Analytical estimation of relative maximum of molecular pairs distribution in shock wave

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Abstract. Results on an analytical study of the translational nonequilibrium effect in the shock wave are presented. They were formulated systematically in authors articles. The analytical models of high-velocity translational nonequilibrium in binary gas mixtures are considered. A correct analytical calculation for maximum value of molecular pairs distribution in the shock-compressed gas mixtures is given.

1. Introduction

At present, there are no definite specific recommendations on the optimal design of an experiment with shock waves, which would make it possible to conduct this experiment optimally, taking into account the strong influence of high-speed translational nonequilibrium in the shock wave front. Such recommendations can be made using an analytical approach to the study of the shock waves structure. This approach may be useful to complement the numerical and semi-analytical methods, the use of which is somehow limited by their accuracy. Difficulties in the application of numerical methods [1-3] are usually due to very small number of particles of the heavy component and the high activation threshold of chemical molecular and cluster reactions. The orientation of the molecules at the interface was considered in [4-6]. The application of analytical methods is free from these difficulties. In the papers [7-9], a number of significant results were obtained:

(i) a necessary and sufficient condition for the effect of high-speed translational nonequilibrium inside the shock wave front;

(ii) universal analytical representation of the velocity coefficients of high-threshold progressively nonequilibrium chemical reactions, taking into account the anisotropy of kinetic temperatures in shock waves.

One of main goals of analytical studies of the effects of high-speed overlap is to obtain as simple as possible estimations of the magnitude of this effect in shock waves.

Analysis of the results of numerical studies of the shock wave structure carried out by the Monte Carlo method allows us to identify four main physical factors of activation of the velocities of inelastic threshold collisions of molecules in the shock wave. These include:

• the resulting decrease in the activation energy of inelastic collisions of molecules pairs in the shock wave, which occurs due to the shift of velocities between the velocities of supersonic and subsonic beams of molecules in the bimodal distribution of Tamm-Mott-Smith;
• a significant decrease in the velocities of equilibrium inelastic collisions in the "hot" region after the jump, due to the strong dilution of the binary gas mixture with a light component;

• a similar decrease in the rate of equilibrium inelastic collisions of molecules pairs of the "hot" region after the jump, due to the presence of a certain number of internal degrees of freedom of molecules of the polyatomic light component of the binary mixture (this is equivalent to a drop at the equilibrium thermodynamic temperature compared to the kinetic inside the wave. The drop will be the greater the more degrees of freedom of the polyatomic light carrier component. An example is the binary mixture is 99% NH$_3$ – 1% C$_{70}$);

• a significant increase in the velocities of inelastic high barrier collisions of vapor molecules due to a significant difference in kinetic temperatures in the directions along the flow and across to it in the heavy component in the shock wave (the effect of anisotropy of the kinetic temperatures of the translational degrees of freedom of the heavy component in the Rayleigh gas mixture) [10].

In this paper, the effect of the first two factors is analyzed in more detail.

2. The hypersonic stabilization in the relative velocity molecular distribution of one component shock–compressed gas

In the shock waves with the binary gas mixtures, three different functions are distinguished: $G^{(ll)}, G^{(lh)}, G^{(hh)}$. They are the functions of the distribution of the molecules pairs modulo the relative velocity. The function $G^{(ll)}$ refers to the distribution of the molecules pairs within the light component. The function $G^{(lh)}$ refers to a pair of molecules from both light and heavy component, and the function $G^{(hh)}$ refers to the molecules pairs of the heavy component.

The evolution of the distribution of pairs of $G^{(ll)}$ molecules is virtually identical to the corresponding function of pairs of molecules in a single-component gas. It has a maximum of $G^{(ll)}_{\max}$ inside the shock front. This maximum $G^{(ll)}_{\max}$ is

$$ G^{(ll)}_{\max} \approx \varepsilon \exp \left( \frac{1}{2\varepsilon} \right). $$

Here $\varepsilon^{-1}$ is the compression ratio in the shock wave, where $\varepsilon = \rho_\infty / \rho_S$, $\rho_\infty$ is the value of the gas density before the jump, and $\rho_S$ is the value of the gas density behind it, $G^{(ll)}_{\max} = G^{(ll)}_{\max}/G^{(ll)}_S$.

The formula (1) is obtained asymptotically for $\varepsilon = \rho_\infty / \rho_S \to 0$. It is important to note that the overlap effect, i.e. the ratio $\tilde{G}^{(ll)}_{\max} = G^{(ll)}_{\max}/G^{(ll)}_S$, (where $G^{(ll)}_S$ is the equilibrium distribution function of the molecules pairs per jump), depends only on the degree of compression in the jump $\varepsilon^{-1}$.

This fact has not been noted in the numerical studies and demonstrates the usefulness of the analytical methods in determining the value of $G^{(ll)}_{\max}$. Thus, we see that the law of hypersonic stabilization, i.e. the dependence of macroparameters of the flow behind the shock wave only on the compression ratio $\varepsilon^{-1}$, obey not only the gas dynamic macroparameters (temperature, velocity, gas flow density), but also the parameters of molecular kinetics, in particular the ratio $G^{(ll)}_{\max}/G^{(ll)}_S$ (flow microparameter).

