SURVEY

ROTATIONAL RELAXATION IN GASES

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1. Introduction

Rotational relaxation first attracted the attention of physicists in the beginning of the 20th century in connection with the study of transport phenomena in polyatomic gases. The internal (rotational) degrees of freedom of polyatomic molecules give an additional contribution to the thermal conductivity compared to the case of a monatomic gas (the energy carried by a particle is different) and for rapid changes in the volume causes a new dissipative process (described by the bulk viscosity).

In the past 50 years, because of the development of chemical kinetics, interest in rotational relaxation has increased. Analysis of the products of exothermal reactions has shown that in many cases they have excess rotational energy. For example, direct measurements of the radiation intensity of OH radicals in oxygen acetylene flares give a "rotational temperature" much higher than the temperature of the flare. Because of progress in experimental ultrasonic methods, frequency regions became accessible in this period which permitted the study of rotational relaxation in gases.

However, the greatest development of rotational kinetics came in the 1960s and 1970s with the wide use of lasers in physics and chemistry. The creation of lasers using vibrational—rotational transitions demanded a deeper study of rotational kinetics. The use of lasers in physical-chemistry experiments for the first time allowed the selection of molecules with a selectivity that was unobtainable earlier and allowed the detection of molecular states with very high sensitivity. This opened up new possibilities in the theoretical and experimental study of rotational nonequilibrium.

2. Characteristic Relaxation Time of the Average Rotational Energies

Of the different forms of internal energy (rotational, vibrational, electronic), the rotational energy is distinguished by the small magnitude of the quantum (for the lower levels). For example, in diatomic molecules the distance between the neighboring rotational levels with quantum numbers j + 1 and j is $2B_e(j + 1)$ where the rotational constant B_e is 0.053°K for J_2, 0.357°K for Cl_2, 2.86°K for N_2, 15.2°K for HCl, and 86.6°K for H_2.

The small magnitude of the rotational quantum implies that the exchange of energy between the translational and rotational degrees of freedom (RT exchange) in molecular collisions can be treated using classical mechanics and the quantum rotational energies can be neglected.

To estimate the rotational relaxation time τ_{RT} we use the expression

$$\tau_{RT} = \tau_0 \frac{E_R^0}{\overline{\Delta E}_R}. \tag{1}$$

Here τ_0 is the average time of a free path (the collision time), E_R^0 is the equilibrium value of the rotational energy per molecule, $\overline{\Delta E}_R$ is the average energy transferred into the rotational degrees of freedom in RT exchange per collision.

Equation (1) has a simple physical interpretation. Suppose after one collision the molecule acquires (on average) an energy $\overline{\Delta E}_R$, then to attain the equilibrium value of the energy of an initially unperturbed molecule, $E_R^0/\overline{\Delta E}_R$ collisions are required on average and this corresponds to the time $\tau_0 E_R^0/\overline{\Delta E}_R$.

For qualitative estimates the absolute value of the rotational relaxation time is not of interest, but rather the order of magnitude of the ratio of the rotational and translational relaxation times.

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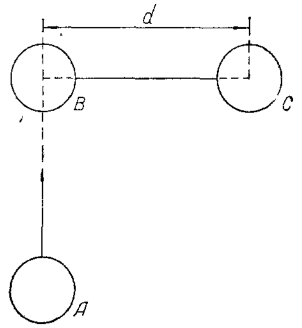

Fig. 1. Collision of an atom with the rotator.

In analogy with τ_{RT}, the translational relaxation time τ_{TT} can be defined as

$$\tau_{TT} = \tau_0 \frac{E_T^0}{\overline{\Delta E_T}},$$

where E_T^0 is the equilibrium value of the translational energy per molecule, $\overline{\Delta E_T}$ is the average energy transferred into the translational degrees of freedom of the molecule per collision. Since $E_T^0 \sim E_R^0$, we have $\tau_{RT}/\tau_{TT} \sim \overline{\Delta E_T}/\overline{\Delta E_R}$.

