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The relaxation of diatomic molecules (harmonic oscillators) in a relatively light inert gas, which plays the part of a thermostat, is considered within the framework of classical mechanics. The gas-kinetic equation for the distribution function of diatomic molecules is approximated by the Fokker-Planck equation in the space of the energies of translational, rotational and vibrational motions on the assumption of strong nonadiabaticity of the collisions. In the approximation discussed, relaxation processes with different degrees of freedom develop independently, although the characteristic times of these processes are quantities of the same order. The vibrational relaxation time, expressed in terms of the gas-kinetic integral  $\Omega^{*(1,1)}(T^*)$ , is obtained.

Studies of the vibrational relaxation of diatomic molecules are usually based on the assumption of steady-state equilibrium with respect to the translational and rotational degrees of freedom. This is valid if the process of establishing equilibrium is more rapid than the process of vibrational relaxation. However, in our case — heavy diatomic molecules constituting a small impurity in a light inert gas (for example,  $I_2$  in He) — the characteristic times of all three processes are quantities of the same order, and therefore they must be investigated jointly.

Henceforth, we shall assume that: a) the molecules and atoms interact according to the laws of classical mechanics; b) the oscillations of a molecule are harmonic and in practice do not affect the moment of inertia of the molecule; c) collisions between molecules and atoms are strongly nonadiabatic — during the collision the coordinates of the molecule remain practically unchanged; d) during collision an atom interacts only with the nearest atom of a molecule.

The vibrational relaxation time in such a system can be found in the same way as the rotational (and translational) relaxation times (see [1]). The Boltzmann gas-kinetic equation for the distribution function of the molecules, correct to terms  $\sim m/M$  inclusive ( $m$  and  $M$  are the mass of an atom of inert gas and the mass of an atom of the molecule) can be replaced by the Fokker-Planck equation for the distribution function  $f(E_1, E_2, E_3, t)$  of the molecules in the space of the translational ( $E_1$ ), rotational ( $E_2$ ), and vibrational ( $E_3$ ) energies:

$$\frac{\partial f}{\partial t} = \sum_{i,k} \frac{\partial}{\partial E_i} \left\{ B_{ik} \left( \frac{\partial f}{\partial E_k} - f \frac{\partial \ln f^\circ}{\partial E_k} \right) \right\} \quad \left( B_{ik} = \frac{\langle \Delta_i \Delta_k \rangle}{2} \right), \quad \Delta_i \equiv \Delta E_i. \quad (1)$$

Here  $\Delta_i$  is the increment of the energy  $E_i$  upon collision between a molecule and an atom of the inert gas;  $\langle \Delta_i \Delta_k \rangle$  is the result of the averaging over all the collisions of the molecules;  $\tau$  stands for the free time of the molecules;  $f^\circ$  is the equilibrium distribution function of the molecules corresponding to a temperature  $T$  of the light gas. The normalization condition is

$$\iiint f dE_1 dE_2 dE_3 = N \quad (2)$$

where  $N$  is the number of molecules per unit volume. To a first approximation ( $m/M \ll 1$ ):

$$\begin{aligned} \Delta_1 &= \frac{\sqrt{E_1}}{\sqrt{M}} 2mv \sin \frac{\chi}{2} \cos \gamma & \Delta_2 &= \frac{\sqrt{E_2}}{\sqrt{M}} 2mv \sin \frac{\chi}{2} \sin \alpha \cos \beta \\ \Delta_3 &= \frac{p_r}{M} 2mv \sin \frac{\chi}{2} \cos \alpha \end{aligned} \quad (3)$$

where  $v$  is the velocity of the atom at infinity;  $\chi$  is its angle of deviation from the initial direction;  $p_r$  is the momentum of vibrational motion of the molecule before collision;  $\alpha$  and  $\beta$  are the orbital and azimuthal angles of the momentum increment vector of the light atom (the axis of the molecule lies along the  $z$ -axis) and  $\gamma$  is the angle between the momentum vector of the center of mass of the molecule and the momentum increment vector of the light atom. Averaging  $\Delta_i \Delta_k$  over all the orientations of the molecule, we obtain:

$$B_{ik} = 0 \quad \text{for } i \neq k. \quad (4)$$

Integrating Eq. (1) with respect to  $dE_1$  and  $dE_2$  from 0 to  $\infty$  for condition (4) and bearing in mind that

$$f^\circ \sim \sqrt{E_1} \exp \left( - \frac{E_1 + E_2 + E_3}{kT} \right),$$

we obtain for the distribution function of the molecules with respect to the vibrational energy  $\Phi(E_3t)$

$$\frac{\partial \Phi_3}{\partial t} = \frac{\partial}{\partial E_3} \left\{ B_{33} \left( \frac{\partial \Phi}{\partial E_3} + \frac{\Phi}{kT} \right) \right\} \quad (5)$$

with the conditions

$$B_{33} \left( \frac{\partial \Phi}{\partial E_3} + \frac{\Phi}{kT} \right) \Big|_{E_3=0, \infty} = 0, \quad \Phi(E_3, 0) = \frac{N}{kT_0} \exp - \frac{E_3}{kT_0} \quad (6)$$

