Hypersonic approximation for distribution function of pairs of molecules in shock wave

M M Kuznetsov, Y D Kuleshova, A A Perov and L V Smotrova
Moscow Region State University, Vera Voloshina str., 24, Mytishchi, Moscow Region, 141014, Russia

E-mail: kuznets-omm@yandex.ru, juliaybogdanova@mail.ru, xok91.91@mail.ru, lilysmotrova@mail.ru

Abstract. New results of an analytical study of translational nonequilibrium in a shock wave are presented that are associated with the use of the exact expression for the longitudinal kinetic temperature $T_x$ in a simple gas. It is shown that the relative magnitude of the overshoot effect for the distribution function of the pairs of molecules inside the shock front satisfies the principle of independence from the Mach number. Asymptotically exact expressions are obtained for the effect of high-speed overshoot of the pair distribution function: “light” - “heavy” component.

1. Introduction

Earlier, in our previous papers [1–4] on the analytical study of the overshoot in the shock waves, a number of significant results were obtained based on commonly used analytical representations of single-particle functions with respect to the velocities of molecules in a shock wave. As is known, these include the Tamm - Mott - Smith approximations, the ellipsoidal distribution of Holway over the velocities of molecules, etc. The essence of the effects of overshoot, as you know, is to exceed the values of any macroscopic parameter or the distribution function of the pairs of molecules inside the shock wave front over the corresponding values behind it. In the latter case, this type of overshoot for the distribution function of the molecules pairs is also called high-speed translational nonequilibrium [5]. The main attention was paid to obtaining a general form of the analytical dependence of the distribution function of pairs of molecules on the determining parameters both in simple (single-component) and in binary mixtures [2]. This original result of the authors allowed them to identify four main physical factors that control the mechanism of effects of overshoot inside the shock front:

- effective reduction of the threshold of chemical reactions inside the front of the shock wave due to the "beam" nature of the bimodal distribution function of the Tamm-Mott-Smith;
- a decrease in the rate of equilibrium chemical reactions in the "hot" zone behind the front of the shock wave due to the strong dilution of the "Rayleigh" gas by the predominant light carrier;
- a decrease in the rate of equilibrium high-threshold chemical reactions in the “hot” zone behind the front of the shock wave due to the energy costs of dissociation (a decrease in the equilibrium statistical temperature compared with the kinetic temperature inside the shock wave front);
- acceleration of the rates of the high-threshold chemical reactions due to the anisotropy of the kinetic temperature field inside the shock wave.
In order for the overshoot effect in the rates of physicochemical processes to significantly affect the flow behind the front, it is necessary, as shown by numerical experimental studies, that its value should be no less than 10⁴. Such a multi-order separation in the rates of kinetic translational-nonequilibrium processes orients First of all, on the accurate account of orders of magnitude, and not coefficients of the order of unity. This justifies the use of the previously used authors in the corresponding a priori analytical approximations.

At the same time, with such analytical approximations, the influence of the collision cross section of the molecules on the form of their distribution function is missed. Full consideration of this fifth factor determining the overshoot effect requires an exact solution of the Boltzmann kinetic equation. At present, such a solution for the structure of the shock wave has been obtained only by numerical methods [6]. Obtaining a similar analytical solution within the entire front of the shock wave is much more difficult. However, as shown in this paper, it can be obtained locally, in separate sections of the flow. Along with this, in this work, we use the exact distribution of the longitudinal kinetic temperature to estimate the effect of the overshoot of the distribution function of the pairs of molecules in a simple gas.

2. The relative value overshoot effect of the distribution function of pairs molecules in shock wave with ellipsoidal distribution

The ellipsoidal velocity distribution function of individual molecules was previously used in [1] to calculate the profiles of macroparameters. However, for the analytical calculation of the acceleration of the rates of activated physicochemical processes, that is, the effect of their overshoot in the shock wave, knowledge of the one-particle function is not enough. For this purpose, a distribution function of pairs of colliding molecules is required. Such a function was obtained earlier in the authors' work [2].

