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Direct Shocks in Vibrationally Nonequilibrium Diatomic Gases at Various Distances from Critical Cross-Section of Nozzle

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Abstract: The high-temperature diatomic gas flows are considered in expanding nozzles under the conditions of a disturbance of the equilibrium distribution over vibrational levels of the molecules. The investigation of such flows is bound up with the problem of the inversion of the vibrational populations in the active mediums of molecular lasers. Under diverse values of the pressure overfall on coming out of the nozzle the shock waves can arise at various distances from critical cross-section. Under these conditions the research of the molecular distributions over vibrational levels behind such shocks acquires special significance. Relaxation processes behind a shock-wave front in a vibrationally nonequilibrium gas have been analyzed previously using differential equations for the vibrational populations. In our paper a shock wave is modeled by a thin transient layer between two vibrationally nonequilibrium quasi-stationary states. Generalized conditions of dynamic consistency are derived. The methods of kinetic theory are used. This approach does not allow one to determine the vibrational populations behind a shock wave at various distances from its front. However, it enables one to find the velocity of the gas, the total number of molecules in unit volume, the gas temperature and the temperature, called by Treanor the temperature of the 1st vibrational level, directly behind a shock wave (outside the relaxation zone). The knowledge of these values allows one to determine all parameters of interest using the kinetic theory methods. An advantage of this approach is that the considerably less number of equations is used and the need to know the probabilities of different vibrational transitions is eliminated. Earlier it was shown that the inversion of vibrational populations decreases when the flows pass through a shock wave. In present paper we note two competing factors. The further direct shock is from critical cross-section of the nozzle, the more the nonequilibrium degree of vibrational distributions and the inversion of vibrational populations are. In connection with that the intensity of a shock wave increases. It leads to a decrease of the vibrational nonequilibrium and the inversion of vibrational populations.

Keywords: Nonequilibrium Distribution Functions Over Vibrational Levels, Additive Invariants of Collisions, Expanding Flows, Critical Cross-Section of Nozzle, Direct Shocks

Introduction

The gas flows in expanding nozzles are founded in many technological processes (see, for example, References in the works (Gordiets *et al*., 1988; Iqbal and Besar, 2007; Bulat, 2014).

Experimental studies have shown that the distribution functions over vibrational levels of diatomic molecules can differ significantly from the Boltzmann distribution in high-enthalpy flows in expanding nozzles (Center and Caledonia, 1971). It can be the cause of so important phenomena as absolute or relative inversion of the populations of molecular vibrational levels. Therefore our paper is devoted to the research of such flows.

For theoretical description of experimental results (Center and Caledonia, 1971) on lower vibrational levels the Treanor distribution (Treanor *et al*., 1968) was usually used. For theoretical description of these results on the intermediate and high levels the set of nonequilibrium quasi-stationary distributions was proposed (see, for example, works of Gordiets *et al*., 1988; Kustova and Nagnibeda, 1995; Nagnibeda and Kustova, 2009; Rydalevskaya, 1995a; 2003). In this study we use the description model of nonequilibrium distributions over vibrational levels which were proposed in the works (Rydalevskaya, 1995a; 2003).

For the investigation of gas-dynamic parameters and nonequilibrium populations of molecular vibrational levels in the expanding nozzles are applied the results of the work (Rydalevskaya and Ryabikova, 1999).

In supersonic nozzles the shock waves can arise at various distances from critical cross-section of nozzle. 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 (Courant and Friedrichs, 1977). By analogy, under nonequilibrium conditions it can be treated as a transient layer between two nonequilibrium quasi-stationary states (Rydalevskaya, 1995b). This approach is applied in our work to the research of direct shocks in vibrationally nonequilibrium expanding flows.

For the determination of the nonequilibrium gas states behind the shocks the generalized dynamic consistency conditions and the methods of kinetic theory are used by analogy with work (Voroshilova and Rydalevskaya, 2004).

Nonequilibrium Distributions in Gas of Anharmonic Oscillators

In high-temperature diatomic gas the rotational and vibrational degrees of freedom of the molecules are excited. The vibrational energy ε_v, counted from the zero level, is usually described by the model of an harmonic oscillator Equation 1:

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

where, v is a number of a vibrational level (v changes from 0 to the level v_d, corresponding to the dissociation energy), ε_1 is energy of the first vibrational level, x is a coefficient of anharmonicity, h is the Planck's constant, ν_* is the atom-vibration frequency in the molecule.

