

There are a number of important advantages in using free jets, compared to other experimental methods in physical kinetics [1]: the possibility of realizing the simplest one-dimensional radial steady flow; the self-modeling nature of the structure of the jet and the distribution of parameters in it; and the possibility of controlling the rates of relaxation processes.

These factors considerably facilitate the theoretical analysis of the results. The latest measured nonequilibrium molecular distribution functions for velocity [2, 3], rotational [4, 5], and vibrational [6-8] energy levels have been used to find the parameters of the elastic and anisotropic interaction potentials [3], and also the rate constants for energy exchange between the internal degrees of freedom [9, 10]. This is done by solving the kinetic equations describing the corresponding relaxation process, with the help of certain model-dependent expressions for the interaction potential or the rate constants. The parameters of the model are determined by comparing the experimental data with the solution of the system of kinetic equations; the problem is drastically simplified if the solution can be found in analytical form. An analytical solution of the system of relaxation equations would also simplify the study of the effect of coupling between different relaxation processes in jets (for example, the effect of condensation on the rotational [11] and vibrational [8] relaxation).

In this connection we develop an analytical method [12, 13] of solving a system of relaxation equations of the detailed balance type, describing, for an appropriate choice of rate constants, rotational and vibrational relaxation, and also nonequilibrium condensation (in the quasichemical model). After transforming from the population densities to smoother functions, and after a nonlinear change of variables, the system reduces to a form which is much easier to solve (both analytically and numerically). It is shown that for isentropic flow, there are several zones along the axis of the jet having different relaxation mechanisms. An iterative method of solving the system of relaxation equations is described. The method uses an optimum choice of the zeroth approximation in each of the zones.

1. Statement of the Problem. In a freely expanding jet, the rotational (vibrational) relaxation of a dilute diatomic gas impurity in a monatomic gas solvent is described by the system of relaxation equations

$$\frac{u}{d} \frac{dN_j}{dx} = n \sum_{\delta} [K_{j+\delta, j} N_{j+\delta} - (K_{j, j+\delta} + K_{j, j-\delta}) N_j + K_{j-\delta, j} N_{j-\delta}]. \quad (1.1)$$

Here $N_j = n_j/n$; $n \equiv \sum_j n_j$ is the number density of the molecular gas; n_j is the population density of the j -th energy level; u is the hydrodynamic velocity; x is the coordinate along the axis of the jet, normalized to the nozzle diameter d ; $K_{i, j}(T)$ is the rate constant of energy exchange between the internal degrees of freedom of the relaxing gas and the translational degrees of freedom of the monatomic gas at temperature T .

The variation of the gasdynamical parameters along the axis of the jet will be described by the isentropic formulas

$$\frac{T(x)}{T_0} = \frac{1}{F(x)} \quad \frac{u(x)}{a_0} = \frac{M(x)}{\sqrt{F(x)}}, \quad \frac{n(x)}{n_0} = [F(x)]^{-1/(\gamma-1)}, \quad \gamma = c_p/c_v, \quad (1.2)$$

where

$$F(x) \equiv 1 + \frac{\gamma-1}{2} M^2(x); \quad (1.3)$$

T_0 , a_0 , n_0 are the temperature, speed of sound, and density in the adiabatically and isentropically braked gas. For the Mach number $M(x)$ the following empirical formula [14] is used

$$M(x) = \begin{cases} A(x-x_0)^{\gamma-1} - \frac{1}{2A} \frac{\gamma+1}{\gamma-1} \frac{1}{(x-x_0)^{\gamma-1}} + \frac{C}{(x-x_0)^{3(\gamma-1)}}, & x \geq x_* \\ M(x_*) \exp\left\{\frac{dM(x_*)}{dx} \frac{x-x_*}{M(x_*)}\right\}, & x < x_*. \end{cases} \quad (1.4)$$

The parameter x_* is chosen from the condition $M(0) = 1$. The exponential approximation in (1.4) gives a smooth matching of the two curves at the point $x = x_*$.

We assume a Boltzmann distribution over the cross section of the nozzle. The corresponding temperature is given by $T = T_* = T_0 \left/ \left(1 + \frac{\gamma-1}{2}\right)\right.$ and

$$N_j^0 \equiv N_j(0) = \frac{g_j}{Q(T_*)} \exp\left(-\frac{E_j}{kT_*}\right) = N_j^B(T_*). \quad (1.5)$$

Here g_j is the multiplicity of the degenerate level j ; $Q(T_*)$ is the partition function; E_j is the energy of the j th level.

