LITERATURE CITED

1. J. Cont-Bello, Turbulent Flow in a Channel with Parallel Walls [Russian translation], Mir, Moscow (1968).
2. H. Schlichting, Boundary Layer Theory, 7th Ed., McGraw-Hill (1979).
3. Proceedings of the IX All-Union School Seminar "Numerical Methods in Viscous Liquid Dynamics," [in Russian], Novosibirsk (1983).
4. A. A. Samarskii, Introduction to the Theory of Difference Systems [in Russian], Nauka, Moscow (1971).
5. B. F. Gordiets, A. I. Osipov, and L. A. Shelepin, Kinetic Processes in Gases and Molecular Lasers [in Russian], Nauka, Moscow (1980).
6. Yu. M. Gershenzon, V. B. Rozenshtein, and S. Ya. Umanskii, "Heterogeneous relaxation of oscillatory molecular energy," in: Plasma Chemistry [in Russian], 4th Ed., Atomizdat, Moscow (1977).

GENERALIZED RELAXATION EQUATIONS FOR VIBRATIONAL AND ROTATIONAL MOLECULAR KINETICS IN GAS FLOWS

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A system of kinetic equations for the distribution functions of gas particles over quantum states (over vibrational and rotational molecular levels) is usually used to describe nonequilibrium relaxation processes in molecular gases [1]. Here we consider impurity relaxation of a molecular gas in a monatomic gas flow, when molecular collisions can be neglected and the distributions of gasdynamic parameters are known.

The kinetic equations are in this case

$$\frac{dN_i}{dt} = n_g \sum_j (K_{ij}N_j - K_{ji}N_i), \qquad (1)$$

where N_i is the population of the i-th molecular quantum level with energy E_i, satisfying the normalization condition $\sum_i N_i = 1$; $K_{ij}(T)$ are rate constants of molecular transitions from state j into state i during collisions with atoms of the gas flow, having temperature T and density n_g and satisfying the detailed balance rule $K_{ij}N_j^* = K_{ij}N_i^*$; N_i^* are molecular equilibrium Boltzman distributions over quantum states, $N_i^* = g_i \exp(-E_i kT)/S$; g_i is the statistical weight of the state; and S is the partition function for the system of levels under consideration, $S = \sum_i g_i \exp(-E_i/kT)$.

For known dependences of K_{ij} on quantum numbers and temperature, as well as for known distributions of the gasdynamic parameters of the monatomic gas, Eqs. (1) can be solved numerically. However, the numerical solutions of the kinetic equations are not always convenient, as a large amount of calculations is required, particularly if it is necessary to take into account the large number of quantum levels.

Besides, the shape of the constants $K_{ij}(T)$ is usually unknown, and the absence of reliable constants leads to the necessity of using semiempirical dependences with adjustable parameters in solving the kinetic equations, selected by comparison with experiment. This also increases the bulk of calculations, and the problem of choosing an adequate set of rate constants, describing experimental data, remains nonsimple. The matter is that rate constants with different dependences on quantum numbers and temperature can lead to nearly equal distributions in the populations of molecular quantum levels.

Here we propose to represent the populations N_i in the form of an expansion in orthogonal functions. As a result, the system of kinetic equations (1) transforms to an equivalent system of moment equations, characterized by some set of time relaxations ω_{km}^{-1}, which in some

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cases are simpler to determine experimentally than the rate constants $K_{ij}(T)$. The method suggested makes it possible to explain a wide class of exactly solvable kinetic problems, to obtain the necessary relaxation condition of an arbitrary molecular system in terms of a sequence of Boltzmann states, and to explain the validity condition of the diffusion approximation. Besides, for cases of not too large a deviation from equilibrium the population expansion can be confined to its first terms, which substantially shortens and simplifies the description of nonequilibrium molecular systems.

Population Expansion in Orthogonal Polynomials. A system of orthogonal functions will be sought, starting from the shape of the molecular energy spectrum E_i and the corresponding spectrum of equilibrium populations N^*_i. Among the whole molecular system we isolate independent modifications, i.e., molecular groups with energy levels, between which transitions are possible during collisions with gas atoms, i.e., molecules for which $K_{ij} \neq 0$. For homonuclear molecules, for example, transitions are almost totally forbidden between ortho- and para-modifications, i.e., transitions from even to odd rotational states, and vice versa. A number of almost exact selection rules also exists for symmetric and asymmetric tops [2, 3], leading to substantially independent modifications in vibrational or rotational transitions.

