STATISTICAL MODELING OF THE STATES OF A GAS MIXTURE WITH ALLOWANCE FOR ENERGY EXCHANGE BETWEEN TRANSLATIONAL AND INTERNAL DEGREES OF FREEDOM

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1. Statement of the Problem

Recently considerable progress has been achieved in the investigation of flows of a rarefied monatomic gas analytically and by numerical methods [1, 2]. Ever closer attention is being attracted by problems in which, first, one cannot be confined to a simple gas alone, and second, during a particle collision energy exchange is possible between translational and internal degrees of freedom, such as the excitation of vibrational, rotational, and electronic levels of molecules, the occurrence of ionization, dissociation, and recombination reactions, etc. Some problems of the theory of a chemically reactive gas mixture either under close to equilibrium conditions or in strongly nonequilibrium states in the presence of a small parameter are considered in [3]. There are also attempts at the numerical solution of such problems [4-7].

A numerical method of statistical modeling of collisions was suggested in [8, 9] to solve problems of the kinetics of a multicomponent gas mixture in a homogeneous space. In the present report this method is extended to gas mixtures in which energy exchange occurs between translational and internal degrees of freedom of the particles [10]. The method being developed is built on the basis of a model of a monatomic gas with elastic collisions [11, 12], whose asymptotic equivalence to the Boltzmann equation was established in [13].

A nonsteady statistical model of a gas mixture is constructed using the basic concepts of [10, 11] and an algorithm modeling collisional relaxation.

2. Construction of the Model

Let the gas mixture consist of M components. We designate each component by the index a_l, where $l = 1, 2, \ldots, M$, and the mass of a particle of the a_l-th component as m_l, while the velocity is $\mathbf{v}^l$.

We isolate some volume V in physical space in which we replace the gas mixture by a system of $N = N_1 + \ldots + N_M = \sum_{l=1}^{M} N_l$ model particles with velocities $\mathbf{v}_1^1, \ldots, \mathbf{v}_{N_1}^1; \ldots; \mathbf{v}_1^M, \ldots, \mathbf{v}_{N_M}^M$. Here N_l is the number of particles of component a_l. The state of the system of model particles as a whole will be characterized by the vector

$$\mathbf{X} = \{(\mathbf{v}_1^1, \ldots, \mathbf{v}_{N_1}^1), \ldots, (\mathbf{v}_1^M, \ldots, \mathbf{v}_{N_M}^M)\} = \{\mathbf{v}_1, \ldots, \mathbf{v}_N\}.$$

We introduce the statistical model of the gas mixture with the help of two definitions, the first of which establishes the concept of the collision of model particles while the second defines the time interval separating collisions [12, 10].

The first definition is based on the laws of conservation of particle number, energy, and momentum for a given interaction potential, the use of which permits a calculation of the velocity following the collision. Through the second definition the physical properties of the model particles assign the probability characteristics describing the model, on the basis of which one obtains an exponential distribution of the waiting time for the next collision of any pair of N particles,

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$$\mathscr{F}(\tau) = P\{\Delta t^* \leqslant \tau\} = 1 - \exp(-\lambda\tau),$$

where the interval τ does not depend on the choice of the origin of the time frame; $\lambda = \omega_{ij}$, collision frequency; $\omega_{ij} = g_{ij}\sigma_{ij}(g_{ij})/V$, probability of the collision of a pair of particles; $g_{ij} = |\mathbf{v}_i - \mathbf{v}_j|$; $\sigma_{ij}(g_{ij})$, collision cross section; Δt^*, waiting time. Consequently, the probability that the pair of particles (i, j) collided at the time t, with the condition that a collision of one of the pair occurred at this time, is $W_{ij} = \omega_{ij}/\lambda$.

In modeling the change in internal energy of the particles in the collision it is convenient to choose the mass m_l, the velocity $\mathbf{v}^l$, and the internal energy $E_l = E_l(\Lambda_l)$ of the particles as the main parameters, where Λl is the set of quantum numbers defining the particles of the given component (type). The transition of a particle from type to type occurs with observation of the laws of conservation of total energy and momentum of the colliding particles.

