This analysis has shown that the form of the discharge strongly depends on the pressure inside the discharge pipe and on the atmospheric humidity. Under certain experimental conditions, the volume occupied by the plasma was minimal due to cooling of the plasma by water vapor.

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NONMONOTONIC RELAXATION IN AN ATOMIC GAS AND THE KINETICS OF THRESHOLD PROCESSES

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Deviations from equilibrium in the high molecular energy range can have a significant effect on the kinetics of threshold processes such as thermonuclear synthesis, gas phase chemical reactions, etc. The nonequilibrium tails of energy distributions must be considered in interpreting the results of physical diagnostics employing selective excitation of a gas. In this connection the effect of nonequilibrium on relaxation properties and transport processes in gases has attracted much attention [1-7]. However, the pattern of global evolution of the distribution function of gas molecules has been studied little, even for the simple case of homogeneous relaxation of an atomic gas. This is due to the complexity of the kinetic equation in Boltzmann's theory of gases [8].

Individual results obtained with asymptotic estimates [4, 5, 8] and on the basis of simple exactly soluble models [7, 9] are basically of a qualitative nature and have limited applicability. In particular, for the hydrodynamic moments of the distribution function we have Maxwell's estimate, according to which their evolution to local equilibrium is monotonic and completed in two or three mean free molecular path times [8]. This property of transition to equilibrium in the region of the "dome" of the distribution function is the basis of the hydrodynamic expansions of the Chapman–Enskog method. But extrapolation of this estimate to the process of relaxation of the distribution function as a whole, often found in the literature (see, for example, [10]), is in general erroneous. Krook's kinetic model with a single relaxation time for the entire energy spectrum also distorts the pattern of evolution of the distribution function tail significantly [11]. For example, for finite distributions, in which a tail is completely absent at the initial moment, the time required for

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transition to equilibrium in the high energy range may comprise decades of mean free path times [1].

The present paper describes a quantitative study of relaxation processes of an atomic gas for phase distribution isotropic in velocity space. The processes of nonmonotonic Maxwellization will be studied for initial data with exponential and powerlike tail asymptotes, as well as finite ones. The main results on time evolution of the phase distribution were obtained by direct numerical integration of the nonlinear Boltzmann kinetic equation for Maxwellian molecules. The time evolution of the distribution functions presented will be analyzed together with individual populations and higher-order scalar moments up to the transition to the linear stage of relaxation. It will be shown that the characteristic amplitudes and existence times of the overpopulations which develop are such that they may have a significant effect on the kinetics of processes having an energy barrier which develop against the background of translational relaxation. Calculations of a high threshold chemical reaction are presented as a quantitative example of the effect.

1. The study of homogeneous relaxation of an atomic gas at the kinetic level involves solution of the Cauchy problem for the nonlinear Boltzmann equation. For Maxwellian molecules and initial conditions isotropic in velocity space the basic mathematical formulation of the problem has the form

$$\partial f(v,\ t)/\partial t = J(f,\ f),\quad f(v,\ 0) = f^{(0)}(v),$$
$$J(f,\ f) = \int\int d\mathbf{w}d\mathbf{n}B\left(\frac{\mathbf{u}\cdot\mathbf{n}}{|\mathbf{u}|}\right)[f(\mathbf{w}',t)f(\mathbf{v}',t) - f(\mathbf{w},t)f(\mathbf{v},t)], \tag{1.1}$$

where f(v, t) is the gas molecule distribution function over velocities, dependent on the modulus of the velocity $v = |\mathbf{v}|$; J(f, f) is the collision integral; $(\mathbf{v}, \mathbf{w})$ and $(\mathbf{v}', \mathbf{w}')$ are velocities of molecular pairs before and after collision; $\mathbf{u} = \mathbf{v} - \mathbf{w}$; $\mathbf{n}$ is the unit vector in the direction of the relative velocity of the particles after collision; $d\mathbf{n} = \sin\theta d\theta d\varepsilon$; θ, ε are the singular scattering variables; and B is the scattering indicatrix.