We represent the molecular populations for the modification considered in the form of the expansion

$$N_i = N_i^* \sum_{k=0} \eta_k(\beta)\, \Psi_k(\varepsilon_i), \tag{2}$$

where $\varepsilon_i = E_i/\Theta$; $\beta = \Theta/T$; Θ is a characteristic temperature proportional to the rotational or vibrational molecular constant, and $\Psi_k(\varepsilon_i) \equiv \Psi_k(i)$ is a set of functions satisfying the orthogonality condition

$$\langle \Psi_m \Psi_k \rangle = \sum_i N_i^* \Psi_m(i)\, \Psi_k(i) = \delta_{mk}. \tag{3}$$

Here the summation is carried out over all energy levels of the modification considered, and the brackets <> denote averaging of the functions $\varphi(\varepsilon_i)$ over the equilibrium molecular distribution over quantum levels: $\langle \varphi \rangle = \sum_i N_i^* \varphi(\varepsilon_i)$. The averaging over nonequilibrium distribution functions is denoted by a bar: $\overline{\varphi} = \sum_i N_i \varphi(\varepsilon_i)$.

We select the functions $\Psi_k(\varepsilon_i)$ in the form of polynomials of order k: $\Psi_k(\varepsilon_i) = \sum_{l=0}^{k} p_{k\ell}(\beta)(\varepsilon_i\beta)^k$, $k = 0, 1, 2, \ldots$, where the coefficients $p_{k\ell}$ may be temperature dependent. The polynomials $\Psi_k(\varepsilon_i)$, for an arbitrary spectrum ε_i, are nonclassical orthogonal polynomials, introduced in [4], but their properties have not been investigated.

As shown in [5], the expansion coefficinets $p_{k\ell}$ can be found by solving the system of equations $p_{mm} \sum_{n=0}^{m} p_{mn} Z_{n+k} = \delta_{mk}$, $k \leqslant m$, $p_{00} \equiv 1$. Here Z_n are determined in terms of the partition function S:

$$Z_n = \beta^n \langle \varepsilon_i^n \rangle = \beta^n \sum_i N_i^* \varepsilon_i^n = (-1)^n \frac{\beta^n}{S} \frac{\partial^n S}{\partial \beta^n}. \tag{4}$$

The polynomials $\Psi_k(\varepsilon_i)$ and the coefficients $p_{k\ell}$ satisfy the recurrence relations

$$\Psi_k(\varepsilon_i) = p_{kk}\left[(\varepsilon_i\beta)^k - \sum_{n=0}^{k-1} \Psi_n(\varepsilon_i) \sum_{l=0}^{n} p_{nl} Z_{k+l}\right] = \left[\varepsilon_i^k - \sum_{n=0}^{k-1} \langle \varepsilon^k \Psi_n \rangle\, \Psi_n(\varepsilon_i)\right] \Bigg/ \sqrt{\langle \varepsilon^{2k} \rangle - \sum_{n=0}^{k-1} \langle \varepsilon^k \Psi_n \rangle^2}; \tag{5}$$

$$p_{kk} = (-1)^k \left[Z_{2k} - \sum_{m=0}^{k-1} \left(\sum_{n=0}^{m} p_{mn} Z_{k+n}\right)^2\right]^{-1/2}, \tag{6}$$

$$p_{kl} = -\, p_{kk} \sum_{m=l}^{k-1} p_{ml} \sum_{n=0}^{m} p_{mn} Z_{k+n} \quad (l < k),$$

$$p_{kl} = -\, p_{ll} \sum_{m=l+1}^{k} p_{km} \sum_{n=0}^{l} p_{ln} Z_{n+m} \quad (l < k).$$

$$\Psi_{k+1}(\varepsilon_i) = \frac{p_{k+1,k+1}}{p_{kk}} \left\{ \Psi_k(\varepsilon_i) \left[\varepsilon_i \beta + \left(\frac{p_{k+1,k}}{p_{k+1,k+1}} - \frac{p_{k,k-1}}{p_{kk}} \right) \right] - \frac{p_{k-1,k-1}}{p_{kk}} \Psi_{k-1}(\varepsilon_i) \right\}.$$

Using the orthogonality conditions, we obtain (see [5]) the relation used below to derive the generalized relaxation equations:

$$\left\langle \Psi_k \frac{d\Psi_m}{d\beta} \right\rangle = \sum_i N_i^* \Psi_k(\varepsilon_i) \frac{d\Psi_m(\varepsilon_i)}{d\beta} = \left(\frac{1}{p_{mm}} \frac{dp_{mm}}{d\beta} + \frac{m}{\beta} \right) \delta_{km} + \frac{p_{m-1,m-1}}{\beta p_{mm}} \delta_{k,m-1}. \tag{7}$$

Multiplying the expansion (2) by $\Psi_m(\varepsilon_i)$ and summing over all i, with account of the orthogonality relations (3), we find the expression

$$\eta_m = \sum_i N_i \Psi_m(\varepsilon_i) = \sum_{n=0}^{m} p_{mn} \beta^n \overline{\varepsilon^n}, \tag{8}$$

the inverse transformation with respect to expansion (2). The seond part of equality (8) implies that the expansion coefficinets are moments of the internal energy, calculated from the nonequilibrium distribution function. In particular, we have

$$\eta_1 = \frac{\langle \varepsilon \rangle - \bar{\varepsilon}}{\sqrt{\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2}} = (Z_1 - \beta\bar{\varepsilon}) / \sqrt{Z_2 - Z_1^2}. \tag{9}$$