2. Analysis of the System of Relaxation Equations. In place of the concentrations $N_j(x)$, we introduce the smooth functions $z_j(x)$ which give the deviation of the distribution functions from the equilibrium distribution functions:

$$z_j(x) = N_j(x)/N_j^B(T(x)). \quad (2.1)$$

It follows from (1.1) that z_j satisfies

$$\frac{dz_j}{dx} = \frac{nd}{u} \sum_{\delta} \left[K_{j+\delta,j} \frac{N_{j+\delta}^B}{N_j^B} z_{j+\delta} - (K_{j,j+\delta} + K_{j,j-\delta}) z_j + K_{j-\delta,j} \frac{N_{j-\delta}^B}{N_j^B} z_{j-\delta} \right] - \frac{z_j}{N_j^B} \frac{dN_j^B}{dx} \equiv K(z). \quad (2.2)$$

We represent $z_{j+\delta}$ in the form

$$z_{j+\delta}(x) = z_j(x) \prod_{i=0}^{\delta-1} a_{j+i}(x) f_{j+i}(x), \quad a_m \equiv \frac{K_{m,m+1}}{K_{m+1,m}} \frac{N_m^B}{N_{m+1}^B}. \quad (2.3)$$

After substitution of (2.3) into (2.2) and a series of reductions similar to those discussed in [13], we obtain the following system of equations for the new unknown functions $f_j(x)$:

$$\frac{1}{f_j} \frac{df_j}{dx} = R_j(f_j, x) + \varepsilon_j(f, x) + \Gamma_j(x), \quad (2.4)$$

where

$$R_j = \frac{nd}{u} \sum_{\delta} [\alpha_j^{(\delta)} f_j^{\delta} + \beta_j^{(\delta)} + \gamma_j^{(\delta)} f_j^{-\delta}], \quad \varepsilon_j = \frac{nd}{u} \sum_{\delta} \varepsilon_j^{(\delta)},$$

$$\Gamma_j = \frac{d}{dx} \ln \frac{K_{j+1,j}}{K_{j,j+1}}, \quad \alpha_j^{(\delta)} = \Pi_{j+1,\delta}^+ - \Pi_{j,\delta}^+, \quad \gamma_j^{(\delta)} = \Pi_{j+1,\delta}^- - \Pi_{j,\delta}^-, \quad \beta_j^{(\delta)} = (K_{j,j+\delta} - K_{j+1,j+\delta+1}) + (K_{j,j-\delta} - K_{j+1,j-\delta+1}); \quad (2.5)$$

$$\varepsilon_j^{(\delta)} = f_j^{\delta} \left[\left(1 - \prod_{i=0}^{\delta-1} \frac{f_{j+i}}{f_j}\right) \Pi_{j,\delta}^+ - \left(1 - \prod_{i=0}^{\delta-1} \frac{f_{j+i+1}}{f_j}\right) \Pi_{j+1,\delta}^+ \right] + f_j^{-\delta} \left[\left(1 - \prod_{i=0}^{\delta-1} \frac{f_j}{f_{j+i-\delta}}\right) \Pi_{j,\delta}^- - \left(1 - \prod_{i=0}^{\delta-1} \frac{f_j}{f_{j+i-\delta+1}}\right) \Pi_{j+1,\delta}^- \right].$$

In (2.5) we have introduced the notation:

$$\Pi_{j,\delta}^+ = K_{j+\delta,j} \frac{N_{j+\delta}^B}{N_j^B} \prod_{i=0}^{\delta-1} a_{j+i}, \quad \Pi_{j,\delta}^- = K_{j-\delta,j} \frac{N_{j-\delta}^B}{N_j^B} \prod_{i=0}^{\delta-1} a_{j+i-\delta}^{-1}.$$

In order to satisfy the principle of detailed balance, we must set $\alpha_j = 1$ for all j . Then $\Pi_{j,\delta}^{\pm} = K_{j,j\pm\delta}$,

$$\Gamma_j = \frac{d}{dx} \ln \frac{N_j^B(T(x))}{N_{j+1}^B(T(x))} = -\frac{E_{j+1} - E_j}{kT} \frac{d}{dx} \ln T(x) > 0, \quad (2.6)$$

and the coefficients in the expression for R_j satisfy the condition

$$\alpha_j^{(\delta)} + \beta_j^{(\delta)} + \gamma_j^{(\delta)} = 0. \quad (2.7)$$