It is known, that the probability of vibrational transition Equation 2:

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

Depends on the ratio of vibrational energy resonance defect to its value before a collision, i.e., on the quantit:

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

The value α is relative resonance defect of vibrational energy under the transition (2).

The results of some research (Osipov and Uvarov, 1992) have shown that the probability of the transitions (2) increases by more than an order of magnitude if the value α decreases twice.

Under certain conditions (under certain correlation between the flow velocity and the diameter of the nozzle, (Center and Caledonia, 1971) it must be taken into account only the changes of translational, rotational energy between the molecules and those changes of vibrational energy (2), when $\alpha \le 1/2$. These changes of energy form the distribution functions, which can be represented as (Rydalevskaya, 1995a; 2003) Equation 3:

$$f_{vr}^{(0)} = s_{vr}\frac{m^3}{h^3}\exp\left(\sum_{\lambda=0}^{2}\gamma_\lambda\psi_{vr}^{(\lambda)}\right) \tag{3}$$

Here index "*vr*" indicates the numbers of vibrational and rotational energy levels of the molecule; s_{vr} is corresponding statistical weight (as the weight of vibrational levels of diatomic molecules $s_v = 1$, *so* $s_{vr} = s_r$): $\psi_{vr}^{(0)} = mc^2/2 + \varepsilon_r + \varepsilon_v$; $\psi_{vr}^{(1)} = 1$ and $\psi_{vr}^{(2)} = \psi_{1/2}(v)\varepsilon_1$ are the invariants of the taken into account collisions. The invariant $\psi_{vr}^{(0)}$ corresponds to the whole energy of the molecule (m, ε_r and ε_v are its mass, rotational and vibrational energy, $\vec{c} = \vec{u} - \vec{v}$ is its peculiar velocity, $\vec{u}$ is its velocity in the motionless coordinate system, $\vec{v}(\vec{r},t)$ is local gas-dynamic velocity). The invariant $\psi_{vr}^{(1)} = 1$ corresponds to the preservation of the molecules number at the collisions. The additional invariant $\psi_{vr}^{(2)} = \psi_{1/2}(v)\varepsilon_1$ is a certain generalization of the Treanor invariant $\psi_{vr}^{(2)} = v\varepsilon_1$ (Treanor *et al*., 1968). The multiplier $\psi_{1/2}(v)$ is continuous piecewise linear function of the vibrational level v. This function is quasi-harmonic approximation of the vibrational energy (1) (Rydalevskaya, 1995a; 2003). The coefficients $\gamma_\lambda\left(\lambda=\overline{0,2}\right)$ at the invariants $\psi_{vr}^{(\lambda)}$ are macroscopic parameters, depending only on the coordinates and time.

The curve 1 corresponds to $T_1/T = 10$; 2-$T_1/T = 5$; 3-$T_1/T = 2$; 4-$T_1/T = 1$; 5-$T_1/T = 0, 1$.

Integrating the functions $f_{vr}^{(0)}$ over the peculiar velocities $\vec{c}$ and summing over r, we obtain the populations n_v of vibrational levels. The relative populations $x_v = n_v/n_0$ can be written in the following form (Rydalevskaya, 1995a; 2003) Equation 4:

$$x_v = exp\left\{-\frac{\varepsilon_1}{kT_1}\left[\frac{\varepsilon_v}{\varepsilon_1} - \left(\psi_{1/2}(v) - \frac{\varepsilon_v}{\varepsilon_1}\right)\left(\frac{T_1}{T} - 1\right)\right]\right\},\\ v = \overline{0, v_d} \tag{4}$$

There are the notations:

$$\gamma_0 = -\frac{1}{kT}, \qquad \gamma_2 = \frac{1}{kT} - \frac{1}{kT_1},$$

where, k is the Boltzmann constant, T is the gas temperature, T_1 is so-called temperature of the first vibrational level (Treanor *et al*., 1968).

The relations (4) determine the dependence of the relative populations of vibrational levels x_v on the ratio T_1/T.

At the lower vibrational level the distribution of relative populations x_v and the Treanor distribution (Treanor *et al*., 1968) coincide.

