10. V. A. Gorelov and L. A. Kil'dyushova, "Features of electrical probe characteristics in a transfer regime in a supersonic plasma flow," Teplofia. Vys. Temp., 23, No. 2 (1985).
11. Chen Sin-Li and T. Sekiguchi, "Instantaneous direct-display system of plasma parameters by means of a triple probe," J. Appl. Phys., 36, No. 10 (1965).
12. N. M. Kuznetsov, Thermodynamic Functions and Shock Adiabats for Air at High Temperatures [in Russian], Mashinostroenie, Moscow (1965).
13. G. Grim, Plasma Spectroscopy [in Russian], Atomizdat, Moscow (1969).
14. V. A. Gorelov, A. S. Korolev, and V. S. Nikol'skii, "Ionization of a gas in a viscous shock layer and modeling of this process in a laboratory experiment," Zh. Prikl. Mekh. Tekh. Fiz., No. 6 (1985).

---

# DIFFUSION MODEL OF VIBRATIONAL RELAXATION IN A BINARY MIXTURE OF DIATOMIC MOLECULES (QUANTUM OSCILLATORS)

O. V. Skrebkov

UDC 533.601.18

Chemical activation of a system involving the crossing of an activation barrier was treated for the first time by Kramers [1] as a stochastic diffusion process in phase space with the use of the formalism of the theory of Brownian motion due to Einstein. In later years the diffusion model was applied to various kinetic processes such as condensation [2], electronic excitation and ionization [2], the approach to equilibrium of the translational degrees of freedom of molecules (TT-relaxation) [3], rotational–translational RTT and RT-relaxation [4, 5], vibrational–translational VT-relaxation [6-9] (including dissociation and recombination [10-12] and radiative deactivation [13]), vibrational–rotational–translational VRT-relaxation and dissociation [14], vibrational VVT-relaxation in a one-component gas [15-17] (including loss of excited particles in chemical reactions [18]), and vibrational VVV'T-relaxation in binary gas mixtures [19-22].

In all of these cases the term "diffusion process" refers to one-dimensional [1-3, 5-18, 20-23] or two-dimensional [4, 14, 19] diffusion in the continuous space of the momenta, angular momenta, and (or) the energies (or the corresponding quantum numbers*) and is described by a generalized diffusion equation of the Fokker–Planck type or by a system of such equations when there are discrete states [22, 23]. The fundamental condition for the applicability of the diffusion model is that the change $\Delta\varepsilon$ of a coordinate $\varepsilon$ (such as the vibrational or rotational energy, angular momentum, mass of a condensation nucleus) must be small in an elementary event, such as a vibrational or rotational transition, the attachment of a molecule to a condensation nucleus, and so on. That is

$$\Delta\varepsilon \ll \varepsilon \text{ or } n \ll v \tag{1.1}$$

(v is the quantum number and n is its change in an elementary event). On the other hand, in relaxation problems the space of the problem (energy or the corresponding quantum number, for example) can be approximated as continuous only if the system is classical. For example, if $\varepsilon$ is the energy of an oscillator, then $\varepsilon \simeq kT$ and the classical diffusion model will be applicable if

$$\Delta\varepsilon \ll kT \text{ or } n\hbar\omega_v \ll kT, \tag{1.2}$$

where $\Delta\varepsilon$ is the change in the vibrational energy due to a collision; n is the change in the vibrational quantum number; $\omega_v \equiv \omega_{v+1,v}$ is the frequency of the vibrational transition $v + 1 \to v$; T is the temperature; k is the Boltzmann constant.

It is not difficult to see that when there are transitions between highly-excited states, the condition (1.1) is significantly less strict than (1.2). When we have transitions between low-lying states and multiquantum transitions can be neglected (n = 1), the single-quantum system of balance equations for the population densities can be written without

---

*In the treatment of condensation according to the theory of Zel'dovich (1942; see [2]), the process is diffusion in the "space" of the sizes of the nuclei of the condensed phase.

Chernogolovka. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 6, pp. 28-35, November-December, 1987. Original article submitted November 10, 1985.

