Journal of Applied Mechanics and Technical Physics, Vol. 45, No. 5, pp. 634–638, 2004

DIRECT SHOCKS IN A VIBRATIONALLY NONEQUILIBRIUM GAS

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UDC 533.6 (075 8)

Direct shocks in flows of a high-temperature diatomic gas with rotational and vibrational degrees of freedom are considered. Gas-dynamic parameters and populations of molecular vibrational levels behind a shock are studied for the case of disturbance of vibrational equilibrium in an incident flow.

Key words: *anharmonic oscillators, vibrational nonequilibrium, shock wave.*

An increase in temperature leads to excitation of rotational and then vibrational degrees of freedom of gas molecules. The associated physical processes can have a significant effect on the gas flow pattern.

It is known that changes in the translational and rotational energies of molecules due to collisions occur much more frequently than changes in their vibrational energy [1, 2]. Under these conditions, the relaxation time of vibrational degrees of freedom exceeds the relaxation time of translational and rotational degree of freedom. In some cases, the vibrational relaxation time can be comparable or even exceed the characteristic gas-dynamic time. In this connection, zones of vibrational nonequilibrium can form in gas flows. For example, experimental and numerical studies have shown that in supersonic gas flows in divergent nozzles, the distribution of molecules over vibrational levels can differ significantly from the Boltzmann distribution [2–4]. Vibrational nonequilibrium of gas was also observed at altitudes of about 60–70 km during spacecraft entry into the Earth's atmosphere. Therefore, in recent decades, there has been considerable interest of researches in vibrationally nonequilibrium flows. The greatest attention has been paid to the so-called quasistationary modes of vibrational relaxation, in which nonequilibrium quasistationary distributions of molecules over vibrational levels are formed in each physically infinitesimal gas volume against the background of an equilibrium Maxwell–Boltzmann distribution over the translational and rotational energies.

The vibrational energy of a high-temperature gas is commonly described using the model of an anharmonic oscillator. In this case, the vibrational energy of a molecule reckoned from the zero level has the form

$$\varepsilon_v = v\varepsilon_1 - \Delta\varepsilon v(v-1), \qquad \varepsilon_1 = h\nu(1-2x),$$
$$\Delta\varepsilon = xh\nu, \qquad v \in [0, v_d], \tag{1}$$

where v is the vibrational-energy level number, h is Planck's constant, ν is the atom-vibration frequency in the molecule, x is the anharmonicity constant ($x \ll 1$), and v_d is the vibrational level corresponding to the dissociation energy.

The probability of vibrational transitions for anharmonic oscillators

$$(v) + (v_1) \quad \longleftrightarrow \quad (v') + (v_1') \tag{2}$$

depends on the ratio of the vibrational-energy resonance defect to the energy value before collision, i.e., on the quantity

$$\alpha = |\varepsilon_{v'} + \varepsilon_{v_1'} - \varepsilon_v - \varepsilon_{v_1}|/(\varepsilon_v + \varepsilon_{v_1}).$$

The results of some studies given in [2, 5] lead to the conclusion that the probability of vibrational transitions (2) increases by more than an order of magnitude as the value of α decreases by a factor of two. In this case, the

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vibrational relaxation process can be divided into several stages [6, 7] corresponding to the situations where the formation of local quasistationary distributions involves, in addition to the translational–rotational transitions of molecules, transitions (2) in which the relative resonance defect α changes in definite ranges. In particular, it is possible to distinguish relaxation stages with $\alpha \approx 1$, $\alpha \leqslant 1/2$, $\alpha \leqslant 1/4$, and $\alpha \leqslant 1/8$. Along with locally equilibrium flows, for which $\alpha \approx 1$, nonequilibrium quasi-stationary flows with $\alpha \leqslant 1/2$ are widely occurring.

It has been shown [6, 7] that under the conditions considered, the gas flow can be considered to be in equilibrium over translational and rotational energy levels and the distribution of molecules over vibrational levels can be written as

$$n_v = \frac{n}{\tilde{Z}_{\mathrm{vibr}}(T, T_1)} \exp\Big\{ -\frac{\psi_{1/2}(v)\varepsilon_1}{kT_1} + \frac{\psi_{1/2}(v)\varepsilon_1 - \varepsilon_v}{kT}\Big\}. \tag{3}$$