In order to estimate the ratio $\overline{\Delta E_T}/\overline{\Delta E_R}$ we consider a gas in which the relaxing diatomic molecules BC (modeled as rigid rotators) are a weak impurity in an equilibrium monatomic gas A. We assume for simplicity that at the initial instant of time the rotational and translational energies of the rotators are equal to zero. Then in each collision of a rotator with an atom of energy $\Delta E_R(v)$ is transferred into the rotational degrees of freedom and an energy $\Delta E_T(v)$ is transferred into the translational degrees of freedom. $\overline{\Delta E_T}$ and $\overline{\Delta E_R}$ are obtained from $\Delta E_T(v)$ and $\Delta E_R(v)$ by averaging over a Maxwellian distribution of incident particles A, hence

$$\frac{\overline{\Delta E_T}}{\overline{\Delta E_R}} \sim \frac{\Delta E_T(v)}{\Delta E_R(v)}.$$

In order to determine $\Delta E_T(v)/\Delta E_R(v)$ we consider the collision of an atom (mass m_A) with the rotator BC (mass $m_{BC} = 2m_B$) and we choose the situation most favorable for the transfer of rotational energy. This is the case where the incident atom moves along a line perpendicular to the axis and passing through one of the atoms of the rotator (see Fig. 1). We will assume that before the collision the angular velocity ω and the velocity v_2 of the center of mass of the rotator are equal to zero, and that the velocity of the incident atom is v_1. We denote the corresponding quantities after the collision by v_1', v_2', and ω'.

We express the ratio $\Delta E_T/\Delta E_R$ in terms of v_2', ω' and the moment of inertia about the center of mass of the rotator ($J = 2m_B(d/2)^2$):

$$\frac{\Delta E_T}{\Delta E_R} = \left(\frac{2m_B v_2'^2}{2} \bigg/ \frac{J\omega'^2}{2}\right) = \frac{4v_2'^2}{d^2\omega'^2}.$$

For this collision geometry, $\Delta E_T/\Delta E_R$ can be determined with the help of the two conservation laws: momentum

$$m_A v_1 = m_A v_1' + 2m_B v_2'$$

and angular momentum (with respect to the center of mass of the rotator)

$$m_A v_1 d/2 = m_A v_1' d/2 + J\omega'.$$

It then follows that $v_2' = d\omega'/2$. Therefore, for this collision geometry we have

$$\frac{\Delta E_T(v)}{\Delta E_R(v)} = 1$$

and hence $\tau_{RT} = \tau_{TT}$.

Since not all collisions are favorable in exciting the rotational degrees of freedom, we will actually have $\tau_{RT} \geqslant \tau_{TT}$.

For an arbitrary distribution of colliding particles, the conservation laws are insufficient to determine the energies transferred into the translational and rotational degrees of freedom and it is necessary to solve the equations of motion, which involve the intermolecular interaction potential. In this approach a new parameter appears in the problem, the ratio of the duration of a collision τ_{CT} to the period of rotation ω^{-1}, and $\omega\tau_{CT}$ determines the magnitude of the transferred energy.

The parameter $\omega\tau_{CT}$ is known in the literature as the adiabatic parameter (adiabatic factor) or Mossi parameter. In a quantum treatment ω is replaced by $\Delta E/\hbar$, where ΔE is the energy difference of the states of the transition.

For molecular collisions accompanied by rotational transitions the adiabatic parameter is much less than unity for most molecules. An order of magnitude estimate is $\tau_{CT} \sim a/\bar{v}$, where a is the range of the intermolecular interaction ($a \sim 10^{-8}$ cm) and $\bar{v}$ is the average velocity of the molecules ($\bar{v} \sim 3 \cdot 10^4$ cm/sec) so that $\tau_{CT} \sim 0.3 \cdot 10^{-12}$ sec. Then $\frac{\Delta E}{\hbar} = \frac{B_e}{\hbar} 2(j + 1)$. For $B_e \sim 1°K$ and $j = 1$, $\Delta E/\hbar \sim 5 \cdot 10^{11}$ sec^{-1} therefore $\Delta E\tau_{CT}/\hbar \sim 0.15$. An increase of temperature weakly affects the magnitude of the Mossi parameter in transitions with rotational energies in the thermal region since then the average value of j and the velocity are proportional to $\sim\sqrt{T}$. A molecular collision under these conditions is instantaneous and nonadiabatic and can be correctly described (in a qualitative sense) by the above method based on the conservation laws.