0021-8944/87/2806-0830$12.50

making any further assumptions in the form of finite-difference equations of the diffusion type in the discrete energy space [24, 25]. Such equations, which do not require the condition (1.2), and which can be used to include approximately the effect of multiquantum transitions (the quantum diffusion model) have been obtained from the complete (including multiquantum transitions) balance equations for the population densities for electronic excitation and ionization [26], VT-relaxation [24-25], and VVV'T-relaxation in a system with a small admixture of nonequilibrium molecules to a Boltzmann thermostat [27]. In [27] it was shown by comparison with the exact multiquantum calculation that the region of applicability of the quantum diffusion approximation is wide enough for it to be useful in practice. The theory gives a better account of the effect of multiquantum transitions the smaller the value of n in comparison with v.

In the present paper we derive a system of finite-difference equations of the diffusion type (the quantum diffusion approximation) from the complete (including multiquantum transitions) balance equations for the population densities for vibrational VVV'T-relaxation in a binary gas mixture with arbitrary concentrations of the components. In the limit (1.2) the equations obtained here reduce to those of the classical diffusion model [19, 22].

1. Kinetic Equation. We consider a gas mixture* of diatomic molecules (quantum oscillators) of two kinds 1 and 2. The system is initially in a nonequilibrium state with respect to the vibrational degrees of freedom. The state of the system at time t† is completely described by two one-particle distribution functions (population densities) $x_{v_1}$, $x_{v_2}$ over the vibrational states $v_i$ (i = 1, 2) or by three two-particle distribution functions corresponding to the three types of collisions (1–1, 1–2, 2–2) possible in the system. These three distribution functions are denoted by $\rho_{v_1,v_1'}$, $\rho_{v_1,v_2'}$, and $\rho_{v_2,v_2'}$, and they are related to $x_{v_1}$ and $x_{v_2}$ by the equations

$$x_{v_i} = \sum_{v_1'} \rho_{v_i,v_1'} + \sum_{v_2'} \rho_{v_i,v_2'}; \tag{1.3}$$

$$\rho_{v_i,v_j'} = x_{v_i} x_{v_j'}, \quad i, j = 1, 2. \tag{1.4}$$

The kinetic behavior of the system can be described by two methods (to the same degree of completeness): either a system of two equations for $x_{v_1}$ and $x_{v_2}$ (the balance equations of the population densities; see [28], for example):

$$\frac{dx_{v_i}}{dt} = \sum_{v_1'} C_{i1} + \sum_{v_2'} C_{i2}, \quad i = 1, 2, \quad v_i(v_j) = 0, 1, \ldots, \tag{1.5}$$

or by three equations for $\rho_{v_1,v_1'}$, $\rho_{v_1,v_2'}$, and $\rho_{v_2,v_2'}$:

$$\frac{d\rho_{v_i,v_j'}}{dt} = C_{ij}, \quad i, j = 1, 2. \tag{1.6}$$

Here

$$C_{ij} = \sum_{n,m\neq 0} \left( \rho_{v_i+n,v_j'+m} Q_{v_i+n,v_i}^{v_j'+m,v_j'} - \rho_{v_i,v_j'} Q_{v_i,v_i+n}^{v_j',v_j'+m} \right) \tag{1.7}$$

is the collision integral; $Q_{v_i,w_i}^{v_j,w_j}$ is the rate constant of the energy exchange process when a molecule of type i makes a transition from state $v_i$ to state $w_i$, and a molecule of type j makes a transition from state $v_j$ to state $w_j$.

Omitting the indices i and j in the interest of brevity, and using the notation

$$\varphi_v(t) = x_v(t)/x_v^0, \quad x_v^0 \equiv x_v(\infty),$$

$$\Phi_{v,v'}(t) = \rho_{v,v'}(t)/\rho_{v,v'}^0, \quad \rho_{v,v'}^0 \equiv \rho_{v,v'}(\infty),$$

$$\Omega(v, v'; n, m) = \rho_{v,v'}^0 Q_{v,v+n}^{v',v'+m} = \rho_{v+n,v'+m}^0 Q_{v+n,v}^{v'+m,v'}$$

we can write (1.6) in the form

---

*The gas is sufficiently rarefied such that trinary collisions can be neglected.
†t is assumed to be larger than the characteristic lifetimes of the nondiagonal elements of the density matrix.

$$\frac{d\rho_{v,v'}}{dt}=\sum_{n,m}(\Phi_{v+n,v'+m}-\Phi_{v,v'})\,\Omega(v,v';n,m). \tag{1.8}$$