Expressions (2) and (8) can also be represented in the form

$$N_i / \sqrt{N_i^*} = \sum_k \sqrt{N_i^*} \Psi_k(\varepsilon_i) \eta_k = \sum_k C_{ik} \eta_k,$$

$$\eta_k = \sum_j \sqrt{N_j^*} \Psi_k(\varepsilon_j) N_j / \sqrt{N_j^*} = \sum_j C_{kj}^{-1} N_j / \sqrt{N_j^*},$$

where the unitary matrix C_{ik} was introduced with elements: $C_{ik} = C_{ki}^{-1} = \sqrt{N_i^*} \times \Psi_k(\varepsilon_i)$. The unitarity of C_{ik} determines one more orthogonality relation for the polynomials

$$\sqrt{N_i^* N_j^*} \sum_k \Psi_k(\varepsilon_i) \Psi_k(\varepsilon_j) = \sum_k C_{ik} C_{ki}^{-1} = \delta_{ij} \tag{10}$$

and the equality of norms in the population (for $N_i/\sqrt{N_i^*}$) and momentum (for η_k) representations $\sum_i N_i^2 / N_i^* = \sum_{k=0} \eta_k^2$, which is a completeness condition for expansion (2).

Generalized Relaxation Equations. We multiply the right- and left-hand sides of the kinetic equation (1) by the polynomial $\Psi_m(\varepsilon_i)$ and sum over all i, replacing the populations N_i by their expansions (2). Using the orthogonality condition (3) and relation (7), as well as taking into account that the polynomials Ψ_m depend on time through their parametric dependence on temperature, we obtain a system of moment equations

$$d\eta_m/dt = -n_g \sum_{k=1} \omega_{mk} \eta_k + \left[\left(\frac{\beta}{p_{mm}} \frac{dp_{mm}}{d\beta} + m \right) \eta_m - \frac{p_{m-1,m-1}}{p_{mm}} \eta_{m-1} \right] \frac{1}{\beta} \frac{d\beta}{dt}, \tag{11}$$

where the elements of the symmetric matrix $\omega_{mk} = \omega_{km}$ are defined in terms of the rate constants

$$\omega_{mk} = \sum_i \Psi_m(i) \sum_j K_{ij} N_j^* (\Psi_k(i) - \Psi_k(j)) = \tag{12}$$

$$= \sum_{i=0} \sum_{j>i} K_{ij} N_j^* (\Psi_m(i) - \Psi_m(j)) (\Psi_k(i) - \Psi_k(j))$$

and vanish if k = 0 or m = 0. Equations (11) are equivalent to (1); more accurately, they are a system of kinetic equations written in a different basis, since the populations N_i are related to the moments η_k by the linear unitary transformation (2).

Consider (11) for the first moment η_1. Taking into account Eq. (9), we obtain after elementary transformations

$$\frac{d\bar{\varepsilon}}{dt} = -n_g \omega_{11} (\bar{\varepsilon} - \langle \varepsilon \rangle) - n_g \omega_{12} \eta_2 / \beta p_{11} - \ldots \tag{13}$$

It is hence seen that if all matrix elements ω_{mk} for m = 1 and k > 1 vanish, then (13) represents the usual relaxation equation for the mean energy of internal degrees of freedom, while $(n_g \omega_{11})^{-1}$ is the energy relaxation time:

$$\tau_1^{-1} = n_g \omega_{11} = n_g \sum_{i=0} \sum_{j<i} K_{ij} N_j^* (\Psi_1(i) - \Psi_1(j))^2 = n_g (\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2)^{-1} \sum_{i=0} \sum_{j<i} K_{ij} N_j^* (\varepsilon_i - \varepsilon_j)^2.$$

Therefore the whole system (11) is called generalized relaxation equations or the relaxation representation (1), while the matrix ω_{mk} is called the relaxation matrix.

The system of obtained generalized relaxation equations is most convenient for use under conditions of insignificant deviation from equilbrium, when the moments η_k satisfy the system of inequalities $1 \gg \eta_1 \gg \eta_2 > \ldots$. This condition makes it possible to truncate the system (11) and restrict the solution to the first few equations, while at the same time, in (1) it is necessary to solve a system of equations of substantially larger size. In a number of cases the relaxation matrix ω_{mk} is diagonal, making it possible to obtain directly a solution of system (11) under arbitrary conditions (the system (1) always has a nondiagonal structure, even for one-quantum transitions). The diagonal elements ω_{mm} are always positive, which follows from definition (12). The nondiagonal elements ω_{mk}, due to the fact that in expression (12) the polynomials $\Psi_m(\varepsilon_i)$ and $\Psi_k(\varepsilon_i)$ "oscillate" out of phase, decay quickly with increasing difference $|k - m|$. This makes it possible to use effectively methods of perturbation theory. The generalized relaxation equations can also be used to solve the opposite problem, i.e., to determine the relaxation matrix elements ω_{mk} and primarily the relaxation time $\tau_1 = (n_g\omega_{11})^{-1}$.