Since the translational relaxation time is of order τ_0 (for comparable masses of the colliding particles we have $\overline{\Delta E_T} \sim \Delta E_T^0$) then we also have that $\tau_{RT} \sim \tau_0$. Therefore in nonadiabatic collisions RT exchange occurs relatively easily after a time of the order of the collision time.

For light molecules (H_2, HD, D_2) or for molecules with large rotational quantum numbers, the adiabatic parameter can be of order unity, or even much larger. In this case the collisions are approximately adiabatic and the energy transferred into the rotational degrees of freedom is small. Indeed, for adiabatic collisions ($\omega\tau_{CT} \gg 1$) the rapidly rotating molecule is like a structureless particle with a spherically symmetric intermolecular potential, and there is no RT exchange in the collision of an atom with such a particle.

Consequently for light molecules with high values of the rotational quantum numbers the rotational relaxation time will be significantly larger than the translational relaxation time. For example, at room temperature the rotational relaxation time in H_2 is about 350 times the collisional, and in D_2 it is about 200 times larger.

The above estimate of the rotational relaxation time is qualitative and serves to distinguish the time scale in which it is necessary to take into account rotational nonequilibrium. In the solution of specific problems where the scale of rotational nonequilibrium is already determined, it is usually necessary to find the nonequilibrium distribution function of the rotational energies. This is especially necessary for kinetic studies.

3. Nonequilibrium Rotational Energy Distribution Function

Gas-kinetic Equation for the Population Densities. The most widely used method of describing rotational relaxation is based on the gas-kinetic equations for the population densities of the rotational levels. We first consider a gas in which the relaxing diatomic molecules (rotators) are a weak impurity in a monatomic gas. We also assume that the rotational relaxation time is much larger than the translational time. Then rotational relaxation occurs for a Maxwellian distribution of velocities for all particles and therefore the system of equations for the rotational population densities can be written without the equations for the velocity distribution functions.

From the balance of the number of particles in each rotational level we can write a system of gas-kinetic equations for the population densities N_j of the rotational levels:

$$\frac{dN_j}{dt} = Z(\Sigma P_{ij} N_i - \Sigma P_{ji} N_j), \quad i, j = 0, 1, \ldots \tag{2}$$

Here P_{ij} is the probability of the rotational transition i → j in one collision of the molecule with an inert atom, averaged over the Maxwellian velocity distribution, and Z is the number of molecule–atom collisions per unit time.

The system of equations (2) takes into account only RT exchange in collisions with atoms; collisions of molecules with each other are neglected because of their small concentration.

Since a sufficiently accurate and general theoretical expression for P_{ij} is unknown, normally semiempirical formulas are used. The most widely used expressions are the exponential and inverse power-law forms [1-3]:

$$P_{ij} = G_0 \exp(-\alpha_1 |\Delta E_{ij}| / kT),$$

$$P_{ij} = G_1 \left(\frac{kT}{|\Delta E_{ij}|}\right)^{\alpha_2}, \tag{3}$$

where α_1 and α_2 are empirical constants, $\Delta E_{ij} = E_i - E_j$, and the factors G_0 and G_1 take into account the degeneracy of the rotational levels and the condition of detailed balance.

The expressions (3) have an obvious physical interpretation. They show that the transition probability depends mainly on the transition energy $|\Delta E_{ij}|$ and decreases as the transition energy increases.

An obvious deficiency of (3) is the necessity of empirical determination of the constants in these formulas. This is possible only in limited intervals of temperature and quantum number since in actuality the dependence of the transition probability on $|i-j|$ is more complex [4-7].

An analytical solution of the system (2) with the probabilities (3) is unknown, and it is unlikely that one could be obtained. There are, however, a large number of papers devoted to the numerical solution of (2) for specific problems. For example, rotational relaxation in jets was studied in [3, 8, 9].

Although numerical calculations are highly important in the description of specific cases, they are unsuitable in bringing out the general features of relaxation processes because of the large number of parameters in the problem. A way out of this difficulty is the use of the diffusion approximation to the system of equations (2), as this approximation admits an analytical solution.

