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EFFECT OF VIBRATIONAL EXCITATION OF MOLECULES ON THE VELOCITY OF SOUND IN A HIGH-TEMPERATURE DIATOMIC GAS

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A formula for the velocity of sound, which is valid not only for barotropic gases, is derived on the basis of methods of the kinetic theory of gases. This formula is specified for various stages of relaxation of a high-temperature diatomic gas in the approximation of the model of anharmonic oscillators. A dependence between the populations of vibrational levels of molecules and the velocity of sound is found.

Key words: *velocity of sound, anharmonic oscillators, vibrational relaxation, populations of vibrational levels.*

The velocity of sound, which is one of the most important characteristics of gaseous media, is usually considered as the velocity of propagation of small perturbations. For vortex-free flows, the squared velocity of sound is identified with the coefficient in the wave equation for the velocity potential (see, e.g., [1, 2]). In the Lagrangian integral for a vortex-free flow of a barotropic gas moving in the field of conservative forces independent of time, the squared velocity is neglected, the resultant expression is differentiated with respect to time, and the continuity equation with omitted terms of the second order of smallness is used. As a result, we obtain the wave equation

$$\frac{\partial^2\varphi}{\partial t^2} = \frac{dp}{d\rho}\operatorname{div}\boldsymbol{v} = \frac{dp}{d\rho}\,\Delta\varphi,$$

where $\boldsymbol{v}$ is the macroscopic velocity of the gas, φ is the potential of this velocity, p is the pressure, and ρ is the density. Hence, we obtain $a^2 = dp/d\rho$ (a is the velocity of sound).

In most cases, the gas with its physical and chemical processes cannot be considered as barotropic. Under these conditions, methods of the kinetic theory of gases [3–5] can be used to choose the governing macroparameters and to close the system of gas-dynamic equations.

Collisions of molecules accompanied by exchange of energy and elementary chemical acts occur with different frequencies [6]. In addition to locally equilibrium flows, therefore, we have to consider various relaxation regimes of the flow in the approximation of an ideal fluid.

The limiting solutions f_i^0 of the kinetic equations corresponding to different stages of gas relaxation are written as [5]

$$f_i^0 = \frac{s_i m_i^3}{h^3}\exp\Big[\gamma_0\Big(\frac{m_i c^2}{2} + \tilde{\varepsilon}_i\Big) + \sum_{\lambda=1}^{\Lambda}\gamma_\lambda\psi_i^\lambda\Big], \qquad i = \overline{1, I}. \tag{1}$$

Here f_i^0 is the distribution function of microparticles (atoms and molecules) of the ith kind (the subscript i indicates the particle kind and the set of quantum numbers characterizing the level of its internal energy), h is the Planck constant, m_i and s_i are the mass and statistical weight of the ith molecule, $\boldsymbol{c} = \boldsymbol{u} - \boldsymbol{v}$ is the own (thermal) velocity of the ith molecule, $\boldsymbol{u}$ is the microparticle velocity in the global (motionless) coordinate system, $\boldsymbol{v}(\boldsymbol{r}, t)$ is its local

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gas-dynamic velocity, $\tilde{\varepsilon}_i$ is the internal energy of the molecule, which can transform to translational energy (and back) in collisions participating in formation of distributions (1), $\psi_i^0 = m_i c^2/2 + \tilde{\varepsilon}_i$ and ψ_i^λ ($\lambda = \overline{1, \Lambda}$) are the independent additive invariants of such collisions (the set of the invariants ψ_i^λ depends on the gas composition and on the relaxation stage considered), and γ_λ ($\lambda = \overline{0, \Lambda}$) are the parameters depending on coordinates and time.