Here n_v is the population of the vth vibrational level, n is the total number of molecules in unit volume, k is the Boltzmann constant, ε_1 and ε_v are the energies of the 1-st and vth vibrational levels, and T is the gas temperature that corresponds to the distribution of molecules over the translational and rotational energies, T_1 is the temperature called by Treanor [8] the temperature of the 1-st vibrational level;

$$\tilde{Z}_{\mathrm{vibr}}(T, T_1) = \sum_{v=0}^{v_d} \exp\Big\{ -\frac{\psi_{1/2}(v)\varepsilon_1}{kT_1} + \frac{\psi_{1/2}(v)\varepsilon_1 - \varepsilon_v}{kT}\Big\}$$

is the vibrational statistical sum under the nonequilibrium conditions considered and $\psi_{1/2}(v)$ is an additional additive invariant of the vibrational transitions (2) for $\alpha \leqslant 1/2$; the dependence of the invariant $\psi_{1/2}$ on the vibrational-level number v corresponds to the quasiharmonic approximation of the vibrational energy (1) according to the model proposed in [6, 7].

The relative populations of the vibrational levels $x(v) = n_v/n_0$ corresponding to the nonequilibrium distribution (3) can be written as [6, 7]

$$x(v) = \exp\Big\{ -\frac{\varepsilon_1}{kT_1}\Big(\frac{\varepsilon_v}{\varepsilon_1} - \Big(\psi_{1/2}(v) - \frac{\varepsilon_v}{\varepsilon_1}\Big)\Big(\frac{T_1}{T} - 1\Big)\Big)\Big\}. \tag{4}$$

At the low levels with $v \in [0, v_1]$, they are close to or slightly exceed the Boltzmann populations at temperature T_1. At these levels, the invariant $\psi_{1/2}(v) = v$ and the distribution (3) coincides with the Treanor distribution [8]. At the middle levels with $v \in [v_1, v_*]$, the additional invariant $\psi_{1/2}(v)$ is a piecewise-continuous linear function which exceeds the vibrational energy. On this segment of the vibrational spectrum, the excess of the populations (4) over the Boltzmann populations at temperature T_1 is greater the larger the ratio T_1/T. For $T_1/T \approx 10$, the curve of the relative populations $x(v)$ has a distinct plateau (see [2–5]). The vibrational energy (1) reaches the maximum value when $v = v_{\max}$. In this case, at the upper levels close to $v_{\max}$, the vibrational energy hardly changes. Accordingly, the quasiharmonic approximation $\psi_{1/2}(v)$ [6, 7] can be considered constant beginning with a certain level v_* that satisfies the equation

$$\psi_{1/2}(v_{\max}) - \psi_{1/2}(v_*) \approx \psi_{1/2}(v_*)/2.$$

Under these conditions, at the upper levels with $v \in [v_*, v_d]$, the invariant $\psi_{1/2}(v) = \psi_{1/2}(v_*)$ and the relative populations (4) decrease according to the Boltzmann distribution at a gas temperature T.

In the perfect fluid approximation, the system of gas-dynamic equations for such flows can be written as [6, 7]

$$\begin{aligned} &\rho\frac{d\boldsymbol{V}}{dt} = \boldsymbol{F}n - \nabla p, \qquad &&\frac{dn}{dt} + n\,\mathrm{div}\,\boldsymbol{V} = 0, \\ &\frac{de}{dt} = -(p+e)\,\mathrm{div}\,\boldsymbol{V}, \qquad &&\frac{d\langle\psi_{1/2}\rangle}{dt} = \langle\Delta\psi_{1/2}\rangle. \end{aligned} \tag{5}$$

Here $\boldsymbol{F}$ is the external force that acts on the gas molecules, ρ is the mass density of the gas, p is the pressure, n and e are the densities of the particle number and the total energy, $\boldsymbol{V}$ is the mass velocity of the gas, $\langle\psi_{1/2}\rangle$ is the average value of the approximate additional collision invariant $\psi_{1/2}(v)$, which was mentioned above, and $\langle\Delta\psi_{1/2}\rangle$ is the change in the average value of this invariant due to the vibrational transitions for $\alpha > 1/2$.

Incidence of supersonic gas flows on an obstacle results in formation of shock waves in the gas. In classical gas dynamics, a shock wave is modeled by a thin (compared to the characteristic flow dimension) transient layer between two states of thermodynamic equilibrium (see, for example, [9]). Under nonequilibrium conditions, a shock wave can be treated by analogy as a transient layer between two nonequilibrium quasi-stationary states, and generalized conditions of dynamic consistency can be derived [10].