We choose a system of dimensionless quantities such that the equilibrium Maxwell distribution [8], which is a steady state solution of Eq. (1.1) as $t \to \infty$, can be represented in the form

$$f_0(v) = (2\pi)^{-3/2}\exp(-v^2/2). \tag{1.2}$$

Correspondingly, the laws of conservation of gas mass and energy in the problem of Eq. (1.1) can be written in the form

$$M_0 = 4\pi\int_0^\infty dvv^2f(v,\ t) = 1,\quad M_1 = \frac{4}{3}\pi\int_0^\infty dvv^4f(v,\ t) = 1. \tag{1.3}$$

The mean time between collisions is chosen as the unit of time. Then for the case of isotropic scattering considered here $B = (4\pi)^{-1}$.

The basic difficulty in numerical integration of relaxation problem (1.1) is connected with the necessity of multiple calculation of the collision integral J(f, f), fivefold calculation in the general case. Although in the case of isotropic distribution functions the dimensionality of J(f, f) can be reduced [9, 12], with increased requirements for accuracy in calculating the distribution function at larger energy intervals and time the use of conventional numerical quadratures in Eq. (1.1) proves to be ineffective. The present study will use the spectral approach proposed in [13]. This approach is based on a discrete analog of the Fourier representation of the homogeneous Boltzmann equation [14], which in the case under consideration has the form

$$\frac{\partial\varphi(k,\ t)}{\partial t} = G(\varphi,\ \varphi),\quad \varphi(k,\ 0) = \varphi^{(0)}(k),$$
$$G(\varphi,\ \varphi) = 2\int_0^1 dss\left[\varphi(ks,\ t)\varphi\left(k\sqrt{1-s^2},\ t\right) - \varphi(k,\ t)\varphi(0,\ t)\right], \tag{1.4}$$

where $s = \sin\theta/2$; $k = |\mathbf{k}|$ is the modulus of the wave vector. Equation (1.4) is related to the original Eq. (1.1) by Fourier transform expressions

$$\varphi(k) = \frac{2}{k}\int_0^\infty dvvf(v)\sin 2\pi kv,\quad f(v) = \frac{2}{v}\int_0^\infty dkk\varphi(k)\sin 2\pi kv.$$

As was shown in [13], integration of Eq. (1.4) in combination with a fast numerical Fourier transform allows a reduction in the volume of numerical computation by a factor of $O(N)$ times as compared to the use of conventional numerical quadratures in Eq. (1.1) [where N is the number of grid points in the interval of change of the velocity (spectral) variable]. In the majority of calculations N = 512 and the integration step in time $\tau_e = 0.2$.

In calculating relaxation at large times near the transition to the linear stage, together with a solution of the problem in the form of Eq. (1.4) use was made of a Fourier representation of a segment of the series

$$f(v, t) = f_0(v)\left(1 + \sum_{\{p\}, p\geq 1} a_p(t)\,\frac{\Gamma(p+3/2)}{\Gamma(3/2)\,\Gamma(p+1)}\,{}_1F_1(-p, 3/2, v^2/2)\right) \tag{1.5}$$

in eigenfunctions of the linearized collision operator. Here $\Gamma(x)$ is a gamma function; ${}_1F_1(\alpha, \beta, x)$ is a degenerate hypergeometric function; $\{p\}$ is some even set of numbers, closed with respect to addition [6]. The coefficients of the series of Eq. (1.5) are calculated by integration of a system of differential equations

$$\frac{da_p(t)}{dt} + \lambda_p a_p(t) = \frac{1}{p+1}\sum_{r+q=p} a_r(t)\,a_q(t), \quad \{p\}, \quad p > 1, \tag{1.6}$$

where $\lambda_p = (p-1)/(p+1)$ are eigenvalues of the linearized collision operator. Using this same system with appropriate changes in initial conditions [5, 12] we studied the behavior of reduced moments of the distribution function

$$M_n(t) = \frac{4\pi}{(2n+1)!!}\int_0^\infty dv\,v^{2n+2} f(v, t), \tag{1.7}$$

where n are integers which at high values are sensitive indicators of tails.