At the middle levels the relative populations x_v (4) are lower than the Boltzmann populations, but near them, if the ratio $T_1/T<1$. If the ratio $T_1/T>1$, the populations (4) are higher than the Boltzmann populations and can differ significantly from them. When $T_1/T>4$, the dependence of the values x_v (4) on the number v takes the form of sloping plateau.

At the high levels, close to v_d, the relative populations x_v (4) decrease by the increase of v like the Boltzmann distribution with the gas temperature T.

The dependence of the relative vibrational populations (4) on the ratio T_1/T in molecular nitrogen N_2 is presented on the Fig. 1 (Rydalevskaya, 2003). The data (Huber and Herzberg, 1979): $\omega = v_*/C_* = 2358, 57$ cm^{-1}, $\omega X/ = 14, 324$ cm^{-1}, (c_* is the light velocity) are used by the calculations.

Nonequilibrium Flows in the Nozzles

The system of gas-dynamic equations for the description of vibrationally nonequilibrium flows of the inviscid and non-conducting gas can be written in the form (Rydalevskaya, 1995a; 2003):

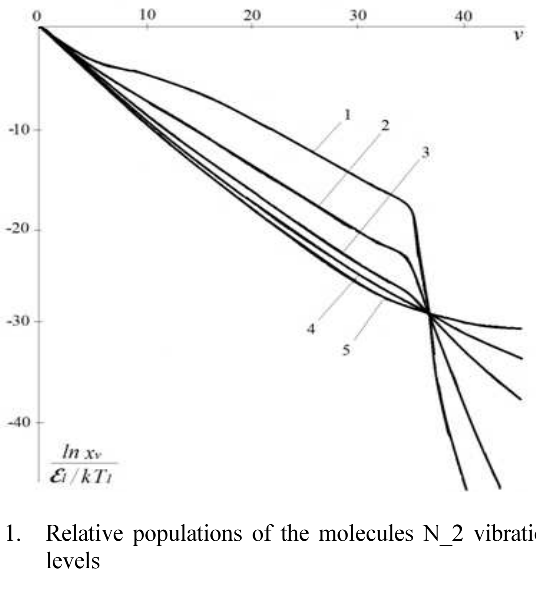

Fig. 1. Relative populations of the molecules N_2 vibrational levels

$$\begin{aligned}
&\varrho \frac{d\vec{v}}{dt} = -\nabla p, \\
&\frac{dn}{dt} + n\,\mathrm{div}\vec{v} = 0, \\
&\frac{de}{dt} = -(e+p)\,\mathrm{div}\vec{v}, \\
&\frac{d\psi_2}{dt} + \psi_2 \mathrm{div}\vec{v} = \Delta\psi_2.
\end{aligned} \tag{5}$$

Here p = nkT is a pressure; the parameters $n = \sum_v n_v$, $\varrho = mn$ and $e = \frac{5}{2}nkT + \sum_v n_v\varepsilon_v$ are the densities of the molecules number, mass and energy of gas; $\psi_2 = \sum_v n_v \psi_{1/2}(v)\varepsilon_1$ is a density of summary value of additional invariants $\psi_{vr}^{(2)}$; $\Delta\psi_2$ is a change of the value ψ_2 due to the vibrational transitions (2) with $\alpha>1/2$. We assume for simplicity that external forces are absent.

The system of Equation (5) in quasi-one-dimensional approximation was used in the works (Rydalevskaya and Ryabikova, 1999) for the investigation of the molecular nitrogen flows in expanding nozzles of diverse configuration.

As it was to be expected, the gas temperature T and the temperature of the first vibrational level T_1 decrease when the gas moves along the nozzle axis. The temperature T decreases by the increase x/d_0 much more than T_1. It leads to significant deformation of initial Boltzmann distribution by the gas movement along the nozzle axis. The nonequilibrium quasi-stationary distributions are formed, which were discovered in (Center and Caledonia, 1971).

The dependences of the temperatures T and T_1 on x/d_0 in the flow of molecular nitrogen are presented on Fig. 2 (Rydalevskaya and Ryabikova, 1999).

The calculation results correspond to conic nozzle with the half-spread angle 15° in prechamber the temperature $T_0 = 3000\ K$ and the pressure $p_0 = 1\,atm$ are.