The following formulas are used to expand the equations into series of finite differences (see [29])

$$\begin{aligned}f(v+n,v'+m)&=f(v,v')+n\Delta f(v+1,v')+\\&+m\Delta'f(v,v'+1)+\frac{1}{2}n(n-1)\Delta^2f(v+2,v')+nm\Delta\Delta'f(v+1,v'+1)+\\&+\frac{1}{2}m(m-1)\Delta'^2f(v,v'+2)+\ldots;\end{aligned} \tag{1.9a}$$

$$\begin{aligned}f(v-n,v'-m)&=f(v,v')-n\Delta f(v,v')-\\&-m\Delta'f(v,v')+\frac{1}{2}n(n-1)\Delta^2f(v,v')+nm\Delta\Delta'f(v,v')+\frac{1}{2}m(m-1)\Delta'^2f(v,v')+\ldots,\end{aligned} \tag{1.9b}$$

$$\Delta f(v,v')=f(v,v')-f(v-1,v'),\quad \Delta'f(v,v')=f(v,v')-f(v,v'-1),\quad \Delta^2f=\Delta(\Delta f),$$

which are valid in the approximations

$$\omega_{v+1,v}\simeq\omega_{v,v-1},\ \omega_{v+n,v}\simeq n\omega_{v+1,v}. \tag{1.10}$$

Applying expansion (1.9a) to the function $\Phi_{v+n,v'+m}\equiv\Phi(v+n,v'+m)$ in Eq. (1.8), we obtain

$$\begin{aligned}\frac{d\rho_{v,v'}}{dt}&=A_1(v,v')\rho^0_{v,v'}\left(\Delta\Phi_{v,v'}+\frac{1}{2}\Delta^2\Phi_{v+1,v'}\right)+\\&+A_2(v,v')\rho^0_{v,v'}\left(\Delta'\Phi_{v,v'}+\frac{1}{2}\Delta'^2\Phi_{v,v'+1}\right)+B_{11}(v,v')\rho^0_{v,v'}\Delta^2\Phi_{v+2,v'}+\\&+2B_{12}(v,v')\rho^0_{v,v'}\Delta\Delta'\Phi_{v+1,v'+1}+B_{22}(v,v')\rho^0_{v,v'}\Delta'^2\Phi_{v,v'+2};\end{aligned} \tag{1.11}$$

$$\begin{aligned}&A_1=\sum_{n,m\neq0}nQ^{v',v'+m}_{v,v+n},\quad A_2=\sum_{n,m\neq0}mQ^{v',v'+m}_{v,v+n},\ B_{11}=\frac{1}{2}\sum_{n,m\neq0}n^2Q^{v',v'+m}_{v,v+n}\simeq\sum_{n,m\geqslant1}n^2Q^{v',v'+m}_{v,v-n},\\&B_{12}=\frac{1}{2}\sum_{n,m\neq0}nmQ^{v',v'+m}_{v,v+n}\simeq-\sum_{n,m\geqslant1}nmQ^{v',v'+m}_{v,v-n},\\&B_{22}=\frac{1}{2}\sum_{n,m\neq0}m^2Q^{v',v'+m}_{v,v+n}\simeq\sum_{n,m\geqslant1}m^2Q^{v',v'+m}_{v,v-n}.\end{aligned} \tag{1.12}$$

Since n and m can be positive or negative, (1.6), (1.7) can be written in the form

$$\frac{d\rho_{v,v'}}{dt}=\sum_{n,m\neq0}\left(\rho_{v-n,v'-m}Q^{v'-m,v'}_{v-n,v}-\rho_{v,v'}Q^{v',v'+m}_{v,v+n}\right). \tag{1.13}$$

Applying the expansion (1.9b) to $\rho_{v-n,v'-m}\equiv\rho(v-n,v'-m)$ and $Q^{v'-m,v'}_{v-n,v}\equiv Q(v-n,v'-m;n,m)$ in (1.13), we obtain

$$\begin{aligned}\frac{d\rho_{v,v'}}{dt}&=-\Delta\left\{\Phi_{v,v'}\rho^0_{v,v'}A_1(v,v')+\frac{1}{2}\Delta'\left[\Phi_{v,v'}\rho^0_{v,v'}A_1(v,v')\right]\right\}-\\&-\Delta'\left\{\Phi_{v,v'}\rho^0_{v,v'}A_2(v,v')+\frac{1}{2}\Delta'\left[\Phi_{v,v'}\rho^0_{v,v'}A_2(v,v')\right]\right\}+\\&+\Delta^2\left[\Phi_{v,v'}\rho^0_{v,v'}B_{11}(v,v')\right]+2\Delta\Delta'\left[\Phi_{v,v'}\rho^0_{v,v'}B_{12}(v,v')\right]+\Delta'^2\left[\Phi_{v,v'}\rho^0_{v,v'}B_{22}(v,v')\right].\end{aligned} \tag{1.14}$$

