RELAXATION OF ANHARMONIC MOLECULES

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The inclusion of anharmonic effects is important in vibrational population inversions in CO-lasers [1, 2], in relaxation processes in jets [3], in thermal dissociation [1], in the kinetics of chemical reactions with high thresholds [4], etc. Usually these effects are studied by including anharmonic corrections to the kinetic constants in the discrete model of single-quantum transitions or in the diffusion approximation [1, 2]. In [5] a method was given of solving the relaxation equations fro arbitrary forms of the rate constants and the spectrum of the molecule. The method is valid when the ratio of the population densities of neighboring levels varies smoothly with quantum number. It was shown in [5] that this approximation can be used to construct analytical solutions for a wide class of problems. In the present paper the method of [5] is extended to the case of equations with variable coefficients. The properties of the solutions for VT-relaxation of anharmonic molecules are analyzed, and the inclusion of sources is considered. A simple method of taking into account multiple-quantum transitions is given, as well as an extension of the method to an arbitrary mixture of gases. The population densities are calculated and the possibility of using our solutions in relaxation gas dynamics is discussed.

1. Harmonic Model with Single-Quantum Transitions. We present briefly the principal results of the harmonic model [1, 2] for a mixture of gases as needed below. The vibrational relaxation of a mixture of harmonic molecules of types $s = 1, 2, \ldots$ in the single-quantum approximation reduces to a system of equations for the population densities $n_s(\nu, t)$ where ν is the number of the vibrational level, and their first moments $\alpha_s(t) = n_s^{-1} \sum_\nu \nu n_s(\nu, t)$ (the average numbers of quanta per molecule):

$$\dot{n}_s(\nu, t) = G_s[\alpha(t)](\nu + 1)n_s(\nu + 1, t) - \{F_s[\alpha(t)](\nu + 1) + G_s[\alpha(t)]\nu\}n_s(\nu, t) + F_s[\alpha(t)]\nu n_s(\nu - 1, t); \quad (1.1)$$

$$\dot{\alpha}_s(t) = K_{01}(s) - [K_{10}(s) - K_{01}(s)]\alpha_s(t) + \sum_{s_1 \neq s}\left[K_{10}^{01}(s, s_1)\alpha_s(t)\left(1 + \alpha_{s_1}(t)\right) - K_{01}^{10}(s, s_1)\alpha_{s_1}(t)(1 + \alpha_s(t))\right]n_{s_1}. \quad (1.2)$$

Here

$$G_s[\alpha(t)] = K_{10}(s) + K_{10}^{01}(s, s)n_s(1 + \alpha_s(t)) + \sum_{s_1 \neq s}K_{10}^{01}(s, s_1)n_{s_1}\left(1 + \alpha_{s_1}(t)\right); \quad (1.3)$$

$$F_s[\alpha(t)] = K_{01}(s) + K_{01}^{10}(s, s)n_s\alpha_s(t) + \sum_{s_1 \neq s}K_{01}^{10}(s, s_1)n_{s_1}\alpha_{s_1}(t), \quad (1.4)$$

where $K_{10}(s)$, $K_{10}^{01}(s, s) = K_{01}^{10}(s, s)$, $K_{10}^{01}(s, s_1) = K_{01}^{10}(s_1, s)$ are the rate constants of the corresponding transitions for VT, VV, and VV' processes; $\alpha \equiv (\alpha_1, \alpha_2, \ldots, \alpha_s, \ldots)$. For a Boltzmann heat reservoir the detailed balance relation holds between the rate constants of the fundamental transitions:

$$K_{01}(s) = K_{10}(s)\exp\left(-\frac{\Theta_s}{T}\right); \quad K_{10}^{01}(s, s_1)\exp\left(-\frac{\Theta_s}{T}\right) = K_{01}^{10}(s, s_1)\exp\left(-\frac{\Theta_{s_1}}{T}\right), \quad (1.5)$$

where T is the temperature of the gas, and $\Theta_s \equiv \hbar\omega_s/k$ is the characteristic vibrational temperature of a molecule of type s.

The exact solution of the system (1.1), (1.2) is not known. In applications one usually uses approximate or quasistationary solutions, which are valid for certain relations

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between the characteristic times of the VV, VV', and VT relaxation processes [1, 2]. This is also the case for the solution of the corresponding equations in the presence of delta-function sources [6]. The most interesting result of the harmonic model is canonical invariance, which states that an initial Boltzmann distribution in a single-component system preserves its form in time

$$n_s(v, t) = n_s \left[1 - \exp\left(-\frac{\Theta_s}{T_s(t)} \right) \right] \exp\left(-\frac{v\Theta_s}{T_s(t)} \right), \tag{1.6}$$

and only the vibrational temperature $T_s(t)$ changes. The latter is related to $\alpha_s(t)$ by the equation

$$\exp\left(-\frac{\Theta_s}{T_s(t)} \right) = \frac{\alpha_s(t)}{1 + \alpha_s(t)}, \quad \alpha_s(0) = \alpha_{s0}. \tag{1.7}$$