For finite initial conditions with an exponential asymptote, where $\{p\} = \{n\}$ and a base consisting of Laguerre polynomials $L_n^{1/2}(v^2/2)$, 20 base functions were chosen for calculation of Eqs. (1.5), (1.6), and the moments of Eqs. (1.7) were calculated up to n = 20 (cf. [9, 15, 16]).

Analysis of results of test and preliminary calculations revealed that the complex of algorithms and programs used provided the necessary accuracy in distribution function calculation, including high energy tails up to $v \sim 10$ over a time interval to $t \sim 15$ with low expenditures of machine time on a BÉSM-6 computer.

2. The possibility of nonmonotonic relaxation of an atomic gas was first noted in [17], where a self-similar solution of Boltzmann's equation was presented for an intermolecular interaction with potential $U \sim r^{-4/3}$, in which at each moment of time within some energy interval the value exceeds the equilibrium value of the distribution function. Tjon [2] demonstrated the nonmonotonic relaxation of an initial distribution of two monoenergetic beams separated in velocity space. Examples of other initial conditions during the evolution of which overpopulation develops in the high particle energy range were considered in [3, 6, 15, 16]. In [15], for distribution functions with an initial particle concentration in the tail below the equilibrium value of Eq. (1.2) criteria were formulated for the existence of the effect. It follows from the asymptote of the reduced distribution function for high energy and large time [see Eq. (1.5)]

$$F(v, t) = f(v, t)/f_0(v) \simeq 1 + a_2(0)\left(\frac{v^2}{2}\right)^2 e^{-\lambda_2 t} \tag{2.1}$$

that the effect is realized if $a_2(0) > 0$. This is a sufficient condition for development of repopulation at high energies where at the initial moment the distribution function was below its equilibrium value.

We note that nonmonotonic relaxation can also be created in the region of the distribution dome, if at the initial moment a reduced particle concentration is created there. In this case the sufficient condition will coincide with that of [15], since the asymptote in the the low-energy range for large times t [see Eq. (2.1)] is defined by the free term of the polynomial $L_2^{1/2}(v^2/2)$, which is always positive [18].

The condition of [15] contains no assumptions as to the character of distribution function evolution in the nonlinear stage of relaxation. The quantitative characteristics of the

process can be obtained only by numerical solution of the relaxation problem. It should be said that only in [2] has the effect been studied by integrating the Boltzmann equation for a model two-dimensional gas. In [3, 6, 15, 16] etc. calculations were performed on the basis of truncated systems of the form of Eq. (1.6). The number of base functions used did not exceed 15, which imposed well-known limitations on the calculation results [6, 15]. In the present study the overall characteristics of the nonmonotonic relaxation process were studied using the method of [13], direct numerical integration of the Boltzmann equation.

Three families of initial conditions were considered:

A. The model distribution of [2, 15], consisting of two monoenergetic beams

$$f_{\delta\delta}^{(0)}(v) = \rho_1\delta(v-a) + \rho_2\delta(v-b),\ 0<a<b<\infty, \tag{2.2}$$

where the generalized function $\delta(v - a)$ is specified by the expression

$$4\pi\int_0^\infty dvv^2\varphi(v)\,\delta(v-a) = \varphi(a).$$

All parameters defining Eq. (2.2) were chosen to be nonnegative. Instead of the criterion of [15], here and below its equivalent

$$M_2(0) > 1, \tag{2.3}$$

was used, being simpler for practical calculations. It can be obtained from the known relationship [12] between the reduced moments M_n of the distribution function and the coefficients a_n [see Eq. (1.5)] of the expansion in Laguerre polynomials $L_n^{1/2}(v^2/2)$

$$M_n = \sum_{k=0}^{n}(-1)^k\binom{n}{k}a_k.$$

From the conservation laws Eq. (1.3) we have $\rho_1 + \rho_2 = 1$, $\rho_1a^2 + \rho_2b^2 = 3$.

With consideration of this, it follows from Eq. (2.3) that the processing of filling of the tail and dome (!) will be nonmonotonic (compare [15]), if the beam energies satisfy the inequality $15 - 3(a^2 + b^2) + a^2b^2 < 0$.