The calculation of the kinetic coefficients is a separate dynamical problem, but there is actually no need to determine $A_k$ and $B_{ks}$ separately, since they can be expressed in terms of one another from the condition that the flux vanish in equilibrium

$$-\Delta\left[\rho^0A_1+\frac{1}{2}\Delta(\rho^0A_1)\right]-\Delta'\left[\rho^0A_2+\frac{1}{2}\Delta'(\rho^0A_2)\right]+\Delta^2(\rho^0B_{11})+2\Delta\Delta'(\rho^0B_{12})+\Delta'^2(\rho^0B_{22})=0. \tag{1.15}$$

Indeed, performing term-by-term "differentiation"* on (1.4), and using (1.11) and (1.15) and the relations $\Delta^2f_{v+2}\simeq\Delta^2f_{v+1}\simeq\Delta^2f_v$, $\Delta\Delta'f_{v+1,v'+1}\simeq\Delta\Delta'f_{v,v'}$, we have to order $O(\Delta^3f)$:

---

* $\Delta(f_vg_v)=f_v\Delta g_v+g_v\Delta f_v-\Delta f_v\Delta g_v$.

$$\frac{d\rho_{v,v'}}{dt} = \Delta\left[\rho^0_{v,v'}B_{11}(v, v')\Delta\Phi_{v,v'} + \rho^0_{v,v'}B_{12}(v, v')\Delta'\Phi_{v+1,v'+1}\right] + \\ + \Delta'\left[\rho^0_{v,v'}B_{12}(v, v')\Delta\Phi_{v+1,v'+1} + \rho^0_{v,v'}B_{22}(v, v')\Delta'\Phi_{v,v'}\right]. \tag{1.16}$$

Therefore in the approximations (1.1) and (1.10) and to second order in expansions of the type (1.9), the process of vibrational relaxation in a binary mixture of diatomic molecules can be described by three independent "differential" finite-difference equations of the diffusion type for $\rho_{v_1,v_1'}$, $\rho_{v_1,v_2'}$, $\rho_{v_2,v_2'}$

$$\frac{d\rho_{v_i,v_j}}{dt} = D_{ij}(v_i, v_j), \quad i, j = 1, 2, \tag{1.17}$$

or [in correspondence with (1.3)] by two coupled "integrodifferential" finite-difference equations of the diffusion type for $x_{v_1}$ and $x_{v_2}$

$$\frac{dx_{v_i}}{dt} = \sum_{v_1'} D_{i1} + \sum_{v_2'} D_{i2}, \quad i = 1, 2. \tag{1.18}$$

Where, from (1.16)

$$D_{ij} = \Delta\left[\rho^0_{v_i,v_j}B^{ij}_{11}(v_i, v_j)\Delta\Phi_{v_i,v_j} + \rho^0_{v_i,v_j}B^{ij}_{12}(v_i, v_j)\Delta'\Phi_{v_i,v_j}\right] + \\ + \Delta'\left[\rho^0_{v_i,v_j}B^{ij}_{12}(v_i, v_j)\Delta\Phi_{v_i,v_j} + \rho^0_{v_i,v_j}B^{ij}_{22}(v_i, v_j)\Delta'\Phi_{v_i,v_j}\right]. \tag{1.19}$$

Using the relations $\Delta\left(\sum_\alpha a_\alpha\right) = 0$ and

$$\sum_{\alpha=0}^{\infty} a_\alpha \Delta b_{\alpha+1} = -\sum_{\alpha=0}^{\infty} b_\alpha \Delta a_\alpha \tag{1.20}$$

