Lennard–Jones law; the interaction involves each atom of the unit. All the atoms in the unit are also interrelated, i.e., each lattice position interacts with all the others, of which there are a finite number, according to the assumed finite unit dimensions.

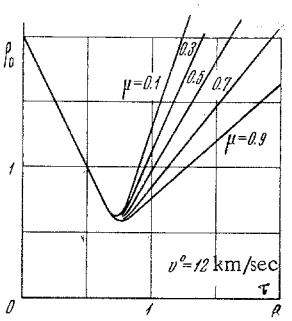

Fig. 1

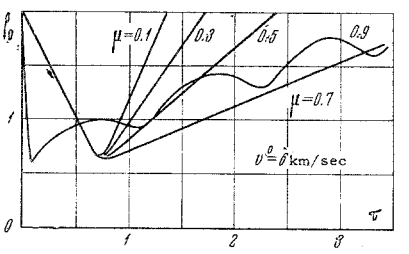

Fig. 2

Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, Vol. 11, No. 2, pp. 162–166, March-April, 1970. Original article submitted September 5, 1969.

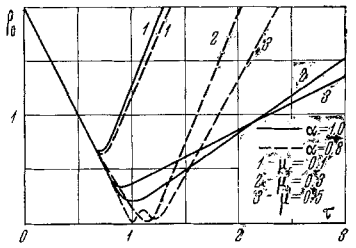

Fig. 3

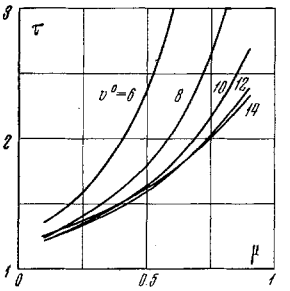

Fig. 4

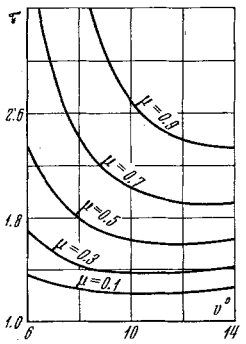

Fig. 5

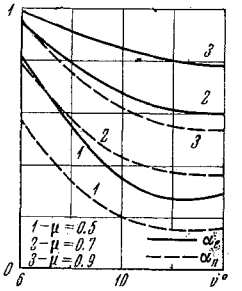

Fig. 6

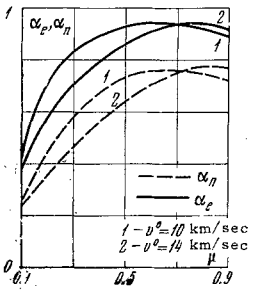

Fig. 7

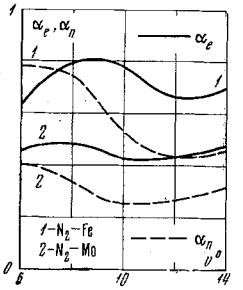

Fig. 8

TABLE 1

μ	$v^\circ = 6$	$v^\circ = 8$	$v^\circ = 10$	$v^\circ = 12$	$v^\circ = 14$
0.1	114.8	153.1	191.3	229.6	267.9
0.3	66.3	88.4	110.5	132.6	154.6
0.5	51.3	68.4	85.5	102.7	119.8
0.7	43.4	57.8	72.3	86.8	101.2
0.9	38.3	51.0	63.8	76.5	89.3

TABLE 2

	δ	β	γ	δ_1	β_1	γ_1	μ	α
N_2 — Fe	150.0	0.800	6.124	8.71	0.930	5.402	0.500	0.773
N_2 — W	365.0	0.676	11.100	63.00	0.405	18.500	0.152	0.853
N_2 — Mo	238.0	0.880	5.237	8.69	0.990	5.301	0.292	0.849

TABLE 3

α	μ	$v^\circ = 10$		$v^\circ = 12$		$v^\circ = 14$	
		α_e	α_n	α_e	α_n	α_e	α_n
0.8	0.1	0.301	0.164	0.341	0.188	0.356	0.198
	0.3	0.476	0.277	0.562	0.338	0.600	0.361
	0.5	0.648	0.415	0.720	0.477	0.719	0.471
	0.7	0.795	0.550	0.846	0.608	0.800	0.571
	0.9	0.925	0.700	0.937	0.730	0.895	0.678
1.0	0.1	0.380	0.213	0.388	0.218	0.385	0.216
	0.3	0.720	0.478	0.702	0.458	0.702	0.455
	0.5	0.928	0.700	0.874	0.656	0.854	0.625
	0.7	0.935	0.760	0.927	0.730	0.935	0.759
	0.9	0.826	0.708	0.900	0.710	0.924	0.786
1.2	0.1	0.360	0.200	0.361	0.201	0.367	0.205
	0.3	0.669	0.430	0.646	0.406	0.665	0.422
	0.5	0.835	0.613	0.821	0.579	0.812	0.568
	0.7	0.935	0.745	0.945	0.740	0.922	0.724
	0.9	0.960	0.840	0.995	0.870	0.990	0.850