Consequently, the following relations are satisfied for the velocity $\mathbf{G}$ of the center of inertia and the relative velocity $\mathbf{g}$ of the colliding particles before and after the collision in each collision:

$$G^{ln} = G^{l'n'}, \quad g^{l'n'} = \left\{\frac{m_{ln}}{m_{l'n'}}(g^{ln})^2 - \frac{2\Delta E_{ln}^{l'n'}}{m_{l'n'}}\right\}^{1/2}, \tag{2.1}$$

where $m_{ln} = m_l m_n/(m_l + m_n)$ and $m_{l'n'} = m_{l'} m_{n'}/(m_{l'} + m_{n'})$ are the reduced masses; $\Delta E_{ln}^{l'n'} = E_{l'} + E_{n'} - E_l - E_n$ is the change in internal energy in the process under consideration; the prime refers to quantities after the collision. The latter parameter determines the type of collision: $\Delta E_{ln}^{l'n'} = 0$, $l' = l$, $n' = n$ is an elastic collision of the particles; $\Delta E_{ln}^{l'n'} = 0$. $l' \neq l$, $n' \neq n$ is a resonance inelastic collision, which is characterized by conservation of the energy of internal degrees of freedom and of the energy of translational degrees of freedom separately; $\Delta E_{ln}^{l'n'} > 0$ is a nonresonance inelastic collision, in which there is a conversion of a certain fraction of the kinetic energy of the colliding particles into internal energy of the particles; $\Delta E_{ln}^{l'n'} < 0$ is a nonresonance inelastic collision in which there is a conversion of part of the internal energy of the particles into kinetic energy (if one of the particles does not possess an internal energy, an electron, e.g., then this will be a case of a so-called superelastic collision).

As a result of collision, the number of model particles for each component will be variable, but the total number of particles is conserved owing to the paring of the collisions. The total collisional cross section for model particles of types a_l and a_n can be assigned in the form (2.2)

$$\sigma_{ln}^T(g^{ln}) = \sigma_{ln}(g^{ln}) + \sum_{l'n'} \sigma_{ln}^{l'n'}(g^{ln}), \tag{2.2}$$

where σ_{ln} is the cross section for an elastic interaction, $\sigma_{ln}^{l'n'}$ is the cross section of the interaction for the process $a_l + a_n \to a_l' + a_n'$.

Equation (2.2) is used to calculate the probability characteristics W_{ij}^{in} for this process, so that

$$\omega_{ij}^{ln} = (\omega_{ij}^{ln})^{e} + (\omega_{ij}^{ln})^{i}, \tag{2.3}$$

where the quantity $(\omega_{ij}^{ln})^{e}$ is the probability of an elastic collision; $(\omega_{ij}^{ln})^{i}$ is the probability of an inelastic collision of the particles. Thus, the waiting times for the next collision are calculated through the collision frequency using Eqs. (2.2) and (2.3), which contain information about the inelastic processes.

The numerical algorithm corresponding to the given statistical model of a gas mixture with physicochemical processes is based on the statements presented above and allows for the changes in the internal energy of the particles and the changes in the types of particles during collisions. The realization of the algorithm consists of a numerical solution by the Monte Carlo analog method by the finite-difference scheme of the Kolmogorov equation $\partial\varphi(X, t)/\partial t = K\varphi(\mathbf{X}, t)$ for the probability distribution $\varphi(\mathbf{X}, t)$ of the state $\mathbf{X}(t)$ of the system of particles. In this case the macroscopic characteristics of the components of the mixture at an arbitrary time t can be calculated as the mathematical expectations of the corresponding average quantities [10].

3. System of Determining Parameters

In the numerical experiments the physical quantities characterizing the state of the mixture are represented in dimensionless form with the following determining parameters: mass m, density n, temperature T, and some effective length α, depending on the interaction potential. The quantities $\lambda \sim 1/\pi n d^2$ and $\bar{v} \sim \sqrt{kT/m}$, the mean free path and the mean velocity, connect the parameters determining the physical experiment with the characteristics of the mathematical model: with the statistical volume constant $V_0 \sim \lambda^3$, the time scale $\tau = \lambda/\bar{v}$, and the number $N \sim n$ of model particles. The determining parameters of one of the components (with the arbitrary number $l = 1$) are chosen as the base quantities in the calculations, and the normalization is carried out with respect to these quantities and their combinations.