The distribution functions (1) are usually normalized to the quantities $\psi_0 = \tilde{e}$, ψ_λ, and $\lambda = \overline{1, \Lambda}$ (densities of the total values of energy of the above-considered types and invariants ψ_i^λ):

$$\psi_0(\boldsymbol{r}, t) = \tilde{e} = \sum_i \int f_i^0 \Big(\frac{m_i c^2}{2} + \tilde{\varepsilon}_i \Big)\, d\boldsymbol{c} = \sum_i n_i^0 \Big(-\frac{3}{2}\frac{1}{\gamma_0} + \tilde{\varepsilon}_i \Big); \tag{2}$$

$$\psi_\lambda(\boldsymbol{r}, t) = \sum_i \int f_i^0 \psi_i^\lambda \, d\boldsymbol{c} = \sum_i n_i^0 \psi_i^\lambda, \qquad \lambda = \overline{1, \Lambda}; \tag{3}$$

$$n_i^0 = \int f_i^0 \, d\boldsymbol{c} = s_i \exp\Big(\gamma_0 \tilde{\varepsilon}_i + \sum_{\lambda=1}^{\Lambda} \gamma_\lambda \psi_i^\lambda \Big) \Big(-\frac{2\pi m_i}{\gamma_0 h^2} \Big)^{3/2}. \tag{4}$$

The right side of Eq. (2) implies the equality $\gamma_0 = -1/(kT)$ (k is the Boltzmann constant and T is the gas temperature).

The densities of the extensive macroparameters ψ_λ ($\lambda = \overline{0, \Lambda}$) and the velocity $\boldsymbol{v}$ satisfy the equations that are derived from the kinetic equations and have the form [7]

$$\frac{d\boldsymbol{v}}{dt} = \boldsymbol{F} - \frac{1}{\rho} \nabla p; \tag{5}$$

$$\frac{d\tilde{e}}{dt} + (\tilde{e} + p) \operatorname{div} \boldsymbol{v} = \Delta \tilde{e}; \tag{6}$$

$$\frac{d\psi_\lambda}{dt} + \psi_\lambda \operatorname{div} \boldsymbol{v} = \Delta \psi_\lambda, \qquad \lambda = \overline{1, \Lambda}. \tag{7}$$

Here

$$p = \frac{1}{3} \sum_i \int f_i^0 m_i c^2 \, d\boldsymbol{c} = -\frac{n^0}{\gamma_0} = n^0 kT; \tag{8}$$

$\boldsymbol{F}$ is the external force acting on a unit mass of the gas; $n^0 = \sum_i n_i^0$ and $\Delta\tilde{e}$, and $\Delta\psi_\lambda$ are the relaxation terms characterizing the changes in the governing macroparameters due to nonequilibrium processes at this stage of relaxation.

It should be noted that the mass density ρ can be presented as a linear combination of the parameters ψ_λ ($\lambda = \overline{1, \Lambda}$). Indeed, some of the additive invariants ψ_i^λ correspond to the condition of conservation of microparticles, which do not change during collisions forming the quasi-steady state considered. In this case, the mass density ρ equals the sum of the quantities ψ_λ, which are products of the densities of these particles and their mass m_λ. The continuity equation follows from Eq. (7).

It follows from the facts discussed above and from Eqs. (2)–(4) and (8) that the dependence of the parameters in Eqs. (5)–(7) on coordinates and time is determined by the functions $\gamma_0(\boldsymbol{r}, t)$ [or $T(\boldsymbol{r}, t)$] and $\gamma_1(\boldsymbol{r}, t), \ldots, \gamma_\Lambda(\boldsymbol{r}, t)$.

By studying the Boltzmann entropy corresponding to different quasi-steady states of gas mixtures, Rydalevskaya [5] demonstrated that the quantities γ_λ are intensive parameters conjugated with extensive parameters whose densities ψ_λ are determined by Eqs. (2)–(4). It was also shown in [5] that the Jacobian of the transition from extensive to intensive parameters is positive:

$$\det = \frac{D(\psi_0, \psi_1, \ldots, \psi_\Lambda)}{D(\gamma_0, \gamma_1, \ldots, \gamma_\Lambda)} > 0. \tag{9}$$

Hence, system (5)–(7) can be considered as a system of differential equations for the unknown functions $\gamma_0(\boldsymbol{r}, t)$ [or $T(\boldsymbol{r}, t)$], $\gamma_1(\boldsymbol{r}, t), \ldots, \gamma_\Lambda(\boldsymbol{r}, t)$, and $\boldsymbol{v}(\boldsymbol{r}, t)$ [8].

