FLOWS OF A DISSOCIATING GAS IN THE ABSENCE OF LOCAL THERMODYNAMIC EQUILIBRIUM

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Abstract

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FLOWS OF A DISSOCIATING GAS IN THE ABSENCE OF LOCAL THERMODYNAMIC EQUILIBRIUM

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Consider flows of a dissociating homonuclear diatomic gas without taking into account viscosity, thermal conductivity, and processes at the walls. For simplicity it is assumed that the heat capacity of the molecular component is constant. The dissociation and recombination reactions proceed according to the scheme $A_2 + M \rightleftarrows 2A_1 + M$ and are assumed to be simple. Under these conditions the gas flow is described by the system of equations:

$$P = \frac{k}{2m_1}(1+\alpha)\rho T, \qquad \frac{d\ln\rho}{dt} + \nabla\mathbf{v} = 0, \qquad \frac{\rho}{P}\frac{d\mathbf{v}}{dt} = -\nabla\ln P,$$

$$\frac{1}{\gamma_f - 1}\frac{d\ln T}{dt} - \frac{d\ln\rho}{dt} + \frac{\alpha}{1+\alpha}\left(\frac{D}{kT} + \frac{2\gamma_1}{\gamma_1 - 1} - \frac{\gamma_2}{\gamma_2 - 1} - 1\right)\frac{d\ln\alpha}{dt} = 0, \quad (1)$$

$$\frac{d\ln\alpha}{dt} = -\left(\frac{\rho}{m_1}\right)^2 \frac{\alpha}{2}\left[(1-\alpha)k_2 + 2\alpha k_1\right](1-\varkappa) = -\frac{1-\varkappa}{\tau_\alpha}.$$

Here α is the degree of dissociation of the gas; D is the dissociation energy of the molecule; $\gamma_i = c_{pi}/c_{vi}$ is the ratio of specific heats for the i-th component;

$$\gamma_f = \left(\frac{1-\alpha}{1+\alpha}\frac{\gamma_2}{\gamma_2 - 1} + \frac{\alpha}{1+\alpha}\frac{2\gamma_1}{\gamma_1 - 1}\right) \Big/ \left(\frac{1-\alpha}{1+\alpha}\frac{\gamma_2}{\gamma_2 - 1} + \frac{\alpha}{1+\alpha}\frac{2\gamma_1}{\gamma_1 - 1} - 1\right);$$

k_i is the recombination-rate constant in which $M = A_i$ $(i = 1, 2)$;
$\varkappa = \alpha_{eq}^2(1-\alpha)/\alpha^2(1-\alpha_{eq})$ is a variable characterizing the deviation of the gas composition from equilibrium; α_{eq} is the degree of dissociation of the gas in the presence of local thermodynamic equilibrium, determined by the equation

$$\frac{\alpha_{eq}^2}{1-\alpha_{eq}} = \frac{g_{01}^2}{16 g_{02}} \frac{m_1^{5/2}}{\pi^{3/2}} \frac{\omega}{I} \frac{\exp(-D/kT)}{\rho\,(kT)^{1/2}}; \tag{2}$$

g_{0i} is the statistical weight of the normal state of the i-th particle; ω and I are the vibrational frequency and moment of inertia of the molecule; $\tau_\alpha = (m_1/\rho)^2(2/\alpha) \times [(1-\alpha)k_2 + 2\alpha k_1]^{-1}$ is the characteristic reaction time. Constants referring to atoms are assigned the subscript 1, those referring to molecules the subscript 2. It is easy to see that $\alpha = \alpha_{eq}$ for $\varkappa = 1$, $\alpha > \alpha_{eq}$ for $\varkappa < 1$, and $\alpha < \alpha_{eq}$ for $\varkappa > 1$.

In the case under consideration there is dispersion of sound. In this case high-frequency disturbances propagate with the frozen speed of sound a_f, and low-frequency disturbances with the equilibrium speed of sound a_{eq}. In the latter case formula (2) holds.

From equations (1) and (2) we find

$$a_f^2 = (dP/d\rho)_f = \gamma_f P/\rho, \qquad a_{eq}^2 = (dP/d\rho)_{eq} = \gamma_{eq} P/\rho, \tag{3}$$

$$\gamma_{eq} = \left[\frac{\alpha}{1+\alpha}\frac{1-\alpha}{2-\alpha}\left(\frac{D}{kT}-\frac{1}{2}\right)\left(\frac{D}{kT}+\frac{2\gamma_1}{\gamma_1-1}-\frac{\gamma_2}{\gamma_2-1}\right)+\frac{D}{kT}-\frac{2}{1+\alpha}\left(\frac{\gamma_2}{\gamma_2-1}-\frac{\gamma_1}{\gamma_1-1}\right)+\frac{1-\alpha}{1+\alpha}\frac{\gamma_2}{\gamma_2-1}+\right.$$

$$\left[\frac{\alpha}{1+\alpha}\frac{1-\alpha}{2-\alpha}\left(\frac{D}{kT}-\frac{1}{2}\right)\left(\frac{D}{kT}+\frac{2\gamma_1}{\gamma_1-1}-\frac{\gamma_2}{\gamma_2-1}-1\right)+\frac{1-\alpha}{1+\alpha}\frac{\gamma_2}{\gamma_2-1}+\frac{\alpha}{1+\alpha}\frac{2\gamma_1}{\gamma_1-1}-1\right].$$