The choice of the time step Δt in the algorithm is limited, on the one hand, by the condition $\omega_{ij}^{l} n \Delta t < 1$ and $\Delta t \ll 1$, in which the total number S of collisions in the system of model particles is determined by the Poisson distribution, and, on the other hand, by the condition of accuracy of construction of the algorithm for the Markov chain being realized, corresponding to the process $\mathbf{X}(t)$.

As follows from [10, 12], the nonsteady statistical model approximates the Boltzmann equation with the accuracy of the quantity $O(1/N)$, which is a result of the replacement of the actual medium by a finite number of model particles, while the finite-difference scheme to which the algorithm is reduced is conditionally stable and provides an approximation accuracy of $O(\Delta t)$ [11]. The preliminary estimate of the error $O(1/N + \Delta t)$ is dependent on the choice of the total number of particles in the experiment and the time step Δt of the algorithm.

4. Relaxation with Respect to Translational Degrees of Freedom

In solving the problem of the relaxation of translational degrees of freedom at a given initial temperature nonuniformity it is assumed that the internal degrees of freedom of the particles are in equilibrium.

A mixture consisting of three gases ($M = 3$) was investigated. The number of model particles of each of the components is chosen as proportional to the initial densities.

The initial values of the velocities of each of the model particles were assigned in accordance with an initial distribution function assumed to be Maxwellian with the corresponding temperature.

The following problems were examined: The relaxation of two components of a gas mixture in a thermostatic medium formed by the third component, the relaxation of a mixture of gases with the same physical properties (one gas with an assigned initial temperature nonuniformity, with a determination of the relaxation time and an estimate of the accuracy of the results); an investigation of the dependence of the relaxation times of the gas mixture on the parameters of the model: the volume V and the number N of particles; an analysis of the evolution of the velocity distribution function of the initial state of each component of the mixture in the process of collisional relaxation; a comparison between the results obtained using the statistical model and the results of calculations of the relaxation of a mixture of two gases by other finite-difference and statistical methods.

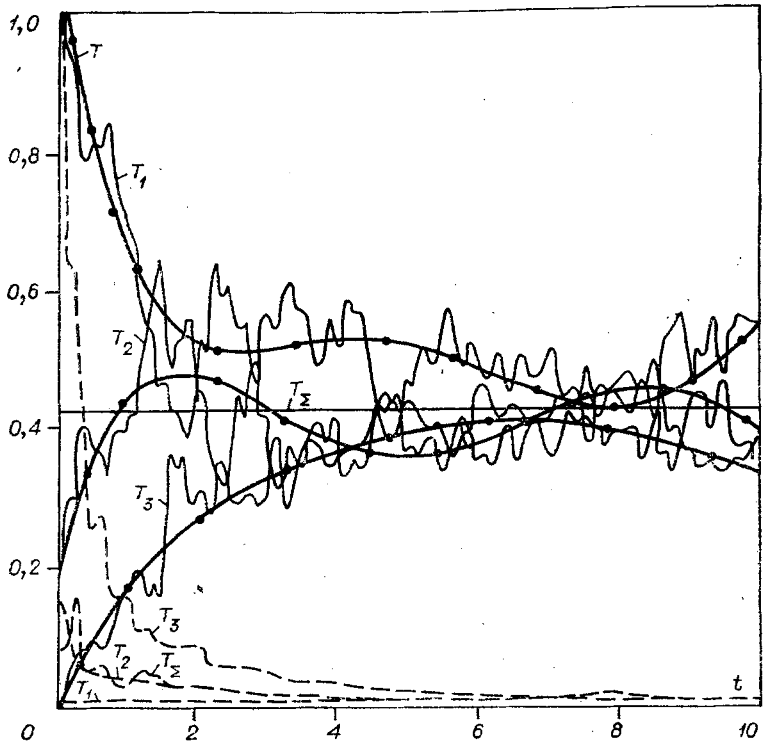

Fig. 1

In the solution of the first of the enumerated problems the velocity distribution function of the particles of one of the components, the so-called thermostatic medium, is kept constant, and the temperatures of the relaxing components of the mixture must approach it.