The present paper deals with shock waves in vibrationally nonequilibrium gas. Shock waves are considered for the case where the nonequilibrium vibrational distribution (3) forms in the incident flow and the macroscopic equations (5) hold. If we confine the consideration to direct shock waves, the dynamic consistency conditions can be written in symmetric form [11]:

$$n^{(+)}V^{(+)} = n^{(-)}V^{(-)}, \qquad \rho^{(+)}V^{(+)2} + p^{(+)} = \rho^{(-)}V^{(-)2} + p^{(-)},$$
$$\frac{V^{(+)2}}{2} + \Big(\frac{e}{\rho}\Big)^{(+)} + \Big(\frac{p}{\rho}\Big)^{(+)} = \frac{V^{(-)2}}{2} + \Big(\frac{e}{\rho}\Big)^{(-)} + \Big(\frac{p}{\rho}\Big)^{(-)}, \qquad \langle\psi_{1/2}\rangle^{(+)} = \langle\psi_{1/2}\rangle^{(-)}, \tag{6}$$

where $\beta^{(-)}$ and $\beta^{(+)}$ are the values of the parameter β ahead of and behind the shock wave. Along with the gas molecule number density n and the velocity $\boldsymbol{V}$, relations (6) contain quantities that can be treated as functions of the parameters n, T and T_1. The pressure p and the density ρ satisfy the formulas $p = nkT$ and $\rho = nm$. Using the Maxwell–Boltzmann distribution over the translational and rotational energies and the nonequilibrium quasistationary distribution (3) over the vibrational levels, we obtain the following analytic dependence of the average value of the invariant $\langle\psi_{1/2}\rangle$ and the energy density e on two temperatures — T and T_1:

$$\langle\psi_{1/2}\rangle = \frac{1}{n}\sum_{v=0}^{v_d} n_v\psi_{1/2}(v) = \frac{\displaystyle\sum_{v=0}^{v_d}\exp\Big\{-\frac{\psi_{1/2}(v)\varepsilon_1}{kT_1} + \frac{\psi_{1/2}(v)\varepsilon_1 - \varepsilon_v}{kT}\Big\}\psi_{1/2}(v)}{\displaystyle\sum_{v=0}^{v_d}\exp\Big\{-\frac{\psi_{1/2}(v)\varepsilon_1}{kT_1} + \frac{\psi_{1/2}(v)\varepsilon_1 - \varepsilon_v}{kT}\Big\}}; \tag{7}$$

$$e = (5/2)nkT + n\langle\varepsilon_{\mathrm{vibr}}\rangle. \tag{8}$$

Here the translational and rotational energies are calculated in the classical approximation and

$$\langle\varepsilon_{\mathrm{vibr}}\rangle = \frac{1}{n}\sum_{v=0}^{v_d} n_v\varepsilon_v = \frac{\displaystyle\sum_{v=0}^{v_d}\exp\Big\{-\frac{\psi_{1/2}(v)\varepsilon_1}{kT_1} + \frac{\psi_{1/2}(v)\varepsilon_1 - \varepsilon_v}{kT}\Big\}\varepsilon_v}{\displaystyle\sum_{v=0}^{v_d}\exp\Big\{-\frac{\psi_{1/2}(v)\varepsilon_1}{kT_1} + \frac{\psi_{1/2}(v)\varepsilon_1 - \varepsilon_v}{kT}\Big\}}. \tag{9}$$

Substituting the expressions for the density and pressure and formulas (7)–(9) into the consistency conditions (6), we have

$$n^{(+)}V^{(+)} = n^{(-)}V^{(-)}, \qquad mn^{(+)}V^{(+)2} + n^{(+)}kT^{(+)} = mn^{(-)}V^{(-)2} + n^{(-)}kT^{(-)},$$
$$\frac{V^{(+)2}}{2} + \frac{7}{2}\frac{kT^{(+)}}{m} + \frac{\langle\varepsilon_{\mathrm{vibr}}\rangle^{(+)}}{m} = \frac{V^{(-)2}}{2} + \frac{7}{2}\frac{kT^{(-)}}{m} + \frac{\langle\varepsilon_{\mathrm{vibr}}\rangle^{(-)}}{m}, \qquad \langle\psi_{1/2}\rangle^{(+)} = \langle\psi_{1/2}\rangle^{(-)}. \tag{10}$$

If the incident-flow parameters are known, relations (10) can be treated as a system of algebraic equations for the unknown parameters $n^{(+)}$, $V^{(+)}$, $T^{(+)}$ and $T_1^{(+)}$. The corresponding system of equations can be solved using the Newton method. The solution of the equations yields the values of the gas-dynamic parameters and the relative vibrational populations (4) behind the shock wave.

