ON THE COLLISION OF AN ATOM WITH THE SURFACE OF A SOLID

MECHANICS

1966

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

UDC 539.219.1

MECHANICS

V. V. MAZHUGA

ON THE COLLISION OF AN ATOM WITH THE SURFACE OF A SOLID

(Presented by Academician Ya. B. Zelʹ dovich, 10 VII 1965)

To understand a number of physical and chemical processes it is important to know the mechanism of the interaction of atoms with the surface of a solid. In view of the complexity of a quantum-mechanical treatment of this problem, one has to use simple models and describe the motion of atoms within the framework of classical mechanics.

A number of works ($^{1-5}$) are devoted to this question. To simplify the problem, the solid is usually approximated by a semi-infinite linear chain of elastically bound atoms, with the end atom of the chain playing the role of the surface atom with which the atom incident from the gas phase interacts. Cabrera and Zwanzig (^{2,3}) found a closed-form solution of the equations of motion for this system under the assumption that all force constants of the interaction of the atoms are equal to one another, for two special cases: a) the mass of all atoms is the same; b) the mass of the incident atom is one half the mass of each of the atoms of the chain. McCarroll and Ehrlich (^{4}) and Lehmann (^{5}), for several values of the mass of the incident atom and of the force constant of the interaction of the gas-phase atom with the surface, carried out a numerical solution of the equations of motion of this system of particles on an electronic computer.

Below, a solution of this problem will be given in closed form for arbitrary values of the mass of the incident atom and of the force constant.

In the model indicated above (Fig. 1), all interatomic distances are assumed to be equal.

Fig. 1

Since the forces of interatomic interaction decrease rapidly with distance, it is

Fig. 2

Figure 2: Fig. 2

approximately possible to restrict oneself to taking into account the interaction of each atom with its two nearest neighbors. The interaction of the atoms is considered in the harmonic approximation. We shall denote the force constant of the chain by K, and the mass of each atom by M. This chain of atoms interacts with an atom A, incident from the gas phase, whose mass is equal to M_0.

Figure 2 shows the potential of interaction between atom A and the end atom of the chain B, representing a truncated harmonic oscillator with force constant K_0. For this oscillator the truncation distance has a fixed value $x(0)$, and the binding energy Q is varied by changing the force constant according to the relation $Q = K_0 x^2(0)/2$. The numbering of the atoms is clear from Fig. 1. The system of equations describing the motion of the atoms has the form:

$$\begin{aligned} M_0 \ddot{r}_0(t) &= -K_0(r_0 - r_1), \\ M \ddot{r}_1(t) &= K_0(r_0 - r_1) - K(r_1 - r_2), \\ M \ddot{r}_n(t) &= K(r_{n-1} - 2r_n + r_{n+1}), \quad n \geqslant 2, \end{aligned} \tag{1}$$

where r_i is the displacement from the equilibrium position of the i-th atom.

We consider the lattice at a temperature of 0°K, i.e., at the initial instant all atoms of the lattice are at rest. Taking this remark into account, the initial conditions are written in the form:

$$r_0(0) = a, \qquad \dot{r}_0(0) = v,$$

$$r_n(0) = 0, \qquad \dot{r}_n(0) = 0, \qquad n \geqslant 1, \tag{2}$$

where v is the velocity of atom A.

We introduce new variables $x(\tau) = r_0(\tau) - r_1(\tau)$, $\tau = 2(K/M)^{1/2} t = \omega_0 t$, and denote $\beta = K_0/K$, $\mu = M/M_0$. By means of the generating-function method proposed by Schrodinger (^{6}) and developed by Rubin (^{7}), MacCarroll and Ehrlich (^{4}), for the quantity $x(\tau)$ we obtained the integro-differential equation

$$\ddot{x}(\tau) = -\frac{1}{4}\beta(1+\mu)x(\tau) + \frac{1}{2}\int_0^\tau ds\, \frac{J_2(s)}{s}\, x(\tau - s), \tag{3}$$

with $x(0) = a$, $\dot{x}(0) = v/\omega_0$, and $J_2(s)$ the Bessel function.