B. To consider possible practical applications of the effect, initial conditions of the form

$$f_{M\delta}^{(0)}(v) = \rho_1(2\pi T_1)^{-3/2}\exp(-v^2/2T_1) + \rho_2\delta(v-a), \tag{2.4}$$

were studied, these simulating the result of selective excitation ($\rho_2 > 0$) or absorption ($\rho_2 < 0$), imposed on an equilibrium Maxwell background. Accordingly, it was assumed that ρ_1, T_1 are nonnegative.

On the basis of the conservation laws, Eq. (1.3), the partial densities are expressed by

$$\rho_1 = (a^2-3)/(a^2-3T_1),\ \rho_2 = 3(1-T_1)/(a^2-3T_1). \tag{2.5}$$

With selective excitation, where $\rho_2 > 0$, the condition of nonmonotonic relaxation (2.3) with substitution of Eq. (2.5) leads to the inequalities

$$0<a^2<a_-^2,\ a_+^2<a^2<\infty,\ a_\pm^2 = \frac{1}{2}\left[5(1+T_1)\pm\sqrt{(25T_1-10)T_1+25}\right]. \tag{2.6}$$

The requirement of reduced population of the tail is insured by the selection of $T_1 < 1$. It then follows from the positive values of the densities (2.5) that the beam energy must exceed the mean energy of thermal molecular motion ($a^2 > 3$) and must be chosen from the second inequality of Eq. (2.6). The alternative choice $T_1 > 1$ may produce nonmonotonic relaxation in the region of the distribution dome. In this case the positiveness of ρ_1, ρ_2 is insured by the condition $a^2 < 3$ and the beam energy must be chosen from the first inequality of Eq. (2.6).

For selective absorption ($\rho_2 < 0$) in a similar manner we find that for nonmonotonic relaxation in the high energy region the absorption line must satisfy the inequalities

$$a_-^2<a^2<3T_1,\quad T_1<1. \tag{2.7}$$

For $T_1 > 1$ nonmonotonic relaxation will occur if $3T_1 < a^2 < a_+^2$.

C. Smooth initial conditions were considered using the example of a one-parameter family of [3]:

$$f_\mu^{(0)}(v) = f_0(v)\, F_\mu^{(0)}(v^2/2),$$
$$F_\mu^{(0)}(x) = \left(\frac{3}{2}\right)^{3/2} \exp\left(-\frac{x}{2}\right)\left[\frac{5}{8} + \frac{9\cdot 35}{32}\mu + \frac{9}{16}x^2\left(\frac{2}{5} - 21\mu\right) + \frac{27}{32}\mu x^4\right]. \quad (2.8)$$

Here the conservation laws are considered directly in the form of Eq. (2.8). The distribution function of Eq. (2.8) is positive at $0 \leqslant \mu \leqslant 0.02563$. The condition for nonmonotonic evolution of the tail (2.3) is equivalent to the inequality (see [3]) for the family parameter $44/45 + (28/3)\mu > 1$. In accordance with these inequalities the evolution of $f_\mu^{(0)}(v)$ was studied in the range $0.00238 \leqslant \mu \leqslant 0.0256$.

Analysis of the calculation results reveals that the process of nonmonotonic relaxation in the high energy region has a number of characteristic features common to all the initial conditions considered, Eqs. (2.2), (2.4), (2.8).

The typical evolution of the process can be traced clearly by the time dependences of relative populations (solid curves of Fig. 1a). Here we use the result of initial conditions (2.8) for $\mu = 0.0256$. To characterize the rate of nonmonotonic relaxation of individual energy groups (populations) the expression

$$\gamma(v, t) = \frac{1}{\tau_e} \ln\left|\frac{F(v, t) - 1}{F(v, t+\tau_e) - 1}\right|$$

was calculated — the evolution rate. Characteristic curves of the evolution rate together with time profiles of individual populations are shown in Fig. 1b for initial conditions of Eq. (2.4) at $T_1 = 0.2$, $\alpha = 3$.

It is evident from Fig. 1 that beginning at some particle energy the evolution of the developing overpopulation has the character of a variable amplitude wave with steep leading and sloped trailing edges, propagating in the direction of higher energies. The moment of arrival of this wave in some region of velocity space is characterized by an abrupt increase in the evolution rate of the local population (the steep leading edge). After achievement of the maximum the relative repopulation slowly decreases to the equilibrium value of unity (the sloping trailing edge). As it moves into higher energy regions, the amplitude of the overpopulation wave decreases, which can be explained by an increase in the local contributions to the integrals of the conservation laws Eq. (1.3).