The results of the numerical experiment for the case of $T_1^0 < T_2^0$, T_3^0, $T_1 = T_1^0 = \mathrm{const}$ ($N = 30$, $\Delta t = 0.1$) are presented in Fig. 1 (dashed lines); the temperatures of the components, which are compared with the temperature T_Σ of the mixture, calculated from the values of T_1, T_2, and T_3, are also presented here, while the values of T_1, T_2, and T_3 smoothed by the method of least squares are denoted by smooth lines with dots.

The accuracy of the calculation can be increased through an increase in the number of particles taking part in the numerical experiment and a decrease in the time step in the algorithm, but to conserve the initial physical characteristics of the gas it is necessary to conserve the value of the parameter N/V as one of the similarity parameters.

To estimate the accuracy, the numerical experiments were carried out with the following parameters of the numerical model: $T_1:T_2:T_3 = 1:0.01:0.001$, $n_1 = n_2 = n_3 = 1.0$; $m_1 = m_2 = m_3 = 1$, $d_1 = d_2 = d_3 = 1$; and

a) $\Delta t = 0.2$, $V = 5V_0$, $N_l = 5$, $l = 1, 2, 3$;
b) $\Delta t = 0.1$, $V = 10V_0$, $N_l = 10$, $l = 1,2,3$

with a number L of independent realizations equal to three.

The data obtained confirm the preliminary estimates of the accuracy of the statistical model. Thus, in the calculations for variant "a" the temperatures of the components are determined with a deviation δ_Σ of up to 20% from the mean value T_Σ of the temperature of the mixture, whereas the preliminary upper estimate of the accuracy gives 26%. For case "b" the macroscopic parameters are determined with an accuracy of up to 10% (preliminary estimate 13%).

In analyzing the value of the dispersion D_Σ of the macroscopic parameters with respect to the number of realizations, one can draw the conclusion that its value is insignificant even for a small number ($L = 3$) of realizations of the numerical experiment and the value of the dispersion does not grow with time, while slight fluctuations are observed within the limits of accuracy of the determination of the values.

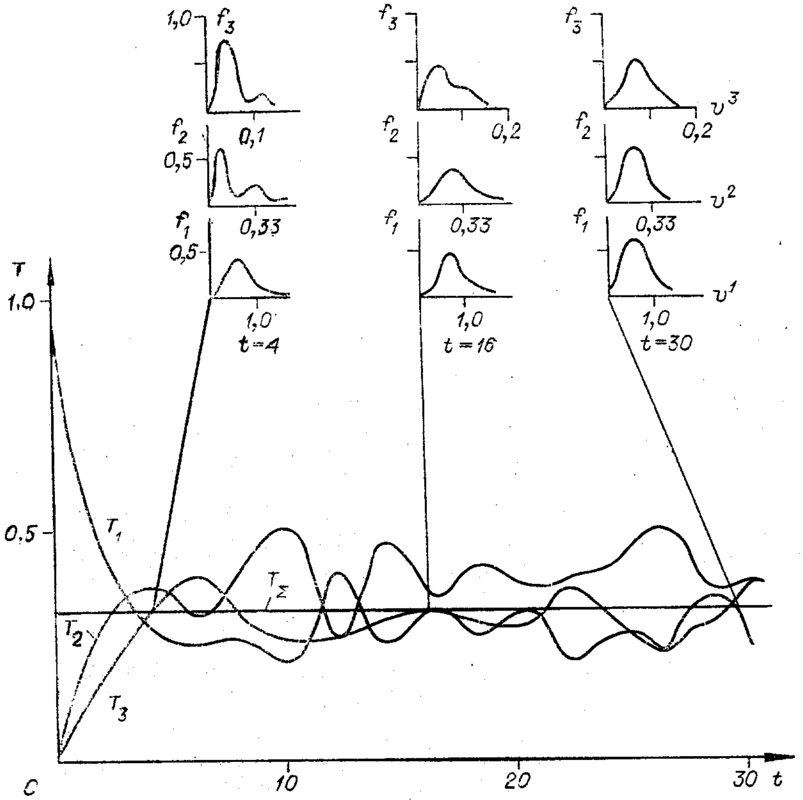

Fig. 2

In Fig. 2 we show the time variation of tne temperatures of the components of the mixture and the evolution of the velocity distribution functions of the particles of each of the components, which have a mass ratio of 1:10:100 and a ratio of particle diameters of 1:2:3, while the remaining parameters coincide with case "b." Here it is shown how the analysis of the distribution functions of the components in the process of relaxation provides additional information about the course of the process.

