ENERGY EXCHANGE ON COLLISION OF MOLECULES WITH A SOLID WALL

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The study of the laws of energy and momentum transfer when particles strike the surface of a solid is of great interest in connection with calculation of the heating and deceleration of flight vehicles in the upper layers of the atmosphere. Since, under these conditions, the relative collision energies reach 10–20 eV, one might expect the internal degrees of freedom of the molecules in the incident flow to have a considerable effect on the pattern of energy exchange with the wall. The influence of the internal degrees of freedom may manifest itself not only under the conditions of free molecular flow, but also in flows with slip. These degrees of freedom may serve as a source (positive or negative) of additional heat fluxes; it is entirely possible that they affect the laws of momentum transfer.

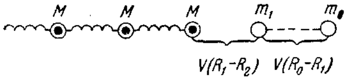


Fig. 1

One may attempt a qualitative evaluation of the effect of internal degrees of freedom at these relative collision energies on the basis of data on the vibratory relaxation and dissociation of molecules behind a shock wave, although the available data relate to a limited temperature range. Since the probability of exciting vibrations is usually small for an individual collision, the single collisions characteristic of the conditions existing in rarefied gas flows may materially weaken the influence of these degrees of freedom. Quantitative estimates of the effect of vibrational degree of freedom may be obtained by making use of the scheme described in [1].

In that article, which was devoted to an analysis of the collision of an atom with a linear chain of elastically bound atoms, a model and scheme for solution of the problem were described in detail. In this article, we consider the energy exchange and momentum loss when a fast vibrationally excited molecule collides with a linear chain of atoms.

First, let us consider the quantitative characteristics of the model in question (Fig. 1). The interaction of the atoms in the molecule was described by the Lennard-Jones potential

$$V_{01} = 4\varepsilon_1 \left[\left(\frac{\sigma}{R_0 - R_1} \right)^{12} - \left(\frac{\sigma}{R_0 - R_1} \right)^{6} \right].$$

Here ϵ_1 is the dissociation energy of the molecule, σ is the distance at which the potential vanishes, and R_i is the coordinate of the particle. The interaction of the first (Fig. 1), and the second atom is also described by the Lennard-Jones potential; in this case, however, $\epsilon_2 = 0.01\,\epsilon_1$. The atoms in the chain are bound by elastic forces with the potential

$$V = K(R_i - R_{i+1}) .$$

Here K is the elastic lattice constant. The reduced mass $\mu = m_0/M = m_1/M$ (Fig. 1) was chosen equal to 0.2, as in [1]. The initial relative collision energy E_0 was taken equal to $0.1\epsilon_1$, $0.5\epsilon_1$, and $5\epsilon_1$; in