Diffusion Approximation. As indicated above, for most molecules we have $kT \gg |\Delta E_{ij}|$ for reasonably small i and j. In this case one can ignore the quantum rotational energies and describe the rotational relaxation process in terms of a classical distribution function $f(\varepsilon, t)$, which is the distribution of molecules in the space of the rotational energies ε at the instant of time t. For function $f(\varepsilon, t)$ we obtain a single integrodifferential equation of the Smolukhovskii type in place of the system (2). It can be transformed into a diffusion equation of the Fokker–Planck type if the rotational transition probabilities go to zero with increasing energy transfer sufficiently rapidly.

Hence in place of the system (2) we obtain the equation

$$\frac{\partial f(\varepsilon, t)}{\partial t} = \frac{\partial}{\partial \varepsilon}\left[\frac{\overline{\Delta^2}}{2\tau_0}\left(\frac{\partial f}{\partial \varepsilon} + \frac{1}{kT} f\right)\right], \tag{4}$$

where $\overline{\Delta^2}$ is the mean square energy transferred into the rotational degrees of freedom per collision and τ_0 is the time duration corresponding to a mean free path of the rotator in the inert gas.

Actual calculations are most simply carried out in two limiting cases: adiabatic collisions with probabilities determined by relations of the type (3); and nonadiabatic collisions where the mass of an inert atom is much less than that of a rotator. In the first case $\overline{\Delta^2} = \text{const}$ [10] and in the second $\overline{\Delta^2} = 2b\tau_0\varepsilon$ [11].

For adiabatic collisions (4) takes the form

$$\frac{\partial f}{\partial t} = \frac{(kT)^2}{\tau}\left(\frac{\partial^2 f}{\partial \varepsilon^2} + \frac{1}{kT}\frac{\partial f}{\partial \varepsilon}\right), \tag{5}$$

and for nonadiabatic collisions

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial \varepsilon}\left[b\varepsilon\left(\frac{\partial f}{\partial \varepsilon} + \frac{1}{kT} f\right)\right]. \tag{6}$$

Here $\tau = 2\tau_0 \frac{(kT)^2}{\overline{\Delta^2}}$, $b = \frac{32}{3}\frac{m}{M} nkT\,\Omega_{12}^{(11)}$, where m and M are the mass of the atom and rotator, respectively, ($m \ll M$), n is the number density of the atoms, and $\Omega_{12}^{(11)}$ are the gas-kinetic collision integrals. For hard spheres with a collision diameter given by $\sigma = (\sigma_1 + \sigma_2)/2$, where σ_1 and σ_2 are the diameters of the rotator and atom, respectively, we have $b = \frac{8}{3}\frac{m}{M}\frac{kT}{\tau_0}$, where $\tau_0 = (2n\sigma\sqrt{2\pi kT/m})^{-1}$.

The solution of (5), subject to the boundary and initial conditions

$$\left(\frac{\partial f}{\partial \varepsilon} + \frac{f}{kT}\right)\bigg|_{\varepsilon=0,\,\infty} = 0,\ f(\varepsilon,\ t=0) = \varphi(\varepsilon) \tag{7}$$

has the form [10]

$$f(\varepsilon,\ t) = \int\limits_0^\infty G(\varepsilon,\ \varepsilon',\ t)\,\varphi(\varepsilon')\,d\varepsilon', \tag{8}$$

where the Green's function is given by

$$\begin{gathered}G(\varepsilon,\ \varepsilon',\ t) = \frac{i}{kT}\frac{1}{2}\left(\frac{\pi t}{\tau}\right)^{-1/2}\left\{\exp\left[-\left(\frac{\varepsilon-\varepsilon'}{kT}+\frac{t}{\tau}\right)^2\frac{\tau}{4t}\right]+\exp\left[-\left(\frac{\varepsilon+\varepsilon'}{kT}+\frac{t}{\tau}\right)^2\frac{\tau}{4t}\right]\exp(\varepsilon'/kT)\right\}+\\ +\frac{1}{2kT}\left\{1-\Phi\left[\left(\frac{\varepsilon+\varepsilon'}{kT}-\frac{t}{\tau}\right)\frac{1}{2}\sqrt{\frac{\tau}{t}}\right]\right\}\exp(-\varepsilon/nT);\\ \Phi(z) = \frac{2}{\sqrt{\pi}}\int\limits_0^z \exp(-y^2)\,dy\end{gathered} \tag{9}$$

and $\Phi(z)$ is the error function.