The relaxation of the cold component CH_4 toward the equilibrium temperature in a mixture of methane and argon is reflected in Fig. 3.

At the initial time it was assumed that the concentrations of the Ar and CH_4 components were the same ($\sim 10^{18}$ cm^{-3}), while the temperatures had the values $T_{Ar} = 10^4$ °K and $T_{CH_4} = 3 \cdot 10^2$ °K. The modeling was carried out with the following values of the parameters: $T_1 : T_2 = 1 : 0.03$, $N_1 = N_2 = 10$, $V = 20V_0$, $\Delta t = 0.1$. Here we also present the results of [14] (dashed line) and [6] (dash-dot line), carried out under the same initial physical conditions. Such a comparison with results obtained in the solution of the system of Boltzmann equations by the finite-difference method [14] and the Monte Carlo method [6] shows the good accuracy and efficiency of the nonsteady statistical model which we used. For example, in [14] the calculation time is greater by about an order of magnitude, while in [6] the number of particles to assure the required accuracy is two to three orders of magnitude larger.

5. Relaxation of Excited States

The problem of the relaxation of excited states is analyzed within the framework of a quasiclassical approximation, when the collisions of particles having translational degrees of freedom are described classically, while the spectrum of values of the internal particle energy is discrete. It is assumed that the exchange of energy between degrees of freedom of the gas in the process of collisions is possible with the exception of resonance inelastic exchange.

Let us consider a mixture of two gases, one of which consists of structureless particles (such as electrons) while the second consists of particles possessing two internal energy levels: ground and excited. In the statistical model we will have three components, where one of them (the first for determinacy) is structureless while the second and third

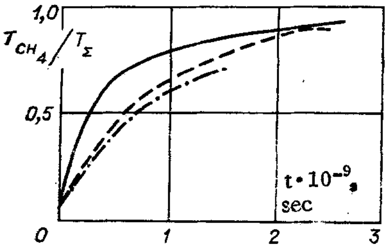

Fig. 3

components consist of particles with the same mass but different internal energies (E_n and E_m, respectively, with $\Delta E_n^m = E_m - E_n > 0$).

The main process determining the behavior of the system of particles under consideration is the paired collision, the time of which is negligibly small compared with the time between collisions. The lifetime of the excited state is assumed to be infinitely long, which eliminates the possibility of a collisionless transition of particles of the third component to the ground state. The possibility of the ionization and recombination of particles of the mixture is not considered, and neither is emission, which can arise in the relaxation of the excited state, modeled here. Only three types of collisions are possible: elastic, inelastic, and superelastic (collisions of the second type).

As a result of collisions of the first type $\Delta E_n^n = 0$ and only the velocities $\mathbf{v}^l$ and $\mathbf{v}^n$ of a structureless particle and a particle in the ground state can change (the internal energy E_n is constant).

Collisions of the second type take place with fulfillment of the condition $E = m_{ln} \cdot (g^{ln})^2/2 \geqslant E^*$, where $g^{ln} = |v_l - v^n|$ is the relative velocity of the colliding particles; m_{ln} is the reduced mass of the particles; E^* is the threshold value of the energy determining the given inelastic process. The formation of a particle of the third component with an internal energy E_m and the disappearance of particles in the ground state occur in this case. In accordance with the fact that a model of two internal energy levels is considered here, the fraction of kinetic energy transferred in a collision from translational to internal degrees of freedom is limited by the energy difference of these levels — of the ground and excited states. In order for the energy transfer between degrees of freedom to be efficient, it is necessary to satisfy the condition of nonadiabaticity of the transfer process [15], which is satisfied in the mixture model under consideration [8].

In the process of collisions of the third type under consideration we have $\Delta E_m^n < 0$, and because of the fact that the sign of the quantity ΔE_m^n is opposite to the sign of the same quantity in the second type of collisions, superelastic collisions can be called opposite to inelastic collisions.