Eqs. (1.18) and (1.19) finally take the form

$$\frac{dx_{v_i}}{dt} = \sum_{j=1}^{2} \Delta J^{(j)}_{v_i}, \quad i = 1, 2, \quad v_i = 0, 1, 2, \ldots, \tag{1.21}$$

where

$$J^{(j)}_{v_i} = \left[\sum_{v_j} B^{ij}_{11}(v_i, v_j)\, x^0_{v_j}\varphi_{v_j}\right] x^0_{v_i}\Delta\varphi_{v_i} - x^0_{v_i}\varphi_{v_i-1}\sum_{v_j}\varphi_{v_j}\Delta'\left[x^0_{v_j}B^{ij}_{12}(v_i, v_j)\right] \tag{1.22a}$$

or

$$J^{(j)}_{v_i} = \left[\sum_{v_j} B^{ij}_{11}(v_i, v_j)\, x_{v_j}\right]\left(x_{v_i} - \frac{x^0_{v_i}}{x^0_{v_i-1}}\, x_{v_i-1}\right) - \frac{x^0_{v_i}}{x^0_{v_i-1}}\, x_{v_i-1} \times \\ \times \sum_{v_j}\left[B^{ij}_{12}(v_i, v_j) - \frac{x^0_{v_j-1}}{x^0_{v_j}} B^{ij}_{12}(v_i, v_j - 1)\right] x_{v_j}, \quad v_j = 0, 1, 2, \ldots \tag{1.22b}$$

It is not difficult to see the advantage of the diffusion formulation of the kinetic equations for the $x_{v_i}$ (or $\varphi_{v_i}$): the coupling between the equations for the different components is confined to the coefficients of $x_{v_i}$ (or $\varphi_{v_i}$ ) and is in the form of an average over the entire spectrum. Hence approximate analytical methods of solution developed in the single-quantum case can be applied, as well as the method of trials for numerical solution; this is quite significant when the number of equations is large.

## 2. Equation for the Average Energies in a System of Harmonic Oscillators.

Introducing the normalization $\sum_{v_i} x_{v_i} = \gamma_i$, we define the average energy $E_i$ of the molecules of type i by the relation $\sum_{v_i} v_i x_{v_i} = \gamma_i E_i$. Multiplying (1.21) by $v_i$ and summing over $v_i$, we have, using (1.20)

$$\gamma_i \frac{dE_i}{dt} = -\sum_{j,v_i} J^{(j)}_{v_i}. \tag{2.1}$$

For harmonic oscillators

$$x^0_{v_i} = \gamma_i \left(E^0_i\right)^{v_i} / \left(1 + E^0_i\right)^{v_i+1} \quad \left(E^0_i \equiv E_i(\infty) = \mathrm{e}^{-\theta_i}\left(1 - \mathrm{e}^{-\theta_i}\right)^{-1}, \quad \theta_i = \hbar\omega_i/kT\right); \tag{2.2}$$

$$Q^{v_j, v_j - m}_{v_i - n, v_i} = \frac{v_i!}{(v_i - n)!\, n!} \frac{v_j!}{(v_j - m)!\, m!} Q^{m0}_{0n}. \tag{2.3}$$

For times $t \gg \tau^{VV}_1$, where $\tau^{VV}_1$ is the characteristic time of single-quantum VV-exchange (the time required to establish a quasi-Boltzmann distribution in each of the components),

$$x_{v_i} = \gamma_i E_i^{v_i} / (1 + E_i)^{v_i+1}. \tag{2.4}$$

After summing the right-hand side of (2.1) over $v_i$ and $v_j$, we find, with the use of relations (2.2) through (2.4)

$$\frac{dE_i}{dt} = \sum_{j=1}^{2} \gamma_j \sum_{n,m \geqslant 1} n Q^{0m}_{n0}(i, j) \frac{E^0_i E_i^{n-1} (1 + E_i)(1 + E_j)^m}{1 + E^0_i} \times \left[ \frac{n\left(E^0_i - E_i\right)}{E^0_i (1 + E_i)} - \frac{m\left(E^0_j - E_j\right)}{E^0_j (1 + E_j)} \right], \quad i = 1, 2. \tag{2.5}$$

These equations describe the relaxation of the average energies in a binary mixture of diatomic molecules (harmonic oscillators) of types 1 and 2. When m, n > 1, these equations are approximate* [in the same sense as the approximate diffusion equations (1.21) and (1.22)]. Single-quantum exchange processes are described by (2.5) exactly, as expected. Indeed, when n = 1, m = 0 (single-quantum VT-exchange) we have

$$\frac{dE_i}{dt} = \left(E^0_i - E_i\right)\left(1 + E^0_i\right)^{-1} \sum_{j=1}^{2} \gamma_j Q_{10}(i, j), \quad i = 1, 2,$$

and when n = m = 1 (single-quantum VV'-exchange)

$$\frac{dE_i}{dt} = \gamma_j Q^{01}_{10}(i, j) \left[ \frac{E^0_i}{1 + E^0_i} \frac{1 + E^0_j}{E^0_j} (1 + E_i) E_j - E_i (1 + E_j) \right], \qquad i, j = 1, 2, \quad i \neq j, \tag{2.6}$$

and these equations agree with the corresponding equations of [28, 31], obtained directly from the single-quantum balance equations for the population densities (see also [30]).