The range of velocities between the frozen and equilibrium speeds of sound will be called the sound zone. In an extremely weakly dissociated gas, and also in an almost completely dissociated gas, when $\alpha(1-\alpha)(D/kT)^2 \ll 1$, the sound zone degenerates into the ordinary speed of sound ($\gamma_{eq} = \gamma_f$). For $\alpha(1-\alpha)(D/kT)^2 \gg 1$ and $D/kT \gg 1$, the equilibrium speed of sound coincides with the isothermal speed of sound ($\gamma_{eq} = 1$).

Let us consider a one-dimensional steady flow. Writing equations (1) for this case and solving them with respect to the derivatives, we obtain

$$(M_f^2-1)\frac{d\ln p}{dx} = -(M_f^2-1)\frac{d\ln v}{dx} = -\frac{\gamma_f-1}{\gamma_f}\frac{\alpha}{1+\alpha}\left[\frac{D}{kT}-\frac{2}{1+\alpha}\left(\frac{\gamma_2}{\gamma_2-1}-\frac{\gamma_1}{\gamma_1-1}\right)\right]\frac{d\ln\alpha}{dx},$$

$$(M_f^2-1)\frac{d\ln T}{dx} = -(\gamma_f-1)\left[M_f^2-\frac{1}{\gamma_f}\left(\frac{D}{kT}+\frac{2\gamma_1}{\gamma_1-1}-\frac{\gamma_2}{\gamma_2-1}\right)\Big/\left(\frac{D}{kT}+\frac{2\gamma_1}{\gamma_1-1}-\frac{\gamma_2}{\gamma_2-1}-1\right)\right]\frac{\alpha}{1+\alpha}\left(\frac{D}{kT}\right. \tag{4}$$

$$\frac{d\ln\alpha}{dx} = -\frac{1}{2v}\left(\frac{\rho}{m_1}\right)^2 \alpha\left[(1-\alpha)k_2 + 2\alpha k_1\right](1-\chi).$$

Here $M_f^2 = v^2/a_f^2$.

Analogous equations can be written for M_f^2 and χ:

$$(M_f^2-1)\frac{d\ln(M_f^2)}{dx} = \frac{(\gamma_f-1)^2}{\gamma_f}\left[M_f^2 + \left\{\left[\frac{D}{kT} - \frac{2}{1+\alpha}\left(\frac{\gamma_2}{\gamma_2-1} - \frac{\gamma_1}{\gamma_1-1}\right)\right]\frac{1}{\gamma_f-1} + \frac{2}{1+\alpha}\left(\frac{\gamma_2}{\gamma_2-1} - \frac{\gamma_1}{\gamma_1-1}\right)\right.\right.$$

$$\times\left[\frac{D}{kT} - \frac{2}{1+\alpha}\left(\frac{\gamma_2}{\gamma_2-1} - \frac{\gamma_1}{\gamma_1-1}\right)\right]\frac{\gamma_f}{\gamma_f-1} - \frac{2}{1+\alpha}\left(\frac{\gamma_2}{\gamma_2-1} - \frac{\gamma_1}{\gamma_1-1}\right)\Bigg]^{-1}\times$$

$$\times\frac{\alpha}{1+\alpha}\left\{\left[\frac{D}{kT} - \frac{2}{1+\alpha}\left(\frac{\gamma_2}{\gamma_2-1} - \frac{\gamma_1}{\gamma_1-1}\right)\right]\frac{\gamma_f}{\gamma_f-1} - \frac{2}{1+\alpha}\left(\frac{\gamma_2}{\gamma_2-1} - \frac{\gamma_1}{\gamma_1-1}\right)\right\}\frac{d\ln\alpha}{dx}, \quad (5)$$

$$(M_f^2-1)\frac{d\ln\chi}{dx} = -(\gamma_f-1)\left(M_f^2 - \frac{\gamma_{eq}^*}{\gamma_f}\right)\times$$

$$\times\left[\frac{\alpha}{1+\alpha}\left(\frac{D}{kT} - \frac{1}{2}\right)\left(\frac{D}{kT} + \frac{2\gamma_1}{\gamma_1-1} - \frac{\gamma_2}{\gamma_2-1} - 1\right) + \frac{2-\alpha}{1-\alpha}\frac{1}{\gamma_f-1}\right]\frac{d\ln\alpha}{dx}.$$

Here γ_{eq}^* is determined by formula (3), where α is the current, and not the equilibrium, degree of dissociation. The factor $M_f^2 - \gamma_{eq}^*/\gamma_f$ entering the right-hand side of the last equation can be written in the form $(\gamma_{eq}^*/\gamma_f)(M_{eq}^{*2} - 1)$, where $M_{eq}^{*2} = \rho v^2/\gamma_{eq}^* P$. Note that $\gamma_f^{-1} \leq \gamma_{eq}^*/\gamma_f \leq 1$.