If the nonequilibrium processes are "frozen" or the flow is locally equilibrium, the right sides of Eqs. (6) and (7) are equal to zero. System (5)–(7) written in terms of intensive parameters has the form [8]

$$\frac{d\boldsymbol{v}}{dt} = \boldsymbol{F} + \frac{1}{\gamma_0}\Big(\tilde{H}\nabla\gamma_0 + \sum \Psi_\lambda \nabla\gamma_\lambda\Big); \tag{10}$$

$$\frac{d\gamma_\lambda}{dt} = -\chi_\lambda \operatorname{div}\boldsymbol{v}, \qquad \lambda = \overline{0,\Lambda}. \tag{11}$$

In Eqs. (10) and (11), $\tilde{H} = (\tilde{e}+p)/\rho$ is the specific enthalpy of the gas, $\Psi_\lambda = \psi_\lambda/\rho$ are the specific values of the summed additive invariants ψ_λ $(\lambda = \overline{1,\Lambda}\,)$ and $\chi_\lambda = \det_\lambda / \det$, where det is the determinant of Eq. (9) and $\det_\lambda$ are the determinants of Eq. (9) with the columns of derivatives with respect to γ_λ replaced by the column of coefficients at $\operatorname{div}\boldsymbol{v}$ in Eqs. (6) and (7).

From Eqs. (6) and (7) with zero right sides, Eq. (8) for the pressure p, and the equation of continuity, we obtain the integrals of motion [7]

$$\Psi_\lambda = \psi_\lambda/\rho = \text{const}, \qquad \lambda = \overline{1,\Lambda}; \tag{12}$$

$$\gamma_0\tilde{H} + \sum_{\lambda=1}^{\Lambda}\gamma_\lambda\Psi_\lambda = \text{const}. \tag{13}$$

Note that equality (13) can be considered as a generalization of the adiabat.

For vortex-free flows and $\boldsymbol{F} = -\nabla U$, we obtain the Lagrangian integral in the form

$$\frac{\partial\varphi}{\partial t} + \frac{v^2}{2} + U + \tilde{H} = 0. \tag{14}$$

In studying the velocity of sound considered as the velocity of propagation of small perturbations, the gas velocity is assumed to be small, and the remaining gas-dynamic parameters, including γ_λ $(\lambda = \overline{0,\Lambda})$, are assumed to be only slightly different from constants.

Restricting ourselves to quantities of the first order of smallness and neglecting terms of the form $(\boldsymbol{v}\cdot\nabla)\gamma_\lambda$ in Eq. (11) and $v^2/2$ in Eq. (14), we obtain

$$\frac{\partial\gamma_\lambda}{\partial t} = -\chi_\lambda \operatorname{div}\boldsymbol{v}, \qquad \lambda = \overline{0,\Lambda}; \tag{15}$$

$$\frac{\partial\varphi}{\partial t} + U + \tilde{H} = 0. \tag{16}$$

Using the conventional approach [1, 2], we differentiate Eq. (16) with respect to time. Assuming the potential U to be independent of time, we obtain the equality $\partial^2\varphi/\partial t^2 + \partial\tilde{H}/\partial t = 0$. After that, using the integrals of motion (12) and (13) to calculate $\partial\tilde{H}/\partial t$, replacing the partial derivatives $\partial\gamma_\lambda/\partial t$ in the resultant formula by expressions (15), and taking into account the relation $\operatorname{div}\boldsymbol{v} = \Delta\varphi$, we obtain the wave equation [8]

$$\frac{\partial^2\varphi}{\partial t^2} = -\frac{1}{\gamma_0}\Big(\tilde{H}\chi_0 + \sum_\lambda \Psi_\lambda\chi_\lambda\Big)\Delta\varphi, \tag{17}$$

where the coefficient can be identified with the squared velocity of sound a.