In a system of harmonic oscillators, single-quantum VV-exchange between molecules of the same kind do not change the $E_i$ [and therefore the terms with i = j are equal to zero in (2.6)], and the only possible result in the case when VV-exchange is fast in comparison with VT-exchange ($\tau^{VV}_1 \ll \tau^{VT}_1$) is the establishment of the quasistationary distribution (2.4). In the general case of anharmonic oscillators, conservation of the number of vibrational quanta in single-quantum VV-exchange $\left(\sum\limits_{v_i} J^{(i)}_{v_i} = 0\right)$ implies that $\varphi_{v+1}/\varphi_v = c = \mathrm{const}$, and we then have the well-known Treanor distribution $x_v = x_0 c^v \exp(-\varepsilon_v/kT)$.

3. Classical Limit of the Kinetic Equations. In the framework of the approximation (1.10), Eqs. (1.17) and (1.19) transform in the classical limit ($\hbar\omega_v/kT \ll 1$)† to a system of three two-dimensional differential equations of the diffusion type:

$$\begin{gathered} \frac{\partial \rho_{ij}}{\partial t} = \operatorname{div} \mathbf{J}^{ij}, \quad i, j = 1, 2, \\ J^{ij}_{\varepsilon} = \rho^0_{ij} B^{ij}_{11} \frac{\partial}{\partial \varepsilon}\left(\rho_{ij}/\rho^0_{ij}\right) - \rho^0_{ij} B^{ij}_{12} \frac{\partial}{\partial \varepsilon'}\left(\rho_{ij}/\rho^0_{ij}\right), \\ J^{ij}_{\varepsilon'} = \rho^0_{ij} B^{ij}_{12} \frac{\partial}{\partial \varepsilon}\left(\rho_{ij}/\rho^0_{ij}\right) - \rho^0_{ij} B^{ij}_{22} \frac{\partial}{\partial \varepsilon'}\left(\rho_{ij}/\rho^0_{ij}\right). \end{gathered} \tag{3.1}$$

Here $\rho_{ij}(\varepsilon, \varepsilon', t) = f_i(\varepsilon, t) f_j(\varepsilon', t)$; $\rho^0_{ij}(\varepsilon, \varepsilon', t) = f_i(\varepsilon, \infty) f_j(\varepsilon', \infty)$; $f_i(\varepsilon, t)$ is the classical distribution function of molecules of type i over the vibrational energies $\varepsilon$; $J^{ij}_{\varepsilon}$ and $J^{ij}_{\varepsilon'}$ are the components of the diffusion flux vector $\mathbf{J}^{ij}$ in the space of the energies $\varepsilon$, $\varepsilon'$ of the interacting molecules; the coefficients $B^{ij}_{ks}$ are given by the relations

$$B^{ij}_{11}(\varepsilon, \varepsilon') = \frac{(\hbar\omega_v)^2}{2} \sum_{n,m \neq 0} n^2 Q^{v', v'+m}_{v, v+n}(i, j) = \frac{\langle(\Delta\varepsilon)^2\rangle}{2\tau_{ij}},$$

---

*The corresponding exact equations are obtained in [30].

†For more detail, see [24, 25], where the limiting procedure was carried through for VT-exchange.

$$B_{12}^{ij}(\varepsilon, \varepsilon') = \frac{\hbar\omega_v \hbar\omega_{v'}}{2} \sum_{n,m\neq 0} nmQ_{v,v+n}^{v',v'+m}(i, j) = \frac{\langle \Delta\varepsilon\Delta\varepsilon' \rangle}{2\tau_{ij}},$$

$$B_{22}^{ij}(\varepsilon, \varepsilon') = \frac{(\hbar\omega_{v'})^2}{2} \sum_{n,m\neq 0} m^2 Q_{v,v+n}^{v',v'+m}(i, j) = \frac{\langle (\Delta\varepsilon')^2 \rangle}{2\tau_{ij}}$$

and are in the form of moments of the transferred energies averaged with respect to the parameters of the collision; $\tau_{ij}$ is the mean time between collisions of a molecule of type i in a gas of molecules of type j.