2. VT Relaxation of Anharmonic Molecules. In the single-quantum approximation the problem reduces to the solution of the system of equations

$$\dot{n}(v, t) = K_{v+1,v}\, n(v+1, t) - [K_{v,v+1} + K_{v,v-1}]n(v, t) + K_{v-1,v}n(v-1, t), \tag{2.1}$$

whose coefficients can depend on time through the temperature of the gas. We introduce, as in [5], the ratio of neighboring population densities

$$\frac{n(v, t)}{n(v-1, t)} = a(v-1)f(v-1, t), \quad a(v-1) \equiv \frac{K_{v-1,v}}{K_{v,v-1}}. \tag{2.2}$$

After substitution of (2.2) into (2.1), and after several reductions analogous to those in [5], we obtain a system of equations for the functions $f(v, t)$:

$$\dot{f}(v, t) = A(v, t)f^2(v, t) + B(v, t)f(v, t) + C(v, t) + \varkappa(v, t)f(v, t), \tag{2.3}$$

where $A(v, t) = K_{v+1,v+2} - K_{v,v+1}$;

$$B(v, t) = K_{v,v+1} + K_{v,v-1} - K_{v+1,v+2} - K_{v+1,v};$$
$$C(v, t) = K_{v+1,v} - K_{v,v-1};$$
$$\varkappa(v, t) = \varepsilon(v, t) - \frac{d}{dt} \ln a(v, t);$$
$$\varepsilon(v, t) = K_{v,v-1} \left[1 - \frac{f(v, t)}{f(v-1, t)} \right] f^{-1}(v, t) - K_{v+1,v+2} \left[1 - \frac{f(v+1, t)}{f(v, t)} \right] f(v, t).$$

When the dependence of $f(v, t)$ on v is smooth we have, approximately

$$\frac{f(v, t)}{f(v-1, t)} \simeq \frac{f(v+1, t)}{f(v, t)} \simeq 1, \quad |\varepsilon(v, t)| \ll 1. \tag{2.4}$$

If the time scales of $f(v, t)$ and $\ln a(v, t)$ are significantly different, the quantity $\varkappa(v, t)$ is small. Therefore the solution of the system (2.3) can be written as a power series in $\varkappa$

$$f(v, t) = \sum_l f^{(l)}(v, t)\varkappa^l(v; f^{(l-1)}(t)), \quad f(v, 0) = f^{(0)}(v, 0) \equiv f_0(v). \tag{2.5}$$

To zero order in $\varkappa$, (2.3) is a general Riccati equation, whose coefficients satisfy $A(v, t) + B(v, t) + C(v, t) = 0$. In this case the general solution is [7]

$$f^{(0)}(v, t) = \frac{1 + f_0(v) + [1 - f_0(v)]\left\{ \int_0^t E(v, t')[A(v, t') + C(v, t')]\, dt' - E(v, t) \right\}}{1 + f_0(v) + [1 - f_0(v)]\left\{ \int_0^t E(v, t')[A(v, t') + C(v, t')]\, dt' + E(v, t) \right\}}; \tag{2.6}$$

$$E(v, t) \equiv \exp\left\{ \int_0^t [A(v, t') - C(v, t')]\, dt' \right\}. \tag{2.7}$$

336

After substitution of (2.5) into (2.3) we obtain a linear equation for the ℓ-th correction

$$\dot{f}^{(l)}(v,t) = \left[2A(v,t)f^{(0)}(v,t) + B(v,t)\right]f^{(l)}(v,t) + A(v,t)\sum_{k=1}^{l-1} f^{(k)}(v,t)f^{(l-k)}(v,t) + f^{(l-1)}(v,t). \qquad (2.8)$$

Hence

$$f^{(l)}(v,t) = D(v,t)\int_0^t D^{-1}(v,t')\left[A(v,t')\sum_{k=1}^{l-1} f^{(k)}(v,t')f^{(l-k)}(v,t') + f^{(l-1)}(v,t')\right]dt', \qquad (2.9)$$

$$D(v,t) \equiv \exp\left\{\int_0^t \left[2A(v,t')f^{(0)}(v,t') + B(v,t')\right]dt'\right\}.$$

Successive application of (2.2) gives for the population densities n(ν, t) the expression

$$n(v,t) = nQ^{-1}(t)\prod_{k=0}^{v-1} a(k)f(k,t), \quad Q(t) = 1 + \sum_{v=1}^{v_0}\prod_{k=0}^{v-1} a(k)f(k,t), \qquad (2.10)$$

where v_0 is the limiting value of the discrete vibrational spectrum.

