STEADY FLOW OF A VIBRATIONALLY EXCITED GAS OF DIATOMIC MOLECULES

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The study of the flow of a vibrationally excited gas has acquired particular importance in connection with the solution of problems of gasdynamical stability of strongly nonequilibrium states of active media, and also in the physics of nonequilibrium discharges in gas flows. In [1, 2] the problem of steady shock waves in a gas of diatomic molecules with excited vibrational degrees of freedom was studied. It was shown that the flow of a nonequilibrium gas can be steady in the shock wave only for a certain intensity and the propagation of these waves is analogous to detonation waves. It was noted in [3] that weak shock waves in a vibrationally excited gas can be amplified and transform into the steady regime of normal Jouguet detonation. The condition for the amplification of weak discontinuities propagating in a nonuniform flow of excited molecules was considered in [4]. In [5], using the Landau–Teller theory of vibrational relaxation, the structure of steady detonation waves is described for the Jouguet regime. In [6] the effect of a dissociation nonequilibrium in a vibrationally excited gas on the propagation of detonation waves was studied.

In the solution of many applied problems, such as the loss of flow uniformity and the separation of ejections of gases in rapidly flowing discharges [7], together with the study of shock-type flows, the study of shockless flows of vibrationally excited diatomic gases is of great value.

In the present paper we describe the steady regimes of these flow types in a pipe of constant cross section. Analogies with the theory of combustion are pointed out. Using the kinetic theory of vibrational relaxation in a system of anharmonic oscillators, we study the structure of the characteristic steady flow types (shock and shock-free types) of vibrationally excited nitrogen.

Let a vibrationally excited gas flow along the X axis (one-dimensional flow). Three characteristic regions can be identified. In the first region ($x < 0$) there is a uniform nonequilibrium medium in which there are (on average) S_0 vibrational quanta per molecule. The temperature T_0 of the translational–rotational motion of the molecule is such that $S_0 > S_p(T_0)$, where $S_p(T_0)$ is the average number of vibrational quanta per molecule in the equilibrium state corresponding to the gas temperature T_0. The gas has a density ρ_0 and moves with velocity D. The nonequilibrium nature of the medium in this region can be ensured by using a discharge or a supersonic jet, for example. The second region is a transition region. Here the incident vibrationally excited gas relaxes. The origin of the coordinate system is chosen to be inside this region. In the third region, coming after the relaxation zone, the gas is uniform and in equilibrium.

From the conservation laws and the equation of state of an ideal gas, we obtain a relation between the thermodynamic quantities of the gas on either side of the relaxaton zone [1]:

$$Y = \frac{Z + 6 + 2m\left(\varepsilon_0 - \varepsilon_p(T_1)\right)/kT_0}{6Z + 1}. \tag{1}$$

Here $Y = V_1/V_0$, $Z = p_1/p_0$; $V = 1/\rho$ is the specific volume; p is pressure, $\varepsilon = \hbar\omega_0/m$; S is the vibrational energy per unit mass of the gas; $\hbar\omega_0$ is the energy of a vibrational quantum of the molecule; m is the mass of a molecule. The quantities with subscript 1 refer to the equilibrium gas region.

From conservation of mass and momentum we also have the relation

$$Y = 1 - \frac{Z - 1}{1{,}4\,M^2}, \tag{2}$$

where $M = D/c_0$ is the Mach number and $c_0 = (1.4kT_0/m)^{1/2}$.

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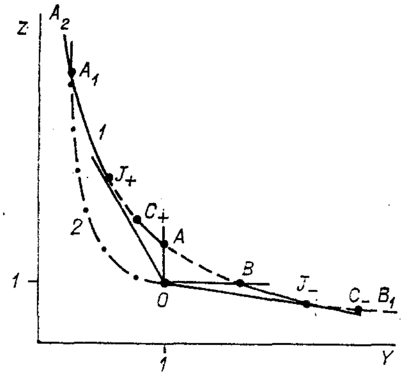