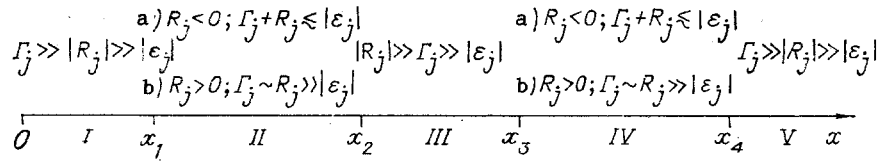


Fig. 1

If the functions $f_j(x)$ depend only weakly on j , then we obtain from (2.5)

$$|\varepsilon_j(\mathbf{f}, x)| \ll 1. \quad (2.8)$$

In the case of a Boltzmann distribution we have from (2.3)

$$f_j^B = 1, \quad (2.9)$$

and hence

$$\varepsilon_j(\mathbf{f}^B) \equiv 0, \quad R_j(f_j^B) \equiv 0. \quad (2.10)$$

For small deviations from equilibrium [$f_j = 1 + \lambda \varphi_j$, $\lambda \ll 1$, $\varphi_j - \varphi_i = O(\lambda)$] we have from (2.7) and (2.10)

$$R_j = O(\lambda), \quad \varepsilon_j = o(\lambda). \quad (2.11)$$

For the isentropic flow of a gas mixture described by (1.2) through (1.4) with $\gamma > 3/2$ (a weak diatomic gas impurity in a monatomic gas) it follows from (2.6) that $\Gamma_j'(x) > 0$, i.e. $\Gamma_j(x)$ increases monotonically from the initial value

$$\Gamma_j(0) = \frac{E_{j+1} - E_j}{kT_0} (\gamma - 1) \frac{dM(x_*)}{dx} \exp \left\{ -\frac{x_*}{M(x_*)} \frac{dM(x_*)}{dx} \right\} \quad (2.12)$$

and behaves at large x as

$$\Gamma_j(x) \underset{x \gg x_*}{\sim} \frac{E_{j+1} - E_j}{kT_0} A^2 (\gamma - 1)^2 (x - x_0)^{2\gamma - 3}.$$

However the factor $n(x)d/u(x)$ in $R_j(x)$ in (2.4) decreases monotonically and for $x \gg x_*$

$$\frac{n(x)d}{u(x)} \underset{x \gg x_*}{\sim} \frac{n_0 d}{a_0} \frac{2}{(\gamma - 1) A^3 (x - x_0)^{3(\gamma - 1)}}. \quad (2.13)$$

Since at low temperature the deactivation rate constants in $R_j(f_j, x)$ become slowly varying functions of T [15], at large x the dominant contribution to the right hand side of (2.4) is the term $\Gamma_j(x)$.

From these estimates we draw the following conclusions:

1. If the Boltzmann distribution (1.5) is specified at the cross section of the nozzle, then in view of (2.9) and (2.10), the departure of the internal degrees of freedom from equilibrium in the initial part of the jet is determined by the term $\Gamma_j(x)$ in (2.4), and hence, according to (2.6) by the gasdynamical characteristics of the flow and by the spectrum of the molecules, and not by the properties of the intermolecular interaction.

2. Suppose $R_j(x) < 0$ in a certain region. Then in this region there can be a situation in which the terms $\Gamma_j(x)$ and $R_j(x)$ cancel out one another [$\Gamma_j + R_j = o(\lambda)$] and then it is necessary to take into account all of the terms on the right hand side of (2.4), in spite of (2.8) and (2.11). In this case we obtain a "quasistationary" distribution given by the condition

$$R_j(f_j, x) + \Gamma_j(x) + \varepsilon_j(\mathbf{f}, x) = 0. \quad (2.14)$$

3. In all other cases the nondiagonal term in \mathbf{f} in (2.4) ε_j can contribute significantly to the rate of change of $f_j(x)$ only for distributions with a strong dependence of f_j on j , i.e., only in the case of a significant deviation from equilibrium. For distributions which are smooth in j , this term can be included using perturbation theory.

4. When $x \gg x_*$ the rate of change of f_j , according to (2.12) and (2.13), is determined by the term $\Gamma_j(x)$, as in the initial part of the jet.

Hence there are five zones on the axis of the jet, characterized by different relaxation regimes (Fig. 1).

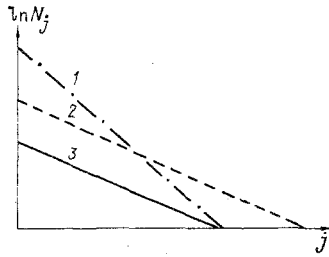


Fig. 2

3. Solution of the System of Relaxation Equations. We attempt to solve the system (2.4) by iteration. However since the contributions of the different terms on the right hand side of (2.4) are significantly different in the different regions along the axis of the jet (Fig. 1), it is necessary to consider the optimum choice of a zeroth approximation in each of the relaxation regimes.

