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N. A. GENERALOV, S. A. LOSEV, A. I. OSIPOV

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Abstract

Full Text

AERODYNAMICS

N. A. GENERALOV, S. A. LOSEV, A. I. OSIPOV

RELAXATION OF THE VIBRATIONAL ENERGY OF AIR MOLECULES BEHIND THE FRONT OF A DIRECT SHOCK WAVE

(Presented by Academician G. I. Petrov, January 25, 1964)

The process of establishing equilibrium with respect to the vibrational degrees of freedom of molecules behind a shock-wave front occurs as a result of the conversion of the translational energy of colliding molecules into vibrational energy. However, when molecules collide, along with the transition of translational energy into vibrational energy, an exchange of vibrational energy between molecules also takes place. The latter process is unimportant in one-component systems: without changing the total vibrational energy of the system, it leads only to a redistribution of molecules over vibrational levels. A different situation arises in a mixture of several polyatomic gases. In this case, processes of vibrational-energy exchange may lead to a rapid redistribution of vibrational energy among the different components of the gas, which may be accompanied by a change in the relaxation time of individual components. Such effects have been observed in experiments and in a number of limiting cases have been studied theoretically ([1]).

Air may be regarded as a binary mixture of diatomic gases N_2 and O_2. Let us determine the conditions under which the exchange of vibrational energy between N_2 and O_2 molecules may prove to be significant. To this end, in the present work we calculate the distribution of the vibrational energy of N_2 and O_2 molecules behind the front of a direct shock wave in air, both with and without allowance for exchange effects.

The distribution of the vibrational energy of air molecules behind the shock-wave front is determined from the solution of a combined system of hydrodynamic equations expressing the laws of conservation of mass flux, momentum, and energy in the nonequilibrium zone, the equation of state, and the relaxation equations.

Since we are interested only in vibrational relaxation, it may be assumed that at each point behind the shock-wave front there exists an equilibrium distribution of energy over translational and rotational degrees of freedom and, moreover, that the processes of dissociation, electronic excitation, and ionization may be completely neglected. In these approximations the hydrodynamic equations may

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be written in the form

$$\rho v = \rho_0 V,$$

$$P + \rho v^2 = P_0 + \rho_0 V^2, \tag{1}$$

$$\frac{7}{2}\frac{RT}{\mu} + \frac{E_{O_2}}{\rho} + \frac{E_{N_2}}{\rho} + \frac{v^2}{2} = \frac{7}{2}\frac{RT_0}{\mu} + \frac{V^2}{2}.$$

In relations (1), ρ, P, v, T are the density, pressure, velocity, and temperature of the gas in the nonequilibrium region. The corresponding quantities with subscript zero refer to the undisturbed gas ahead of the front. V is the shock-wave velocity. E_{O_2}, E_{N_2} are the vibrational energies of O_2 and N_2 molecules in the nonequilibrium zone, referred to unit mass.

The relaxation equations describing the change in the vibrational energy of the individual components in a binary mixture are obtained in (1) and have the form

$$\frac{d\alpha_i}{dt} = \left(z_{ii}P_{10}^{ii}N_i + z_{ik}P_{10}^{ik}N_k\right)\left(1 - e^{-\theta_i/T}\right)\left(\frac{N_i}{e^{\theta_i/T} - 1} - \alpha_i\right) +$$

$$+ z_{ik}Q_{10}^{ik}\left\{(\alpha_i + N_i)\alpha_k e^{-\theta_i/T + \theta_k/T} - (\alpha_k + N_k)\alpha_i\right\}, \qquad \theta_i = \frac{h\nu_i}{k}, \quad i, k = \mathrm{O}_2, \mathrm{N}_2. \tag{2}$$

In equation (2), α_i is the number of vibrational quanta of the i-component per unit volume ($h\nu_i\alpha_i = E_i$), z_{ik} is the collision frequency of molecules i and k in calculation per one molecule i and k; P_{10}^{ik} is the probability of transition of molecule i from the first vibrational level to the ground state upon collision with molecule k, accompanied by conversion of vibrational energy into translational energy; Q_{10}^{ik} is the probability of transfer of a vibrational quantum by a molecule i, in the first vibrational state, to a molecule k in the ground state; N_i, N_k are the total numbers of molecules of the i-th and k-th components per unit volume.

Fig. 1. Distribution of vibrational energy behind the shock-wave front in air with account (**a**) and without account (**b**) of exchange by vibrational quanta at shock-wave velocities $M = 5$, $M = 9$, and $M = 20$ and initial pressure 1 mm Hg. For the case $M = 5$, the values of β are increased by a factor of 10.

The system of equations (2) describes the change in vibrational energy occurring as a result of the transition of the translational energy of gas molecules into the vibrational energy of one of the components (the first term on the right-hand side) and as a result of the process of exchange of vibrational energy between components i and k (the second term).