Fig. 1

Using (2) we reduce (1) to the form

$$Z_{(\pm)} = 1 + \frac{7(M^2-1)}{12}\left[1 \pm \left(1 - \frac{9{,}6\,M^2 F}{7(M^2-1)^2}\right)^{1/2}\right] \tag{3}$$

$$\left(F = \frac{\hbar\omega_0}{kT_0}[S_0 - S_p(T_1)]\right).$$

With the help of (3) we can divide the relaxation adiabatic curve into segments corresponding to shock and shock-free flow. In order to do this, it is only necessary to take into account that (3) [as well as (2)] is satisfied at each point of the transition region if we let $Z \to p/p_0$, $Y \to V/V_0$, $S_p(T_1) \to S$; here p, V, and S are the values of the quantities in the transition region. We note that with this substitution (2) determines the equation of the Michelson lines. The type of flow depends only on the sign in front of the square root in (3). This is obvious when applied to the beginning of the transition region, where $S = S_0$. The solution $Z_{(+)}$ describes a flow containing shock jumps in the parameters of the gas. The solution $Z_{(-)}$ describes a flow with continuous parameters. The change in the parameters is due entirely to vibrational relaxation in the transition layer.

Figure 1 gives a qualitative representation of the relaxation and shock adiabatic curves (lines 1 and 2). The first is described by (1), and the second by the relation $Y = (Z + 6)\cdot(6Z + 1)^{-1}$. According to (3), the relaxation adiabatic curve can be broken up into three regions corresponding to steady-state solutions of the system of equations for the state of the moving nonequilibrium gas. The solution $Z_{(+)}$ corresponds to the segment A_2C_+ of the relaxation adiabatic curve; the solution $Z_{(-)}$ corresponds to the segments C_+A and BC_- (the segment AB is not considered because $M^2 < 0$ everywhere on this segment, and the segment C_-B_1 is also not considered because it corresponds to a flow with a shock jump of rarefaction). On the relaxation adiabatic curve the symbols J_+ and J_- denote its points of tangency to the Michelson lines drawn from the point 0 of the initial state, while the symbols C_+ and C_- denote the points for which the radical in (3) vanishes.

Straightforward but lengthy calculations show that the pairs of points (C_+, J_+) and (C_-, J_-) are not coincident with each other. The points J_+ and J_- lie above the corresponding points C_+ and C_- (this is due to the fact that the heat released and the heat capacity of the gas depend upon the temperature). It is not difficult to see that for the points $J_\pm$ we have the relation

$$\left(\frac{\partial Z}{\partial Y}\right)_{\text{rel}} = \left(\frac{\partial Z}{\partial Y}\right)_P, \tag{4}$$

where $\left(\frac{\partial Z}{\partial Y}\right)_{\text{rel}}$ and $\left(\frac{\partial Z}{\partial Y}\right)_P$ are the derivatives along the relaxation adiabatic curve and the Poisson adiabatic curve [relation (4) leads to an equation between the quantities $Y_{J_\pm}$ and $T_{J_\pm}$ equivalent to the condition of tangency of the Michelson lines to the relaxation adiabatic curve). Therefore, all of the properties of the Jouguet point of the detonation adiabatic curve are characteristic of the points $J_\pm$. Taking into account the equality determining the properties of the points $J_\pm$, and $Z_{C_\pm} = {}^1/_{12}(7M_{C_\pm}^2 + 5)$, $Y_{C_\pm} = {}^1/_{2.4}(1.4 + M_{C_\pm}^{-2})$, we obtain the relation $v = c_{f1}$ (for the points $C_\pm$) and $v = c_{e1}$ (for the points $J_\pm$), where v is velocity of flow of the equilibrium gas, $c_{f1} = (1.4p_1V_1)^{1/2}$ is the speed of sound in a gas with "frozen" vibrational degrees of freedom, and $c_{e1} = c_{f1}\left[\frac{1+\frac{2\hbar\omega_0}{7k}\frac{dS_{1p}}{dT_1}}{1+\frac{2\hbar\omega_0}{5k}\frac{dS_{1p}}{dT_1}}\right]^{1/2}$ is the speed of sound in the equilibrium gas with the vibrations of the molecules taken into account.

We now discuss the case of interest here, that of the flow of a vibrationally excited gas. We note first that steady flows corresponding to the segments J_+C_+ and J_-C_- of the relaxation adiabatic curve do not occur. In fact, because the segments J_+C_+ and J_-C_- lie below the corresponding Jouguet points J_+ and J_-, when the gas goes into the final state corresponding to these segments, it reaches equilibrium (with larger entropy) sooner than for the points above these segments of the adiabatic curve (this can easily be seen, if we take note that on the ZY diagram a change in the stage of a gas particle in the relaxation zone is represented by a displacement of the point along the Michelson lines).