It is evident from the asymptote (2.1) that with approach of the gas toward equilibrium for the initial conditions considered here a linear relaxation stage sets in, where $\gamma(v, t) \sim \lambda_2 = 1/3$. The time interval in which the process develops nonlinearly can be estimated from the time t_r, beginning at which for all $t > t_r$ the inequality

$$|\gamma(v, t) - \lambda_2|/\lambda_2 < 0{,}1. \quad (2.9)$$

is satisfied.

Analysis of the results using criterion (2.9) reveals that the time for transition to the linear stage of relaxation in the region $v \leqslant 10$ lies in the range $t_r = 15$–20 for all initial conditions studied.

The time evolution of the reduced moments, Eq. (1.7), for $n \geqslant 5$ is also nonmonotonic in character. The form of the functions $M_n(t)$ is shown in Fig. 2a for initial conditions (2.2) at $\alpha = 1$, $b = 3$.

The mean level of the overpopulations which develop can range over wide limits, depending on the parameters chosen in the initial conditions. Thus, for an initial distribution function Eq. (2.4) at $T_1 = 0.9$, change in the beam velocity in the interval $\alpha = 3$–4.5 leads to a growth in the local overpopulation in the tail of two orders of magnitude (see Fig. 2b). In general, it can be said that under conditions of well developed nonmonotonic relaxation the overpopulation in the velocity range $4 \leqslant v \leqslant 10$ exceeds the equilibrium value on the average by a factor of 2-3. For the given particle energy excitation continues for $t = 5$–6, while the total relaxation time of the repopulation wave reaches $t \approx 20$.

An example of nonmonotonic relaxation in the region of the distribution function dome is shown in Fig. 3a, which depicts results for initial conditions (2.4) at $T_1 = 1.8$, $\alpha = 1$. A similar process, developing in parallel to nonmonotonic relaxation in the tail region, can be observed for all initial conditions (2.2) at $M_2(0) > 1$, which corresponds to the generalization of the criterion of [15] to low energies. The overpopulation amplitudes and relaxation times obtained for the redistribution dome are approximately an order of magnitude

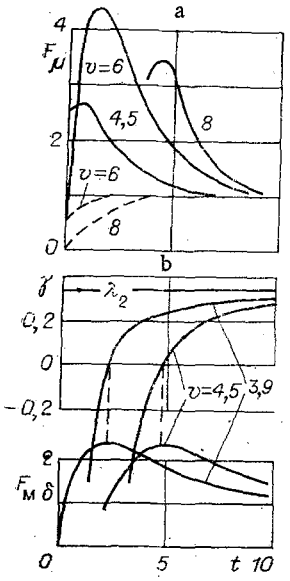

Fig. 1

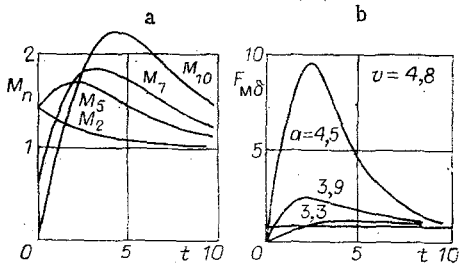

Fig. 2

lower than for the developed effect in the tail region.

3. An additive contribution of the form

$$f_0(v)\,{}_1F_1\left(-p, \frac{3}{2}, \frac{v^2}{2}\right), \tag{3.1}$$

where p is not an integer, will transform the initial conditions of Eqs. (2.2), (2.4), (2.8) to the class of distribution functions with a powerlike tail asymptote [14, 4]. In fact, in this region [18] $f_0(v)\,{}_1F_1(-p, 3/2, v^2/2) \sim (v^2/2)^{-p-3/2}$. The present study considers the effect of small additions of the form of Eq. (3.1) at p = 3/2 on the process of nonmonotonic relaxation. In this case the criterion of [15] is inapplicable, since at the initial moment the distribution function tail is overpopulated and $M_2(0)$ does not exist. In addition, at moderate velocity values ${}_1F_1(-3/2, 3/2, v^2/2)$ behaves like a Laguerre polynomial $L_2^{1/2}(v^2/2)$ [18], and it can be expected that in this region the nonmonotonic relaxation effect will be maintained.