The values y = $\ln x_v/(\varepsilon_1/(kT_1))$, which correspond to the relative vibrational populations in diverse sections of the same nozzle, are presented on Fig. 3.

It is easy to see that the further a cross-section of nozzle from critical section, the more the populations of vibrational levels differ from equilibrium populations.

Direct Shocks in Diverse Cross-Sections of Expanding Nozzles

As it was said in Introduction, a shock wave in nonequilibrium gas flow can be treated as a transient layer between two nonequilibrium states (Rydalevskaya, 1995b).

In expanding flows of vibrationally nonequilibrium gases it can be modeled by a thin transient layer between two vibrationally nonequilibrium quasi-stationary states.

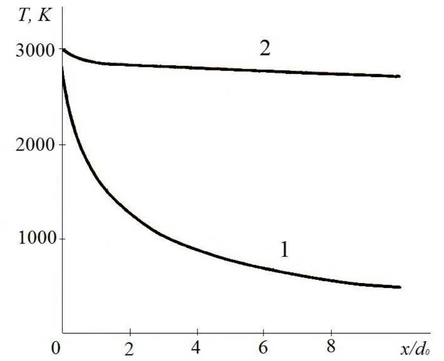

Fig. 2. The change of the temperatures T (the curve 1) and T1 (the curve 2) by the molecular nitrogen movement along the nozzle axis

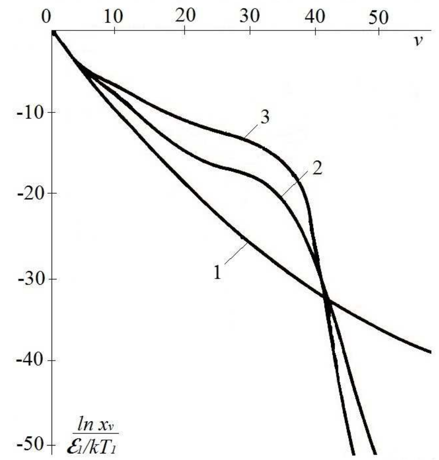

Fig. 3. Relative populations of vibrational levels of the molecules N_2 in diverse sections of the nozzle. The curve 1 corresponds to x/d0 = 0; 2-x/d0 = 6; 3-x/d0 = 12

In this case the distribution functions and relative populations of vibrational levels have the forms (3) and (4) both before and after shock wave. The dynamic consistency conditions involve the additional relation for the densities ψ_2 of summary value of invariants $\psi_{vr}^{(2)}$.

If we confine the consideration to direct shocks, the consistency conditions can be written in symmetric form (Voroshilova and Rydalevskaya, 2004) Equation 6:

$$\begin{aligned}
&n^{(+)}v_x^{(+)} = n^{(-)}v_x^{(-)},\\
&\varrho^{(+)}v_x^{(+)2} + p^{(+)} = \varrho^{(-)}v_x^{(-)2} + p^{(-)},\\
&\frac{v_x^{(+)2}}{2} + \left(\frac{e}{\varrho}\right)^{(+)} + \left(\frac{p}{\varrho}\right)^{(+)} = \frac{v_x^{(-)2}}{2} + \left(\frac{e}{\varrho}\right)^{(-)} + \left(\frac{p}{\varrho}\right)^{(-)},\\
&\psi_2^{(+)}v_x^{(+)} = \psi_2^{(-)}v_x^{(-)},
\end{aligned} \tag{6}$$

where, $\beta^{(-)}$ and $\beta^{(+)}$ are the value of the parameter β ahead of and behind the shock.

The consistency conditions (6) contain the values, which can be expressed through the functions (3) and (4). If the gas parameters are known before the shock wave, the relations (6) can be treated as a system of algebraic equations for the unknown parameters $v_x^{(+)}, \gamma_0^{(+)}, \gamma_1^{(+)}$ and $\gamma_2^{(+)}$ (or $v_x^{(+)}$, $n^{(+)}$, $T^{(+)}$ and $T_1^{(+)}$).

The corresponding system can be solved using the Newton method (Voroshilova and Rydalevskaya, 2004).

