

COLLISION OF AN ATOM WITH THE SURFACE OF A SOLID

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The energy exchange between atoms and solids is very important to the theory of adsorption or catalysis, as well as to the theory of processes in which a major part is played by interaction of a crystal surface with initial compounds or intermediates. The problem has been considered [1, 2] in the one-phonon approximation. Experiment [3, 4] indicates that condensation of atoms occurs with a probability of the order of unity when the translational energy equals the energy needed to excite several phonons in the solid. Hence the rate of energy exchange is much greater than that predicted in [1, 2]. The quantum-mechanical argument is very complicated, so I use simple models and describe the motion of the atoms within the framework of classical mechanics.

There are several papers [5-9] on this topic. The solid is usually represented as a semiinfinite linear chain of elastically bound atoms, the end atom acting as the surface atom that interacts with the incident atom. A closed solution has been found [6, 7] for the equations of motion of this system on the assumption that all the force constants for the atomic interactions are equal for two particular cases: a) all the atoms have the same mass, b) the mass of the incident atom is half that of an atom in the chain. The equations have been solved numerically [8, 9] for several different masses of the incident atom and for various force constants for the interaction of this with the surface. Here I give a solution in a closed form for arbitrary values of the force constant at the surface and of the mass of the incident atom.

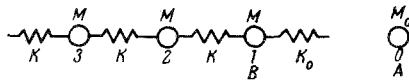


Fig. 1

1. General. All the interatomic distances are assumed equal. Interatomic forces are rapidly decreasing functions of distance, so we consider only the interaction of an atom with its two nearest neighbors, and that in the harmonic approximation. Let K be the force constant of the chain, whose atoms are of mass M. This chain interacts with an atom A (Fig. 1), whose mass is M₀. Figure 2 shows the potential for the interaction of A with the end atom B, which is represented as the truncated potential for a harmonic oscillator of force constant K₀. The cutoff distance has a value x(0), while the binding energy Q obeys Q = K₀x²(0)/2. The numbering of the atoms will be clear from Fig. 1. The system of equations of motion is

$$\begin{aligned} M_0 r_0''(t) &= -K_0(r_0 - r_1), \\ M r_1''(t) &= K_0(r_0 - r_1) - K(r_1 - r_2), \\ M r_n''(t) &= K(r_{n-1} - 2r_n + r_{n+1}) \quad (n \geq 2), \end{aligned} \quad (1)$$

in which r_n is the deviation of atom n from its equilibrium position.

In this case we consider a lattice at 0°K, i.e., all the lattice atoms are initially at rest. The initial conditions are then written as

$$\begin{aligned} r_0(0) &= a, & r_0'(0) &= v, \\ r_n(0) &= 0, & r_n'(0) &= 0 \quad (n \geq 1), \end{aligned} \quad (2)$$

in which v is the velocity of atom A.

We introduce the new variables x and τ, together with the quantities β and μ,

$$x(\tau) = r_0(\tau) - r_1(\tau), \quad \tau = 2\left(\frac{K}{M}\right)^{1/2} t = \omega_L t, \quad \beta = \frac{K_0}{K}, \quad \mu = \frac{M}{M_0}.$$

Schrödinger's method [10], as developed by others [7, 8, 11], is

applied to get for x(τ) the integrodifferential equation

$$x''(\tau) = -\frac{1}{4}\beta(1+\mu)x(\tau) + \frac{1}{2}\beta \int_0^\tau \frac{I_2(s)}{s} x(\tau-s) ds, \quad (3)$$

in which x(0) = a, x'(0) = v/ω_L and I₂(s) is a Bessel function.

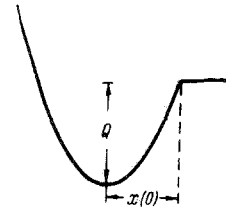


Fig. 2

2. Solution of the equation of motion. The solution is found via a Laplace transformation. Let X(p) be the transform of the desired function; then we have

$$X(p) = \frac{4x(0)p + 4x'(0)}{4p^2 + \beta(1+\mu) - \beta(\sqrt{p^2 + 1 - p})^2}. \quad (4)$$

The solution to (3) is expressed via the contour integral

$$x(\tau) = \frac{1}{2\pi i} \int_{a-i\infty}^{a+i\infty} X(p) e^{p\tau} dp. \quad (5)$$

Here a is a constant greater than the real part of any singularity in X(p). Integration along the straight line Re p = a may be replaced by integration along any closed path in a finite part of the plane that encloses all singularities of X(p).