On the whole the calculations performed confirm this assumption. For initial conditions

$$f^{(0)}(v) = f_0(v)\left[F_\mu^{(0)}(v^2/2) + 0.002\,{}_1F_1\left(-\frac{3}{2}, \frac{3}{2}, \frac{v^2}{2}\right)\right] \tag{3.2}$$

Fig. 3b shows the change over time of the relative populations; for comparison the dashed lines show corresponding data for the initial distribution of Eq. (2.8) (see also Fig. 1a). It is evident from Fig. 3b that the nonmonotonic character of relaxation is maintained for $4.5 \leqslant v \leqslant 5.5$, and in the high velocity region the distribution function evolves monotonically. The results indicate that the addition of Eq. (3.1), although low in absolute value, significantly affects the nonlinear effect, and a criterion for nonmonotonic relaxation applicable to initial conditions with a powerlike tail is necessary.

The evolution of initial conditions of the type of Eq. (3.2) was studied in [6] by integrating system (1.6). The set was defined by the expression p = (3 + n)/2, n = 0, 1,.... In the expansion of Eq. (1.5) 15 base functions were maintained, which according to the estimates of [6] provided usable accuracy in distribution function calculations only for t > 10. The results of the present study were obtained by integrating the kinetic equation, and are valid for $t \geqslant \tau_e$, where τ_e is the time step used in integrating Eq. (1.4). Control calculations revealed that the results obtained in the interval $\tau_e \leqslant t \leqslant 10$ agree well with numerical solution of Eq. (1.6) with 37 base functions.

4. The Krook model is often used in calculating kinetic processes in gases. For isotropic relaxation in the notation used herein the corresponding kinetic equation can be written in the form

$$\partial f(v, t)/\partial t = f_0(v) - f(v, t). \tag{4.1}$$

The shortcomings of this equation relative to homogeneous relaxation problems were considered in [9, 11]. However, the disagreement noted normally did not lead to total distortion of the picture of distribution function evolution. In the given case nonmonotonic

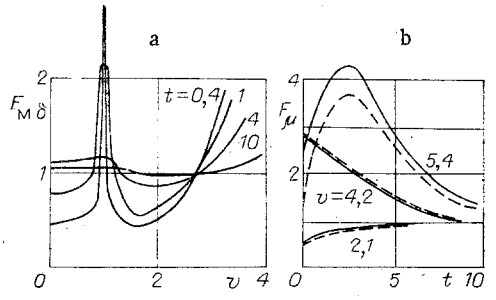

Fig. 3

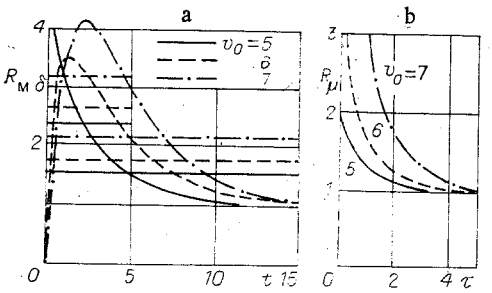

Fig. 4

relaxation is an example of a process which in principle cannot be described by the relaxation-type equation (4.1). In fact, the solution of the evolution problem for Eq. (4.1) has the form

$$f(v,\ t) = f_0(v) + (f^{(0)}(v) - f_0(v))e^{-t}, \tag{4.2}$$

whence it follows that for any initial conditions for all molecular velocity values the process of transition to equilibrium is monotonic. For a clear comparison, the dashed lines of Fig. 1a show the evolution of relative populations according to Eq. (4.2) for initial conditions (2.8) at $\mu = 0.0256$. The evolution of the reduced moments of all orders is also monotonic [see Eqs. (1.7), (4.2)].