We discuss the basic properties of the solution. First, it has the correct normalization for any form of the function f(ν, t). If the coefficients of the system (2.1) do not depend on time (relaxation into a heat reservoir), then the solution (2.6) reduces to that found in [5]. Indeed, in this case

$$\tau^{-1}(v) \equiv C(v) - A(v) = K_{v+1,v} - K_{v+1,v+2} + K_{v,v+1} - K_{v,v-1}, \qquad (2.11)$$

and (2.6), with the help of (2.11), takes the form

$$f^{(0)}(v,t) = \frac{[1-f_0(v)]\exp[-t/\tau(v)]\beta(v) + f_0(v) - \beta(v)}{[1-f_0(v)]\exp[-t/\tau(v)] + f_0(v) - \beta(v)}, \qquad (2.12)$$

$$\beta(v) \equiv (K_{v+1,v} - K_{v,v-1})/(K_{v+1,v+2} - K_{v,v+1}).$$

For a monotonic dependence of the rate constants on the quantum numbers and temperature it follows from (2.7) that E(ν, t) → 0. Therefore when $t \gg \tau(v)$ $f^{(0)}(v,t) \simeq 1$ and the solution (2.10) gives the quasistationary distribution $n^q(v)$ determined by the well-known condition [8]

$$n^q(v)/n^q(v-1) = a(v-1). \qquad (2.13)$$

For a Boltzmann heat reservoir $a(v-1) = \exp\{-[e(v)-e(v-1)]/kT\}$ and with the help of (2.13), equation (2.10) reduces to a Boltzmann distribution with the exact anharmonic spectrum e(ν):

$$n^q(v) = n^B(v) = nQ_B^{-1}\exp[-e(v)/kT], \quad Q_B = \sum_{v=0}^{v_0}\exp[-e(v)/kT]. \qquad (2.14)$$

If τ(ν) in (2.11) is interpreted as the relaxation time of the function f(ν, t), then the evolution of the population density of level ν is determined, as seen from (2.10), by all τ(μ) with $0 \le \mu \le v-1$.

We consider the behavior of the solution (2.10) in the harmonic approximation for a non-Boltzmann heat reservoir, when $\tau^{-1} = K_{10} - K_{01}$, $\beta = K_{10}/K_{01} = a^{-1}$, $f_0(v) = \beta n(v,0)/n(v-1,0) \equiv \beta\varphi(v)$:

$$af(v,t) \equiv q(v,t) = \left\{e^{-\frac{t}{\tau}}[1-\beta\varphi(v)] + \varphi(v) - 1\right\}\Big/\left\{e^{-\frac{t}{\tau}}[1-\beta\varphi(v)] + \beta[\varphi(v)-1]\right\}. \qquad (2.15)$$

We see from (2.15) that for the harmonic model the dependence of q(ν, t) on ν is determined by the initial conditions only. If this dependence is weak then q(ν, t) ≅ q(t) and the solution (2.10) gives

$$n(v, t) = n[1 - q(t)]\dot{q}^v(t).$$

(2.16)

The function q(t) can be expressed in terms of $\alpha(t)$, whose explicit form (with the inclusion of VT transitions only) is found from (1.2) without the terms inside the square brackets:

$$\alpha(t) = 1/(\beta - 1) + [\alpha(0) - 1/(\beta - 1)] \exp(-t/\tau).$$

(2.17)

Combining (2.17) and (2.15), we have $q(t) = \alpha(t)/[1 + \alpha(t)]$, $\alpha(0) = \varphi(v)/[1 - \varphi(v)]$. With the help of (1.7) the solution (2.16) transforms into (1.6), i.e., it has the property of canonical invariance. Therefore canonical invariance is a consequence of the harmonic approximation for the rate coefficients and the smoothness of the initial distribution. The solution (2.16) can be considered as a generalization of (1.6) for a non-Boltzmann heat reservoir and when q(v, t) is weakly dependent on v.

A simplification of the general solution (2.10) is possible by expressing the functions A...E, $f_0(v)$, a(v, t) in terms of the VT transition rate constants.

As an illustration we calculated the distribution function, as given by (2.10), for the system Ar + N_2 in a Boltzmann heat reservoir, for both the harmonic model (Fig. 1, dashed curves) and the anharmonic model (solid curves) for various gas temperatures T and initial vibrational temperatures $T_V(0)$. Figure 1, which presents graphs of the distribution function at the times t = 10^{12}, 10^{13}, 10^{14}, 10^{15} a.e. (curves 1 through 4) for $T_V(0)$ = 1000°K, T = 300°K, shows that anharmonic effects lead to a slowing of the relaxation and to a violation of canonical invariance. When we have the opposite relation between the temperatures ($T_V(0)$ = 300°K, T = 1000°K) the relaxation time to equilibrium is comparable in the two models (Fig. 2, t = 10^7, 10^8, 10^9, 10^{10} a.e.; curves 1 through 4), however the deviation from canonical invariance becomes much more significant when anharmonic effects are taken into account. In the calculations the data for the VT exchange rate constants in the system Ar + N_2 was taken from [9].

3. Relaxation of Anharmonic Molecules in the Presence of Sources. In the presence of external sources the original system of equations (2.1) is more conveniently written in vector form (n(t) = (n(0, t), n(1, t), ..., n(v_0, τ)))

$$\dot{n}(t) = K \cdot n(t) + \Pi[n(t), t], \quad n(0) = n_0,$$

(3.1)

where the vector Π, which in general depends on the population densities n(t) and the time t, describes a set of sources.