From the condition that the derivatives remain finite in the section where $M_f = 1$, it follows that the flow velocity can reach the frozen speed of sound only when the gas reaches the equilibrium state ($\chi = 1$). (At the end of a channel such a speed can also be attained for values of χ different from unity.)

Equations (5) make it possible to obtain, in the phase plane χ, M_f^2, a picture of all possible types of gas flows brought out of an equilibrium state in some way. Figure 1 gives a qualitative picture of the behavior of the integral curves in this plane. The arrows indicate the direction of change of the variables along the flow. In regions 1–4 the flows of a dissociating gas are similar to the flows of a nonreacting gas with distributed heat addition or removal. However, in region 5 the gas, on the contrary, tends to depart from the equilibrium state, which at

Fig. 1. Qualitative picture of possible types of one-dimensional stationary flows of dissociated gas brought out of the equilibrium state

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first glance seems paradoxical. The departure of the gas from the equilibrium state is accompanied by its deceleration. It continues until the gas is decelerated to the speed $a^*_{eq} = (\gamma^*_{eq} P/\rho)^{1/2}$. After this the gas relaxes to the equilibrium state.

Parameters lying in region 6 cannot correspond to unbounded steady flows, since in this case the condition is not satisfied

finiteness of discontinuities of the derivatives for $M_f^2 = 1$. This means that, in a real flow, in this case a nonstationary process must arise that will lead to a change in the initial conditions. However, in channels of finite length such a prohibition does not apply. In that part of region 6 where the flow velocity is less than the frozen speed of sound, but greater than

$$a^*_{eq} = \left(\gamma^*_{eq} P/\rho\right)^{1/2},$$

the gas will depart from the equilibrium state, accelerating in the process. In this case the maximum velocity that can be

Fig. 1. Qualitative picture of the possible types of one-dimensional stationary flows of dissociated gas brought out of the equilibrium state

attained at the end of the channel is equal to the frozen speed of sound. In that part of region 6 where the flow velocity is less than the speed

$$a^*_{eq} = \left(\gamma^*_{eq} P/\rho\right)^{1/2},$$

the gas will approach the equilibrium state until it reaches the speed

$$a^*_{eq} = \left(\gamma^*_{eq} P/\rho\right)^{1/2}.$$

After this it will begin to depart from the equilibrium state in accordance with what was said above.

It follows from this that, for flow velocities lying in the sound zone, a one-dimensional stationary flow of an equilibrium dissociated gas cannot occur. Accordingly, equilibrium theory is not applicable for describing flows in this range of velocities, whatever the values of the characteristic reaction times. Thus, the nonequilibrium theory passes into the equilibrium theory not as the characteristic reaction time tends to zero, but when the sound zone degenerates into the ordinary speed of sound (the condition for such degeneration was given above).

The departure of the gas from the equilibrium state in the sound zone can be explained as follows. It is known that, in the flow of an ordinary nonreacting gas, in the region where its velocity is less than the adiabatic but greater than the isothermal speed of sound, removal of heat from the gas leads to such a deceleration of the flow that the gas temperature increases, while addition of heat to the gas leads to such an acceleration of the flow that the gas temperature decreases. The sound zone lies in this range of velocities, coinciding with it under the conditions indicated above. If within it $\alpha < \alpha_{eq}$, then the gas, tending to return to the equilibrium state, will begin to dissociate. But dissociation is accompanied by absorption of heat, which in this zone must lead to an increase in temperature and in the equilibrium value of the degree of dissociation. (We note that the maximum temperature, to within a quantity small relative to D/kT, is reached at the isothermal speed of sound.) This will cause further dissociation, etc. The departure of the gas from the equilibrium state is explained analogously in the case when $\alpha > \alpha_{eq}$ (in a channel of finite length).

Obviously, such a departure of the gas from the equilibrium state must occur in any reversible endothermic processes. (The departure of the gas from the equilibrium state in the case of excitation of the vibrational degree of freedom was found earlier in [1].)