On the segment $[0, x_1]$ we choose as a zeroth approximation the solution of the Cauchy problem

$$\frac{1}{f_{j,0}^{(I)}} \frac{df_{j,0}^{(I)}}{dx} = \Gamma_j(x), \quad f_{j,0}^{(I)}(0) = 1. \quad (3.1)$$

Using (2.1), (2.3), and (2.6), we find from (3.1)

$$f_{j,0}^{(I)}(x) = \frac{N_j^B(T(x))/N_j^B(T_*)}{N_{j+1}^B(T(x))/N_{j+1}^B(T_*)} \quad (3.2)$$

or

$$\frac{N_{j+1,0}^{(I)}(x)}{N_{j,0}^{(I)}(x)} = \frac{N_{j+1}^0}{N_j^0} \equiv \frac{N_{j+1}^B(T_*)}{N_j^B(T_*)}. \quad (3.3)$$

The solution (3.3) describes a set of population densities in which the upper levels become overpopulated and the lower levels becomes depopulated (Fig. 2); this is consistent with the experimental data [4, 5] on the rotational relaxation of nitrogen molecules in free jets (curves 1 and 2: $N_j^B(t(x))$, $N_j(x)$ for $x > 0$; curve 3: $N_j^B(T_*)$ for $x = 0$).

We obtain from (2.4) for the successive approximations

$$\frac{1}{f_{j,h+1}^{(I)}} \frac{df_{j,h+1}^{(I)}}{dx} = R_j(f_{j,h}^{(I)}, x) + \varepsilon_j(f_{j,h}^{(I)}, x) + \Gamma_j(x), \quad (3.4)$$

from which it follows, with the help of (3.1), that

$$f_{j,h+1}^{(I)}(x) = f_{j,0}^{(I)}(x) \exp \left\{ \int_0^x [R_j(f_{j,h}^{(I)}, \xi) + \varepsilon_j(f_{j,h}^{(I)}, \xi)] d\xi \right\}. \quad (3.5)$$

Since all functions appearing in (2.4) are continuous on $[0, x_1]$, and $f_j(x) > 0$, the right-hand side of this equation satisfies the Lipschitz condition, which ensures that the sequence of iterations (3.5) converges to the solution of the Cauchy problem. The concentrations $N_j^{(I)}(x)$ can be found in terms of the functions $f_j^{(I)}(x)$ using relations (2.3) and (2.1).

On the segment $[x_1, x_2]$ in case *a* (see Fig. 1) the zeroth approximation can be taken to be the "quasistationary" distribution given by the condition (2.14). However it is simpler to find it by solving the following system of equations derivable from (2.2) in this case, rather than by solving the system (2.14):

$$\begin{aligned} K_{j,j+1} z_{j+1}^{(II)} &= K_{j,j} z_j^{(II)} - K_{j,j-1} z_{j-1}^{(II)}, \\ K_j &\equiv K_{j,j+1} + K_{j,j-1} + \frac{u}{nd} \frac{d}{dx} \ln N_j^B(T(x)). \end{aligned} \quad (3.6)$$

Because the temperature of the gas drops rapidly along the axis of the jet, only single-quantum transitions ($\delta = 1$) are taken into account in (3.6); multi-quanta transitions will be taken into account in the higher order approximations. The solution of (3.6) can be written in the form

$$z_{j+1,0}^{(II)} = \prod_{i=0}^j \frac{K_i}{K_{i,i+1}} \left[1 - \sum_{i=0}^{j-1} \frac{K_{i+1,i} K_{i,i+1}}{K_i K_{i+1}} + p_j \right] z_{0,0}^{(II)}, \quad (3.7)$$

where the coefficients p_j are calculated from the recursion relation

$$p_j = p_{j-1} + \frac{K_{j,j-1} K_{j-1,j}}{K_{j-1} K_j} \left(\sum_{i=0}^{j-3} \frac{K_{i+1,i} K_{i,i+1}}{K_i K_{i+1}} - p_{j-2} \right), \quad p_0 = p_1 = p_2 = 0,$$

and $z_{0,0}^{(II)}(x)$ is calculated from the normalization condition

$$\sum_j N_j(x) = \sum_j z_j(x) N_j^B(T(x)) = 1.$$

For the higher-order approximations it follows from (2.2) that $dz_{j,k+1}^{(II)}/dx = K(z_k^{(II)})$, and therefore

$$z_{j,k+1}^{(II)}(x) = \int_{x_1}^x K[z_k^{(II)}(\xi)] d\xi + z_j^{(I)}(x_1).$$

As a zeroth approximation on the segment $[x_2, x_3]$ we take the solution of the Cauchy problem

$$\frac{1}{f_{j,0}^{(III)}} \frac{df_{j,0}^{(III)}}{dx} = R_j(f_{j,0}^{(III)}), \quad f_{j,0}^{(III)}(x_2) = \frac{z_{j+1}^{(II)}(x_2)}{a_j(x_2) z_j^{(II)}(x_2)}. \quad (3.8)$$