Presenting the specific enthalpy $\tilde{H}$ and the summed additive invariants Ψ_λ in Eq. (17) in the form of the ratios of the densities of the corresponding quantities $\tilde{e}+p$ and ψ_λ to the mass density of the gas ρ, multiplying and dividing the right side of Eq. (17) by the total number of particles n^0 in a unit volume, and using Eq. (8) for the pressure p, we obtain the expression for the squared velocity of sound in the form

$$a^2 = \varkappa\frac{p}{\rho}, \qquad \varkappa = \langle\tilde{h}\rangle\chi_0 + \sum_\lambda\langle\psi_\lambda\rangle\chi_\lambda \tag{18}$$

[$\langle\tilde{h}\rangle = (\tilde{e}+p)/n^0$ and $\langle\psi_\lambda\rangle = \psi_\lambda/n^0$ are the mean enthalpy and invariants ψ_i^λ per one molecule]. It should also be noted that Eq. (8) for the pressure p, the dependence of $n^0 = \sum\limits_i n_i^0$ on the parameters γ_λ [see Eq. (4)], the equation of continuity, and Eqs. (11) allow us to present the coefficient at $\Delta\varphi$ in Eq. (17) (and, hence, the value of a^2) in the form $a^2 = dp/d\rho$. (Note that this expression in our case is the ratio of the total differentials of pressure and density.)

A chemically homogeneous diatomic gas is a fairly simple subject of research, which, nevertheless, makes it possible to study various stages of translational-rotational and vibrational relaxation. Owing to the development of molecular lasers in last decades, there appeared many publications dealing with research of nonequilibrium states of a high-temperature diatomic gas (see, e.g., [3–6] and the references therein).

Diatomic molecules are known to possess rotational and vibrational degrees of freedom at high temperatures; vibrational degrees of freedom are usually described by the anharmonic oscillator model:

$$\varepsilon_v = v\varepsilon_1 + \Delta\varepsilon v(v-1), \quad \varepsilon_1 = h\nu(1-2x), \quad \Delta\varepsilon = xh\nu, \quad v \in [0, v_d]. \tag{19}$$

Here ε_v is the vibrational energy of the molecule, counted from the zero level, v is the number of the level of vibrational energy, ν is the frequency of vibrations of atoms in the molecule, $x \ll 1$ is the anharmonicity constant, and v_d is the vibrational level corresponding to dissociation energy.

During molecular collisions, changes in translational and rotational energies of molecules occur much more often than vibrational energy exchange:

$$(v) + (v_1) \quad \leftrightarrows \quad (v') + (v_1'), \tag{20}$$

which can also occur with different frequencies [6].

According to [9, 10], the probability of vibrational exchange (20) increases by more than an order of magnitude owing to halving of the quantity $\alpha = |\varepsilon_{v'} + \varepsilon_{v_1'} - \varepsilon_v - \varepsilon_{v_1}|/(\varepsilon_v + \varepsilon_{v_1})$, which is the ratio of the defect of the resonance of vibrational energy to its value before the collision. Under these conditions, we can divide the process of vibrational relaxation of a diatomic gas into several stages and write the system of inequalities in the form [5]

$$\tau_{RT} \ll \tau_{VT}^{1/8} \ll \tau_{VT}^{1/4} \ll \tau_{VT}^{1/2} \ll \tau_{VRT}.$$

Here τ_{RT} is the time of relaxation in terms of translational and rotational degrees of freedom, τ_{VT}^{α} are the times of partial vibrational relaxation [at these stages, formation of quasi-steady states involves, in addition to translational and rotational transitions of molecules, transitions (20) where the relative defect of the resonance is $\alpha < 1/8$, $1/4$, and $1/2$, respectively), and τ_{VRT} is the total relaxation time (time needed for thermodynamic equilibrium to be established).

The behavior of gas-dynamic parameters and populations of vibrational levels on the boundaries of the corresponding relaxation zones inside the region of the normal shock wave arising in equilibrium and vibrationally nonequilibrium flows of a diatomic gas and behind this region was studied in [11–13]. Closed systems of gas-dynamic equations were obtained for different stages of relaxation of a diatomic gas in these papers, and the properties of these systems were considered for conditions of local equilibrium and in the cases where the influence of slow physical and chemical processes can be neglected. In the present paper, we consider the changes in the velocity of sound at these stages of relaxation.