Elastic collisions are characterized by a constant scattering cross section

$$\begin{cases} \sigma_{ik}(g^{ik}) = (\sigma_{ik})_0, \\ d\sigma_{ik} = \frac{1}{4\pi}\sigma_{ik}(g^{ik})\, d\Omega, \end{cases} \quad i, k = l, n, m,$$

where $(\sigma_{ik})_0 \sim 10^{-15}$-$10^{-16}$ cm^2 coincides with the elastic collisional cross sections of the main atmospheric components.

In the case of inelastic collisions of structureless particles with atoms in the ground state the cross section of the process is approximated here by the expression

$$\begin{cases} \sigma_{ln}^{lm}(g^{ln}) = \begin{cases} 0, & g^{ln} < g_{\mathrm{i}}^{ln}, \\ (\sigma_{ln}^{\mathrm{i}})_0 \left(1 - \left(\frac{g_{\mathrm{i}}^{ln}}{g^{ln}}\right)^2\right), & g^{ln} \geqslant g_{\mathrm{i}}^{ln}, \end{cases} \\ d\sigma_{ln}^{lm} = \frac{1}{4\pi}\sigma_{ln}^{lm}(g^{ln})\, d\Omega, \end{cases}$$

where $g_i^{ln} = \{2\Delta E_n^m/m_{ln}\}^{1/2}$ is the threshold value of the relative velocity of the colliding particles, the quantity $(\sigma_{ln}^i)_0 \sim 10^{-17}$–$10^{-18}$ cm^2 is the mean characteristic value of the cross section for inelastic excitation of an atom by an electron.

The superelastic scattering cross section can be represented in the form

$$\sigma_{lm}^{ln}(g^{lm}) = (\sigma_{lm}^{s})_0 \left(1 - g^{lm^2}/g_{as}^2\right), \quad d\sigma_{lm}^{ln} = \frac{1}{4\pi}\,\sigma_{lm}^{ln}(g^{lm})\,d\Omega,$$

where $(\sigma_{lm}^{s})_0 \sim 10^{-17}$ cm^2 to provide agreement with experimental data, $g_{as} = 4 - 7$.

Thus, the given model can permit the analysis of a number of physicochemical processes of the type of the excitation of atoms by electron impact in a gas. It becomes possible to investigate the influence of outside action on the gas, expressed either in the establishment of equilibrium in the gas or in the maintenance of nonequilibrium states. A determination of the characteristic times of energy exchange between degrees of freedom of a gas can permit an estimate of the limits of applicability of equilibrium models for gases in which one cannot be confined to collisional relaxation with respect to the translational degrees of freedom. The possibility in a numerical experiment of estimating the efficiency of energy transfer from one degree of freedom to another and of calculating the rates of the processes taking place in the gas are important.

In particular, a condition for equilibrium with respect to internal degrees of freedom is time constancy of the level-population temperature

$$T_{nm}^{\text{lev}} = -\Delta E_n^m / \ln\left(\frac{n_m}{n_n}\right),$$

while the rate constants of the inelastic processes are determined by the equations

$$(K_{ln}^{l'n'})_\sigma = \frac{1}{n_l n_n}\int f_l(\mathbf{v}^l, t)\, f_n(\mathbf{v}^n, t)\, g^{ln}\sigma_{ln}^{l'n'}(g^{ln}, \theta)\, d\Omega\, d\mathbf{v}^l d\mathbf{v}^n,$$

where $f_l(\mathbf{v}^l, t)$ and $f_n(\mathbf{v}^n, t)$ are the values of the distribution functions of particles of types α_l and α_n at a given time t.

The following model problems are considered: an estimate of the relaxation time of an initial nonequilibrium populated excited state in the gas under consideration; an estimate of the efficiency of energy transfer from translational to internal degrees of freedom of the gas as a function of the energy of the structureless particles and the energy difference between the ground and excited states; the populating of the excited level of gas particles through the supply of translational energy to the mixture, when the distribution function of the structureless particles does not change; an investigation of the process of establishment of equilibrium with respect to the translational degrees of freedom of the gas with an initial temperature nonequilibrium of the gas components under the condition of an initial equilibrium population of the internal degrees of freedom; an analysis of the evolution of the initial velocity distribution functions as a result of the realization of inelastic processes; an estimate of the rate constants of processes of excitation of internal degrees of freedom by inelastic particle collisions and of relaxation of the excited state in superelastic impacts.