The values of the function $G^{(ll)}_{\max}$, given by the formula (1) are given in table 1 for different values of the parameters $\gamma$ or $\varepsilon$, $\varepsilon = \gamma - 1/\gamma + 1$.

The symbol A denotes a variety of gas molecules with different number of atoms. Thus, symbols (A), (A$_2$), (A$_3$) denote molecules of monatomic, diatomic and triatomic gases respectively. The last column of the table shows the values of the parameters $\gamma$ and $\varepsilon$ of the polyatomic molecule CsH$_{16}$.

The numerical values of the function $G^{(ll)}_{\max}$ given in table 1 indicate that it increases very rapidly (exponentially) with a relatively small change in the parameter $\varepsilon$. For the practical use
Table 1. Maximum ”overshoot” $\tilde{G}_{\text{max}}^{(ll)}$ in the mixture of two gases

| Gas  | $A$ | $\gamma$ | $\varepsilon$ | $\tilde{G}_{\text{max}}^{(ll)}$ |
|------|-----|----------|---------------|-------------------------------|
| $A_2$ | linear, none vibration | $5/3$ | $1/4$ | $1.31$ |
| $A_2$ | linear, with vibration | $7/5$ | $1/6$ | $2.37$ |
| $A_3$ | nonlinear | $9/7$ | $1/8$ | $4.84$ |
| $C_8H_{16}$ | | $7/6$ | $1/13$ | $36/28$ |

of the overlap effect of this function, as well as its observation, it is necessary, as the experiment shows, that its value is of the order of $10^4$ and more. We see that only the data of the last column of table 1 meet this requirement. This raises the question of the possibility of excitation of the required number of degrees of freedom of a polyatomic molecule at the thickness of the shock wave. Note those possible cases where such excitation has time to occur. The first case is the preliminary excitation of the required number of vibrational degrees of freedom before the shock wave front. The second case is the implementation of the effect of high-speed overlap in the Rayleigh gas mixture, appropriately selected components of this mixture. It is necessary that at the equalization lengths (relaxation lengths) of the temperature and velocities of the heavy and light components in the light polyatomic component (type NH$_3$) the required number of oscillations is excited. Such a mixture may include, for example, 99% NH$_3$ – 1% C$_{70}$ or the Rayleigh mixture in a cluster thermonuclear.

3. The hypersonic stabilization in the relative velocity molecular distribution of disparate concentration shock–compressed gas mixtures

The distribution functions of the component pairs $G^{(ll)}$ (light component) and $G^{(lh)}$ (light–heavy) detect the effect of a high-speed ”overlap”, quantitatively close to the corresponding effect in the single–component gas, during their evolution inside the shock wave front. The strongest effect is observed for function $G^{(hh)}$ (heavy component).

It can be shown that the strengthening effect of the ”overlap” for the heavy component is due to the fact that the mod $\tilde{G}_{01}^{(hh)}$ contains in the exponent of the exponential the ratio of the mass of the heavy component to the equilibrium temperature of the gas behind the shock wave, defined by the predominance of the light component in the gaseous mixture.

For the Rayleigh mixture with a significant predominance of the $n_l$ concentration of the light component over the concentration of heavy $n_h$, for example, in the case of inequality $10 < n_l/n_h < 10^4$, it is not difficult to calculate the maximum effect of the high-speed overlap, similar to the calculation made earlier for a simple gas [7, 11]. For the maximum value of the distribution function of the pairs of the heavy component of the mixture $\tilde{G}^{(hh)}$, when the ratio of the mass of the molecule of the heavy component $m_h$ to the mass of the molecule of the light $m_l$ is two and four, one can make table 2.

It clearly follows from the table that both the increase in the number of excited internal degrees of freedom of the predominant light carrier (leading to a decrease in the $\varepsilon$ parameter) and the decrease in its molecular weight (leading to an increase in the $m_h/m_l$ ratio) lead to an increase in the value of the high–speed overlap $\tilde{G}_{\text{max}}^{(hh)}$.

It is to note that the possibility of this analytical consideration of the overlap effect in the heavy component of the Rayleigh gas, is strongly diluted with the light polyatomic component with internal degrees of freedom, was previously justified by the results of numerical calculations in [12].
Table 2. Maximum "overshoot" $\tilde{G}_{\text{max}}^{(hh)}$ in the mixture of two gases

| Gas   | A     | $(A_2)$ linear molecule without vibrational degree freedom | $(A_2)$ linear molecule factored in vibrational degree freedom | A     | $(A_2)$ linear molecule without vibrational degree freedom | $(A_2)$ linear molecule factored in vibrational degree freedom |
|-------|-------|----------------------------------------------------------|-----------------------------------------------------------|-------|----------------------------------------------------------|-----------------------------------------------------------|
|       | γ     | 5/3                                                      | 7/5                                                       | 9/7   | 5/3                                                      | 7/5                                                       |
|       | ε     | 1/4                                                      | 1/6                                                       | 1/8   | 1/4                                                      | 1/6                                                       |
|       | $G(h, h)$ | 1.86                                                  | 2.8                                                       | 11.7  | 3.1                                                      | 3.9                                                       | 119 |

4. Conclusion
This analytical estimate can be useful when conducting aerodynamic experiment in shock tubes. Such experiments could include study of an initial stage of translational non-equilibrium processes of pyrolysis with high velocity overshoot effect.

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