Specifying Eq. (18) for the above-indicated stages of relaxation of a diatomic gas modeled by anharmonic oscillators, we can estimate the effect of molecular collisions of various types on the velocity of sound.

At the stage of completion of translational-rotational relaxation, the additive invariants in distributions (1) are the translational-rotational energy and the number of the level of vibrational energy of the molecule, which are described by the following governing macroparameters: density of translational-rotational energy $\tilde{e} = e_{RT}$, population of vibrational levels n_v ($v = \overline{0, v_d}$), and mean-mass velocity $\boldsymbol{v}$. The coefficient $\varkappa$ in Eq. (18) has the form

$$\varkappa = \langle h_{RT}\rangle \chi_0 + \sum_{v=0}^{v_d} \langle n_v\rangle \chi_{v+1}. \tag{21}$$

Here $\langle h_{RT}\rangle = (e_{RT} + p)/n$, $\langle n_v\rangle = n_v/n$, $n = \sum\limits_{v=0}^{v_d} n_v$, $n_v = Z_{RT}(\gamma_0)\exp\gamma_{v+1}$, and $Z_{RT}(\gamma_0)$ is the statistical sum of the molecule over the translational and rotational degrees of freedom. It can be easily demonstrated that $\varkappa = 7/5$ in the classical description of rotational degrees of freedom [7].

At the stages of completion of partial vibrational relaxation $VT(\alpha)$ ($\alpha = 1/8$, $1/4$, and $1/2$), in addition to the invariant corresponding to the total (translational–rotational–vibrational) energy of the molecule and $\psi_i^1 = 1$, distribution (1) contains another additive invariant $\psi_i^2 = \psi_\alpha(v)\varepsilon_1$ ($\Lambda = 2$), which is a quasi-harmonic approximation of vibrational energy (19) of the anharmonic oscillator with a relative accuracy α (see [5]). The governing

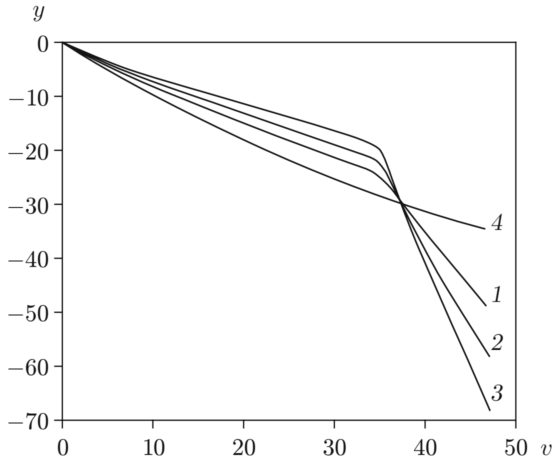

Fig. 1

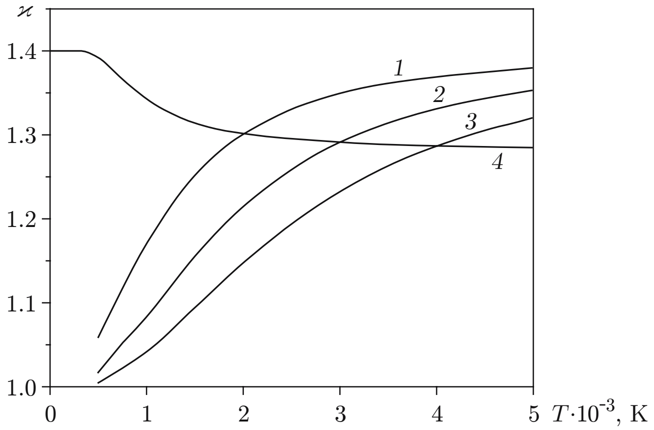

Fig. 2

Fig. 1. Relative populations of vibrational levels of nitrogen molecules for different values of T_1/T: curves 1–3 show the stages of partial vibrational relaxation $VT(1/2)$ for $T_1/T = 4$ (1), 6 (2), and 8 (3); curve 4 shows the equilibrium state.