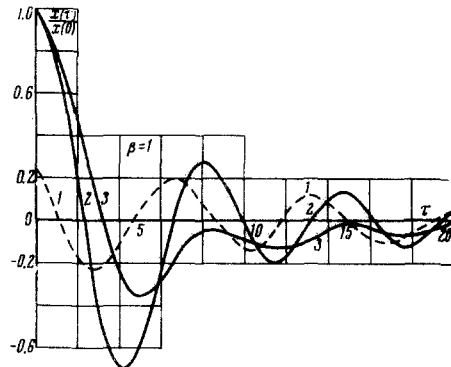


Fig. 3

The integral of (5) may be expressed in terms of Lommel and Bessel functions together with trigonometric functions. The Lommel functions U_ν(y, z) of two independent variables* are defined by

$$U_\nu(y, z) = \sum_{m=0}^{\infty} (-1)^m \left(\frac{y}{z}\right)^{\nu+2m} I_{\nu+2m}(z), \quad (6)$$

where I_{ν+2m}(z) are Bessel functions.

*See [12] for tables of these functions.

The function $\sqrt{p^2 - 1}$ has singularities at $p = i$ and $p = -i$. We join these points by a line. The function $w = \sqrt{p^2 - 1} - p$ images the plane with the section of p within unit circle $w = 1$ in the plane of the complex variable w . To the circles $r = \text{const}$ in the w plane correspond ellipses in the p plane, whose foci lie at the critical points.

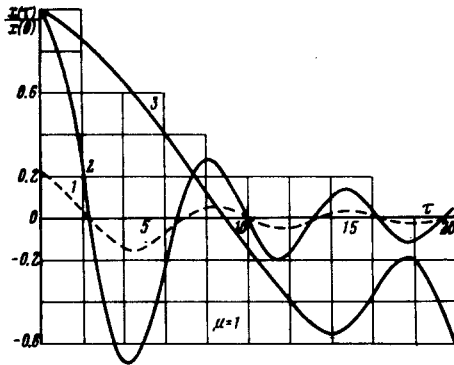


Fig. 4

Counterclockwise (positive) traversal of an ellipse corresponds to clockwise (negative) traversal of a circle. We now replace the variables via the formula [13] $w = \sqrt{p^2 - 1} - p$ to get

$$x(\tau) = \frac{1}{2\pi i} \int_{|w|=1} X(w) \exp\left[\frac{\tau}{2} \left(\frac{1}{w} - w\right)\right] dw,$$

$$X(w) = \frac{x(0)(1-w^4) + 2x'(0)w(1+w^2)}{w[(1-\beta)w^4 + (\beta + 3\mu - 2)w^2 + 1]} \quad (7)$$

As our contour l we may take a circle of unit radius, $|w| = 1$. Here and subsequently we assume that the origin is traversed in the positive direction. We put the rational function $X(w)$ in the form of a sum of fractions

$$X(w) = \frac{x(0)}{w} + \sum_{n=0}^2 \sum_{s=1}^2 \frac{A_{ns} w^n}{w^2 - w_s},$$

$$w_{1,2} = \frac{2 - \beta - 3\mu \pm \gamma}{2(1 - \beta)}, \quad \gamma = \sqrt{\beta^2 \mu^2 + \beta^2 - 4\beta\mu + 2\beta^2 \mu} \quad (8)$$

The integral of (7) splits up into a sum of integrals of the form

$$\frac{1}{2\pi i} \int_{|w|=1} \frac{1}{w} \exp\left[\frac{\tau}{2} \left(\frac{1}{w} - w\right)\right] dw, \quad (9)$$

$$F = \frac{1}{2\pi i} \int_{|w|=1} \frac{w^n}{w^2 - w_s} \exp\left[\frac{\tau}{2} \left(\frac{1}{w} - w\right)\right] dw. \quad (10)$$