Relaxation processes behind a shock-wave front in a vibrationally nonequilibrium gas has been analyzed previously using differential equations for the vibrational populations n_v, $v \in [0, v_d]$ (see, for example, [12]). The research method proposed in the present study uses generalized dynamic-consistency conditions does not allow one to determine the vibrational populations behind a shock wave at various distances from its front. It only enables one to find all parameters of interest directly behind a shock wave (on the boundary of the relaxation zone considered). An advantage of this method is that the number of equations is decreased by more than an order of magnitude and the need to know the probabilities of different vibrational transitions (2) is eliminated.

The possibility of determining the state of gas behind shock-wave fronts on the boundaries of the zones of partial vibrational relaxation by solving algebraic systems of the form (10) was demonstrated in [11]. In the cited

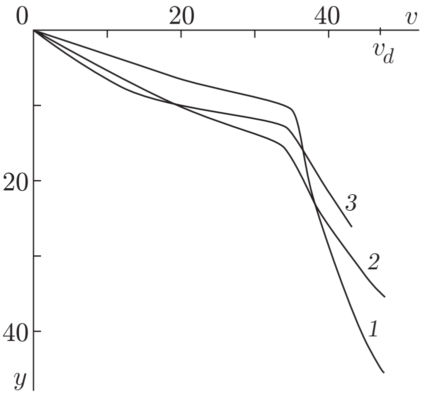

Fig. 1

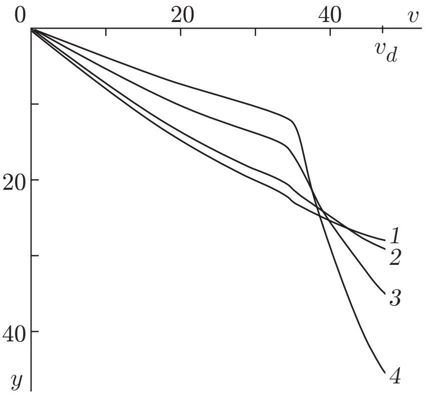

Fig. 2

study, direct shock waves in an equilibrium flow were considered. In the present study, it is proposed to explore the states of a vibrationally nonequilibrium gas behind shock waves by solving system (10).

Using the generalized consistency relations (10), we investigated shock waves in molecular oxygen, nitrogen, and carbon dioxide. The incident-flow parameters $n^{(-)}$, $V^{(-)}$, $T^{(-)}$, and $T_1^{(-)}$ were varied in the following ranges: $n^{(-)} = 0.5n_{\rm L}$–$5n_{\rm L}$ ($n_{\rm L}$ is Loschmidt's number), $V^{(-)} = 500$–3500 m/sec, $T^{(-)} = 500$–1000 K, and $T_1^{(-)} = 1000$–5000 K.

The calculation results show that under nonequilibrium conditions, the gas-temperature jump coincides with an accuracy of a few degrees with that under conditions of an equilibrium incident flow. Nonequilibrium effects also have a weak effect on the magnitudes of density and velocity jumps, and the jump in the temperature of the first vibrational level T_1 can be ignored. Under these conditions, the ratio T_1/T decreases with passage through the shock wave. Accordingly, the plateau level on the curve $x(v)$ is lowered, and on the vibrational-spectrum segment $[0, v_*]$, the relative vibrational populations $x^{(+)}(v)$ become closer to the Boltzmann population at temperature $T_1^{(-)}$ than the populations $x^{(-)}(v)$. Similar effects were observed behind a direct shock wave in molecular nitrogen at a certain distance from the shock front in [12].

Figure 1 shows the quantities $y = \ln x(v)/(\varepsilon_1/(kT_1^{(-)}))$, where $x(v)$ are the relative vibrational populations (4) of nitrogen molecules ahead of and behind the shock formed in a nonequilibrium flow at a velocity $V^{(-)} = 1000$ m/sec, a molecule number density $n^{(-)} = n_{\rm L}$, a gas temperature $T^{(-)} = 500$ K, and a temperature of the first vibrational level $T_1^{(-)} = 5000$ K. The curve 1 refers to the populations $x^{(-)}(v)$ ahead of the shock; curve 2 refers to the populations $x^{(+)}(v)$ behind the shock with the parameters found from Eqs. (10). Curve 3, corresponding to the populations $x^{(+)}(v)$ at a distance of 1100 free path lengths from the shock front [12], is given for comparison.

As is evident from the figure, in the interval $0 \leqslant v \leqslant v_*$ (v_* is the vibrational level beginning with which the Boltzmann distribution at a temperature T holds), curves 2 and 3, describing the populations behind the shock, are below curve 1, which describes the populations ahead of the shock. The plateau segment on these curves is less pronounced.