A. Let Π be a constant vector, i.e., in the gas we have a group of sources and sinks with constant intensity $\Pi(v)$. The solution of the linear inhomogeneous system (3.1) is written as a sum of a general solution $n_1(t)$ of the homogeneous system (as found in Sec. 2), and a particular solution $n_2(t)$ of the inhomogeneous system

$$n(t) = n_1(t) + n_2(t).$$

(3.2)

The inhomogeneous solution is written in the form

$$n_2(t) = n^0 \eta t + g(t), \quad \eta \equiv \sum_{v=0}^{v_0} \Pi(v),$$

(3.3)

where the vector n^0 is obtained from the condition

$$K \cdot n^0 = 0, \quad \sum_{v=0}^{v_0} n^0(v) = 1,$$

(3.4)

and hence n^0 is the quasistationary distribution in a system without sources. According to (2.10), the solution of the system (3.4) has the form

$$n^0(v) = n^0(0) \prod_{\mu=0}^{v-1} \frac{K_{\mu,\mu+1}}{K_{\mu+1,\mu}}, \quad n^0(0) = \left[1 + \sum_{v=0}^{v_0} \prod_{\mu=0}^{v-1} \frac{K_{\mu,\mu+1}}{K_{\mu+1,\mu}}\right]^{-1}.$$

(3.5)

After substitution of (3.2) through (3.4) into (3.1), we obtain for g

Fig. 1

Fig. 2
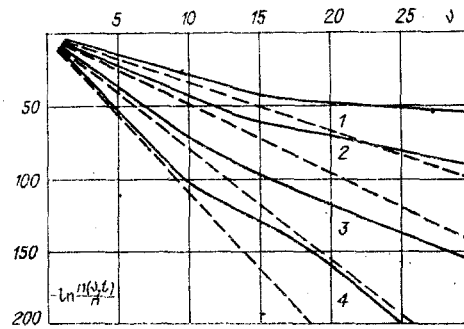
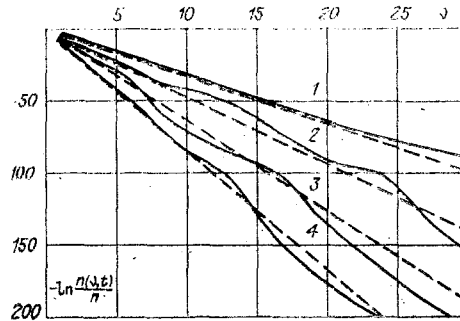$$\dot{\mathbf{g}} = \mathbf{K} \cdot \mathbf{g} + \mathbf{\Pi} - \mathbf{n}^0 \eta. \tag{3.6}$$

Because it is sufficient to find an arbitrary particular solution of the system (3.1), we assume that g = const. Then it follows from (3.6) that

$$\mathbf{K} \cdot \mathbf{g} = \mathbf{n}^0 \eta - \mathbf{\Pi}. \tag{3.7}$$

Equation (3.7) leads (in the single-quantum approximation) to the system of recursion relations between the components of the vector g:

$$g(v+1)K_{v+1,v} = g(v)(K_{v,v+1} + K_{v,v-1}) - g(v-1)K_{v-1,v} + \eta n^0(v) - \Pi(v),$$

and the solution is found in the explicit form

$$g(v) = g(0)\frac{n^0(v)}{n^0(0)} + \sum_{\mu=1}^{v} \frac{n^0(v)}{n^0(\mu)} \frac{R(\mu-1) - P(\mu-1)}{K_{\mu,\mu-1}}, \quad v \geqslant 1; \tag{3.8}$$

where the quantity g(0) is determined from the normalization condition $\sum_{v=0}^{v_0} g(v) = 0$:

$$g(0) = n^0(0) \sum_{v=1}^{v_0} \sum_{\mu=1}^{v} \frac{n^0(v)}{n^0(\mu)} \frac{P(\mu-1) - R(\mu-1)}{K_{\mu,\mu-1}}. \tag{3.9}$$

Here $R(v) \equiv \eta \sum_{\mu=0}^{v} n^0(\mu); \quad P(v) \equiv \sum_{\mu=0}^{v} \Pi(\mu).$

B. We consider the case when Π is a vector which is linear in n(t):

$$\mathbf{\Pi} = \Lambda \cdot \mathbf{n}(t), \tag{3.10}$$

where Λ is a diagonal matrix with elements λ_v. For example $\lambda_v > 0$ for an electron excitation and $\lambda_v < 0$ for dissociation. WIth the help of (3.10), the system (3.1) takes the form

$$\dot{\mathbf{n}}(t) = (\mathbf{K} + \Lambda) \cdot \mathbf{n}(t). \tag{3.11}$$

The general solution of (3.11) is written in the same form as in Sec. 2, where it is assumed that the method of (2.4) still holds when there are sources. After replacing (2.2) and performing a series of reductions, we obtain in place of (2.3)

$$\dot{f}(v, t) = A(v, t)f^2(v, t) + [B(v, t) + \lambda_{v+1}(t) - \lambda_v(t)]f(v, t) + C(v, t) + \varkappa(v, t)f(v, t). \tag{3.12}$$