The solution (8), (9) has a simply physical interpretation. If we choose the initial distribution as a delta function $\varphi(\varepsilon) = N\delta(\varepsilon-\varepsilon_0)$, then the solution $f(\varepsilon,\ t) = NG(\varepsilon,\ \varepsilon_0,\ t)$ will describe the transition of particles from the energy region about the initial value ε_0 (the first term in (9)) into particles with distribution asymptotically approaching the Boltzmann distribution (the second term in (9)).

The solution of (6) with the analogous boundary and initial conditions is written as a series of Laguerre polynomials L_n [11]:

$$f(\varepsilon,\ t) = \Sigma c_n \exp\left(-\frac{nt}{\tau_1}\right)L_n\left(\frac{\varepsilon}{kT}\right)\exp\left(-\frac{\varepsilon}{kT}\right), \tag{10}$$

where

$$c_n = \frac{1}{kT}\int\limits_0^\infty \varphi(\varepsilon)\,L_n\left(\frac{\varepsilon}{kT}\right)d\varepsilon;\ \tau_1 = \frac{kT}{b}.$$

However, here we are more interested in a particular solution of (6), where we assume that the initial condition is given as a Boltzmann distribution with a temperature T_0 different from the reservoir temperature. This case occurs for expansions in nozzles or in a shock wave front. In this case $\varphi(\varepsilon) = \frac{N}{kT_0}\exp\left(-\frac{\varepsilon}{kT_0}\right)$, and

$$f(\varepsilon,\ t) = \frac{N}{k\theta(t)}\exp\left(-\frac{\varepsilon}{k\theta(t)}\right), \tag{11}$$

where

$$\frac{d\theta}{dt} = -\frac{\theta - T}{\tau_1}. \tag{12}$$

Solution (11) means that the process of establishing equilibrium passes through a sequence of Boltzmann distributions of different temperatures. In this case we say that (6) has canonical invariance. Another property of (6) is related to canonical invariance. If we multiply (6) by ε and integrate over all ε then we obtain for the average rotational energy per unit volume $\bar{\varepsilon} = \int\limits_0^\infty \varepsilon f(\varepsilon,t)\,d\varepsilon$ the simple relaxation equation

$$\frac{d\bar{\varepsilon}}{dt} = -\frac{\bar{\varepsilon}-\varepsilon_0}{\tau_1}, \tag{13}$$

where $\varepsilon_0 = kT$.

Equation (13) is often used in gasdynamical calculations. We note that (13) follows directly from (12).

We emphasize that only (6) possesses the property of canonical invariance. Equation (5) does not preserve the form of the Boltzmann distribution and the simple relaxation equation (13) does not follow from it.

We can make the following conclusions from the above analytical treatment of rotational relaxation:

1. The process of rotational relaxation is only weakly sensitive to changes in the rotational transition probabilities P_{ij}. Rather it is determined by certain integral characteristics such as the diffusion coefficient $\overline{\Delta^2}/2\tau_0$.

2. The simple relaxation equation (13) for the average rotational energy and the property of canonical invariance, which allows one to introduce an instantaneous rotational temperature, are only valid for special systems of the Rayleigh gas type with nonadiabatic collisions. In general one cannot use equation (13).

These conclusions are supported by numerical calculations for specific cases (see [8] for example); however, the analytical treatment adds an element of generality to these numerical results.

Joint Translational—Rotational Relaxation. The preceding treatment was limited by the condition that the rotational relaxation time be much larger than the translational relaxation time. This is the case of most interest in practical applications, since the duration of rotational relaxation provides sufficient time both for the removal of energy (for example by laser generation between rotational levels) and for the operation of the relaxation process itself. But there are several problems (rotational distributions in shock waves or high-frequency ultrasonic dispersion are two examples) in which rotational and translational relaxation occur simultaneously.