The substitution $w = u^{-1}$ shows that the integral of (9) is a Bessel function $I_0(\tau)$ of order zero. We assume that the point w_s lies outside the contour $|w| = 1$, which is so for $\beta < 4/(\mu + 2)$. Then

$$\frac{1}{w^2 - w_s} = -\frac{1}{w_s} \left[1 + \frac{w^2}{w_s} + \left(\frac{w^2}{w_s}\right)^2 + \dots\right], \quad (11)$$

We substitute (11) into (10) and make the change of variable $w = u^{-1}$ to get

$$F = \frac{1}{2\pi i} \sum_{m=0}^{\infty} \int_{|u|=1} (-1)^m \times$$

$$\times \left(-\frac{1}{w_s}\right)^{m+1} u^{-n-2m-2} \exp\left[\frac{\tau}{2} \left(u - \frac{1}{u}\right)\right] du. \quad (12)$$

It is permissible to reverse the order of summation and integration because the series in the integral converges uniformly and absolutely.

We use the representation of the Bessel functions in the form of a contour integral

$$I_\nu(y) = \frac{1}{2\pi i} \int_{l_0} t^{-\nu-1} \exp\left[\frac{y}{2} \left(t - \frac{1}{t}\right)\right] dt, \quad (13)$$

in which l_0 is a circle of arbitrary radius with its center at the origin. Comparison of (6), (12), and (13) gives

$$F = \left(-\frac{1}{w_s}\right)^{1/2(\mu+1-n)} U_{n+1}\left[\left(-\frac{1}{w_s}\right)^{1/2} \tau, \tau\right]. \quad (14)$$

Consider the case where w_s lies within the contour $|w| = 1$, which occurs for $\beta > 4/(\mu + 2)$. The integrand in (10) has an essentially special point $w = 0$ and two first-order poles $w = \pm\sqrt{w_s}$. The integral equals the product of $2\pi i$ by the sum of the amounts to be subtracted from the integrand for the poles within the unit circle, plus the integral over a circle of radius $r < |w_s|$. For $n = 1$ we have

$$\frac{1}{2\pi i} \int_{|w|=1} \frac{w}{w^2 - w_s} \exp\left[\frac{\tau}{2} \left(\frac{1}{w} - w\right)\right] dw =$$

$$= \cos \omega \tau + \frac{1}{2\pi i} \int_{l_r} \frac{w}{w^2 - w_s} \exp\left[\frac{\tau}{2} \left(\frac{1}{w} - w\right)\right] dw,$$

$$\omega = \left(\frac{\beta \mu^2}{4\mu - 2\beta\mu - 2\beta + 2\gamma}\right)^{1/2}. \quad (15)$$

Here l_r is a circle of radius $r < |w_s|$. The integral over l_r , by analogy with the above, is expressed via a Lommel function. For $n = 0$ we get

$$\frac{1}{2\pi i} \int_{|w|=1} \frac{1}{w^2 - w_s} \exp\left[\frac{\tau}{2} \left(\frac{1}{w} - w\right)\right] dw =$$

$$= -\left(-\frac{1}{w_s}\right)^{1/2} \sin \omega \tau + \frac{1}{2\pi i} \int_{l_r} \frac{1}{w^2 - w_s} \exp\left[\frac{\tau}{2} \left(\frac{1}{w} - w\right)\right] dw. \quad (16)$$

Simple algebraic operations give us the solution to (3) once the integrals have been calculated. Before giving the final result, we may simplify the notation by writing

$$\alpha = \left(-\frac{1}{w_1}\right)^{1/2}, \quad \delta = \left(-\frac{1}{w_2}\right)^{1/2},$$

$$C = \frac{2(\alpha^2 - 1)}{\gamma\alpha}, \quad E = \frac{2(\delta^2 - 1)}{\gamma\delta}, \quad D = \frac{2\gamma - \beta\gamma - 2\beta + \beta^2 + \beta^2\mu}{2\gamma(\beta - 1)}.$$