339

This is a general Riccati equation and can be integrated only for particular choices of the $\lambda_\nu(t)$ (for example when $\lambda_{\nu+1} - \lambda_\nu + \varkappa \ll 1$). Therefore we assume that the coefficients in the system (3.11) are constants. Then (3.12) can be written as

$$\dot{f}(\nu, t) = A(\nu)[f(\nu, t) - z_1(\nu)][f(\nu, t) - z_2(\nu)] + \varepsilon(\nu, t),\qquad (3.13)$$

where $z_{1,2}(\nu)$ are the roots of the quadratic equation ($z_1 < z_2$)

$$z^2(\nu) + 2\gamma(\nu)z(\nu) + \beta(\nu) = 0 \qquad (3.14)$$

with $\gamma(\nu) \equiv [\lambda_{\nu+1} - \lambda_\nu + B(\nu)]/2A(\nu)$. With the condition (2.4) we find from (3.13), to zero order in ε

$$f(\nu, t) = \frac{e^{-\frac{t}{\tau(\nu)}}z_2(\nu)[z_1(\nu) - f_0(\nu)] - z_1(\nu)[z_2(\nu) - f_0(\nu)]}{e^{-\frac{t}{\tau(\nu)}}[z_1(\nu) - f_0(\nu)] - [z_2(\nu) - f_0(\nu)]},\qquad (3.15)$$

$$\tau^{-1}(\nu) = (K_{\nu+1,\nu+2} - K_{\nu,\nu+1})[z_2(\nu) - z_1(\nu)].$$

If the intensities of the sources are such that there are two identical roots in (3.14), then in place of (3.15) we have ($z_1 = z_2 = \sqrt{\beta(\nu)}$)

$$f(\nu, t) = z_1(\nu) - [z_1(\nu) - f_0(\nu)]\left[1 + (z_1(\nu) - f_0(\nu))\frac{t}{\tau(\nu)}\right]^{-1},\qquad (3.16)$$

$$\tau^{-1}(\nu) = K_{\nu+1,\nu+2} - K_{\nu,\nu+1}.$$

When (3.14) has complex conjugate roots the solution of (3.13) takes the form

$$f(\nu, t) = \frac{f_0(\nu) + \{1 + \gamma(\nu)[\beta(\nu) - \gamma^2(\nu)]^{-1/2}[f_0(\nu) + \gamma(\nu)]\}\,\mathrm{tg}\frac{t}{\tau(\nu)}}{1 - [\beta(\nu) - \gamma^2(\nu)]^{-1/2}[f_0(\nu) + \gamma(\nu)]\,\mathrm{tg}\frac{t}{\tau(\nu)}},\qquad (3.17)$$

$$\tau^{-1}(\nu) = (K_{\nu+1,\nu+2} - K_{\nu,\nu+1})[\beta(\nu) - \gamma^2(\nu)]^{1/2}.$$

Unlike (3.15) and (3.16), the solution (3.17) has an unusual structure: it describes an oscillation of the function $f(\nu, t)$ about the initial value $f_0(\nu)$, which is typical in self-oscillating relaxation regimes [10]. Since in this case the condition (2.4) is rapidly violated, this solution is valid only when $f(\nu, t) \sim f_0(\nu)$.

4. Inclusion of Multiple-Quantum Transitions. We consider now the possibility of approximately taking into account multiple transitions in our method. Multiple-quantum transitions are significant for the vibrational relaxation of strongly excited molecules. We write the right hand side of the system (2.1) as a sum over the number of transferred quanta

$$\dot{n}(\nu, t) = \sum_\delta [K_{\nu+\delta,\nu}n(\nu + \delta, t) - (K_{\nu,\nu+\delta} + K_{\nu,\nu-\delta})n(\nu, t) + K_{\nu-\delta,\nu}n(\nu - \delta, t)].\qquad (4.1)$$

Generalizing (2.2), we find

$$n(\nu + \delta, t) = n(\nu, t)\prod_{\mu=0}^{\delta-1} a(\nu + \mu)f(\nu + \mu, t).\qquad (4.2)$$

Substituting (4.2) into (4.1) we obtain in place of (2.3)

$$\frac{\dot{f}(\nu, t)}{f(\nu, t)}\sum_\delta [b(\nu, \delta)f^\delta(\nu, t) + c(\nu, \delta) + d(\nu, \delta)f^{-\delta}(\nu, t)] + \varepsilon(\nu, t).\qquad (4.3)$$