It will also be useful to note that the relaxation rate function calculated for Eq. (4.2) gives $\gamma(v, t) = 1$, i.e., for the Krook equation the evolution rate is the same at any time for the entire energy spectrum. Such a property is quite often ascribed (see, for example, [4]) to a gas with Maxwellian distribution, which of course, is erroneous (see Fig. 1b).

5. It was noted in [2, 17] that the nonmonotonic character of relaxation may have a significant effect on the nonsteady-state kinetics of processes having an energy barrier. In order to quantitatively estimate the possible size of the effects, the rate of a model high threshold reaction was calculated. In the model used the relative reaction rate was defined by the expression

$$R(t,\ v_0) = N(t,\ v_0)/N_0(v_0),$$
$$N(t,\ v_0) = \int\int d\mathbf{v}_1 d\mathbf{v}_2 B_r(g,\ v_0)\, f(v_1,\ t) f(v_2,\ t). \tag{5.1}$$

The product of the modulus of the relative molecular velocity $g = |\mathbf{v}_1 - \mathbf{v}_2|$ by the differential section of the elastic process was written in the form

$$B_r(g,\ v_0) = \frac{1}{4\pi} H(g - v_0), \quad H(x) = \begin{cases} 1, & x > 0, \\ 0, & x \leqslant 0, \end{cases} \tag{5.2}$$

where H(x) is a Heaviside step function; v_0 is the characteristic velocity defining the value of the energy barrier.

The function $N(t, v_0)$ was calculated for nonsteady-state distribution functions describing translational relaxation of initial distributions (2.2), (2.4), (2.8). Correspondingly, $N_0(v_0)$ was determined for the equilibrium distribution (1.2). It was then assumed that the converse effect of the inelastic process on atomic gas relaxation could be neglected.

For distribution functions isotropic in velocity space, the integral in Eq. (5.1) reduces to the form

$$N(t,\ v_0) = 2\pi \int_0^\infty \int_0^\infty dv_1 dv_2 v_1^2 v_2^2 f(t,\ v_1) f(t,\ v_2) \int_{-1}^{1} dx H[\psi(v_1,\ v_2,\ x) - v_0],$$
$$\psi(v_1,\ v_2,\ x) = (v_1^2 + v_2^2 - 2v_1 v_2 x)^{1/2}. \tag{5.3}$$

The expression for $N_0(v_0)$ can be calculated explicitly:

$$N_0(v_0) = \frac{1}{4\pi}\left[1 - \Phi\left(\frac{v_0}{2}\right) + \frac{1}{\sqrt{\pi}} \exp\left(-\frac{v_0^2}{4}\right)\right] \tag{5.4}$$

(where $\Phi(x)$ is the probability integral [18]).

Using numerical calculations [2, 16] predicted that evolution of the distribution function for nonmonotonic relaxation is determined by the initial conditions and not dependent on the molecular interaction potential. This makes it possible to use the distribution functions calculated in Sec. 2 to estimate the effect of nonmonotonic relaxation on the rate of threshold reactions for other molecular models. In particular, calculations were performed for the hard sphere case. In place of Eq. (5.2) the function

$$B_{rss}(g, v_0) = (4\pi)^{-1} g H(g - v_0).$$

was used. The corresponding relative reaction rate $R_S(t, v_0)$ is determined by the expressions

$$N_s'(t, v_0) = 2\pi \int_0^\infty \int_0^\infty dv_1 dv_2 v_1^2 v_2^2 f(t, v_1) f(t, v_2) \int_{-1}^{1} dx \psi(v_1, v_2, x)$$

$$\times H[\psi(v_1, v_2, x) - v_0], \quad N_{0,s}(v_0) = \pi^{-3/2}(1 + v_0^2/4)\exp(-v_0^2/4).$$

The time dependences of relative rates of threshold reactions for both molecular models were compared in the dimensionless time scale $\tau = \lambda_{2,S} t_S = \lambda_{2,M} t_M$. Here $\lambda_{2,S} = 1.033$; $\lambda_{2,M} = 1/3$, the minimum eigenvalues of the linearized collision operator defining the characteristic linear relaxation times, and t_S, t_M are dimensionless times measured in units of the mean time between collisions for hard spheres and pseudo-Maxwellian molecules, respectively.