In the classical limit, Eqs. (1.21) and (1.22) transform into a system of two integro-differential equations

$$\frac{\partial f_i(\varepsilon, t)}{\partial t} = \frac{\partial}{\partial \varepsilon} \int (J_\varepsilon^{i1} + J_\varepsilon^{i2})\, d\varepsilon', \quad i = 1, 2, \tag{3.2}$$

which can also be obtained from (3.1) with the help of the relation $f_i(\varepsilon, t) = \int \rho_{i1}(\varepsilon, \varepsilon', t)\, d\varepsilon' + \int \rho_{i2}(\varepsilon, \varepsilon', t)\, d\varepsilon'$, $i = 1, 2$, which is the classical analog of (1.3).

Equations (3.1) and (3.2) were obtained in [19] directly from the Boltzmann kinetic equations with the use of the weak interaction condition ($\Delta\varepsilon$, $\Delta\varepsilon' \ll \varepsilon$, $\varepsilon'$).

## LITERATURE CITED

1. H. A. Kramers, "Brownian motion in a field of force and the diffusion model of chemical reactions," Physica, 7, No. 4 (1940).
2. E. M. Lifshits and L. P. Pitaevskii, Physical Kinetics [in Russian], Nauka, Moscow (1979).
3. P. R. Berman, "Brownian motion of atomic systems: Fokker–Planck limit of the transport equation," Phys. Rev., A9, No. 5 (1974).
4. M. N. Safaryan and E. V. Stupochenko, "Rotational relaxation of diatomic molecules in a light inert gas," Zh. Prikl. Mekh. Tekh. Fiz., No. 4 (1964).
5. M. N. Safaryan, "Rotational relaxation of molecules of the type HBr in an inert gas," Teplofiz. Vys. Temp., 10, No. 4 (1972).
6. A. I. Osipov and N. K. Generalov, "Theory of vibrational relaxation," Fiz. Goreniya Vzryva, No. 2 (1966).
7. E. E. Nikitin, "Relaxation of the vibrations of polyatomic molecules in collisions," Teor. Éksp. Khim., 4, No. 3 (1968).
8. M. N. Safaryan and N. M. Pruchkina, "Vibrational relaxation of anharmonic oscillators," Teor. Éksp. Khim., 6, No. 3 (1970).
9. M. N. Safaryan and O. V. Skrebkov, "Kinetics of vibrational–translational exchange of diatomic molecules (anharmonic oscillators) in an inert gas," Fiz. Goreniya Vzryva, No. 4 (1975).
10. J. C. Keck and G. Carrier, "Diffusion theory of nonequilibrium dissociation and recombination," J. Chem. Phys., 43, No. 7 (1965).
11. E. V. Stupochenko and M. N. Safaryan, "A diffusion theory of thermal dissociation of diatomic molecules," Teor. Éksp. Khim., 2, No. 6 (1966).
12. S. A. Losev, "On the vibrational excitation and dissociation of diatomic molecules in the diffusion approximation," Teor. Éksp. Khim., 5, No. 6 (1969).
13. M. N. Safaryan and O. V. Skrebkov, "The effect of spontaneous emission on the kinetics of vibrational deactivation of anharmonic oscillators," Fiz. Goreniya Vzryva, No. 2 (1978).
14. M. N. Safaryan, E. V. Stupochenko, and N. M. Pruchkina, "Effect of the interaction of molecular vibrations and rotations in the diffusion theory of the thermal dissociation of diatomic molecules," Teor. Éksp. Khim., 5, No. 2 (1969).
15. C. A. Brau, "Classical theory of vibrational relaxation of anharmonic oscillators," Physica, 58, No. 3 (1972).
16. B. F. Gordiets and Zh. S. Mamedov, "Distribution function and rate of vibrational energy relaxation in a system of anharmonic oscillators," Zh. Prikl. Mekh. Tekh. Fiz., No. 3 (1974).
17. V. M. Volokhov and O. V. Skrebkov, "Vibrational relaxation of diatomic molecules (anharmonic oscillators) in a Boltzmann reservoir. One-component system," Fiz. Goreniya Vzryva, No. 4 (1981).