The equations of motion have the standard form:

$$M\frac{d^2\mathbf{R}_0}{dt^2} = -\sum_{i,j,k}\frac{\partial U_1(R_0 - R_{ijk})}{\partial(R_0 - R_{ijk})}\frac{\mathbf{R}_0 - \mathbf{R}_{ijk}}{R_0 - R_{ijk}} = \mathbf{F}$$

$$m\frac{d^2\mathbf{r}_{ijk}}{dt^2} = -\mathbf{F} + \sum_{i\neq j\neq k}\frac{\partial U(\rho_{ijk}^{ijk})}{\partial\rho_{ijk}^{ijk}}\frac{\rho_{ijk}^{ijk}}{\rho_{ijk}^{ijk}}$$

$$\mathbf{R}_{ijk} = \mathbf{A}_{ijk} + \mathbf{r}_{ijk}, \quad \rho_{ijk}^{ijk+1} = \mathbf{R}_{ijk} - \mathbf{R}_{ijk+1}$$

on the right side are the Lennard–Jones and Morse potentials

$$U_1(R) = 4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$$

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

Here $\mathbf{R}_0$ is the radius vector of the gas atom; $\mathbf{A}_{ijk}$ is the radius vector of the equilibrium lattice position; $\mathbf{r}_{ijk}$ is the displacement from this position; M and m are the masses of the gas atoms and the lattice atom, respectively; and ε, σ, D, c, and b are potential parameters.

To convert the equation and variables to dimensionless form, we use the characteristic time t°, which we chose to be equal to the ratio $R_0^\circ/v.$, where R_0° and v° are the distance from the origin and the gas velocity at t = 0. We further assume that $t = \tau i^\circ$, $R_{ijk} = \rho_{ijk}\sigma$, $M = \mu m$, $R_0 = \rho_0\sigma$, a lattice constant

$$a = \alpha\sigma, \qquad v^{\circ 2} = v^2\,\varepsilon\,\mu / M$$

$$D = \delta\varepsilon, \quad b = \beta\sigma, \quad \gamma = c\sigma, \quad U_1 = 24\,\omega_1\varepsilon, \quad U = 2\,\omega\,D\,c\sigma.$$

The right sides of the equations of motion will then contain the following derivatives, depending on the potential:

$$\frac{d\omega_1}{d\rho} = \frac{1}{\rho^7} - \frac{2}{\rho^{13}} \quad \text{or} \quad \frac{d\omega}{d\rho} = e^{-\gamma(\rho-\beta)} - e^{-2\gamma(\rho-\beta)}$$

they will be multiplied by the dimensionless coefficient

$$K_0 = 24\,\rho^{\circ 2}/\mu v^2, \quad K_1 = 24\,\rho^{\circ 2}/v^2, \quad K_2 = 2\delta\gamma\rho^{\circ 2}/v^2$$

in the case of an external Lennard–Jones potential and an internal Morse potential, or by the coefficient

$$K_0 = 2\,\delta_1\gamma_1\rho^{\circ 2}/\mu v^2, \quad K_1 = 2\,\delta_1\gamma_1\,\rho^{\circ 2}/v^2, \quad K_2 = 2\,\delta\gamma\rho^{\circ 2}/v^2$$

if the external potential is also of the Morse type (here the index "1" corresponds to the external potential). From the actual values of the other parameters we find $K_0 \approx 10^{-1}$, $K_1 \approx 10^{-2}$, $K_2 \approx 10^{-4}$. In calculations in which the interacting atoms and the lattices were not specified, qualitative results were obtained for the following parameters: α) 0.8, 1.0, 1.2; μ) 0.1, 0.3, 0.5, 0.7, 0.9; v^0) 6, 8, 10, 12, 14 km/sec (the dimensionless parameter v, given in Table 1, depends on μ). Table 2 shows the other parameters.

For certain order-of-magnitude calculations, the depth of the internal potential well was assumed greater than that shown in Table 2 (e.g., $\delta = 0.015$ and 1.50).

Both the displacements from the equilibrium position and the velocities of all the lattice atoms are initially equal to zero (at $\tau = 0$). The target is the area enclosed by a square of side α around the initial atom; within the square, the aiming positions (ξ^*, η^*) are distributed uniformly. The interaction begins at a distance $\zeta = 2$ along the vertical coordinate, so that the components of the radius vector ρ_0 of the gas atom are initially

$$\xi^* + \zeta^* \operatorname{tg}\vartheta \cos\varphi, \quad \eta^* + \zeta^* \operatorname{tg}\vartheta \sin\varphi,$$
$$\rho_0 \cos\vartheta = \zeta^* = 2$$

where the angles ϑ and φ give the spatial position of the velocity of the gas atom ($\vartheta = 0 - 1/2\pi$, $\varphi = 0 - 2\pi$). Each target is penetrated by 625 trajectories (25 target points multiplied by 25 velocity orientations).