The barrier range $1 \leqslant v_0 \leqslant 7$ was studied. It was shown for all distribution functions calculated in Secs. 2, 3 that with increase in v_0 the maximum values of the relative reaction rate $R(t, v_0)$ as well as the mean values $\langle R(t, v_0)\rangle$ over the time interval $[0, t]$ increase. For low barriers the rate $R(t, v_0)$ is a monotonic function of time. With increase in v_0 the character of the time dependence of $R(t, v_0)$ becomes nonmonotonic, which agrees with the behavior of relative populations in the process of tail filling (see Figs. 1, 3b).

A characteristic example of $R(t, v_0)$ curves for initial conditions (2.4) at $T_1 = 0.2$, $\alpha = 3$ and various barrier values is shown in Fig. 4a. The straight lines are values of $\langle R(t, v_0)\rangle_t$ for $t = 5$, 15. The length of the lines indicates the interval of averaging. It is evident that $R(t, v_0)$ approaches its equilibrium value over a time period $t \simeq 15$, which correlates with the relaxation period of the overpopulation wave. Comparison of the curves of $R(t, v_0)$ with curves of the evolution of relative populations shows that the value of the barrier v_0 at which nonmonotonic behavior of $R(t, v_0)$ commences is markedly above the velocity value defining the lower limit of nonmonotonic relaxation of the distribution function tail. In particular, for initial conditions (2.8) at $\mu = 0.0256$ the curves $R(t, v_0)$ for barriers $v_0 \leqslant 7$ behave monotonically (compare Figs. 1a, 4b).

It follows from the calculations that the increase in reaction rate $R(t, v_0)$ produced by small additions of the form of Eq. (3.1) does not exceed 10% for $v_0 \leqslant 7$, although it can be expected that for further increase in barrier height the contribution of powerlike tails may become significant.

Comparison of reaction rates $R_S(t_S, v_0)$ and $R(t_M, v_0)$ calculated for initial conditions (2.2), (2.4), (2.8) shows that to three significant figures the effect of transition from pseudo-Maxwellian molecules to hard spheres reduces to a reduction in the time scale by a factor of $\lambda_{2,M}/\lambda_{2,S}$. When the time scale τ is used the quantities $R_S(\tau, v_0)$, $R_M(\tau, v_0)$ practically coincide on the graph. An example of such curves for initial conditions (2.8) at $\mu = 0.0256$ is shown in Fig. 4b.

Analysis of the results obtained reveals that in the process of nonmonotonic relaxation the mean rates of binary threshold reactions may exceed the equilibrium values by a factor of more than two times. This estimate is valid for all powerlike intermolecular repulsion potentials from the Maxwell model to hard spheres. The time intervals over which the mean reaction rate significantly exceeds the equilibrium value comprise from 5 to 15 mean molecular path times, increasing with decrease in "rigidity" of the potential.

It follows from these quantitative estimates that nonmonotonic relaxation may significantly accelerate barrier type kinetic processes developing with it as a background.

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NONLINEAR WAVES ON THE SURFACE OF A LIQUID FILM RUNNING DOWN A VERTICAL WALL

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It is known from experiments [1, 2] that the flow of a liquid film down a vertical plane has a wave character even for small Reynolds numbers. This is related to the fact that the flow of a film of thickness h with a plane free surface whose velocity profile is semiparabolic, $u = 3u_0(y/h - y^2/2h^2)$, is unstable starting from very small Reynolds numbers, i.e., infinitesimal long-wave disturbances increase exponentially with time [3, 4]. As a result of nonlinear effects stationary periodic and soliton flow regimes may be formed. Since a complete treatment of such problems is extremely complicated, various simplifications are used to solve it.

Thus, for low flow rates ($Re \sim 1$) the problem of wave regimes can be reduced to that of solving a single equation for the film thickness [5]. However, stationary traveling waves are practically not observed at these flow rates, and although the form of the solutions of this equation [6] is in good qualitative agreement with the form of the waves observed in experiment, there is no quantitative agreement. A similar situation occurs also with a two-wave equation [7] which contains only quadratic nonlinear term, and therefore describes the

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