Fig. 2

We shall solve this equation by the Laplace-transform method. By successive transformations one can express the resulting contour integral in terms of Lommel functions, Bessel functions, and trigonometric functions. The Lommel functions $U_\nu(w, z)$ of two independent variables are defined by the relation*

$$U_\nu(w,z) = \sum_{m=0}^{\infty} (-1)^m \left(\frac{w}{z}\right)^{\nu+2m} J_{\nu+2m}(z). \tag{4}$$

In view of the cumbersomeness of the formulas, we give only the final result. If $\beta > 4/(\mu+2)$ and $\beta \neq 1$, then

$$x(\tau) = x(0)\big[(1-\omega A)J_0(\tau) + \omega A\cos\omega\tau + BU_2(\alpha\tau,\tau) - CU_2(\varepsilon\tau,\tau)\big] +$$

$$+\dot{x}(0)\big[A\sin\omega\tau + DU_1(\alpha\tau,\tau) - EU_1(\varepsilon\tau,\tau)\big], \tag{5}$$

where

$$A = \frac{2\beta\mu - 8\varphi^2 + 8\beta\varphi^2 - 4\beta\omega^2 + 2\beta\gamma + B\beta\gamma}{2\beta\gamma\omega},$$

$$B = \frac{8\omega^2(\omega^2-1)}{\gamma(2\omega^2-\alpha^2-1)}, \qquad C = \frac{8\varphi^2(\varphi^2-1)}{\gamma(2\varphi^2-\varepsilon^2-1)},$$

$$D = \frac{8\alpha(\omega^2-1)}{\gamma(\alpha^2-1)}, \qquad E = \frac{8\varepsilon(\varphi^2-1)}{\gamma(\varepsilon^2-1)},$$

$$\omega = \sqrt{\frac{\beta\mu^2}{4\mu - 2\beta\mu - 2\beta + 2\gamma}}, \qquad \varphi = \sqrt{\frac{\beta\mu^2}{4\mu - 2\beta\mu - 2\beta - 2\gamma}},$$

$$\alpha = \sqrt{\frac{\beta\mu^2 + 2\beta\mu - \gamma\mu - 2\mu + \beta - \gamma}{2\mu - \beta\mu - \beta + \gamma}},$$

$$\varepsilon = \sqrt{\frac{\beta\mu^2 - \gamma\mu - 2\mu + \beta + \gamma}{2\mu - \beta\mu - \beta - \gamma}},$$

$$\gamma = \sqrt{\beta^2\mu^2 + \beta^2 - 4\beta\mu + 2\beta^2\mu}.$$

For $\beta < 4/(\mu+2)$ and $\beta \neq 1$, $\beta \neq 4\mu/(\mu+1)^2$, the solution has the form

$$x(\tau) = x(0)\big[J_0(\tau) - BU_2(\delta\tau,\tau) - CU_2(\varepsilon\tau,\tau)\big] -$$

$$-\dot{x}(0)\left[DU_1(\delta\tau,\tau)+EU_1(\varepsilon\tau,\tau)\right], \tag{6}$$

where

$$\delta=\sqrt{\frac{\beta\mu^2+\gamma\mu-2\mu+\beta-\gamma}{2\mu-\beta\mu-\beta+\gamma}}.$$

In the case $\beta=4/(\mu+2)$ we find:

$$x(\tau)=x(0)\left[J_0(\tau)-CU_2(\varepsilon\tau,\tau)\right]-\dot{x}(0)EU_1(\varepsilon\tau,\tau). \tag{7}$$

For $\beta=1$ and $\mu>2$ we obtain:

$$\begin{aligned}x(\tau)=x(0)&\left[\frac{1}{(\mu-1)^2}J_0(\tau)-\frac{1}{\mu-1}J_2(\tau)+\frac{\mu(\mu-2)}{(\mu-1)^2}U_2\left(\frac{\tau}{\sqrt{\mu-1}},\tau\right)\right.\\&\left.+\frac{\mu(\mu-2)}{(\mu-1)^2}\cos\left(\frac{\mu}{2\sqrt{\mu-1}}\tau\right)\right]+2\dot{x}(0)\left[\frac{1}{\mu-1}J_1(\tau)\right.\\&\left.-\frac{\mu-2}{(\mu-1)\sqrt{\mu-1}}U_1\left(\frac{\tau}{\sqrt{\mu-1}},\tau\right)+\frac{\mu-2}{(\mu-1)\sqrt{\mu-1}}\sin\left(\frac{\mu}{2\sqrt{\mu-1}}\tau\right)\right].\end{aligned} \tag{8}$$

For $\beta=1$, $\mu\leq 2$, and $\mu\neq 1$, the solution is as follows:

$$\begin{aligned}x(\tau)=x(0)&\left[\frac{1}{(\mu-1)^2}J_0(\tau)-\frac{1}{\mu-1}J_2(\tau)-\frac{\mu(\mu-2)}{(\mu-1)^2}U_2\left(\sqrt{\mu-1}\,\tau,\tau\right)\right]\\&+2\dot{x}(0)\left[\frac{1}{\mu-1}J_1(\tau)+\frac{\mu-2}{(\mu-1)\sqrt{\mu-1}}U_1\left(\sqrt{\mu-1}\,\tau,\tau\right)\right].\end{aligned} \tag{9}$$