Knowledge of the relaxation matrix makes it possible to determine the transition rate constants K_{ij}. Indeed, multiplying ω_{mk} in expression (12) by $N_q^*N_p^*\Psi_m(p)\Psi_k(q)$ summing over m and k, and taking into acount the orthogonality reation (10), we find $N_q^*N_p^* \sum\limits_k \sum\limits_m \omega_{mk}\Psi_m(p)\Psi_k(q) = \sum\limits_j K_{pj}N_j^*\delta_{qp} - K_{pq}N_q^*$, whence

$$K_{pq} = -N_p^* \sum_{k=1} \sum_{m=1} \omega_{mk}\Psi_m(p)\Psi_k(q),\ p \neq q, \tag{14}$$
$$\sum_{j \neq p} K_{pj}N_j^* = N_p^{*2} \sum_{k=1} \sum_{m=1} \omega_{mk}\Psi_m(p)\Psi_k(p).$$

The last equality also follows directly from (14). Relationship (14) makes it possible to explain a wide range of constants, leading to the splitting of generalized relaxation equations (11). In the simplest case, when $\omega_{mk} = \omega_{11}\delta_{mk}$, from (10) and (14) we directly obtain $K_{pq} = N_p^*\omega_{11}$ for $p \neq q$.

Expressions (12) and (14) make it possible to clarify the reason for difficulties encountered in determining K_{ij} in relaxation processes under moderate deviation from equilibrium. Under these conditions the populations N_j are well described by the first few terms in expansion (2). The evolution of η_k for small k is determined by the lowest elements of ω_{mk}. These ω_{mk} values, found from experimental data with the use of system (11), can be represented with a given accuracy by means of expression (12) by various sets of K_{ij}. If, however, there exist a priori theoretical considerations concerning the dependence of the constants $K_{ij}(T)$ on quantum numbers and on temperature, the values of ω_{mk} obtained can serve to refine the parameters of the selected model.

On the other hand, as seen from Eq. (14), knowledge of a restricted number of ω_{mk} does not uniquely determine K_{ij}. However, "natural" assumptions about the dependence of ω_{mk} on the subscripts m and k and on temperature makes it possible to find a set of model constants, correctly describing the relaxation of lower moments η_k.

To illustrate the use of the generalized relaxation equations, we consider a number of problems for specific energy spectra ε_i and model shapes K_{ij}, particularly for a harmonic oscillator and a rigid rotor.

Harmonic Oscillator. We study the relaxation of a system of harmonic oscillators. Due to its relative simplicity and importance, this problem has been investigated quite well (see [1, 6]), and therefore can serve as a benchmark test for the method suggested in this study. The harmonic oscillator has an equivalent energy spectrum $\varepsilon_i = E_i/\hbar\omega_e = i$ (we omit the constant energy shift $\hbar\omega_e/2$) for all levels). The partition function for the harmonic oscillator equals $S = (1 - e^{-\beta})^{-1}$ ($\beta = \hbar\omega_e/kT$, and ω_e is the vibrational quantum of the oscillator).

Using expressions (4)-(6), after a substantial number of transformations we obtain

$$\Psi_k(i) = e^{-k\beta/2} \sum_{\nu=0} (1 - e^{\beta})^{\nu} C_k^{\nu} C_i^{\nu}, \tag{15}$$

where $C_k^{\nu} = k!/[(k - \nu)!\nu!]$. Expression (15) coincides, accurately within normalization, with the definition of Gottlieb polynomials $\ell_k(i)$ [6]: $\Psi_k(i) = \exp(k\beta/2)\ell_k(i)$.

The elements ω_{mk} for a harmonic oscillator are easily determined in the one-quantum approximation, when for transitions from state i the nonvanishing rate constants are $K_{i-1,i} =$

iK_{01}, $K_{i+1,i} = (i + 1)K_{01}e^{-\beta}$. Substituting them into (12) and using the definition for the polynomials $\Psi_m(i)$ for the harmonic oscillator $\Psi_m(i) = \sum_{n=0}^{m} p_{mn}\beta^n i^n$, we find

$$\omega_{mk} = K_{01}(1 - e^{-\beta})m\delta_{mk} = m\omega_{11}\delta_{mk}. \tag{16}$$