A nonequilibrium initial state corresponds to a situation when there is a nonequilibrium in the system either with respect to translational degrees of freedom (temperature nonequilibrium) or with respect to internal degrees of freedom (the Boltzmann distribution of particle concentrations in the ground and excited states is disturbed).

Processes with a change in internal energy were investigated in cases when the distribution function of the structureless component was assigned in the form of a δ function or a Maxwellian one and was kept constant in time (thermostatic medium) and when the particle system under consideration was assumed to be energetically isolated.

Processes of translational relaxation and of a change in the internal energy are characterized by a dimensionless parameter ΔE_2^3 which, in the case of a monoenergetic initial distribution of the structureless particles, is the ratio of the energy of excitation of the level at the level temperature T_{23}^{lev} either to the kinetic energy of one particle (thermostatic medium) or to the average thermal energy per particle. The characteristic values of this

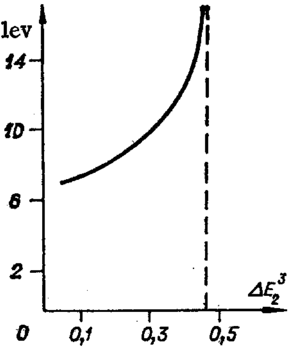

Fig. 4

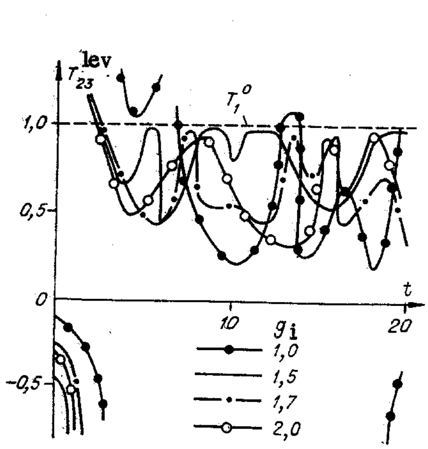

Fig. 5

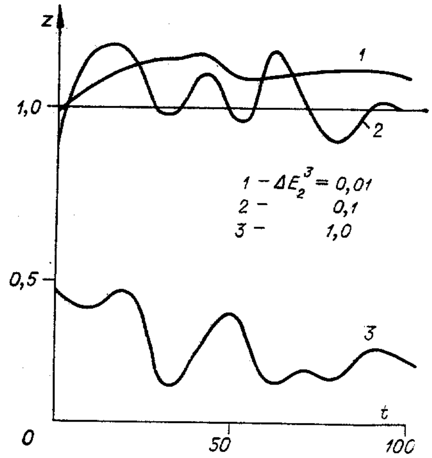

Fig. 6

parameter at which the numerical experiments were carried out are 0.0625, 0.250, 0.3906, 0.490, 0.5625, 0.7225, 1.0, and 1.562. They correspond to the following values of the threshold velocity g_i: 0.5, 1.0, 1.25, 1.4, 1.5, 1.7, 2.0, and 2.5.

The dependence of the time τ_{lev} in which an inversion of the population of the excited state ($T_{23}^{lev} < 0$) occurs on the quantity ΔE_2^3 in the case of a thermostatic medium is presented in Fig. 4.

The results of an investigation of the possibility of maintaining an inverted population of the excited state are presented in Fig. 5; time dependences of the population temperature of the excited state are given for different values of the parameter ΔE_2^3. An upper limit of values of this parameter ($(\Delta E_2^3)_{max}$ = 0.250) is established such that when $\Delta E_2^3 \leq (\Delta E_3^2)_{max}$ it is possible to maintain an inverted population of the excited state in the particle system under consideration. Further, one can isolate a spectrum of values of the translational energy of the structureless particles (ΔE_2^3 = 0.7225-1.5) for which the particle system arrives at a state analogous to an equilibrium state, i.e., T_2, $T_3 \simeq T_1^0$ and $T_{23}^{lev} \simeq T_1^0$, with part of the translational energy of the structureless particles going into the excitation of internal degrees of freedom.