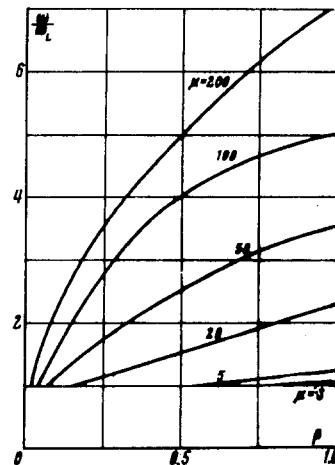


Fig. 5

Then the solution may be written as follows:
for $\beta < 4/(\mu + 2)$, $\beta \neq 1$, $\beta \neq 4\mu/(\mu + 1)^2$

$$x(\tau) = x(0) [I_0(\tau) - \omega C U_2(\alpha\tau, \tau) + D U_2(\delta\tau, \tau)] + x'(0) [C U_1(\alpha\tau, \tau) - E U_1(\delta\tau, \tau)]; \quad (17)$$

for $\beta > 4/(\mu + 2)$ and $\beta \neq 1$

$$x(\tau) = x(0) [(1 - \omega C) J_0(\tau) + \omega C \cos \omega\tau + \omega C U_2(\alpha^{-1}\tau, \tau) + D U_2(\delta\tau, \tau)] + x'(0) [C \sin \omega\tau - C U_1(\alpha^{-1}\tau, \tau) - E U_1(\delta\tau, \tau)]; \quad (18)$$

for $\beta = 4/(\mu + 2)$

$$x(\tau) = x(0) [I_0(\tau) + D U_2(\delta\tau, \tau)] - x'(0) E U_1(\delta\tau, \tau); \quad (19)$$

for $\beta = 1$ and $\mu > 2$

$$x(\tau) = x(0) \left[\frac{1}{(\mu - 1)^2} I_0(\tau) - \frac{1}{\mu - 1} I_2(\tau) + \frac{\mu(\mu - 2)}{(\mu - 1)^2} U_2\left(\frac{\tau}{\sqrt{\mu - 1}}, \tau\right) + \frac{\mu(\mu - 2)}{(\mu - 1)^2} \cos\left(\frac{\mu}{2\sqrt{\mu - 1}}\tau\right) \right] + 2x'(0) \left[\frac{1}{\mu - 1} I_1(\tau) - \frac{\mu - 2}{(\mu - 1)\sqrt{\mu - 1}} U_1\left(\frac{\tau}{\sqrt{\mu - 1}}, \tau\right) + \frac{\mu - 2}{(\mu - 1)\sqrt{\mu - 1}} \sin\left(\frac{\mu}{2\sqrt{\mu - 1}}\tau\right) \right]; \quad (20)$$

for $\beta = 1$, $\mu \leq 2$ and $\mu \neq 1$

$$x(\tau) = x(0) \left[\frac{1}{(\mu - 1)^2} I_0(\tau) - \frac{1}{\mu - 1} I_2(\tau) - \frac{\mu(\mu - 2)}{(\mu - 1)^2} U_3(\sqrt{\mu - 1}\tau, \tau) \right] + 2x'(0) \left[\frac{1}{\mu - 1} I_1(\tau) + \frac{\mu - 2}{(\mu - 1)\sqrt{\mu - 1}} U_1(\sqrt{\mu - 1}\tau, \tau) \right]. \quad (21)$$

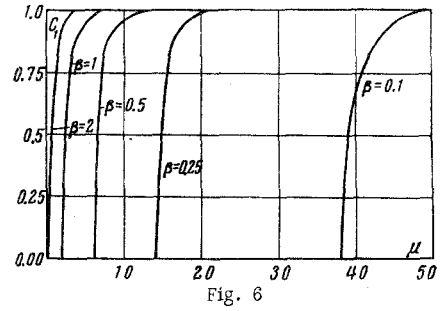
The solution of (22) has been obtained previously [6, 7].
For $\beta = 1$ and $\mu = 1$,

$$x(\tau) = x(0) [I_0(\tau) - I_4(\tau)] + 2x'(0) [I_1(\tau) + I_3(\tau)]; \quad (22)$$

for $\beta = 4\mu/(\mu + 1)^2$,

$$x(\tau) = x(0) \left\{ 2U_0\left[\left(\frac{\mu - 1}{\mu + 1}\right)^{1/2}\tau, \tau\right] - I_0(\tau) - 4\mu \sum_{n=0}^{\infty} \frac{(n + 1)(1 - \mu)^n}{(\mu + 1)^{n+2}} I_{2n+4}(\tau) \right\} + 2x'(0) \left\{ I_1(\tau) + \left(\frac{\mu + 1}{\mu - 1}\right)^{1/2} U_3\left[\left(\frac{\mu - 1}{\mu + 1}\right)^{1/2}\tau, \tau\right] + 2 \sum_{n=0}^{\infty} \frac{(n + 1)(1 - \mu)^n}{(\mu + 1)^{n+1}} I_{2n+3}(\tau) \right\}. \quad (23)$$