Thus, the relaxation matrix ω_{mk} is diagonal for a harmonic oscillator, Eqs. (11) are decoupled in this case, and the solution is easily found. The result for the case of a thermal bath (β = const) is particularly simple. Equations (11) reduce then to $d\eta_m/dt = -m\eta_m/\tau_1$, where the energy relaxation time τ_1 for a harmonic oscillator is introduced: $\tau_1 = (n_g\omega_{11})^{-1} = [n_g K_{01}(1 - e^{-\beta})]^{-1}$. It is seen that each moment η_m relaxes with a time $\tau_m = \tau_1/m$. The solution of system (11) acquires the form $\eta_m = \eta_m^0 \exp(-mt/\tau_1)$, $\eta_k^0 = \sum_i N_i(t = 0)\Psi_k(i)$, $N_i(t) = \sum_k \eta_k^0 \Psi_k(i) N_i^* \exp(-kt/\tau_1)$, which, accurately within the notation, coincides with the results of [6] (see also [1], p. 80).

High-Temperature Rotor Approximation. Consider the model of a rigid rotor, describing the rotation of diatomic or linear polyatomic molecules. The energy spectrum of a rotor is $\varepsilon_i = E_i/k\Theta = i(i + 1)$, $k\Theta = \hbar^2/2I$ (I is the moment of inertia of the rotor). The statistical weight for the rotor is $g_i = 2i + 1$. For all molecules we practically have $\Theta \lesssim 10$ K (exceptions are only hydrogen-containing molecules, such as H_2, D_2, HD, HF, and OH, for which the characteristic rotational temperatures are Θ = 85.6; 43; 64; 30; and 25 K, respectively). Therefore, it is natural to confine oneself to the high-temperature limit, i.e., $T \gtrsim 2\Theta$ or $\beta \ll 1$, when, in calculating the sum over energy states by the modification under consideration, one can transform to integration (the continuous approximation)

$$\sum_i g_i f_i \approx \frac{1}{\alpha}\int d\varepsilon f(\varepsilon), \tag{17}$$

where α = 1 and 2 for heteronuclear and homonuclear molecules.

In the high-temperature approximation the partition function of the rotor is proportional to temperature: $S \sim T/\Theta = \beta^{-1}$ (the proportionality coefficient may differ from unity for homonuclear molecules). It follows from (4) that $\langle\varepsilon^n\rangle = n!\beta^{-n}$, or $Z_n = n!$. Using (6), it is easily shown that

$$p_{kl} = (-1)^l \frac{k!}{(k - l)!\, l!^2}, \tag{18}$$

i.e., the polynomials $\Psi_k(\varepsilon_i)$ coincide, within the high-temperature approximation, with the Laguerre polynomials:

$$\Psi_k(\varepsilon_i) = \sum_{l=0}^{k} (-1)^l \frac{k!}{(k - l)!\, l!^2} (\varepsilon_i\beta)^l = L_k(\varepsilon_i\beta). \tag{19}$$

Taking into account (19), the generalized relaxation equation acquires the form

$$\frac{d\eta_m}{dt} = m(\eta_m - \eta_{m-1})\frac{1}{\beta}\frac{d\beta}{dt} - n_g\sum_{k=1}^{\infty}\omega_{mk}\eta_k, \tag{20}$$

and the relaxation matrix in the continuous approximation, replacing summation by integration according to rule (17), leads to the form

$$\omega_{mk} = \frac{1}{\alpha\beta}\int_0^\infty dx e^{-x}\int_{\delta(x)}^\infty dz P(x, z) e^{-z} (L_m(x + z) - L_m(x))(L_k(x + z) - L_k(x)), \tag{21}$$

where besides the deactivation rate constants K_{ij} ($j > i$), we have introduced the energy transition probabilities $P(x, z) = P(\beta\varepsilon_i, \beta\varepsilon_j - \beta\varepsilon_i) = g_i^{-1}K_{ij}$ for $x = \beta\varepsilon_i$ and $z = \beta(\varepsilon_j - \varepsilon_i)$. The lower limit of integration over z at $\beta \ll 1$ equals $\delta(x) = \beta(\varepsilon_{i+\alpha} - \varepsilon_i) \approx 2\alpha\sqrt{\beta x}$, and, as a rule, $\delta(x)$ can be replaced by zero. The error due to this replacement is easily estimated in each specific case.

Taking into account that $\Psi_m(x)$ is a polynomial of order m, and only the derivatives $\partial^n\Psi_m/\partial x^n$ with $n \le m$ are nonvanishing, expression (21) is written in the form

$$\omega_{mk} = \frac{1}{\alpha\beta}\int_0^\infty dx e^{-x} \sum_{l=1} \sum_{n=1} \frac{1}{n!l!} \frac{\partial^l L_k(x)}{\partial x^l} \frac{\partial^n L_m(x)}{\partial x^n} \int_{\delta(x)}^\infty dz e^{-z} P(x, z)^{n+l}. \tag{22}$$

We calculate ω_{mk} for a number of model constants K_{ij}. Since at the present time the theory of rotational transitions has no simple models, such as the harmonic oscillator model in the theory of vibrational relaxation, we test the most widely used semi-empirical dependences for rate constants [7].