The acceleration of a one-dimensional steady flow of a dissociating gas in a channel of finite length in the sonic zone has not previously been described in the literature. On the contrary, the deceleration of a one-dimensional steady unbounded flow of a dissociating gas in the sonic zone is well known (see [2-4]). However, an explanation of the mechanism of such deceleration, which is quite different from the mechanism of deceleration of a gas in the viscous front of a shock wave, has not previously been given.

The conditions at a shock wave in a dissociating gas can be written in the form

$$\frac{1+\alpha_A}{U_A}\,\gamma_{fA}\,\frac{\left(M_{fA}^2+1/\gamma_{fA}\right)^2}{M_{fA}^2}=\frac{1+\alpha_B}{U_B}\,\gamma_{fB}\,\frac{\left(M_{fB}^2+1/\gamma_{fB}\right)^2}{M_{fB}^2}, \tag{6}$$

$$\frac{1+\alpha_A}{U_A}\,\gamma_{fA}\left(M_{fA}^2+\frac{2}{\gamma_{fA}-1}\right)+2\alpha_A=\frac{1+\alpha_B}{U_B}\,\gamma_{fB}\left(M_{fB}^2+\frac{2}{\gamma_{fB}-1}\right)+2\alpha_B.$$

Here the indices A and B denote the values of the variables before and behind the shock wave, respectively. The equilibrium values $\alpha_{A,B}$ are determined by equation (2), which can be written in the form

$$\frac{\alpha_{A,B}^2}{1-\alpha_{A,B}}=\frac{g_{01}^2}{16\sqrt{2g_{02}G}}\,\frac{m_1^2}{\pi^{3/2}}\,\frac{\omega}{I}\,\sqrt{(1+\alpha_{A,B})\gamma_{fA,B}}\,M_{fA,B}\exp\left(-\frac{D}{kT_{A,B}}\right). \tag{7}$$

Here $G = \rho v = \text{const}$.

In the viscous front one may put $\alpha = \text{const}$. The values of the variables behind the viscous front, denoted by the index C, are related to the values of the variables before the shock-front by the relations

$$M_{fC}^2 = \frac{\gamma_{fA} - 1}{2\gamma_{fA}} \frac{M_{fA}^2 + 2/(\gamma_{fA} - 1)}{M_{fA}^2 - (\gamma_{fA} - 1)/2\gamma_{fA}},$$

$$\frac{T_C}{T_A} = \frac{2\gamma_{fA}(\gamma_{fA} - 1)}{(\gamma_{fA} + 1)^2 M_{fA}^2} \left(M_{fA}^2 + \frac{2}{\gamma_{fA} - 1} \right) \left(M_{fA}^2 - \frac{\gamma_{fA} - 1}{2\gamma_{fA}} \right), \qquad (8)$$

$$\chi_C = \left[\frac{\gamma_{fA} - 1}{2\gamma_A M_{fA}^2} \frac{M_{fA}^2 + 2/(\gamma_{fA} - 1)}{M_{fA}^2 - (\gamma_{fA} - 1)/2\gamma_{fA}} \right]^{1/2} \left\{ \frac{g_{01}^2}{16\sqrt{2g_{02}}} \frac{m_1^2}{\pi^{3/2}} \frac{\omega}{I} \times \right.$$

$$\left. \times \frac{1 - \alpha_A}{\alpha_A^2 G} \left[(1 + \alpha_A)\gamma_{fA} M_{fA}^2 \right]^{1/2} \right\}^{({M_{fA}}^2 - 1)(M_{fA}^2 + 1/\gamma_{fA})^v / [M_{fA}^2 + 2/(\gamma_{fA} - 1)]\, [M_{fA}^2 - (\gamma_{fA} - v)/2\gamma_{fA}]} .$$

On the phase plane χ, M_f^2 in Fig. 1, the values of the variables behind the viscous front are indicated by a dashed line. If $M_{fC}^2 \leq \gamma_{eq}^*/\gamma_f$ ($M_{fA}^2 \geq M_{fAD}^2$), then in the viscous front of the shock wave the gas departs from the equilibrium state, and in the adjacent relaxation zone it reaches a new equilibrium state (the curve N'—N'' in Fig. 1). For $\gamma_{eq}/\gamma_f < M_{fA}^2 < 1$ there always exists a special shock wave without a viscous front (the curves Q—Q'' and R—R'' in Fig. 1). The mechanism of the departure of the gas from the equilibrium state in it, associated with the impossibility of an equilibrium flow in the sonic zone, was described above. The departure of the gas from the equilibrium state in a special shock wave takes place until the gas is decelerated to a velocity equal to $a_{eq}^* = (\gamma_{eq}^* P/\rho)^{1/2}$. After this the gas relaxes to a new equilibrium state. For $1 < M_{fA}^2 < M_{fAD}^2$ both mechanisms of departure of the gas from the equilibrium state act simultaneously in the shock wave (see the curve P'—P''' in Fig. 1).

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Note: Figure translations are in progress. See original paper for figures.