The calculation results had shown that nonequilibrium effects have a week influence on the jumps of the density n and the velocity $\vec{v}$ in diatomic gas of an harmonic oscillators. The magnitude of the gas temperature jump like to the jump of the temperature T in equilibrium flow, while the jump in the temperature of the first vibrational level T_1 can be ignored. Therefore, the ratio T_1/T decreases with the gas passage through a shock wave. Accordingly, the relative vibrational populations $x_v^{(+)}$ become closer to the Boltzmann populations with the temperature $T_1^{(+)} \approx T_1^{(-)}$ than the populations $x_v^{(-)}$.

This effect become apparent the more, the more the shock wave intensity, which increase with an increase of $v_x^{(-)}$ and a decrease of a sound velocity $a^{(-)}$. As it was shown in (Voroshilova and Rydalevskaya, 2008), under nonequilibrium conditions the value of the coefficient k in the formula $a^2 = \kappa p / \varrho$ decreases with an increase of the ratio T_1/T.

The further direct shock is from critical cross-section of the nozzle, the more the temperatures ratio $T_1^{(-)} / T^{(-)}$ and the velocity $v_x^{(-)}$. The degree of the distribution nonequilibrium ahead the shock increase with an increase of $T_1^{(-)} / T^{(-)}$. However, an increase of $v_x^{(-)}$ and a decrease of the sound velocity $a^{(-)}$ favors the approach of the molecules distribution behind the shock to the Boltzmann distribution.

For the illustration of these effects the values $ln x_v/(\varepsilon_1/(kT_1))$ are presented on the Fig. 4.

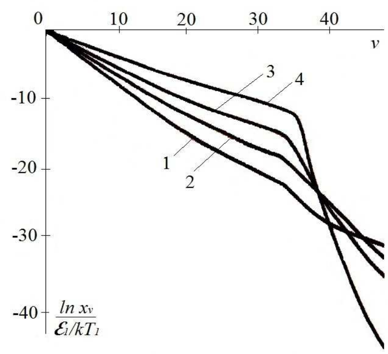

Fig. 4. The relative populations of the vibrational levels of the molecules N_2 after and before the shocks in diverse cross-sections of the nozzle. The curves 1 and 3 correspond to the populations $x_v^{(+)}$ and $x_v^{(-)}$ when x/d_0 = 6; 2 and 4 – to $x_v^{(+)}$ and $x_v^{(-)}$ when $x/d_0 = 12$

These values correspond to the relative populations of vibrational levels of nitrogen molecules ahead and behind the shocks. The direct shocks are at various distances from the critical cross-section of conic nozzle with the half-spread angle 15°. In prechamber the temperature T_0 = 3000 K and the pressure p_0 = 1_{atm} are by the forming of the flow.

Conclusion and Findings

In work vibrationally nonequilibrium flows of diatomic gases in expanding nozzles and direct shocks in diverse cross-sections of a nozzle are considered. The gas states behind the direct shocks are determined using the generalized dynamic consistency conditions (6) and the methods of kinetic theory which allow to put the parameters before and after a shock into the nonequilibrium quasi-stationary distributions (3) and the relative populations of vibrational levels (4). This method can be applied for the investigation of diverse diatomic gases in such diapasons of the temperatures and the pressures when in the gas high vibrational levels of the molecules are excited but one may not consider the dissociation processes.

In present paper under the investigation of molecular vibrational populations behind the direct shocks at various distances from critical cross-section it is noted the action of two competing factors. The moving away from the critical cross-section leads to an increase of the ratio $T_1^{(-)}/T^{(-)}$ and the velocity $v_x^{(-)}$ ahead the shock. The increase of the ratio $T_1^{(-)}/T^{(-)}$ must lead to an increase of vibrational nonequilibrium both before and after shock. At the same time, the intensity of a shock wave and the temperature $T^{(+)}$ increase with an increase of the ratio $T_1^{(-)}/T^{(-)}$ and the velocity $v_x^{(-)}$. In connection with that the ratio $T_1^{(+)}/T^{(+)}$ and the degree of vibrational nonequilibrium decrease after shock.

The results can be the basis of future researches which will allow to determine the dependence of the inversion of molecular vibrational population in the various cross-sections of the nozzle on its form, length and the pressure overfall on coming out of the nozzle.

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Author’s Contributions

All authors equally contributed in this study.

Ethics

This article is original and contains unpublished materials. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved.

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