First consider the case in which the transition probability P(x, z) depends only on the energy difference, i.e., $P(x, z) = P^{(0)}(z)$. It is precisely to this shape that the most widely used semi-empirical dependences of rate constants – power law and exponential – reduce [7].

For $P^{(0)}(z) = Bz^{-1}$ we easily obtain [5], taking account of properties of Laguerre polynomials,

$$\omega_{mk} = \frac{B(\beta)}{\beta} \sum_{l=1}^{k} \frac{1}{l}\, \delta_{mk}. \tag{23}$$

Thus, the transition rate constants

$$K_{ij} = \frac{B(\beta)}{\beta} \frac{g_i}{|\varepsilon_j - \varepsilon_i|} \quad (P(x, z) = B(\beta)\, z^{-1}) \tag{24}$$

in the high-temperature approximation lead to a diagonal relaxation matrix ω_{mk}, and, consequently, to a decoupling of the generalized relaxation equations (20). It is necessary to emphasize, however, that this result is approximate, unlike the result for a harmonic oscillator, since by means of (17) we transformed from the discrete to the continuous description.

In the more general case for power law dependence of the constants on energy difference

$$K_{ij} = \frac{B(\beta)}{\beta^\gamma} \frac{g_i}{|\varepsilon_j - \varepsilon_i|^\gamma} \quad (j > i),\ P(x, z) = Bz^{-\gamma} \tag{25}$$

with $\gamma \neq 1$, but $\gamma < 2$, one can also carry out the integration in expressions (21), (22), for the relaxation matrix

$$\omega_{mk} = \frac{B}{\beta\Gamma(\gamma-1)^2} \sum_{l=0}^{k-1} \sum_{p=0} \frac{\Gamma(\gamma-1+m-l-p)\,\Gamma(\gamma-1+k-l-p)\,\Gamma(1-\gamma-p)}{(m-l-p)!\,(k-l-p)!\ p!}.$$

Comparison of the constants (25) with those calculated by the strong-coupling method, relative to rarely calculated experimental data for a number of molecules [7], shows that the parameter γ is usually near unity ($0.75 \leqslant \gamma \leqslant 1.4$). For $\gamma \approx 1$ we then have, accurate within terms $O(\gamma - 1)$,

$$\omega_{mk} \approx \frac{B}{\beta} \frac{(\gamma-1)}{|m-k|} \sum_{n=1}^{k} \frac{1}{|m-k|+n},\ m \neq k,\ \omega_{mk} \approx \frac{B}{\beta} \sum_{n=1}^{k} [n^{-1} - (\gamma-1)\, n^{-2}].$$

It is hence seen that for $\gamma \neq 1$, nondiagonal elements are generated in the relaxation matrix; these elements are small for $|\gamma - 1| \ll 1$, so that a solution of the system of generalized relaxation equations is possible by perturbation theory methods.

In the general case for transition probabilities depending only energy differences ($P(x, z) = P^{(0)}(z)$), we obtained from expression (22) $\omega_{mk} = \sum_{n=1}^{m} \sum_{l=1}^{k} \frac{a_{mk}^{nl}}{n!l!} D_{l+n}^{(0)}$, where we introduced the functions $D_q^{(0)}$, related to the diffusion coefficients in the energy space:

$$D_q^{(0)} = \int_0^\infty dz e^{-z} P^{(0)}(z)\, z^q,$$

$$a_{mk}^{nl} = \int_0^\infty dx e^{-x} \frac{\partial^n L_m}{\partial x^n} \frac{\partial^l L_k}{\partial x^l} = \frac{(-1)^{l+n}}{(n-1)!\,(l-1)!} \sum_{p=0} \frac{(m-1-p)!\,(k-1-p)!}{(m-n-p)!\,(k-l-p)!}.$$

In particular, for exponential probabilities $P(z) = Be^{-\lambda z}$.

$$\omega_{mk} = \frac{B}{\alpha\beta} \sum_{l=1}^{k} \sum_{n=1}^{m} \frac{a_{mk}^{nl}}{n!k!} (1 + \lambda)^{-(n+l+1)}, \tag{26}$$

whence it follows that for $\lambda \gg 1$, i.e., when the transition probabilities decrease quickly with increasing $\Delta\varepsilon_{ij}$, the main contribution to the relaxation matrix is provided by terms with $n = \ell = 1$.