The ellipsoidal distribution takes into account the anisotropy of the kinetic temperature field inside the shock front. As a rule, the kinetic temperature in the direction of flow is higher than in the direction perpendicular to it. Moreover, this temperature is not only higher than the “perpendicular” temperature, but also exceeds in some region the equilibrium temperature behind the wave front. This is a manifestation of the overshoot longitudinal temperature effect. Note that the effect of the overshoot longitudinal temperature is a fundamental scientific fact. This effect was discovered experimentally [7] and obtained strictly theoretically based on the laws of conservation of mass and momentum flows in a shock wave [8]. An immediate consequence of [8] is that any new theory related to the study of the structure of the shock front must necessarily be checked for coincidence with the reference curve for the longitudinal temperature $T_x$.

In the present work, the reference temperature dependence $T_x$ on a variable particle concentration (or a variable macro velocity of a gas flow) was used to calculate the relative overshoot of pairs of molecules.

As is known the hypersonic approximation used in this work corresponds to the tendency of the Mach number of the free flow to infinity [9]. Based on the previous results of the authors of [2], it can be shown that, in the hypersonic approximation, the relative overlap effect for the distribution function of the pairs of molecules $\tilde{G}_{neq}$ will be equal to:

$$\tilde{G}_{neq} \sim exp \left\{ \left( \frac{g}{u} \right)^2 \left[ \frac{1}{2} \left( \frac{1}{2} - \varepsilon \right)^2 / \varepsilon (1 - \varepsilon) \right] \right\},$$

where $\tilde{G}_{neq} = G_{neq}/G_{eq}$, $G_{neq}$ is the translational nonequilibrium, ellipsoidal distribution function of the pairs of molecules inside the shock front, $G_{eq}$ is the equilibrium distribution function of the pairs of molecules behind the wave front, $g$ is the relative velocity modulus $\tilde{g}$, $u$ is the free flow velocity in front of wave front, $\varepsilon$ is the ratio of the flux densities in front of and behind the wave front.

Table 1 gives an estimate of the overshoot effect value for the ellipsoidal distribution function of pairs of molecules in a simple gas. The parameters in this table are the parametrically set absolute value of the relative velocity of molecules $g$ in gauges of the velocity of the flow $u$ incident on the shock wave. Values of $g$ equal to $3u$ and $5u$ approximately correspond to the activation energies of
high-threshold chemical reactions, starting with values of several eV. The parameter $\varepsilon^{-1}$ corresponds to the ultimate compression in an infinitely strong shock wave with a Mach number $M, M \to \infty$.

### Table 1. The overshoot effect value $G_{\text{neq}}$ in simple gas

| $g/\varepsilon$ | $u$ | $3u$ | $5u$ |
|-----------------|-----|-----|-----|
| $1/4$           | $10^{0.1}$ | $10^{1.3}$ | $10^{3.6}$ |
| $1/6$           | $10^{0.3}$ | $10^{3}$ | $10^{9}$ |
| $1/7$           | $10^{0.4}$ | $10^{4}$ | $10^{10}$ |

It can be directly seen from formula (1) that the effect of high-speed overshoot $G_{\text{neq}} > 1$ satisfies the principle of independence from the Mach number $M$ of the free flow. It should be emphasized that the quantity $G_{\text{neq}}$ is a microscopic characteristic of the gas, since it depends on the modulus of the relative velocity of molecules $g$. Thus, the principle of independence from the Mach number can be satisfied not only for the macrocharacteristics of the hypersonic flow behind the front of the shock wave.

From formula (1) it also follows that the overlap effect $G_{\text{neq}} > 1$ will certainly hold for the values of the parameter $\varepsilon > 1/2$. In a simple gas with a minimum number of degrees of freedom equal to 3, the value of $\varepsilon$ will be equal to 1/4. For a gas with rotational degrees of freedom, when the total number of degrees of freedom becomes equal to 5 (linear molecule) or 6 (non-linear molecule), $\varepsilon$ will be equal to 1/6 and 1/7, respectively. With a further increase of the internal degrees of freedom number, the parameter $\varepsilon$ will be even smaller. Thus, relation (1) is always feasible.

It should also be noted a very fast (exponential) increase of the overshoot effect value with a relatively small change in the parameter $\varepsilon$.

### 3. Estimation of the value of high-speed overshoot $G_{\text{neq}} > 1$ with asymptotically exact knowledge of the distribution function of pairs of molecules in highly dispersed shock-compressed gas mixtures

It is known that in highly dispersed gas mixtures of gases, when the concentration of the light component $n_l$ significantly exceeds the concentration of the heavy component $n_h, n_l \gg n_h$, the effect of high-speed overshoot is significantly enhanced [5]. If we consider the Rayleigh gas, when the inequality $n_l \gg n_h$ is accompanied by another inequality $m_l \ll m_h$, a strong separation arises in the value of the characteristic relaxation times (times of equilibrium) of the light and heavy components. The shock wave bifurcates, as it were. First, the light component comes to equilibrium, passing through the shock wave in its gas. Then, at much longer times (with respect to $m_h/m_l$ [10]), the heavy component comes to equilibrium.

Such an asymptotic situation provides additional opportunities for an exact analytical solution to the problem of high-speed overshoot.

In this regard, we consider a binary Rayleigh mixture of gases and analyze the main physical features of relaxation processes. It is quite clear that in the Rayleigh gas mixture the light component is the first to arrive at the state of thermodynamic equilibrium. By this moment, the heavy component arrives even in the frozen state, which asymptotically coincides with the locally equilibrium state ("cold") in front of the shock wave front.
Thus, it becomes possible to analytically compose the distribution function of pairs of light and heavy molecules based on asymptotically exact single-particle distribution functions for the light (“hot Maxwellian”) and heavy (“cold Maxwellian”) components of the Rayleigh mixture.

We emphasize the radical difference between the use of “cold” and “hot” Maxwellians when constructing the distribution function of pairs of molecules based on the Tamm – Mott Smith method and the asymptotic case of the Rayleigh gas mixture under consideration. In the first case, the “cold” and “hot” Maxwellians are taken in completely different, infinitely distant from each other, in flow sections in front of and behind the shock wave. In the case of a Rayleigh mixture, these Maxwellians are taken in the same section, characterizing the asymptotically final stage of the arrival of the light component of the mixture to thermodynamic equilibrium behind the front of the shock wave in the light gas. At the same time, it can be shown that the so-called Tamm - Mott cross mode of the Smith function of the distribution of pairs of molecules will mathematically exactly coincide with the distribution function of the pairs of molecules of the Rayleigh gas mixture in the cross section of the arrival of the light component to equilibrium.

For the boundary number of excited internal degrees of freedom, the maximum of high-speed overshoot $G_{\text{neq}}^{(th)} > 1$ can be represented in the following table 2:

Table 2. The value of “overshoot” $G_{\text{neq}}^{(th)}$ at the beginning of the relaxation zone of the heavy component

| Gas       | A  | (A2) linear, none vibration | (A2) linear, with vibration | (A3) nonlinear |
|-----------|----|-----------------------------|-----------------------------|----------------|
| $\gamma$  | 5/3| 7/5                         | 9/7                         | 7/6            |
| $\varepsilon$ | 1/4| 1/6                         | 1/8                         | 1/13           |
| $G_{\text{max}}^{(th)}$ | 1.31 | 2.37                        | 4.84                        | 3628           |

Here the symbol $A$ denotes a variety of gas molecules with different number of atoms. Thus, symbols $(A)$, $(A2)$, $(A3)$ denote molecules of monatomic, diatomic and triatomic gases respectively, $G_{\text{neq}}^{(th)} = G_{\text{neq}}^{(th)} / G_{\text{eq}}^{(th)}$, $G_{\text{neq}}^{(th)}$ - the translationally-nonequilibrium distribution function of the pairs of molecules inside the shock front, $G_{\text{eq}}^{(th)}$ is the equilibrium distribution function of the pairs of molecules behind the wave front.

From the data in Table 2, one can draw a conclusion similar to the conclusion from the data in Table 1 about a very fast (exponential) increase in the function $\tilde{G}_{\text{neq}}^{(th)}$ with a relatively small change in the parameter $\varepsilon$.

**Conclusion**

The exact expression for the longitudinal kinetic temperature in a shock wave was used in the calculation of the effect of high-speed overlap in a simple gas.

Asymptotically exact expressions of single-particle distribution functions of the components of the Rayleigh mixture are used to determine the effect of high-speed overlap. The asymptotically exact value of this effect was obtained by the time the process of relaxation of the light component was completed.

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