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Fig. 1. Distribution of vibrational energy behind the front of a shock wave in air with account (a) and without account (b) of exchange by vibrational quanta at shock-wave velocities $M = 5$, $M = 9$, and $M = 20$ and initial pressure 1 mm Hg. For the case $M = 5$, the values of β are increased by a factor of 10.

Figure 1: Fig. 1. Distribution of vibrational energy behind the front of a shock wave in air with account (a) and without account (b) of exchange by vibrational quanta at shock-wave velocities $M = 5$, $M = 9$, and $M = 20$ and initial pressure 1 mm Hg. For the case $M = 5$, the values of β are increased by a factor of 10.

Equations (2) are valid in a system of harmonic oscillators, collisions between which lead only to one-quantum energy transitions. In air such an approximation is suitable up to temperatures of the order of 10 000°K. At higher temperatures, generally speaking, it is no longer possible to restrict consideration to only one-quantum transitions. However, the latter circumstance is unimportant in determining the comparative role of exchange effects.

When considering vibrational relaxation behind the shock-wave front, it is convenient to refer the vibrational energy not to a unit volume (as in equation (2)), but to a unit mass or to 1 mole. For simplicity we shall pass to mole fractions and introduce the quantities

$$\xi_i = \frac{N_i}{N} = \frac{N_i \mu}{\rho \mathcal{N}}, \qquad \beta_i = \frac{\alpha_i \mu}{\rho \mathcal{N}}, \qquad i = \mathrm{O_2}, \mathrm{N_2}. \tag{3}$$

In formulas (3), $\mathcal{N}$ is Avogadro’ s number; N is the number of molecules of the mixture per unit volume, μ is the mean molecular weight of the mixture; ξ_i has the meaning of the relative concentration of the i-th component, while β_i determines the mean number of vibrational quanta of the i-th component calculated per 1 molecule of the mixture.

The transition probabilities appearing in equation (2) were determined in work (2). For simplicity, we shall assume that the potential of the repulsive forces between mo-

cules has the form $V_0 \exp(-\alpha r)$, and the value of α for $O_2 - O_2$, $O_2 - N_2$, and $N_2 - N_2$ is the same and equal to $\alpha = 4 \cdot 10^8$ cm^{-1}. We shall regard as identical all factors in the transition probabilities that are determined by the effects of the orientation of the molecules upon collision, by the attractive forces, and by the value of the gas-kinetic diameter of oxygen and nitrogen. Since the magnitude of these factors depends strongly on the approximations used, we shall regard them as unknown and introduce into all the transition probabilities the same unknown constant C. Generally speaking, C depends on temperature, but this dependence is weak and may be neglected.

Fig. 2. Rate of excitation of vibrations of O_2 and N_2 molecules in air, referred

SovietRxiv

Fig. 2

Figure 2: Fig. 2

to the rate of excitation of N_2 molecules in collisions with O_2: *a*—excitation of O_2, *b*—excitation of N_2 at the expense of the translational energy of N_2 (1) and O_2 (2) molecules; *v*—excitation rate associated with exchange of vibrational quanta.

In the new variables, taking account of the change in density in the relaxation zone, equation (2) can be written in the form

$$\frac{d\beta_i}{dt} = C\frac{P_0}{kT_0}T^{1/3}\frac{\rho}{\rho_0}\left[(\varphi_{ii}+\varphi_{ik})\frac{2\,\mathrm{sh}\,\theta_i/2T}{\theta_i}\left(\frac{\xi}{e^{\theta_i/T}}-\beta_i\right)+\psi_{ik}\right],$$

$$\varphi_{ik} = \frac{\xi_k}{\sqrt{\mu_{ik}}}\frac{(\vartheta_i')^{7/6}}{\exp\left[{}^3/_2\,(\vartheta_i'/T)^{1/3}\right]}, \tag{4}$$

$$\psi_{ik} = \frac{\pi^2}{\sqrt{\mu_{ik}}}\frac{\theta_i\theta_k}{\theta_{\Delta ik}^2}\frac{(\vartheta_{\Delta ik})^{13/6}}{\vartheta_i'\vartheta_k'}\frac{(\beta_i+\xi_i)\beta_k e^{-\theta_{\Delta ik}/T}-(\beta_k+\xi_k)\beta_i e^{\theta_{\Delta ik}/T}}{\exp\left[{}^3/_2\,(\vartheta_i'/T)^{1/3}\right]},$$

$$i, k = \mathrm{O}_2, \mathrm{N}_2.$$

Here

$$\theta_{\Delta ik} = \theta_i - \theta_k, \qquad \vartheta_i' = \frac{16\pi^4 k\overline{m}_i}{h^2\alpha^2}\theta_i^2, \qquad \vartheta_{\Delta ik}' = \frac{16\pi^4 k\overline{m}_{ik}}{h^2\alpha^2}\theta_{\Delta ik}^2$$