The Diffusion Approximation. Consider the connection between the generalized relaxation equations and the kinetic and diffusion approximations [1, 8, 9]. The diffusion equation in the space of energy levels at β = const is represented in the form

$$\frac{\partial}{\partial t}\left(e^{-\beta\varepsilon}\eta(\varepsilon)\right) = \frac{\partial}{\partial \varepsilon}\left[e^{-\varepsilon\beta} D(\varepsilon) \frac{\partial \eta(\varepsilon)}{\partial \varepsilon}\right].$$

Here $D(\varepsilon) = \beta^{-2} \int_0^\infty dz P(x, z) \exp(-z) z^2$ is the diffusion coefficient, $x = \beta\varepsilon$, and $\eta(\varepsilon) = N(\varepsilon)/N^*(\varepsilon)$ is the population of energy state ε, normalized by the equilibrium value.

We expand $\eta(\varepsilon)$ in a series in Laguerre polynomials $L_k(\varepsilon\beta)$: $\eta(\varepsilon) = \sum_k \eta_k L_k(\beta\varepsilon)$. For the coefficents η_k, we then obtain in the diffusion approximation at β = const $d\eta_m/dt = -n_g \sum_{k=1} \omega_{mk}^{(g)} \eta_k$, where $\omega_{mk}^{(g)} = \beta^{-1} \int_0^\infty dx e^{-x} \frac{\partial L_k}{\partial x} \frac{\partial L_m}{\partial x} \int_0^\infty dz e^{-z} P(x, z) z^2$. By comparison with the relaxation matrix (22), it is seen that in the diffusion case the summation over ℓ and n is restricted to one term with $n = \ell = 1$. In the general case only the matrix elements ω_{11} and $\omega_{11}^{(g)}$ coincide, i.e., the energy relaxation times coincide. All remaining matrix elements ω_{mk} and $\omega_{mk}^{(g)}$ can differ substantially, particularly for multi-quantum transitions. For example, for the probability (24): $\omega_{mk}^{(g)} = (B/\beta) \min(m, k)$, which differs substantially from the exact matrix (23). On the other hand, for $P(\varepsilon_i, \varepsilon_j)$, which falls with increasing $\Delta\varepsilon_{ij}$, the relaxation matrix practically coincides with the diffusion matrix (for example, for $\lambda \gg 1$ in expression (26)).

Thus, the diffusion approximation describes the relaxation process only for weak deviation from equilibrium, when $\eta_1 \gg \eta_2 > \eta_3, \ldots$, and in the absence of multiquantum transitions in the system, when in expression (22) one can neglect terms with n and ℓ larger than unity.

Relaxation through a Sequence of Boltzmann States. It is well known [1] that the harmonic oscillator can relax through a sequence of Boltzmann states if the initial distribution has a Boltzmann shape. This property is called canonical invariance. The question arises whether relaxation is possible through a Boltzmann state for other systems of energy levels.

Consider relaxation of a molecular system in a thermal bath for β = const. Let the internal degrees of freedom have a Boltzmann distribution, with $T_r = \beta_r^{-1}$, whose expansion coefficients are, according to (8),

$$\eta_k = \sum_{l=0}^{k} p_{kl}^{(t)} \beta_t^l \langle \varepsilon^l \rangle_r. \tag{27}$$

Here the energy moments $\langle\varepsilon^\ell\rangle_r$ correspond to T_r, and all remaining quantities are determined by T_t. The generalized relaxation equation acquires in this case the form

$$\frac{d}{dt}\left[\sum_{n=0}^{m} p_{mn}^{(t)} \beta_t^n \langle \varepsilon^n \rangle_r\right] = -n_g \sum_{k=1}^{\infty} \omega_{mk} \sum_{l=0}^{k} p_{kl}^{(t)} \beta_t^l \langle \varepsilon^l \rangle_r. \tag{28}$$

We use the expansion of the moment $\langle\varepsilon^n\rangle_r$, determined at the point $\beta = \beta_r$, by a Taylor series in powers of: $\Delta\beta = \beta_r - \beta$: $\langle \varepsilon^n \rangle_r = \langle \varepsilon^n \rangle_t + \frac{\partial \langle \varepsilon^n \rangle_t}{\partial \beta} \Delta\beta + \frac{1}{2} \frac{\partial^2 \langle \varepsilon^n \rangle_t}{\partial \beta^2} (\Delta\beta)^2 + \ldots$. With account of (6) and the relation $\partial\langle\varepsilon^n\rangle/\partial\beta = \langle\varepsilon^n\rangle\langle\varepsilon\rangle - \langle\varepsilon^{n+1}\rangle$, which follows from (4), and equating in expression (28) terms with identical powers of $\Delta\beta$, we obtain in the lowest nonvanishing order

$$\omega_{mk} = m\omega_{11}\delta_{mk}. \tag{29}$$

This relation is the necessary condition for relaxation through a sequence of Boltzmann states and coincides with expression (16), obtained for a harmonic oscillator.