The system of equations was solved by the Runge–Kutta method on a BESM-3M computer. The program, written in ALGOL-60, yields the parameters of the individual trajectories and the individual energy and momentum accomodation coefficients, as well as the average coefficient. The time required for a single calculation (25 trajectories) is of the order of 25-30 min. The reflection was determined from the yield of gas particles at a monitor level ($\zeta = 2$); the capture time was monitored so that the vertical coordinate did not become negative, and the capture or total absorption was monitored so that the vertical coordinates remained negative and within the target. The calculations were restricted to a unit having $3 \times 3 \times 2 + 1$ atoms. Control calculations were carried out for a larger unit, but the results differed very little, while about twice as much computer time was required.

Figures 1-3 show certain trajectories for the case of normal incidence characterizing the interaction for various sets of parameters with an external Lennard–Jones potential and an internal Morse potential. A comparison of the trajectories in these figures shows the dependence of the interaction on the mass ratio, on the one hand, and on the initial gas-atom velocity, on the other.

Figure 2 shows a typical trajectory with temporary capture, for $\mu = 0.9$ and $v^\circ = 6$ km/sec. Figure 3 shows the dependence on the lattice constant in the case of $v^\circ = 6$ km/sec. We note that in the case of $\alpha = 1.0$ (dashed curves), temporary capture may occur; under otherwise equal conditions, this does not occur in the case of a denser lattice ($\alpha = 0.8$, solid curves). Curves 1-3 in Fig. 2 corresponds to $\mu = 0.1$, 0.3, 0.5, respectively. As a rule, heavy atoms are captured temporarily.

It is interesting to compare the collision times as a function of the initial velocity and mass ratio. The corresponding curves are shown in Figs. 4 and 5.

The calculations show a uniform tendency for a decrease in the energy accomodation coefficient α_e and in the normal-momentum coefficient α_n with increasing initial velocity, as is clearly shown by Fig. 6. An increase in the accommodation coefficients occurs also as the mass ratio increases. When a Morse function is used as external potential, there is a weak dependence of the accommodation coefficients on μ (Fig. 7) for the case $\alpha = 1.0$, while in the case of a denser lattice ($\alpha = 0.8$), this dependence is nearly linear. Table 3 shows the accommodation coefficients for three lattice densities ($\alpha = 0.8$, 1.0, 1.2) and for several initial velocities. A comparison shows that there is no clearly defined dependence on the lattice density and that the accommodation coefficients are generally quite similar for different α.

Figure 8 shows α_e and α_n for N_2–Fe and N_2–Mo pairs. In both cases, a Morse function was used as external potential.

A comparison of these results with the analogous results for a harmonic lattice shows that the lattice with an exponential interaction potential is softer and permits gas atoms to penetrate, or at most delays them at the surface (an adsorption layer forms), for essentially all mass ratios and initial energies, except for purely normal collisions.

The interaction time is greater, but the control calculations showed that the size of the unit which (within a specified accuracy) participates in the collision does not change. The overall tendency is for greater accommodation coefficient than in harmonic-lattice case.

For example, the average accommodation coefficients obtained for an FE lattice with Morse binding and with an external N_2–Fe Morse potential are $\alpha_e = 0.371$ and 0.327, $\alpha_n = 0.213$ and 0.180 for velocities

$v^\circ = 6$ and 8 for $\vartheta = 15°$; the tangential-momentum accommodation coefficients are $\alpha_\tau = 0.128$ and 0.177. These values differ from those calculated for a harmonic lattice, examined, in particular, in [8], only by a few percent.

A calculation carried out for a crystal with elastic interaction forces in this version yields $\alpha_e = 0.352$ and 0.327, $\alpha_n = 0.196$ and 0.169, $\alpha_\tau = 0.119$ and 0.169. The dependence of the accommodation coefficients on the gas-surface potential, on the other hand, is stronger. The corresponding accommodation coefficients for the N_2–Fe version with a Lennard–Jones external potential are $\alpha_e = 0.542$ and 0.465, $\alpha_n = 0.282$ and 0.203, $\alpha_\tau = 0.171$ and 0.175.

A determination of quantitative criteria showing the applicability of the harmonic approximation for lattice dynamics would obviously require a detailed calculation for many parameters. Only control versions of these calculations were carried out, from which we derive the qualitative conclusion above. Since the calculation time required for an anharmonic lattice is much greater than that for a harmonic lattice, while the results do not differ greatly from those available, it does not seem worthwile to carry out more numerical calculations in this field until good semiempirical interaction potentials or reliable experimental results are available to justify such potentials or reliable experimental results are available to justify such large expenditures of computer time.

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