18. V. D. Rusanov, A. A. Fridman, and G. V. Sholin, "Population in a nonequilibrium plasma of vibrationally excited states of diatomic molecules in the diffusion approximation," Zh. Tekh. Fiz., 49, No. 3 (1979).
19. V. M. Volokhov, M. N. Safaryan, and O. V. Skrebkov, "Diffusion model of vibrational relaxation of anharmonic oscillators. Two-component system," Teor. Éksp. Khim., 4, No. 4 (1978).
20. V. M. Volokhov and O. V. Skrebkov, "Diffusion model of vibrational relaxation in a binary mixture of diatomic molecules (harmonic oscillators)," Teor. Éksp. Khim., 18, No. 2 (1982).
21. V. M. Volokhov and O. V. Skrebkov, "Vibrational relaxation of diatomic molecules (anharmonic oscillators) in a Boltzmann reservoir. Two-component system," Zh. Prikl. Mekh. Tekh. Fiz., No. 5 (1982).
22. G. V. Dubrovskii, "Simplified kinetic approach to the dynamics of a structural relaxing gas," Zh. Tekh. Fiz., 52, No. 10 (1982).
23. V. I. Osherov, "On the approach to equilibrium in the presence of nonadiabatic transitions," Teor. Éksp. Khim., 4, No. 2 (1968).
24. M. N. Safaryan and O. V. Skrebkov, "Classical diffusion and quantum mechanical methods of calculating the kinetics of VT-exchange and radiative deactivation of diatomic molecules," Preprint, Inst. of Mech. Problems, Acad. of Sciences of the USSR, No. 56, Moscow (1975).
25. M. N. Safaryan and O. V. Skrebkov, "Comparison between classical diffusion and quantum calculations of vibrational—translational relaxation of diatomic molecules," Zh. Prikl. Mekh. Tekh. Fiz., No. 4 (1978).
26. L. M. Biberman, V. S. Vorob'ev, and I. T. Yakubov, "Kinetics of collisional and radiative ionization and recombination," Usp. Fiz. Nauk, 107, No. 3 (1972).
27. V. M. Volokhov and O. V. Skrebkov, "Classical diffusion and quantum calculations of vibrational relaxation in a binary mixture of diatomic molecules (anharmonic oscillators)," Khim. Fiz., 3, No. 2 (1984).
28. E. E. Nikitin an A. I. Osipov, "Vibrational relaxation in gases," Summary of Science and Technology, Ser. Kinetics and Catalysts, Vol. 4, VINITI, Moscow (1977).
29. A. O. Gel'fënd, Calculus of Finite Differences [in Russian], Nauka, Moscow (1967).
30. A. S. Biryukov and B. F. Gordiets, "Kinetic equation of vibrational energy relaxation in mixtures of polyatomic gases," Zh. Prikl. Mekh. Tekh. Fiz., No. 6 (1972).
31. E. V. Stupochenko, S. A. Losev, and A. I. Osipov, Relaxation Processes in Shock Waves [in Russian], Nauka, Moscow (1965).

---

# QUASISTATIONARY RELAXATION AND GAS-DYNAMIC PHENOMENA IN A ONE-COMPONENT SYSTEM OF EXCITED ANHARMONIC OSCILLATORS

V. P. Silakov and A. V. Chebotarev

UDC 531

At the present time the kinetic theory of vibrational relaxation of molecular gases is the most developed branch of physical kinetics. Among important achievements in this field one has to include the development of general methods of description of systems far from equilibrium [1, 2]. In such cases the anharmonicity of the molecular vibration shows a substantial influence on the behavior of the medium. Until now theoretical analysis of vibrational relaxation of systems of anharmonic oscillators was carried out basically for gases at rest.

In addition, due to advances in the physics of nonequilibrium discharge phenomena it became clear that the correct description of the behavior of strongly excited gases should take into account their relaxational motion. Indeed, as an example, such motion can markedly influence the conditions of vibrational relaxation of gases after the discharge [3], and in fast-flow discharge arrangements it can lead to the breakdown of the pumping regime of the vibrational degrees of freedom of the gaseous mixtures [4]. For a theoretical consideration of a selected class of problems one has to complete a substantial amount of computational

---

Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 6, pp. 35-42, November-December, 1987. Original article submitted July 29, 1986.

0021-8944/87/2806-0836$12.50