Including only single-quantum transitions ($\delta = 1$) in R_j , we have [13]

$$\begin{aligned} f_{j,0}^{(III)}(x) &= \frac{1 + f_{j,0}^{(III)}(x_2) + (1 - f_{j,0}^{(III)}(x_2))}{1 + f_{j,0}^{(III)}(x_2) + (1 - f_{j,0}^{(III)}(x_2))} \rightarrow \\ &\rightarrow \frac{\left\{ \int_{x_2}^x \frac{n(\xi) d}{u(\xi)} E_j(\xi) [\alpha_j(\xi) + \gamma_j(\xi)] d\xi - E_j(x) \right\}}{\left\{ \int_{x_2}^x \frac{n(\xi) d}{u(\xi)} E_j(\xi) [\alpha_j(\xi) + \gamma_j(\xi)] d\xi + E_j(x) \right\}} \rightarrow \\ E_j(x) &\equiv \exp \left\{ \int_{x_2}^x \frac{n(\xi) d}{u(\xi)} [\alpha_j(\xi) - \gamma_j(\xi)] d\xi \right\}. \end{aligned} \quad (3.9)$$

The higher order approximations are found from the system (3.4)

$$f_{j,k+1}^{(III)}(x) = f_{j,0}^{(III)}(x) \exp \left\{ \int_{x_2}^x [R'_j(f_{j,k}^{(III)}, \xi) + \varepsilon_j(f_k^{(III)}, \xi) + \Gamma_j(\xi)] d\xi \right\},$$

where only multi-quanta transitions ($\delta \geq 2$) are taken into account in R_j' .

On the segment $[x_3, x_4]$ the solution is constructed in the same way as on the segment $[x_1, x_2]$: from the zeroth approximation (3.7) with an appropriate change of initial parameters. Finally for $x \geq x_4$ the initial approximation is chosen in the same way as on the first segment $[0, x_1]$.

The most complicated case is the choice of the optimum zeroth approximations on segments II and IV (see Fig. 1) in case b, i.e., when the terms Γ_j and R_j in (2.4) are positive quantities of the same order. Even in the approximation of single-quantum transitions, instead of (3.8) we have the following expression from (2.4)

$$\frac{df_{j,0}}{dx} = \frac{nd}{u} [\alpha_j^{(1)} f_{j,0}^2 + \beta_j^{(1)} f_{j,0} + \gamma_j^{(1)}] + f_{j,0} \Gamma_j. \quad (3.10)$$

Each of the equations of the system (3.10) is a general Riccati equation with the sum of the coefficients not equal to zero. Therefore unlike (3.8), their integration requires a separate treatment.

Analyzing the results, we make the following conclusions:

First, the solution (3.2) and (3.3) of the system (3.1) describes the experimentally observed redistribution of internal energy in the free expansion of a molecular gas, in particular the overpopulation of the upper levels and the underpopulation of the lower levels, in comparison with a Boltzmann distribution.

Second, according to (2.6), the right-hand side of (3.1) is proportional to $E_{j+1} - E_j$. Taking into account the dispersion of the rotational spectrum of diatomic molecules, rotational nonequilibrium in an expanding jet appears primarily in the upper levels; this also agrees with the experimental data [4, 5].

Third, in order to reproduce the rate constants of rotational (vibrational) energy exchange from the relaxation experiments, it is necessary to take into account the zones shown in Fig. 1 with different relaxation mechanisms, because the conventional methods are applicable only in zone III, and possibly in the transitional zones II and IV. Therefore in each case the boundaries x_1, x_2, x_3, x_4 of the intervals must be estimated.

Using a generalization of the solution (3.9) of the system (3.8) [13], the iteration method employed in the present paper to integrate (1.1) can also be applied to the case when intermolecular rotational-rotational or vibrational-vibrational energy exchange is taken into account. It can also be useful in the numerical solution of the relaxation equations, since they form a system of stiff equations and the use of special methods is necessary (different variants of the Gere method, for example).

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