Here  $T_0$  is the initial temperature of the heavy gas. In order to calculate  $B_{33}$ , in addition to averaging over the Maxwellian distribution of the light gas, we must average the quantity  $\Delta_3^2$  over all possible values of  $p_r$ . We perform this averaging in the phase space of the harmonic oscillator over a layer bounded by the surfaces

$$\frac{p_r^2}{M} + \frac{1}{2} K (r - r_e)^2 = \begin{cases} E_3 \\ E_3 + \delta \end{cases} \quad (\delta \rightarrow 0) \quad (7)$$

assuming uniform distribution of the probability density of values of  $p_r$  and  $r$  (here  $r_e$  is the equilibrium distance between the atoms in the molecule, and  $K$  is a quasi-elastic (force) constant). We then obtain:

$$\langle p_r^2 \rangle / M = 1/2 E_3 \quad (8)$$

With the aid of result (8) and the equality  $\langle \cos^2 \alpha \rangle = 1/3$  we get:

$$B_{33} = E_3 \frac{m}{M} \frac{4}{3} \langle m v^2 \sin^2 \frac{\chi}{2} \rangle \quad (9)$$

Averaging on the right side (9) with respect to  $v$  and  $\chi$  requires a knowledge of the interaction potential for a molecule and an atom of light gas; if we represent this in the form  $U = \epsilon_{12} \varphi(R/\sigma_{12})$ , where  $\epsilon_{12}$  and  $\sigma_{12}$  are certain parameters, and  $R$  is the distance between interacting atoms, we finally obtain (see [2]):

$$B_{33} = b_3 E_3, \quad b_3 = \frac{2}{3} \frac{m}{M} \frac{kT \Omega^{*(1,1)}(T^*)}{\tau_e} \quad \left( \tau_e = \frac{1}{4n\sigma_{12}^2} \left( \frac{m}{2\pi kT} \right)^{1/2} \right) \quad (10)$$

where  $\Omega^{*(l,s)}(T^*)$  is one of the reduced integrals  $\Omega^{*(l,s)}$  used in calculating transport coefficients in the kinetic theory of gases [2]; and  $n$  is the concentration of the light gas. Multiplying (5) by  $E_3$  and integrating with respect to  $dE_3$  from 0 to  $\infty$ , we obtain the relaxation equation for the average vibrational energy  $\langle E_3 \rangle$ :

$$\langle E_3(t) \rangle = \int_0^\infty E_3 \Phi(E_3, t) dE_3 \quad (11)$$

in the usual form

$$\frac{d \langle E_3 \rangle}{dt} = - \frac{1}{\tau_3} [\langle E_3(t) \rangle - \langle E_3(\infty) \rangle], \quad \tau_3 = \frac{kT}{b_3} = \frac{3}{2} \frac{M}{m} \frac{1}{\Omega^{*(1,1)}(T^*)} \tau_e \quad (12)$$

where  $\tau_3$  is the vibrational relaxation time.

Equating  $\tau_3$  with  $\tau_2$  and  $\tau_1$ , the rotational and translational relaxation times [1], we obtain

$$\tau_3 = 2\tau_2 = 2\tau_1 \quad (13)$$

Thus, the vibrational, rotational and translational relaxation times are of the same order, and these processes may be studied independently in an approximation that satisfies condition (4).

For a solid ball model

$$\tau_3^0 = \frac{3}{2} \frac{M}{m} \tau \quad (14)$$

where  $\tau^0$  is the free time of a molecule in the light gas. In this particular case the result coincides with the expression for the vibrational relaxation time obtained by the Landau-Teller method using a solid sphere model and the quantum mechanical transition probabilities for a harmonic oscillator in nonadiabatic collisions [3, 4] (the possibility of an independent consideration of vibrational relaxation is not discussed in these papers).

In conclusion, we note that, as with translational and rotational relaxation in the system considered [1], the solution of Eqs. (5) and (6) preserves the original form of the Boltzmann distribution throughout the relaxation process, the temperature  $\Theta_3$  of the vibrational degrees of freedom varying according to the law

$$\Theta_3(t) = T + (T_0 - T) e^{-t/\tau_3} \quad (15)$$

## REFERENCES

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