Fig. 2. Coefficient $\varkappa$ of molecular nitrogen versus temperature for different values of T_1: curves 1–3 show the stages of partial vibrational relaxation $VT(1/2)$ for $T_1 = 2 \cdot 10^3$ (1), $3 \cdot 10^3$ (2), and $4 \cdot 10^3$ K (3); curve 4 shows the equilibrium state.

macroparameters are the density of the total energy $\tilde{e} = e$, the number of particles $n^0 = n$, the total value $n\langle\psi_\alpha\rangle\varepsilon_1$ of the additional additive invariant $\psi_\alpha(v)\varepsilon_1$ [$\langle\psi_\alpha\rangle$ is the mean value of $\psi_\alpha(v)$ per one molecule], and the velocity $\boldsymbol{v}$. The coefficients $\varkappa$ in Eq. (18) have the form

$$\varkappa = \langle h\rangle\chi_0 + \chi_1 + \langle\psi_\alpha\rangle\varepsilon_1\chi_\alpha \tag{22}$$

[$\langle h\rangle = (e+p)/n$]. Relations (22) and (18) describe the analytical dependence of the velocity of sound on the parameters γ_0 (or T), γ_1 (or n), and γ_2.

After the relaxation process is completed, distribution (1) contains only the invariants corresponding to conservation of the total energy and the number of particles. The governing macroparameters are e, n, and $\boldsymbol{v}$. Under these conditions, the coefficient $\varkappa$ in Eq. (18) acquires the form

$$\varkappa = \langle h\rangle\chi_0 + \chi_1. \tag{23}$$

Relations (22) and (23) allow us to determine the dependence of the velocity of sound on vibrational populations of the molecules.

At the stages of partial vibrational relaxation, the relative vibrational populations can be presented as $x_v(\alpha) = n_v(\alpha)/n_0(\alpha) = \exp[\gamma_0\varepsilon_v + \gamma_2\psi_\alpha(v)\varepsilon_1]$. At the lower vibrational levels, we obtain a piecewise-linear function $\psi_\alpha(v) = v$. If the equality $\gamma_0 = -1/(kT)$ and the presentation $\gamma_2 = 1/(kT) - 1/(kT_1)$ (T_1 is the so-called temperature of the first vibrational level) are used, the relative populations $x_v(\alpha)$ at these levels are consistent with Treanor's distribution [14]. The ratio of temperatures T_1/T determines the degree of vibrational excitation of gas molecules. The higher the value of T_1/T, the higher the populations of vibrational levels are above the Boltzmann distributions for $T_1/T > 1$ [5]. This phenomenon is most profoundly manifested at the last-but-one stage of vibrational relaxation ($t \sim \tau_{VT}^{1/2}$), which is of greatest interest, because nonequilibrium quasi-steady flows with $\alpha < 1/2$ are also frequently encountered, in addition to locally equilibrium flows ($\alpha \approx 1$).

Figure 1 shows the relative populations of vibrational levels for a nitrogen molecule $y = \ln x_v/(\varepsilon_1/(kT_1))$ at the stage of partial vibrational relaxation $VT(1/2)$ and in the equilibrium state.

Figure 2 shows the dependence of the coefficient $\varkappa(T)$ calculated by Eq. (22) for molecular nitrogen at the stage of relaxation $VT(1/2)$ for $n = n_{\text{L}}$ (n_{L} is the Loschmidt number) and different values of T_1, and also the dependence $\varkappa(T)$ in the state of thermodynamic equilibrium calculated by Eq. (23).

By an example of molecular nitrogen, Figs. 1 and 2 illustrate the dependence between the populations of vibrational levels of molecules and the value of the coefficient $\varkappa$. In the equilibrium state at sufficiently low temperatures (where vibrational excitation can be neglected), we have $\varkappa = 1.4$. As the temperature increases and the populations of vibrational levels also increase, the value of $\varkappa$ monotonically decreases and approaches a certain constant value as the temperature becomes sufficiently high. Under nonequilibrium conditions, an increase in the value of T_1/T increases the populations of the lower and medium vibrational levels and decreases the value of $\varkappa$ in Eq. (18), i.e., the velocity of sound is lower for identical density and pressure. We also obtained similar dependences for other gases.

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