Here b, c, and d are coefficients which can be expressed in terms of the rate constants of multiple-quantum transitions. We assume that these coefficients are constants, and the quantity $\varepsilon(\nu, t)$ is, as before, small ($|\varepsilon| \ll 1$) when the condition (2.4) is satisfied. The general solution of (4.3) to zero order in ε reduces to quadratures

340

$$t = \int_{f_0(v)}^{f(v,t)} dz \left\{ z \sum_\delta [b(v,\delta) z^\delta + c(v,\delta) + d(v,\delta) z^{-\delta}] \right\}^{-1}.$$

Note that if, in addition to (2.4), the condition $a(v) \cong a(v-1)$ is also satisfied, then the solution of (4.3) is simple

$$f(v,t) = \frac{\exp[-t/\tau^*(v)][1-f_0(v)]\beta^*(v) - [\beta^*(v) - f_0(v)]}{\exp[-t/\tau^*(v)][1-f_0(v)] - [\beta^*(v) - f_0(v)]},$$

where

$$[\tau^*(v)]^{-1} \equiv \sum_\delta [\tau(v,\delta)]^{-1} = \sum_\delta [K_{v+1,v+1-\delta} - K_{v,v-\delta} \qquad (4.4)$$
$$- K_{v+1,v+1+\delta} + K_{v,v+\delta}];$$

$$\beta^*(v) = \left[\sum_{\delta \geqslant 2} (K_{v+1,v+1-\delta} - K_{v,v-\delta})\right] \left[\sum_{\delta \geqslant 2} (K_{v+1,v+1+\delta} - K_{v,v+\delta})\right]^{-1}.$$

It is evident that each of the terms in (4.4) can be interpreted as an inverse relaxation time of the function $f(v, t)$ due to transitions where the quantum number changes by the quantity δ.

5. Vibrational Relaxation in a Mixture of Anharmonic Molecules. We consider an arbitrary mixture of anharmonic molecules of types $s = 1, 2, \ldots$ and write the system of equations for the mixture in the form (single-quantum transitions)

$$\dot{n}_s(v,t) = K^*_{v+1,v}(s,t) n_s(v+1,t) - [K^*_{v,v+1}(s,t) + K^*_{v,v-1}(s,t)] n_s(v,t) + K^*_{v-1,v}(s,t) n_s(v-1,t), \qquad (5.1)$$

where the coefficients $K^*_{\mu v}(s, t)$ are determined by

$$K^*_{v+1,v}(s,t) = K_{v+1,v}(s) + M_{v+1,v}(s,t) + M'_{v+1,v}(s,t), \quad K^*_{v,v+1}(s,t) \qquad (5.2)$$
$$= K_{v,v+1}(s) + N_{v,v+1}(s,t) + N'_{v,v+1}(s,t),$$
$$M_{v+1,v}(s,t) = \sum_\mu K^{\mu,\mu+1}_{v+1,v}(s,s) n_s(\mu,t), \quad M'_{v+1,v}(s,t) = \sum_{\mu,s_1} K^{\mu,\mu+1}_{v+1,v}(s,s_1) n_{s_1}(\mu,t),$$
$$N_{v,v+1}(s,t) = \sum_\mu K^{\mu+1,\mu}_{v,v+1}(s,s) n_s(\mu+1,t), \quad N'_{v,v+1}(s,t)$$
$$= \sum_{\mu,s_1} K^{\mu+1,\mu}_{v,v+1}(s,s_1) n_{s_1}(\mu+1,t).$$

If we assume that the dominant contribution to the moments of the distribution function comes from the lower levels, for which the harmonic model in μ can be used for the rate coefficients [1, 2], then it is not difficult to obtain approximate relations for M and N which are analogous to the corresponding terms in (1.3) and (1.4):

$$M_{v+1,v}(s,t) = n_s[1 + \alpha_s(t)] K^{01}_{v+1,v}(s,s), \quad M'_{v+1,v}(s,t) = \sum_{s_1 \neq s} n_{s_1}[1 + \alpha_{s_1}(t)] K^{01}_{v+1,v}(s,s_1), \qquad (5.3)$$

$$N_{v,v+1}(s,t) = n_s \alpha_s(t) K^{10}_{v,v+1}(s,s), \quad N'_{v,v+1}(s,t) = \sum_{s_1 \neq s} n_{s_1} \alpha_{s_1}(t) K^{10}_{v,v+1}(s,s_1).$$

Here $K^{01(10)}_{\mu v}$ are the effective rate constants of the corresponding transitions. In the framework of the approximation (5.3), using the method discussed in Sec. 2, we can obtain an analytical solution of the system (5.1). It is sufficient to replace $K_{\mu v}$ by $K^*_{\mu v}$ in equations (2.6) through (2.10). The time dependence of the functions $\alpha_s(t)$ is determined from the solution of a system analogous to (1.2).