The flow regimes corresponding to points of the segment $J_+A_1A_2(M \geq M_{J_+})$ on the relaxation adiabatic curve. The flow velocity D satisfies $D > c_0$. Hence, the gas is braked in the transition region and its pressure, density, and temperature increase continuously. The velocity of the gas exceeds the local value of the speed of sound everywhere inside the relaxation region. This type of flow of a vibrationally excited gas is known in the theory of combustion as weak detonation flow driven by an external source [8]. It can occur under certain conditions, for example using supersonic jets.

For the steady flow regimes corresponding to the points of the segment BJ_- $(0 < M \leq M_{J_-})$, the speed of the nonequilibrium gas in the first region must be less than the speed of sound, $D < c_0$. In this case, the gas is accelerated and its pressure and density decrease monotonically. The flow remains subsonic everywhere (except for the regime J_-, where $v = c_{e1}$). This type of flow corresponds to the weak deflagration regime in the theory of combustion. It resembles the flow arising in the process of propellant combustion in the chamber of a reaction engine [8]. Besides the condition on the initial velocity, pressure drops must be provided in the first and third regions in order for this type of flow to occur. We note that, unlike the case of deflagration flow, as usually considered in the theory of combustion (when the rate of combustion of the mixture is determined by the propagation mechanism of the flames), shock-free deflagration flow of a vibrationally excited gas can exist for arbitrary values of the Mach number inside the interval $0 < M \leq M_{J_-}$.

For the characteristic steady flow regimes C_+, J_+, and J_-, the velocity of the nonequilibrium gas is found from the conditions determining the positions of the appropriate points on the relaxation adiabatic curve. A straightforward transformation allows one to represent these conditions in the form of equations for $0 < M \leq M_{J_-}$:

$$\begin{gathered} \mathrm{M}_{C_+} = \left(1+\frac{2{,}4F_{C_+}}{7}\right)^{1/2} + \left(\frac{2{,}4F_{C_+}}{7}\right)^{1/2}, \\ F_{C_+} = \frac{\hbar\omega_0}{kT_0}\left[S_0 - S_p\left(T_{C_+}\right)\right], \quad \frac{T_{C_+}}{T_0} = \left(\frac{1{,}4\mathrm{M}_{C_+}^2+1}{2{,}4\mathrm{M}_{C_+}}\right)^2; \end{gathered} \tag{5}$$

$$\mathrm{M}_{J_\pm} = \left[\frac{1-U_{J_\pm}/Y_{J_\pm}}{1{,}4\left(Y_{J_\pm}-1\right)}\right]^{1/2}, \tag{6}$$

where $Y_{J_\pm} = Q_\pm + (Q_\pm^2 + U_{J_\pm})^{1/2}$; $Q_\pm = 0{,}5\alpha\Delta S_\pm - 3\left(U_{J_\pm} - 1\right)$, $\alpha = 2\frac{\hbar\omega_0}{kT_0}$; $\Delta S_\pm = S_0 - S_p\left(U_{J_\pm}\right)$; $U_{J_\pm} \equiv \frac{T_{J_\pm}}{T_0}$ are the roots of the equations $a_\pm Y_{J_\pm} - b_\pm \pm (b_\pm^2 + a_\pm d_\pm)^{1/2} = 0$; $a_\pm = 42 + 8\alpha \left.\frac{dS_p}{dU}\right|_{U=U_{J_\pm}}$; $b_\pm = 42 + 6\alpha\Delta S_\pm + \alpha(7+\alpha\Delta S_\pm)\left.\frac{dS_p}{dU}\right|_{U=U_{J_\pm}}$; $d_\pm = 42 + 7\alpha\Delta S_\pm + \alpha(6+\alpha\Delta S_\pm)\left.\frac{dS_p}{dU}\right|_{U=U_{J_\pm}}$.

We now study the structure of the nonequilibrium flow for the flow regimes J_+, C_+, and J_-. We chose vibrationally excited molecular nitrogen for this study. The distribution of the parameters of the medium in the transition region is given by the system of equations

$$\frac{d\psi_v}{dx} = \frac{N}{DN_{(0)}}(\pi_{v+1} - \pi_v),\ v = 0, 1, \ldots, v_*, \tag{7}$$

which follow from the equations of unsteady vibrational kinetics for a single-component system of anharmonic oscillators [9, Ch. 4, Eq. (2.1)]. Here, $\pi_{v+1} = Z_{st}\left\{P_{v+1,v}\psi_{v+1} - P_{v,v+1}\psi_v + \sum_{v'=0}^{v_*}\left(Q_{v+1,v}^{v',v'+1}\psi_{v'}\psi_{v+1} - Q_{v,v+1}^{v'+1,v'}\psi_v\psi_{v'+1}\right)\right\}$; v_* is the number of the last vibrational level that is taken into account (i.e., excitations with $v > v_*$ are neglected); $\psi_v = N_v/N$; N_v is the number of molecules per unit volume with quantum number v; $N = \sum_{v=0}^{v_*} N_v$; $N_{(0)} = \rho_0/m$; Z_{st} is the frequency of molecular collisions; $P_{v+1,v}$, $P_{v,v+1}$ are the probabilities of VT transitions; $Q_{v+1,v}^{v',v'+1}$, $Q_{v,v+1}^{v'+1,v'}$ are the probabilities of VV transitions. Expressions for the probabilities of VT and VV transitions are presented in [9]. The temperature dependence of the quantities $P_{1,0}(T)$ and $Q_{1,0}^{0,1}(T)$, which enter the expressions for these probabilities, was normalized in accordance with the experimental data [10-12]. The system of equations (7) was integrated with the help of the solution algorithm given in [13] for stiff systems of ordinary differential equations; 50 vibrational levels of the N_2 molecule were taken into account ($v_* = 50$).

The problem was solved numerically, taking into account (2) and (3), the relation $S = \frac{1}{\hbar\omega_0}\sum_{v=1}^{v_*} E_v\psi_v$ (E_v is the energy of an anharmonic oscillator with vibrational quantum number v) and the following boundary condition for the distribution function

$$\psi_v(x = 0) = \psi_0 \exp\left(-\frac{E_v}{kT_{\text{к}}}\right),$$

where T_{vib} is a parameter (the vibrational temperature) determining the excitation of nitrogen molecules emerging from the first region. We give the results for the case when the nonequilibrium flow is characterized by the quantities $S_0 = 1$, $T_0 = 300$ K and $N_{(0)} = 2.67 \cdot 10^{19}$ cm^{-3}. Then it is found from (5) and (6) that, in the flow regimes of interest to us, the gas must be injected with the velocities $DJ_+ = 3.853c_0$, $DC_+ = 3.859c_0$, and $DJ_- = 0.245c_0$.

Graphs of the functions T(x), p(x), and S(x) are shown in Figs. 2 and 3 for shock and shock-free flow, corresponding to the points J_+ and C_+ on the relaxation adiabatic curve. For normal Jouguet detonation (Fig. 2) the pressure and temperature of the vibrationally excited gas jump to the values $p = 17.2p_0$ and $T = 3.82T_0$. In a relaxation zone of width $\delta \approx 2$ cm (the quantity δ was determined from the condition of "emission" by each molecule with vibrational energy equal to $0.7\ \omega_0[S_0 - S_p(T_1)]$), the pressure of the gas decreases monotonically to the value $9.47p_0$, the temperature increases to $5.57T_0$, and the flow velocity increases up to the local speed of sound $c_e = 2.28c_0$. In shock-free deflagration flow C_+ (Fig. 3), the width of the relaxation zone is $\delta \approx 0.5$ m. In this zone, the gas slows down to a velocity equal to the speed of sound in a gas with "frozen" vibrational degrees of freedom ($c_f = 2.36c_0$). The temperature and pressure of the gas increase monotonically to the values $5.56T_0$ and $9.09p_0$.

In Fig. 4, for the shock-free flow regime J_-, the functions T(x), ρ(x), and S(x) are shown. In this case, $\delta \approx 0.6$m. It is clear that the transition region does not have sharp boundaries with the equilibrium gas (a similar situation occurs for J_+). This is explained by the significant rarefaction of the moving gas, which leads to slowing of the final stages of relaxation. In this case the velocity of the gas increases by a factor of 7.38 (the density correspondingly decreases to the value $0.135\rho_0$).