3. Discussion. It is readily shown that all terms tend to 0 as $\tau \rightarrow \infty$ in these formulas, apart from the sine and cosine terms, which correspond to excitation of local vibration, whose frequency lies above the range of allowed frequencies, and the amplitude decreases exponentially away from the surface. In the harmonic approximation, the energy corresponding to this vibration is not dissipated in the lattice but persists on the atom. The other terms correspond to excitation of crystal modes, and it can be shown that the energy corresponding to the crystalline vibrations is transferred to the chain in a time of the order of 10^{-12} sec. The anharmonicity gives the local vibration a finite lifetime of 10^{-8} to 10^{-6} sec.



This solution allows us to discuss the mechanical relaxation of a solid when an atom is adsorbed on it. The mean bond energy in chemisorption is much greater than the mean kinetic energy of the atoms in the gas, so for simplicity we may assume that the velocity of the incident atom is 0. The atom begins to vibrate and gives its energy to the chain when its distance from the surface becomes equal to $x(0)$.

Figure 3 shows the time variation of the distance between the end atom of the chain and the gas atom, as expressed in relative units, for several values of the mass ratio μ , with $\beta = 1$. Curve 1 corresponds to $\mu = 3$; curve 2, to $\mu = 1$; and curve 3, to $\mu = 0.2$. Local oscillation occurs for $\mu = 3$, and the dashed line in Fig. 3 shows the contribution of the crystal oscillations to $x(\tau)/x(0)$. The energy corresponding to the crystal modes is transferred more slowly to the lattice as the mass of the incident atom decreases. For $\mu \ll 1$ the motion is aperiodic.

Figure 4 shows $x(\tau)/x(0)$ for various β for $\mu = 1$. Curve 1 is for $\beta = 2.2$, curve 2 is for $\beta = 1$, and curve 3 is for $\beta = 0.1$. Local oscillation occurs for $\beta = 2.2$; the broken line in Fig. 4 shows the contribution from band oscillations to $x(\tau)/x(0)$. The rate of relaxation of the vibrational energy is directly related to the interaction constant. A large constant implies that the dissipation of the energy of the band modes occurs at roughly the rate applicable if all the force constants are equal.

Figure 5 shows the frequency of the local oscillation in units of ω/ω_L as a function of β for various μ . This frequency substantially exceeds the Debye frequency ω_L when a light atom is adsorbed.

Figure 6 shows the relative amplitude $C_1 = \omega C$ of the local oscillation as a function of $\mu = M/M_0$; for each given β there is some critical mass ratio above which we get local oscillation, the amplitude varying rapidly from 0 to 1 as μ increases. For $C_1 \approx 1$ the motion may be described via a single oscillator; this situation occurs for virtually any β for $\mu \gg 1$.

It is thus clear that vibrationally excited particles can occur in above-equilibrium concentrations in adsorption and when exothermic elementary acts of reaction occur at the surface of a catalyst. The energy of these relatively long-lived hot particles is subsequently used to activate fresh molecules. Active centers in a catalyst can occur at any type of defect in the periodic structure that can give rise to local oscillations. The activation energy comes to the adsorbed molecule from the solid phase and from the active center, which acts as an energy trap. The frequency of local vibration at an active center should coincide with the vibrational frequency of the molecule that leads to the desired reaction, because the probability of exchange is maximal for resonance.

To conclude we note that the above argument applied for times $\tau < \tau^*$, in which τ^* is the characteristic time for energy exchange between normal modes. The solution does not require resort to computers to get the accommodation coefficient for any mass ratio and any binding energy; it also gives the asymptotic value of the velocity of the atom on reflection and so on.

I am indebted to N. D. Sokolov for discussions.

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