Condition (29) is particularly easily proved in the high-temperature approximation ($\beta \ll 1$), when (18) and $\langle \varepsilon^n \rangle_r = n!\beta_r^{-n}$ are valid. In this case the expansion coefficients (27) equal

$$\eta_k = \sum_{l=0}^{k} \frac{(-1)^l k!}{(k-l)!\,l!} \frac{\beta_t^l}{\beta_r^l} = \left(1 - \frac{\beta_t}{\beta_r}\right)^k = \left(1 - \frac{T_r}{T_t}\right)^k \tag{30}$$

and expression (28) acquires the form $m\left(1 - \frac{T_r}{T_t}\right)^{m-1} \frac{d}{dt}\left(\frac{T_r}{T_t}\right) = n_g \sum_{k=1} \omega_{mk} \left(1 - \frac{T_r}{T_t}\right)^k$, whence (29) follows directly.

Consider the condition of canonical invariance for the diffusion approximation. It has been shown in [8] that for $P(x, z) = xP^{(1)}(z)$, the rotor system relaxes through a sequence of Boltzmann states. The diffusion matrix is in this case

$$\omega_{mk}^{(g)} = \beta^{-1} \int_0^\infty dx e^{-x} \frac{\partial L_k(x)}{\partial x} \frac{\partial L_m(x)}{\partial x}\, x \int_0^\infty dz e^{-z} P^{(1)}(z)\, z^2 = m\delta_{mk} D_2^{(1)}$$

$$= m\omega_{11}^{(g)} \delta_{mk}, \quad D_2^{(1)} = \beta^{-1} \int_0^\infty dz e^{-z} P^{(1)}(z)\, z^2,$$

i.e., it coincides with condition (29).

Condition (29) is usually also a sufficient condition for relaxation of system levels through a sequence of Boltzmann states if the initial state is a Boltzman state. For a harmonic oscillator, the proof of this fact is given in [6], while for the diffusion approximation with $P(x, z) = xP^{(1)}(z)$, it is provided in [8]. The proof is easily obtained for a system of rotor with $\beta \ll 1$ in the case of a thermal bath. If condition (29) is satisfied, Eqs. (11) for $\beta = \beta_t = \text{const}$ have the solutions

$$\eta_m(t) = \eta_m^0 \exp(-mt/\tau_1), \quad \tau_1 = (n_g \omega_{11})^{-1}. \tag{31}$$

Since the initial state has a Boltzmann shape for a temperature of internal degrees of freedom $T_r(t = 0) = T_0$, then, as in (30), $\eta_m^0 = \sum_{l=0}^{m} p_{ml} \beta_t^l \langle \varepsilon \rangle_0 = \left(1 - \frac{T_0}{T_t}\right)^m$. Consequently, the solution (31) retains the Boltzmann shape at any moment of time $t > 0$: $\eta_m(t) = [(1 - T_0/T_t) \cdot \exp(-t/\tau_1)]^m = (1 - T_r/T_t)^m$. Here we introduced the temperature of internal degrees of freedom $T_r = T_t + (T_0 - T_t)\exp(-t/\tau_1)$.

We note that if ω_{mk} is diagonal, but the condition of canonical invariance (29) is not satisfied, then relaxation does not occur through a sequence of Boltzmann states, even though the relaxation equations are valid for the mean energy and for other moments.

LITERATURE CITED

1. B. F. Gordiets, L. I. Osipov, and L. I. Shelepin, Kinetic Processes in Gases and Molecular Lasers [in Russian], Nauka, Moscow (1980).
2. T. Oka, "Collision-induced transitions between rotational levels," in: Adv. Atomic and Molecular Physics, D. R. Bates (ed.), Academic Press, Vol. 9 (1973).
3. G. Herzberg, Vibrational and Rotational Spectra of Polyatomic Molecules [Russian translation], IL, Moscow (1949).
4. L. von Waldmann and E. Trübenbacher, Formal kinetic theory of molecular gas mixtures, Z. Naturforschung, 17a, No. 5 (1962).
5. G. I. Sukhinin, "The relaxation representation of kinetic equations," Preprint Inst. Teor. Fiz. Sib. Otd. Akad. Nauk SSSR No. 144, Novosibirsk (1986).
6. E. W. Montroll and K. E. Shuler, "Studies in nonequilibrium rate processes. 1. The relaxation of a system of harmonic oscillators," J. Chem. Phys., 26, No. 3 (1957).
7. T. A. Brunner and D. Pritchard, "Fitting laws for rotationally inelastic collisions," in: Dynamics of the Excited State, K. P. Lawley (ed.), Wiley, New York (1982).
8. A. I. Osipov, "Rotational relaxation in gases," Inzh. Fiz. Zh., 49, No. 1 (1985).
9. G. V. Dubrovskii, "Simplified kinetic approaches to dynamics of a strucural relaxing gas," Zh. Tekh. Fiz., 52, No. 10 (1982).