If the moments $M_{\mu v}$ and $N_{\mu v}$ are slowly varying functions of time over times of the order of the relaxation times $\tau_s(v)$ (determined below) then one can use (2.12) for $f_s(v, t)$ in (2.10). With the help of (2.11) we then obtain the following relation for $\tau_s(v)$

$$\tau_s^{-1}(v) = [K_{v+1,v}(s) + K_{v,v+1}(s) - K_{v+1,v+2}(s) - K_{v,v-1}(s)]$$
$$+ [M_{v+1,v}(s) + N_{v,v+1}(s) - M_{v,v-1}(s) - N_{v+1,v+2}(s)] +$$
$$+ [M'_{v+1,v}(s) + N'_{v,v+1}(s) - M'_{v,v-1}(s) - N'_{v+1,v+2}(s)],$$

which shows that the relaxation time of the function $f_s(v, t)$ is given by the largest of the VT, VV, or VV' relaxation times. The advantage of this solution is that when $t \gg \tau_s(v)$ (2.10) transforms into the quasistationary distribution which is described by an expression analogous to (2.13) [8]:

$$\frac{n_s^q(v)}{n_s^q(v-1)} = \frac{K^*_{v-1,v}(s)}{K^*_{v,v-1}(s)}. \tag{5.4}$$

If we substitute the exact expression for the moments (5.2) into (5.4), then the solution of this system will naturally be the stationary Boltzmann distribution (2.14). Quasistationary distributions are formed for particular times and regions of the spectrum when one of the processes in the limit $t \gg \tau_s(v)$ is dominant. For example, if in a given region of the spectrum VV processes are dominant, then a distribution of the Trinor type [1, 2] is valid

$$n_s^q(v, t) = n_s Q_s^{-1} \exp\{v\chi_s(t) - e_s(v)/kT\},$$

where the partition function Q_S is assumed known over the distribution valid for all v. The quantity $\chi_s(t)$ remains undetermined by the condition (5.4) and the exact expressions (5.2). If we use the approximation (5.3) we can write

$$\exp[\chi_s(t)] = \exp\left(\frac{\Theta_s}{T}\right)\frac{\alpha_s(t)}{1 + \alpha_s(t)}, \quad \Theta_s = e_s(1)/k.$$

A system of equations for $\alpha(t)$ of the form

$$\dot{\alpha} = \Phi(\alpha) \tag{5.5}$$

is obtained by differentiating the relation $\alpha_s(t) = n_s^{-1}\sum_v v n_s(v, t)$ with respect to t, and using (5.1) and the explicit solution from from (5.4). The Trinor exponent $\chi_s(t)$ can have either sign depending on the quantity $\alpha_s(t)$. We see from (1.7) that the sign of $\chi_s(t)$ is the same as that of the difference $T_s(t) - T$.

A more exact quasistationary distribution can be found by using other solutions of (5.4) which are consistent with equations (5.5) or their more exact analogs obtained from (5.3).

6. Dynamical Equations of a Vibrationally Nonequilibrium Gas. The analytical solutions found above can be used to construct a new, more exact model of relaxation gasdynamics allowing a self-consistent treatment of the behavior of the population densities themselves, and also the effect of relaxation processes on the flow dynamics.

We consider a mixture of diatomic molecules with slow vibrational relaxation. The transport equations, including viscous, heat conduction, and relaxation effects are written in the form

$$\frac{d\rho}{dt} + \rho\nabla\cdot\mathbf{u} = 0, \quad \rho\frac{d\mathbf{u}}{dt} + \nabla\cdot\mathbf{P} = 0, \quad \rho\frac{d}{dt}[E(T) + E_r] = -\nabla\cdot\mathbf{q} - \mathbf{P}{:}\nabla\mathbf{u}, \tag{6.1}$$

$$\mathbf{P} = (p - \xi\nabla\cdot\mathbf{u} + p_r)\mathbf{I} - 2\mu\mathbf{S}, \quad p = nkT, \quad \rho E_r = \sum_{s,v} n_s(v)e_s(v),$$

$$n = \sum_{s,v} n_s(v), \quad \rho = \sum_s \rho_s, \quad \mathbf{q} = -\lambda\nabla T - \sum_{s,v} L_s(v)\mathbf{d}_s(v),$$

$$\frac{dn_s(v)}{dt} + n_s(v)\nabla\cdot\mathbf{u} = -\nabla\cdot[n_s(v)\mathbf{u}_s(v)] + I_s(v),$$

$$\mathbf{u}_s(v) = \sum_{\mu s_1} B_{ss_1}(v, \mu)\mathbf{d}_{s_1}(\mu) - C_s(v)\nabla\ln T,$$

$$\mathbf{d}_s(v) = \nabla[n_s(v)/n] + [n_s(v)/n - \rho_s/\rho]\nabla p.$$

Here S in the deformation rate tensor, $d_s(\nu)$ is the vector of the diffusive thermodynamic forces, $u_s(\nu)$ is the velocity of diffusion of molecules of type s in vibrational state ν; μ, ξ, p_r are the coefficients of shear and bulk viscosity, and the relaxation pressure, respectively; λ is the thermal conductivity; $L_s(\nu)$, $B_{ss_1}(\nu, \mu)$ and $C_s(\nu)$ are quantities expressible in terms of the coefficients of diffusion and thermodiffusion; $I_s(\nu)$ is the collision integral, taking into account VT, VV, VV' processes and sources; E(T) is the energy density of the equilibrium degrees of freedom. A detailed discussion of the expressions for μ, ξ, p_r, $L_s(\nu)$, $B_{ss_1}(\nu, \mu)$, $C_s(\nu)$, λ and their connection with the population densities $n_s(\nu)$ for the case of slow relaxation is given in [11]. The general problem (6.1) is extremely complicated, and therefore we discuss briefly possible methods of simplification of the problem which could be used to find a solution for the distribution function $n_s(\nu)$.