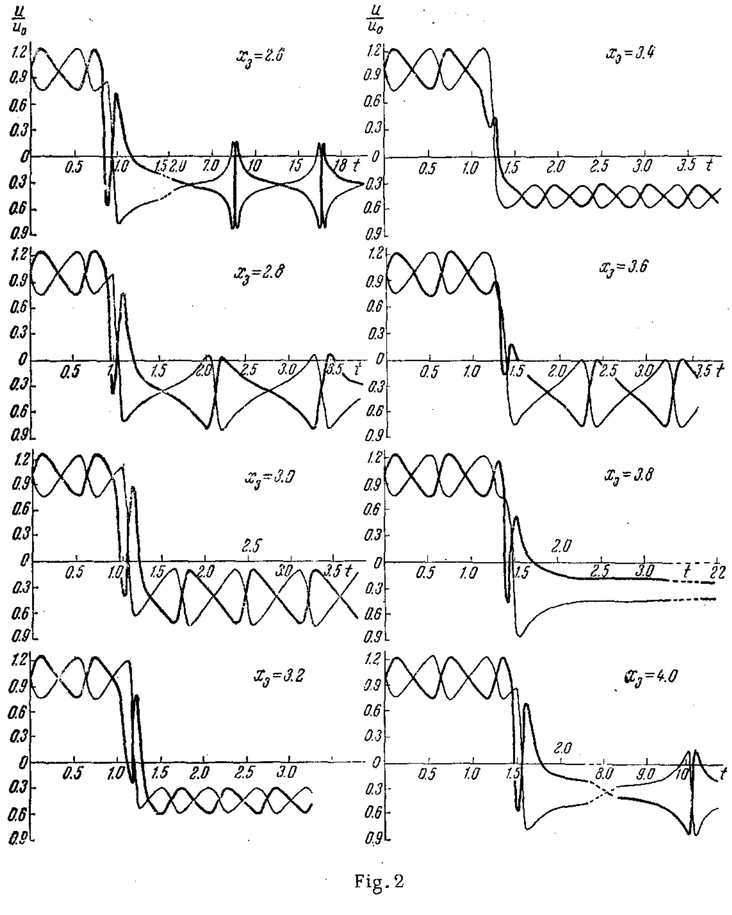


Fig. 2

addition, cases of E_0 equal to 4, 6, and $10\epsilon_1$ were considered. Under actual conditions, this would correspond to energies from about 0.1 to about 50 eV. The initial vibrational excitation of the molecule was fixed by specifying the interatomic distance, which differs from the equilibrium value. Values of the initial vibrational energy $E_0' = 0.22\epsilon_1$, $0.085\epsilon_1$, and $0.018\epsilon_1$ were utilized in the calculations.

The initial kinetic and vibrational energies of the molecule were not sufficient to determine the final state, since the latter also depends on the phase of the vibration, that is, on the magnitude and direction of the vibrational velocity at the time of collision.

In order to take account of the effect of the phase and to obtain phase-averaged results, we varied the initial distance $x_3 = (R_1 - R_2)/\sigma$ of the vibrating molecule from the linear chain. The values of x_3 were varied in the range from 2 to 4, depending on the magnitude of the initial translational and vibrational energies.

A typical series of time diagrams of the collision process for one complete phase change cycle is presented in Fig. 2 ($E_0 = 4\epsilon_1$ and $E_0' = 0.22\epsilon_1$), where the ratio of the variable u and initial u_0 velocities is plotted along the axis of ordinates and the time t along the axis of abscissas. The thin line corresponds to the 0 and the heavy line to the 1 atom (Fig. 1); the dashed line shows the rough course of the curves on converting to a different scale along the axis of abscissas. The antinodes in Fig. 2 correspond to equilibrium positions of the unexcited molecule and the nodes to the extreme excited positions of the molecule; changes in the amplitude of the velocity fluctuations after collision correspond to changes in the vibrational energy during collision. A line drawn through the nodes shows the change in the velocity of the center of mass of the molecule (the initial reduced velocity is equal to unity). Figure 2 clearly shows the phase effect; depending on the latter, the vibrational energy may either increase (right up to dissociation—the case in which $x_3 = 3.8$) or decrease (the case in which $x_3 = 3.2$). It can be seen from Fig. 2 that collisions in states corresponding to transition from compression to expansion are most effective in respect to additional excitation of vibrations, while the opposite situation is least effective. In concluding the qualitative discussion of Fig. 2, we note that the selected molecular model took anharmonicity into account; thus, in states of strong excitation (close to dissociation), the period of the vibrations increase greatly (compare the cases $x_3 = 2.6$ and $x_3 = 3.2$ in Fig. 2).

With the aid of data of the type presented in Fig. 2, the transfer coefficient for translational energy $\alpha = E_1/E_0$ (here E_1 is the value of the translational energy after collision), the transfer coefficient for the translational energy after collision), the transfer coefficient for the total energy $\alpha_2 = (E_1 + E_1')/(E_0')$, and the acquired vibrational energy $(E_1' - E_0')$ were obtained as functions of the collision energy E_0 for different values of the initial vibrational energy E_0'. These relationships are shown in Figs. 3a, 3b, and 3c, respectively, (curve 1 corresponds to the case of collision of an unexcited molecule, curve 2 to that of an excited molecule with $E_0' = 0.22\epsilon_1$, the relationships for $E_0' = 0.085\epsilon_1$ and $0.018\epsilon_1$, which practically coincide with curve 2, are shown by individual points and curves 3 and 4).

The transfer coefficient for translational energy α_1 characterizes the momentum exchange when there are internal degrees of freedom; it is found from the velocity of the center of mass of the molecule, so that the transfer momentum coefficient is equal to the root of the values presented in Fig. 3a. It follows from Fig. 3a that the presence of vibrational degrees of freedom has little effect on momentum exchange during collision, for order a wide range of collision energies and initial vibrational energies, the values of α_1 differ little from those corresponding to elastic collision of a structureless particle (the straight line in Fig. 3a).