For states of the particle system when the translational degrees of freedom are described by a Maxwellian distribution with a temperature T_Σ, the rate constant of the inelastic process can be calculated analytically:

$$(K_{12}^i)_\sigma^0 = \left(\frac{m_{12}}{2\pi T_\Sigma}\right)^{3/2} \int (g^{12})^3 \sigma_{12}^{13}(g^{12}) \exp\left(-\frac{m_{12}(g^{12})^2}{2T_\Sigma}\right) dg^{12}.$$

Using the model proposed above for the excitation of particles in the ground state by structureless particles, we obtain

$$(K_{12}^{i})_{\sigma}^{0} = (\sigma_{12}^{in})_0 \left(\frac{3T_\Sigma}{m_{12}\pi}\right)^{1/2} \exp\left(-\Delta E_2^3/T_\Sigma\right). \qquad (5.1)$$

Under conditions close to equilibrium, the statistical rate constant of a process with a change in internal energy should be close to the quantity (5.1) and the rate constants of inelastic and superelastic processes are close in value.

For the initial conditions $m_1:m_2:m_3 = 1:10:10$ and $n_3:n_2 = \exp(-\Delta E_2^3/\tilde{T}_\Sigma)$, where $\tilde{T}_\Sigma = T_1/3$, and values of the parameter ΔE_2^3 in the range of 0.01-1.0 we calculated the quantities $F^i = (K_{12}^{i})\sigma/K_{12}^{i})_{\sigma}^{0}$ and $F^s = K_{13}^{s})\sigma/(K_{13}^{s})_{\sigma}^{0}$. The ratios $z = F^i/F^s$ obtained for three values of the parameter ΔE_2^3 are presented in Fig. 6. From an analysis of these results it follows that the relaxation time is less for a system of particles containing high-energy structureless particles ($\Delta E_2^3 = 0.01$-0.1), while the rate constants are $(K_{12}^{i})\sigma \simeq (K_{13}^{s})\sigma$ and F^i, $F^s \simeq 1$. If $\Delta E_2^3 \geqslant 1.0$, the establishment of equilibrium with respect to internal degrees of freedom is hindered, since the rate constant of superelastic collisions considerably exceeds the rate constant of inelastic collisions ($z \ll 1$ when $\Delta E_2^3 \geqslant 1.0$), i.e., the collisional processes under consideration are insufficient to describe the establishment of equilibrium distributions. It is possible that in this case we must allow for other mechanisms of relaxation of the internal degrees of freedom, such as allowance for radiative transitions.

Thus, the investigation of the relaxation of a system of particles with respect to translational and internal degrees of freedom using the rate constants of processes with a change in the internal energy confirms the conclusions about the behavior of the system made on the basis of an analysis of the physical properties of the gas mixture modeled by the given system of particles.

The main result of the present work is the extension of the method of nonsteady statistical modeling to a gas mixture in which physicochemical processes occur. A model is constructed allowing the analysis of processes of energy exchange between degrees of freedom in paired particle collisions with allowance for the known discrete spectrum of values of the internal particle energy and the sole requirement of finiteness of the total collisional cross section.

A numerical algorithm was constructed, as a result of the realization of which one can obtain the macroscopic characteristics of the mixture: the density, the temperature, the average macroscopic velocity, the total energy, and the heat capacity of each component of the mixture, as well as the collision frequency, the reaction rate constants, and others.

The results of the calculations in the problem of the investigation of the relaxation of a spatially homogeneous gas when only elastic collisions occur in the mixture confirmed the main physical assumptions about the relaxation of a mixture with respect to translational degrees of freedom, i.e., the establishment of a single temperature of the mixture and the establishment of a Maxwellian velocity distribution function for the particles of the mixture components.

A physicochemical process analogous to the process of excitation of atoms by electron impact was investigated for a gas mixture with internal degrees of freedom. The range of energy supplied to the mixture in which an inverted population of the excited states of the particles is achieved was determined in a numerical experiment. The efficiency of energy transfer from translational to internal degrees of freedom as a function of the supplied energy and the energy difference between the ground and excited states was estimated. The conditions were determined under which a Maxwell-Boltzmann distribution of velocities and internal energies is established in the gas mixture. The rate constants were calculated for processes of excitation of internal degrees of freedom by inelastic particle collisions and for processes of removal of excitation by superelastic collisions, both in nearly equilibrium states and in strongly nonequilibrium states.

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