As is known, the jump in the gas temperature T increases with increase in the incident-flow velocity $V^{(-)}$ (Mach number). If the jump in the temperature T_1 is ignored, then at the same ratio $T_1^{(-)}/T^{(-)}$, the ratios $T_1^{(+)}/T^{(+)}$ behind the shock wave for different values of the velocity $V^{(-)}$ are different. As the velocity $V^{(-)}$ increases, the ratio $T_1^{(+)}/T^{(+)}$ decreases. Accordingly, the relative populations $x^{(+)}(v)$ decrease in the interval $[0, v_*]$, and the curves approach Boltzmann curves at a temperature $T_1^{(-)}$.

This is clearly demonstrated in Fig. 2, which also gives the quantities $y = \ln x(v)/(\varepsilon_1/(kT_1^{(-)}))$ for the case where the nonequilibrium quasistationary distribution (3) with $n^{(-)} = n_{\rm L}$, $T^{(-)} = 500$ K, and $T_1^{(-)} = 4000$ K formed in an incident flow of molecular nitrogen, and the flow velocity $V^{(-)}$ was varied. The relative populations $x^{(+)}(v)$ behind the jump are shown by curves 1–3: $V^{(-)} = 2000$ (1), 1500 (2), and 1000 m/sec (3); curve 4 refers to the population $x^{(-)}(v)$ ahead of the shock.

A similar effect, called a decrease in the anharmonicity effect, was also observed in studies [12] of the vibrational relaxation of molecular nitrogen behind a direct shock.

Calculations of the populations of the vibrational levels of nitrogen, oxygen, and carbon dioxide molecules behind shocks in various nonequilibrium flows using the generalized consistency relations (10) show that an increase in the velocity $V^{(-)}$ at a constant ratio $T_1^{(-)}/T^{(-)}$ has a similar effect on the populations $x^{(+)}(v)$ as a decrease in $T_1^{(-)}/T^{(-)}$ at a constant velocity $V^{(-)}$.

The results suggest that when flows of diatomic gases pass through a shock wave, the degree of their nonequilibrium due to the difference between the temperatures T and T_1 decreases.

The decrease in the temperature ratio T_1/T with passage through a shock wave will be larger the higher the incident-flow velocity $V^{(-)}$.

REFERENCES

1. E. V. Stupochenko, S. A. Losev, and A. I. Osipov, *Relaxation Processes in Shock Waves* [in Russian], Nauka, Moscow (1965).
2. B. F. Gordiets, A. I. Osipov, and L. A. Shelepin, *Kinetic Processes in Gases and Molecular Lasers* [in Russian], Nauka, Moscow (1980).
3. G. E. Caledonia and R. E. Center, “Vibrational distribution functions in anharmonic oscillators,” *J. Chem. Phys.*, **55**, No. 2, 552–561 (1971).
4. E. V. Kustova, E. A. Nagnibeda, T. Yu. Alexandrova, and A. Chikhaoui, “On the nonequilibrium kinetics and heat transfer in nozzles flows,” *Chem. Phys.*, **276**, 139–154 (2001).
5. E. E. Nikitin and A. I. Osipov, *Vibrational Relaxation in Gases: Kinetics and Catalysis* [in Russian], Vol. 4, Khimiya, Moscow (1977).
6. M. A. Rydalevskaya, “Relaxing gas of anharmonic oscillators. Kinetics and gasdynamics,” in: *Rarefied Gas Dynamics-19*, Oxford Univ., Oxford–New York (1995), pp. 578–582.
7. M. A. Rydalevskaya and T. V. Ryabikova, “Different stages of vibrational relaxation of anharmonic oscillators,” in: *Aerodynamics* [in Russian], Izd. St. Petersburg. Univ., St. Petersburg (1997), pp. 97–109.
8. C. E. Treanor, J. W. Rich, and R. G. Rehm, “Vibrational relaxation of anharmonic oscillators with exchange-dominated collisions,” *J. Chem. Phys.*, **48**, No. 4, 1798–1806 (1968).
9. G. G. Chernyi, *Gas Dynamics* [in Russian], Nauka, Moscow (1988).
10. M. A. Rydalevskaya, “Models describing shock waves in reactive gas mixtures,” *Model. Mekh.*, **2**, No, 5, 111–118 (1988).
11. M. A. Rydalevskaya, “Gas-dynamic shock waves in a relaxing gas,” *J. Appl. Mekh. Tekh. Phys.*, **36**, No. 3, 401–405 (1995).
12. I. I. Kovalev and E. A. Nagnibeda, “Disturbance of the canonical invariance of the distribution of molecules in the relaxation zone behind a shock wave,” in: *Dynamic Processes in Gases and Solids* [in Russian], Izd. Leningrad. Univ., Leningrad (1990), pp. 43–49.