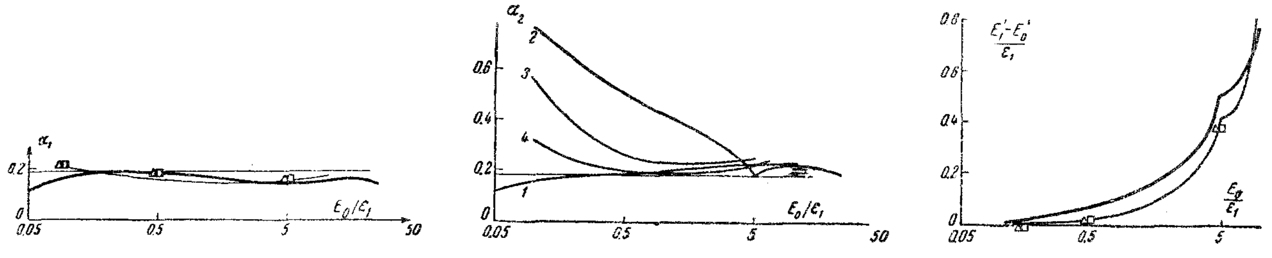
Thus, we may conclude that momentum exchange, and hence the resistance to the motion of a body in a rarefield atmosphere, may depend only slightly on the presence of internal degrees of freedom in the molecules in the flow, and these degrees of freedom may apparently be neglected in practical calculations.

Figure 3b shows the coefficient α_2 as a function of the relative energy for various values of the initial vibrational energy ($E_0' = 0$, $0.018\varepsilon_1$, $0.085\varepsilon_1$, $0.22\varepsilon_1$). The straight horizontal line corresponds to the value of the coefficient for elastic collision of a structureless particle of the same mass. It is clear from Fig. 3b that the initial vibrational excitation will have a noticeable effect on the value of the transfer coefficient α_2, and thus on the amount of energy transferred to the chain. This is connected with the fact that for collisions with energies less than ϵ_1, exchange of vibrational energy is difficult (its initial value is retained). Although the effectiveness of excitation of vibrational degrees of freedom increases with increase in collision energy, the relative proportion of vibrational energy in the total energy decreases. As a result, the total energy transfer coefficient α_2 decreases and approaches the value for elastic collision of structureless particles. As can be seen from Fig. 3b, for the model under consideration, the internal degrees of freedom may be a sink of additional heat fluxes only at energies of about $1\epsilon_1$ to $5\epsilon_1$. In this range, the amount of energy transferred to the body of the flying particle may, depending on the magnitude of the initial excitation, be reduced approximately 10% by energy being "pumped over" into the internal degrees of freedom. In the case of relative collision energies leading to dissociation ($E_0 \geq 5\epsilon_1$), the total energy transfer coefficient was close to the value of the coefficient α.

Thus, when a rareified gas flows at high velocity around a body, the excitation of vibrational degrees of freedom will apparently reduce the heat flux to the body by about 10%, and this reduction should be most effective at the expense of molecules in the flow which possess considerable initial vibrational excitation.

For the same initial vibrational energies, Fig. 3c shows the vibrational energy acquired in collisions with the wall as a function of the value of the initial energy (the energy is expressed in units of dissociation energy ϵ_1).

It can be seen from Fig. 3c that when the initial excitation is low, it has practically no effect on the amount of vibrational energy acquired as a result of collision. However, in the case when $E_0 = 0.22\varepsilon_1$, in the interval of relative collision energies $0.5\epsilon_1$ the effectiveness of the additional excitation is noticeably higher than for undisturbed molecules. When the relative collision energies are greater than $9\epsilon_1$, the value of the vibrational energy acquired may become smaller than for the undisturbed molecule. As may be seen from Fig. 3c, the effectiveness of excitation of the latter is somewhat higher for collision energies exceeding $9\epsilon_1$. It should be noted that when the relative collision energies are low (about $0.1\epsilon_1$), vibrationally excited molecules lose a small part of their vibrational energy. In all cases,



a b c

Fig. 3

however, the magnitude of the loss is so small that it can not be shown in the scale of Fig. 3a.

On the basis of the data of Fig. 3c, one may conclude that on the average for a vibrationally excited molecule within the range of energies of practical interest, collision results only in additional excitation and deexcitation does not take place. Therefore, the vibrational degrees of freedom can apparently be only a negative source of heat flux.

On comparing the above-described results with the available data on moleculear collisions, one notes their qualitative agreement. Thus, for example, according to [2], the probability of dissociation of an excited molecule is exceedingly small, even if the translational energy of the colliding molecules is greater than the binding energy. Dissociation is realized from the upper vibrational levels whose energy is close to the dissociation energy; in this case, the translational energy may not differ from the average thermal energy.

In [3, 4] it is shown that when molecules collide, the cross section for vibrational transition is on the order of the gas kinetic cross section (the transition probability approaches unity) at collision energies an order of magnitude higher than the vibrational quantum.

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