(k, h are the Boltzmann and Planck constants; $\overline{m}_i$ and $\overline{m}_{ik}$ are the reduced masses of the molecule i and of the colliding pair of molecules $i-k$, respectively). In formulas (4), μ_{ik} is the reduced molecular weight of the colliding pairs. The numerical value of the constant C is chosen so that the absolute values of the vibrational relaxation time τ in pure gases O_2 and N_2, obtained from equation (4), coincide with the experimental ones. Good agreement between the calculated and experimental values of τ in the range 2000–7000°K for O_2 [3] and 1900–5600°K for N_2 [4] is obtained for

$$C = 4.482\cdot 10^{-11}\ \mathrm{cm}^3\cdot \mathrm{s}^{-1}\cdot \mathrm{deg}^{-1/2}.$$

The system of equations (1), (4) was solved on an electronic computer. As initial conditions it was assumed that immediately behind the shock-wave front ($t = 0$), $\beta_{O2} = 0$, $\beta_{N2} = 0$. To determine the role of vibrational-energy exchange, the calculations were carried out in two variants—with and without ($\psi_{ik} = 0$) the exchange effects taken into account.

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Fig. 3. Relative difference of the temperature ΔT, with and without allowance for exchange of vibrational quanta, compared with the total temperature change ΔT_k due to excitation of vibrations behind the shock front in air ($M = 5,\ \Delta T_k = 150°;\ M = 7,\ \Delta T_k = 400°;\ M = 9,\ \Delta T_k = 650°;\ M = 20,\ \Delta T_k = 4550°$)

Figure 3: Fig. 3. Relative difference of the temperature ΔT, with and without allowance for exchange of vibrational quanta, compared with the total temperature change ΔT_k due to excitation of vibrations behind the shock front in air ($M = 5,\ \Delta T_k = 150°;\ M = 7,\ \Delta T_k = 400°;\ M = 9,\ \Delta T_k = 650°;\ M = 20,\ \Delta T_k = 4550°$)

The results of the calculations at shock-wave velocities corresponding to $M = 5, 9, 20$ are presented in Figs. 1 and 2. It is seen from Fig. 1 that the exchange of vibrational-quanta affects the relaxation of N_2 and O_2 differently. In the case of N_2, exchange may lead to a significant shortening of the relaxation time. On the other hand, exchange effects increase the relaxation time of O_2 only slightly.

This result is easy to understand. Excitation of the vibrational energy of O_2 molecules occurs under conditions in which the N_2 molecules are practically unexcited; therefore, there is no flux of vibrational energy from N_2 to O_2.

Fig. 3. Relative difference of the temperature ΔT, with and without allowance for exchange of vibrational quanta, compared with the total temperature change ΔT_k due to excitation of vibrations behind the shock front in air ($M = 5,\ \Delta T_k = 150°;\ M = 7,\ \Delta T_k = 400°;\ M = 9,\ \Delta T_k = 650°;\ M = 20,\ \Delta T_k = 4550°$).

The flux of vibrational energy in the opposite direction, from the O_2 component to the N_2 component, can lead only to a slight increase in the vibrational relaxation time of O_2, since these two processes (the vibrational relaxation of O_2 and of N_2) are separated in time. Physically this means that the rate of excitation of O_2 molecules by conversion of translational energy into vibrational energy considerably exceeds the rate of deactivation of O_2 molecules by transfer of vibrational energy from O_2 to N_2. On the other hand, the process of excitation of N_2 molecules occurs in an environment of already excited O_2 molecules. In this case the rate of transfer of vibrational energy from O_2 to N_2 may considerably exceed the rate of direct excitation of N_2 molecules through the conversion of translational-motion energy into vibrational degrees of freedom (Fig. 2, $M = 5$) and lead to a noticeable reduction of the relaxation time of N_2 compared with the case in which exchange is absent. As M increases, as is seen from Figs. 1 and 2, the role of exchange effects decreases. The latter is explained by the fact that, with increasing temperature, the probability of direct excitation of molecules by translational-motion energy grows faster than the probability of exchange. At high temperatures these probabilities differ little, and exchange effects may be neglected (see Figs. 1 and 2 for $M = 20$).

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Allowance for exchange of vibrational quanta leads to a more rapid drop in temperature and to an increase in gas density in the nonequilibrium region behind the wave front. Figure 3 gives the ratio of the temperature difference ΔT obtained in solving the problem with and without allowance for exchange, to the temperature change ΔT_k due to excitation of molecular vibrations throughout the nonequilibrium zone behind the wave front in air. It is seen that the relative effect of exchange decreases with increasing Mach number M of the shock wave.

Moscow State University
named after M. V. Lomonosov

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