For $\beta=1$ and $\mu=1$ the solution was obtained earlier ([2,3]):

$$x(\tau)=x(0)\left[J_0(\tau)-J_4(\tau)\right]+2\dot{x}(0)\left[J_1(\tau)+J_3(\tau)\right]. \tag{10}$$

Finally, for $\beta=4\mu/(\mu+1)^2$ the solution has the form:

---

* For tables of Lommel functions see ([8]).

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

$$x(\tau) = x(0)\left[2U_0\left(\sqrt{\frac{\mu-1}{\mu+1}}\tau, \tau\right) - J_0(\tau) - 4\mu\sum_{n=0}^{\infty}\frac{n+1}{(\mu+1)^{n+2}}J_{2n+4}(\tau)\right]$$
$$+2\dot{x}(0)\left[J_1(\tau) - \sqrt{\frac{\mu+1}{\mu-1}}\,U_3\left(\sqrt{\frac{\mu-1}{\mu+1}}\tau, \tau\right) + 2\sum_{n=0}^{\infty}\frac{n+1}{(\mu+1)^{n+1}}J_{2n+3}(\tau)\right]. \tag{11}$$

This solution makes it possible to consider, for example, the mechanical relaxation of a solid upon adsorption of an atom on its surface. Since usually $Q \gg kT$, for simplicity one may assume that the velocity of the incident atom is zero. After the distance between the atom and the surface becomes equal to $x(0)$, the atom begins to oscillate and to transfer its energy to the chain.

Fig. 3

Fig. 4

In the formulas for $x(\tau)$, all terms tend to zero as $\tau \to \infty$, except for the terms containing the cosine. The latter correspond to the excitation of a localized vibration, whose energy in the harmonic approximation is not dissipated into the lattice but remains on the given atom. The energy of the crystalline vibrations of the incident atom is transferred to the chain in a time of the order of 10^{-12} sec.

Figure 3 shows the dependence of the relative amplitude of the localized vibration $A_1 = \omega A/x(0)$ on $\mu = M/M_0$ for different values of the ratio of the force constants. It is seen from Fig. 3 that for each given

β there is a certain critical mass ratio, above which a localized vibration arises, and its amplitude, as μ increases, rapidly changes from 0 to 1. If $A_1 \simeq 1$, then the vibrations of the system can be described by a single oscillator. For $\mu \gg 1$ such a situation occurs practically for any β.

Figure 4 shows the dependence of $x(\tau)/x(0)$ for different β at $\mu = 1$. At $\beta = 2.2$ a localized vibration arises; in Fig. 4 the dotted line shows only the contribution of the crystal vibrations to the value of $x(\tau)/x(0)$. A decrease in the interaction constant leads to a slowing of the relaxation of the vibrational energy. When the interaction constant is increased, the dissipation of that part of the energy due to the band vibrations of the adsorbed atom proceeds at approximately the same rate as when all the force constants are equal.

It can be shown that when the mass of the incident atom is decreased, the energy corresponding to the crystal vibrations is transferred to the lattice more slowly than in the case when the masses of all atoms are identical. In the collision of a heavy atom with the chain, i.e., for $\mu \ll 1$, the motion is aperiodic in character.

I express my sincere gratitude to Prof. N. D. Sokolov for discussion of the results obtained and for a number of useful suggestions.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
29 VI 1965

REFERENCES

1. J. E. Lennard-Jones, Proc. Roy. Soc. London, A **163**, 127 (1937).
2. N. B. Gerera, Disc. Farad. Soc., **28**, 16 (1959).
3. R. W. Zwanzig, J. Chem. Phys., **32**, 1173 (1960).
4. B. McCarrol, G. Ehrlich, J. Chem. Phys., **38**, 523 (1963).
5. B. B. Leonas, Zhurn. prikl. mekh. i tekhn. fiz., **6**, 124 (1963).
6. E. Schrödinger, Ann. Phys., **44**, 916 (1914).
7. R. J. Rubin, Proc. Intern. Symp. Transport Processes Statist. Mech., Brussels, 1958, p. 155.
8. E. N. Dekanosidze, *Tables of Cylindrical Functions of Two Variables*, Publ. House of the Academy of Sciences of the USSR, 1956.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.