The existence of these steady flow regimes means that we can obtain reliable information on the rate constants of VV and VT exchanges for gas temperatures that are not too high, and we can also determine the parameters of the initial state of the nonequilibrium gas. The simplest method of studying the vibrational relaxation of strongly excited nitrogen is the method of CO (or CO_2) tracing. Using infrared radiation, a small impurity of CO

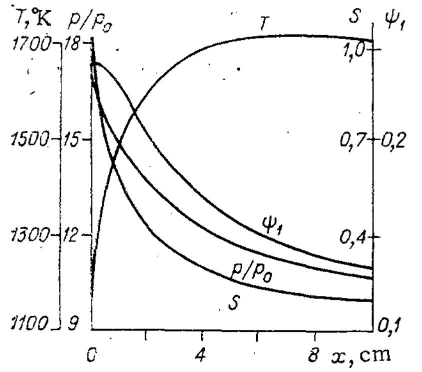

Fig. 2

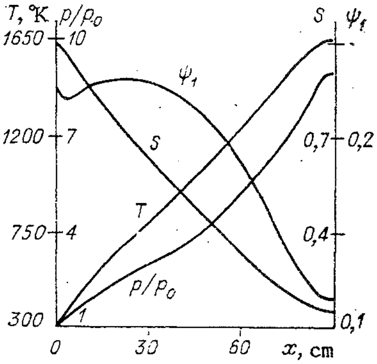

Fig. 3

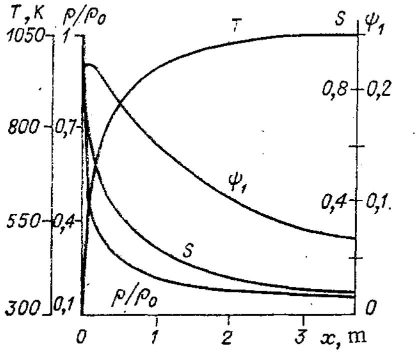

Fig. 4

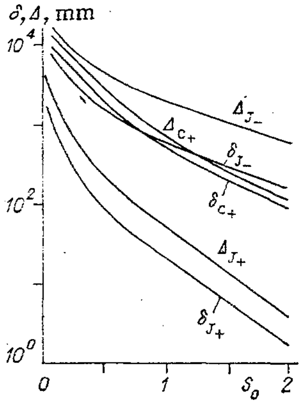

Fig. 5

(or CO_2) molecules allows one to get the spatial dependence of the relative population density of the first vibrational level of the molecules $\psi_1(x)$. This method is used mainly in experiments with shock waves (see, e.g., [14-16]), but recently it has been used to study the dynamics of vibrationally excited and heated nitrogen during and after a UHF pulse discharge [17].

In all of the figures showing the structure of the characteristic nonequilibrium flows, we also show the relative population density ψ_1 of the first vibrational level of the molecules as a function of the coordinate x. The dependence is nonmonotonic in all cases. This is especially noticeable for C_+. The same type of dependence of the quantity ψ_1 was observed in the after-discharge period of relaxation of vibrationally excited nitrogen in [17], where an explanation of this result was given. With the onset of the final stage of relaxation, the relative population of the first vibrational level becomes practically constant. Note that with the help of the CO (or CO_2) trace method, it is possible to determine the size of the transition region.

Figure 5 shows the dependence of the width of the relaxation zone for the flow regimes J_+, C_+, and J_- [for $T_0 = 300$ K and $N(\omega) = 2.67 \cdot 10^{19}$ cm^{-3}] on the initial energy of the vibrational degrees of freedom of the molecules, i.e., $\delta(S_0)$ and $\Delta(S_0)$ (Δ is the width of the transition region as determined from the condition of "emission" by each molecule with vibrational energy equal to $0.9\hbar\omega_0[S_0 - S_p(T_1)]$. The calculation shows that when $S_0 > 0.7$, the widths of the relaxation zones for the regimes J_+ and J_- can be approximated by the relatively simple expressions $\Delta J_+(S_0) \approx 54.1 \exp[-2.67(S_0 - 1)]$ and $\Delta J_-(S_0 \approx 1984 \exp[-1.12(S_0 - 1)]$, where the values of the widths are in millimeters.

In order to study the possibility of a prolonged existence of the flow regimes described above for a vibrationally excited molecular gas, it is also necessary to consider the stability of these regimes to small perturbations of the medium.

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