1. For an inviscid and non-heat-conducting gas ($\mu = \xi = p_r = \lambda = C_s(\nu) = L_s(\nu) = B_{ss_1}(\nu, \mu) = 0$), vibrational relaxation affects the dynamics of the gas only through the nonequilibrium vibrational energ density E_r. Therefore one can include the relaxation in the following approximate way.

When $\tau_s(\nu) \ll T \ll \tau_v$, where τ_v is the time to establish an equilibrium distribution over the vibrational degrees of freedom, and T is the characteristic time scale of the flow, $n_s(\nu)$ can be found from (2.13) and (5.4), considered as simultaneous equations with the gasdynamical equations. It is important to realize that this case does not lead to equilibrium in the theory of jets [3] and quasistationary distributions are possible.

For a stationary, one-dimensional problem (plane flow, flow from a spherical source), we can use solutions taking into account the parametric dependence of the coefficients on time (or the coordinate), as obtained Sec. 2.

For nonstationary problems these solutions can be used if we write the equations in Lagrangian coordinates [3]. In this case, E_r can be calculated by taking a simplified relaxation equation of the type (5.5) for $\alpha(t)$ (in particular, a generalization of the Crookes approximation in the theory of VT relaxation [5]).

2. When viscous and heat-conduction properties of the gas are taken into account, our solutions can be used to calculate both E_r and the other relaxation coefficients. Of special interest is an analytical solution of the problem with sources (Sec. 3). This problem is relevant in the construction of mathematical models describing possible relaxation instabilities.

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GAS-DYNAMIC ACCELERATION OF IONS IN AN INHOMOGENEOUS
MAGNETIC FIELD

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1. Introduction. The basic features of gas-dynamic acceleration of ions in a homogeneous magnetic field were deduced in [1-4], wherein the existence of a Debye discontinuity was indicated, and self-similar solutions constructed, permitting description of ion acceleration for "steplike" application of the accelerating voltage. The form of the potential well for oscillating electrons found in [2] is shown in Fig. 1. The behavior of the potential at the Debye discontinuity is time-independent, while in the region $\phi < \phi_D$ the width of the well increases linearly with time.

As was shown in [3, 4], the efficiency of ion acceleration depends significantly on the thickness of the anode foil. Therefore it is desirable to select the foil such that the electrons transfer their energy to the accelerated ions significantly more rapidly than they lose energy to the foil. However reduction in foil thickness leads not only to increased ion acceleration efficiency, but also to a reduction in angular scattering of electrons within the foil, which finally leads to cutoff of the diode and a reduction in ion current density [4].

In order to weaken the corresponding diode cutoff limitation and increase the efficiency of energy transfer to ions [3] proposed a method of gas-dynamic acceleration of ions in an inhomogeneous magnetic field, of high level in the diode region, but weak in the acceleration region (Fig. 2). An electron beam with supercritical current is injected into the drift chamber between the sandwich of foils A and F, the space between which is filled by a neutralizing plasma. Under such conditions a large portion of the electrons injected into the chamber are reflected and begin to oscillate between the real cathode and a "virtual cathode" which appears in the drift chamber beyond foil F. As a result a dense cloud of oscillating electrons is formed near foils A and F. Under certain conditions the electrons may produce on the surface of foil F, located in the weak magnetic field region, a layer of plasma P, which serves as an ion source. Under the action of the electric field a cloud of ions is extracted from this plasma, and compensating the space charge of the oscillating electrons, is accelerated along the chamber.

The present study will evaluate the method of gas-dynamic acceleration of ions in an inhomogeneous magentic field proposed in [3] in two variants — a strongly scattering and nonscattering foil F. In the first variant the presence of the inhomogeneous magnetic field leads to an increase in ion current related to increase in the flux area in the acceleration region, while in the second the increase in current is insignificant, but nevertheless the efficiency of ion acceleration is increased, because all the energy of the oscillating electrons in the accelerated region will be included in a longitudinal degree of freedom. This fact leads to an increase in the rate of expansion of the plasma synthesized from ions and oscillating electrons. Because of this increase in the mean rate of plasma expansion the efficiency of acceleration increases also.

2. Oscillating Electron Distribution Function. We will consider ion acceleration for the case where the anode foil is strongly scattered and foil F is superthin. The thickness of the anode foil is then such that the following relationships are satisfied: