FORM OF DISTRIBUTION OF ABSOLUTE AND RELATIVE VELOCITIES OF MOLECULES IN A STRONG SHOCK FRONT. MONATOMIC ONE-COMPONENT GAS

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In the hydrodynamics of an ideal fluid the shock wave is a geometrical surface dividing two thermodynamically equilibrium states of the medium. From the molecular-kinetic point of view this discontinuity surface is an approximation of a transition layer, i.e., the shock front, in which there occurs the evolution of the velocity distribution of molecules from one Maxwellian distribution, corresponding to the gas ahead of the shock wave, to another, corresponding to the gas behind the shock wave. The state of the gas in the shock front is so very different from the equilibrium state and changes so rapidly that the only admissible approach for the description of the phenomenon is the use of the nonlinear Boltzmann equation. The solution of this equation, in principle, allows one to obtain detailed information on the nonequilibrium distribution function; however, in the study of the motion of a gas across the transition layer, attention is focused not on the distribution itself, but on the computation of the spatial mean velocities and of the macroscopic quantities (density, mean velocity, and temperature).

The form of the distribution itself (and, in particular, the form of the high-velocity tail of the distribution) becomes especially important in the case when quantities with a threshold nature of the velocity dependence are being averaged and the threshold lies in the range of velocities corresponding to the tail of the distribution. Among such quantities are the cross sections of many chemical reactions whose occurrence is associated with the surpassing of the activation potential barrier at the expense of the energy of the colliding molecules. Therefore, an explanation of the characteristics of the relaxation process in a strong shock front may be of help in understanding the role played by this transition region in chemical transformations initiated by the shock wave.

The object of the present work is to study the evolution of the form of the velocity distribution of molecules and of the relative velocity distribution of molecule pairs in the zone of the shock.

Such investigations have become feasible only in recent years as a result of intense development of numerical methods [1-3].

At present there are two clearly marked directions in this field, which are apparently the most promising.

The first of these is based on computer simulation of the investigated phenomenon and statistical computation of the elementary collision events in a model gas [4-6]. Among the methods using this approach, Bird's method is the best known [5]. Its basic advantages are the relatively low level of demands on the computer memory and the absence of constraints on the form of the desired solution and of the potential of the intramolecular forces, which enable one to investigate the structure of a strong shock wave in a gas consisting of rigid spherical molecules and to obtain the distribution functions of the longitudinal and transverse components of the intrinsic velocities at different points of the wave with Mach number $M = 10$.

The second direction involves the development of schemes of numerical solution of the Boltzmann equation. The main difficulty in its solution, even for one-dimensional stationary motion of a gas (for example, the motion of a gas in a plane shock wave), lies in the evaluation of integrals of large multiplicity. The Monte Carlo method [7], developed for this

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purpose, has been successfully applied to the solution of the problem of shock-wave structure [8].

Another suitable method is to construct successive approximations, specifically choosing the intramolecular potential, the symmetry of the problem, and the initial conditions so that a significant reduction in the multiplicity of the integrals will result.

The use of the method of integral equations [9] in the problem of the shock-wave structure in a gas consisting of Maxwellian molecules has offered the possibility of obtaining, in the first approximation, an analytic form of the velocity distribution function [10]. In spite of the fact that the convergence of the successive approximations is not proved for the general case, it has been confirmed by test numerical solutions, in which the method of integral equations is combined with the statistical method of computing the collision integral [11].

In the present work we compare the distribution functions of the absolute velocities of the molecules and the relative velocities of molecule pairs in a shock wave with M = 5 computed by the method of direct simulation [5].

We consider a one-dimensional stationary shock wave in an ideal monatomic gas. The discrete description of the gas is carried out with the use of the distribution function $f(x, u_x, u_y, u_z) = f(x, \mathbf{u})$, which determines the mean density of the molecules in the phase space composed by the spatial coordinate x and the three velocity coordinates u_x, u_y, and u_z. It is assumed that the gas is in the equilibrium state at infinite distances upstream and downstream; therefore, the distribution function satisfies the asymptotic (boundary) conditions

$$\begin{aligned} f(-\infty,\ \mathbf{u}) &= f_1(\mathbf{u}) = n_1(h_1/\pi)^{3/2}\exp\,[-h_1(\mathbf{u}-\mathbf{U}_1)^2],\\ f(+\infty,\ \mathbf{u}) &= f_2(\mathbf{u}) = n_2(h_2/\pi)^{3/2}\exp\,[-h_2(\mathbf{u}-\mathbf{U}_2)^2], \end{aligned} \tag{1}$$

where $\mathbf{U}_i = (U_i, 0, 0)$; U_1 and U_2 are, respectively, the flow velocities ahead of the wave and behind it. The conditions in the gas on the two sides of the shock wave are related through Rankine–Hugoniot equations, which represent the laws of conservation of mass, momentum, and energy:

$$h_2/h_1 = 16M^2/(M^2+3)(5M^2+1), \quad n_1/n_2 = u_2/u_1 = (M^2+3)/4M^2,$$

where $M = (6/5h_1)^{1/2}U_1$ is the Mach number for the shock wave.

The relative velocity distribution function of the molecule pairs is defined through the function $f(x, \mathbf{u})$ in the following way:

$$G(x, u_{\text{rel}}) = \int\limits_{|v|=u_{\text{rel}}} f(x, \mathbf{u}+\mathbf{v})\, f(x, \mathbf{u})\, d\mathbf{u}d\mathbf{v}.$$

It can be verified by direct integration that for Maxwellian distributions $f_i(\mathbf{u})$ we have

$$G_i(u_{\text{rel}}) = n_i^2\sqrt{\frac{2}{\pi}}\, h_i^{3/2} u_{\text{rel}}^2 \exp\left(-\frac{h_i}{2}\, u_{\text{rel}}^2\right).$$

The method of direct modeling [5] is used for a statistical numerical simulation of the Boltzmann equation by computing the motion of several thousand molecules modeling a one-dimensional stationary shock wave in the gas. The field of the modeled flow is divided into spatial cells which are much smaller than the scale of the changes in the flow. Boundary conditions (1) are set up at the ends of the segment $[-x_0, x_0]$.

At the initial instant of time the molecules with a velocity distribution corresponding to the function $f_1(\mathbf{u})$ are uniformly distributed over the cells on the segment $[-x_0, 0]$. At this instant a mirror-reflecting plane piston whose operating surface is perpendicular to the direction of the flow is introduced into the flow and starts moving from the point $x = 0$ to the point $x = x_0$ with a velocity U_2. The evolution of this system over a time Δt, which is taken small compared to the mean local time between collisions, is divided into two stages. In the first stage only the velocities of the molecules in the cells change because of the collisions during the time Δt. In the second stage the displacement of the molecules occurs in conformity with the time interval Δt and their instantaneous velocities. The collisions between the molecules in each cell are treated statistically and the trajectories of the molecules in between the collisions are computed accurately.

The time interval during which the piston reaches the boundary downstream from the center is sufficient for establishing a stationary shock-wave profile. After this, the required flow characteristics can be measured. The method gives a numerical solution of the Boltzmann equation [12], whose accuracy increases with an increase in the time interval Δt, a decrease in the cell dimensions, and an increase in the number of modeled molecules in each cell.

In the realization of the method adopted by us, the molecular model of elastic spheres is used; the length of the cell is equal to the mean free path of the molecules λ_1 upstream; the total number of cells in the segment $[-x_0, x_0]$ is 30-40; the initial number of molecules was put equal to 300-400; and the final number of molecules in the segment $[-x_0, x_0]$ is 1500-2000. The time Δt is computed during the operation of the program in the following way. After the termination of the next cycle of m displacements of each of the cells lying to the left of the piston, the mean relative velocity of the molecules u_{rel} is calculated. The mean time between collisions t_m is obtained by averaging the quantity $(\pi a^2 n u_{rel})^{-1}$ over all the cells to the left of the piston; here a is the diameter of the molecules, and n is the density of the molecules in a given cell. The time Δt is taken equal to t_m/m. The number m is usually put equal to 5. The velocities after the collision are computed according to the algorithm of [4]. In order to reduce the statistical scatter, several measurements of the distribution function (usually 4-6) are averaged, the measurements being taken after the piston reached point x_0 at intervals equal to t_m. The entire procedure of piston motion is repeated up to 20 times. The computations were done on a BESM-6 computer.

The velocity distribution functions of the molecules f(x, u) at different points of the shock wave are compared in Fig. 1. The distribution functions are normalized so that f(x, u)du = 1. The number above each curve denotes the coordinate x/λ_1 to which the distribution function pertains. The minus sign denotes the region in front of the shock wave and the plus sign denotes the region behind the wave. The most probable thermal velocity of the molecules in the unperturbed flow ahead of the shock wave $c_1 = (1/h_1)^{1/2}$ is taken as the unit of measurement of the velocity.

At large distances upstream from the center of the wave ($x/\lambda_1 = -9.5$) the distribution is close to the equilibrium Maxwellian distribution. As the wave moves deeper, the distribution becomes distorted because of the molecules with small u, which appear during the retardation of the impinging flow. The probability of appearance of such molecules increases toward the center of the wave, where the distribution becomes highly nonequilibrium. Behind the center, a Maxwellian distribution is established again relatively rapidly.

It is interesting to note that the local nonequilibrium functions retain the information about the flow characteristics upstream and downstream, i.e., the maxima of the distributions, while decreasing in magnitude, do not change their position almost up to the center of the wave (curves between $x/\lambda_1 = +9.5$ and $+0.5$ are similar and are omitted in Fig. 1). This fact is reflected in the bimodal shape of the distribution, similar to the distribution in [13].

The nonequilibrium relative velocity distribution function of molecule pairs $G(x, u_{rel})$ is shown in Fig. 2.

A special feature of its evolution consists of the fact that the distribution retains traces of the bimodal nature, which is manifested in the enhanced probability of finding molecules with large relative velocities. The ratios $G(x, u_{rel})/G_2$ are shown in Fig. 3, which illustrates the nature of the departure from equilibrium in the range of moderate and high relative velocities. It is evident that the moderate relative velocities manage to change from one equilibrium value to another even over a few mean free path lengths, whereas for large velocities this requires about 10 lengths.

The rigid-sphere molecular model used in the computations is a limiting case of the real intramolecular potentials. A "softer" intramolecular interaction will apparently increase not only the overall width of the wave, but also the saturability of the zone of the shock by molecules with high relative velocities. Clearly similar effects should be expected also in a mixture of gases having greatly different masses.

An appreciable saturability of the zone of the shock by molecules with high relative velocities would lead to the result that in a shock front propagating in a reacting gas, reactions with rates appreciably exceeding those in the heated gas behind the shock wave will

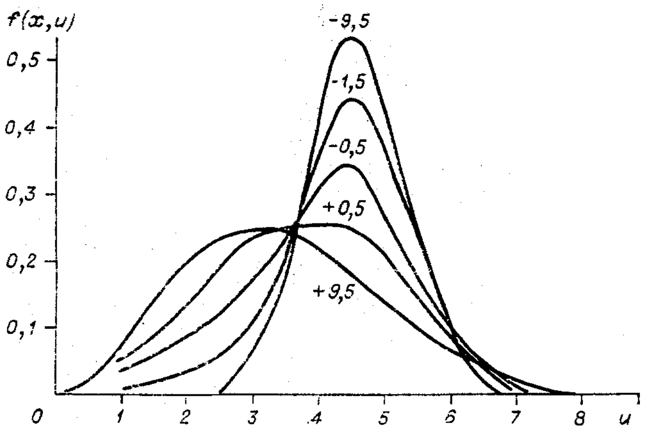

Fig. 1

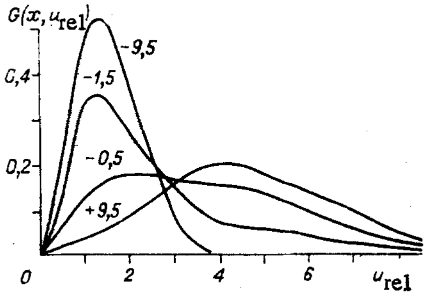

Fig. 2

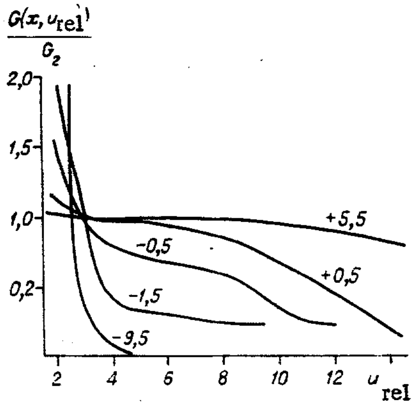

Fig. 3

occur quite efficiently. This would be particularly pronounced in processes having chain (cascade) nature, when even a relatively small transformation depth at the initial instant of time (initiation) has a strong influence on the characteristics of the entire process.

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COMPARISON OF THE RESULTS OF CLASSICAL DIFFUSION AND QUANTUM CALCULATIONS OF VIBRATIONAL–TRANSLATIONAL RELAXATION OF DIATOMIC MOLECULES

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INTRODUCTION

Starting with a numerical solution of the diffusion equation from [2], an investigation was performed in [1] of the vibrational relaxation of anharmonic oscillators in an inert gas medium, the relative effect of anharmonicity on the kinetics of the distribution function and the mean energy was determined, the dependence of the relaxation of the mean energy of the system on its deviation from equilibrium at each instant was shown, etc. The question arises of how far the results in [1] are applicable to quantum systems, and, more generally, what are the limits of applicability of the classical diffusion calculation. A quantitative answer to this question requires a step-by-step comparison with the corresponding quantum-mechanical calculation. We perform such a comparison in the present paper (cf. [3]).

We use the following notation: ε, vibrational energy; ε_i, energy corresponding to the i-th vibrational level; $f(\varepsilon, t)$ distribution function; $f_i(t)$, population of i-th level; f° and f_i°, equilibrium values at temperature T; T, temperature of thermostat; T_0, initial vibrational temperature; $\bar{\varepsilon}(t)$, mean energy; ε_0, energy at zero time; τ_1, vibrational relaxation time of harmonic oscillators; ω_0, μ, and D, fundamental frequency, reduced mass, and dissociation energy of oscillator; N, number of levels of quantum oscillator; ξ_0, adiabaticity parameter; $\xi_0 = (\omega_0\pi/\alpha)\sqrt{M/2kT}$, where M is the reduced mass of the oscillator and particles of the thermostat, and α is the parameter of the intermolecular interaction potential; F(t), force acting on oscillator in a collision; P_{ik}, probability of transition of oscillator from i-th to k-th level per unit time; $a = D/kT$; $a_0 = D/kT_0$; $\omega_{ik} = (1/\hbar)|\varepsilon_i - \varepsilon_k|$, $\tau = t/\tau_1$; $\varphi = f/f^\circ$; $\varphi_i = f_i/f_i^\circ$; $x = \varepsilon/D$; $\theta = \hbar\omega/kT$; $\theta_0 = \hbar\omega/kT_0$.

1. Statement of the Problem. Initial Equations.

It is well known that classical and quantum-mechanical methods of calculation are equivalent if

$$\theta_{\max} = \hbar\omega_0/kT_{\min} \ll 1, \tag{1.1}$$

where $T_{\min}$ is the smaller of the values of T and T_0. This condition is sufficient, but it may or may not be necessary for the determination of a number of kinetic characteristics. Actually, another quantity determining the possibility of applying the classical method of calculation to quantum systems is the time of the kinetic process. It is known that a Fokker-Planck type of equation for an initial distribution function with large spatial derivatives does not give a correct description at times which are very short in comparison with the relaxation time, but starting from a certain instant the size of the initial gradient is of no

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