An analytical treatment of translational—rotational relaxation was carried out in [11], where the problem was solved in the diffusion approximation for a mixture of heavy rotators and light, monatomic particles. In this case the processes of translational and rotational relaxation are independent, although they have a single characteristic time. Independence of simultaneously occuring relaxation processes is the exception rather than the rule. The numerical results indicate [12] that the characteristic rotational and translational relaxation times and the form of the nonequilibrium distribution functions of the energies associated with the translational and rotational degrees of freedom depend on the initial translational—rotational energy distribution. We note that even when there is simultaneous translational and rotational relaxation the synchronism of the rates of the two processes will be disturbed for the high rotational levels, which are populated or depopulated at a slower rate than the rate of translational relaxation.

Resonant Vibrational—Rotational Exchange. Recently, there has been much interest in vibrational and rotational relaxation under conditions of effective vibrational—rotational energy exchange (VR exchange). Numerous calculations of the probabilities of VR exchange in collisions of inert gas atoms with hydrogen-containing molecules (see [13-15] as examples) have shown that the largest probability occurs for transitions close to the resonance condition $\Delta E_{vj \to v'j'} = E_{vj} - E_{v'j'}$. As an example, such transitions for H_2 are ($v' = 1$, $j' = 6$)-($v = 0$, $j = 8$), ($v' = 1$, $j' = 8$)-($v = 0$, $j = 10$), ($v' = 1$, $j' = 10$)-($v = 0$, $j = 12$) [16]. Resonant VR transitions also dominate for the OH radical at large j [14].

Intense VR transitions affect the kinetics of vibrational and rotational relaxation. For example, upon excitation of the vibrational levels, a succession of RT and VR exchanges is more effective than the usual vibrational—translational exchange.

In turn, the lagging RT exchange in the upper rotational levels for an excess occupation of the vibrational levels can lead to the formation of a population inversion in the rotational levels (because of intense VR exchange) with subsequent laser generation in the rotational transitions. Apparently this mechanism explains the formation of rotational inversions and laser generation in purely rotational transitions in OH radicals formed in vibrationally excited states in the reaction $O(^1D) + H_2$ [17, 18].

The cause of the formation of population inversions in the rotational levels in the presence of intense VR exchange is the difference in relaxation times of the rotational energies for the lower and upper rotational levels. Suppose that a nonequilibrium distribution of vibrational energies is formed in a diatomic gas under the action of some effect such as a rapid expansion or a chemical excitation. Then rapid VR exchange synchronizes the rotational distribution of the upper levels with the nonequilibrium vibrational distribution. But rapid RT exchange synchronizes the rotational distribution of the lower rotational levels with a Maxwellian distribution. RT exchange is more effective for the upper rotational levels than VR exchange, therefore the excess population density induced because of VR exchange cannot be eliminated with RT exchange. For strong enough vibrational excitation at low translational temperatures a rotational inversion is immediately induced.

The problem of the formation of a rotational inversion under resonant VR exchange was solved analytically in [19] in the diffusion approximation. A numerical calculation of rotational inversion for an expanding H_2—HF mixture in a nozzle was considered in [20, 21].

Quasistationary Distributions. In the solution of problems of rotational relaxation in conditions of rapid VR exchange, quasistationary distribution functions of the rotational energies are encountered. The quasistationary distribution functions can be most simply obtained by considering the solution of (6) with a delta-function source of particles

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial \varepsilon}\left[b\varepsilon\left(\frac{\partial f}{\partial \varepsilon} + \frac{1}{kT} f\right)\right] + \eta\delta(\varepsilon - \varepsilon_0). \tag{14}$$

This equation describes rotational relaxation in a system in which η particles are supplied with rotational energy ε_0 per unit time and per unit volume. A constant source of particles models VR exchange in a chemical reaction, or in some other type of excitation.

The solution of (14) has the form [22]:

$$f(\varepsilon, t) = \frac{1}{kT} e^{-\varepsilon/kT} \sum_{\nu=1} \alpha_\nu L_\nu\left(\frac{\varepsilon}{kT}\right) e^{-\nu t/\tau_1} + \frac{1}{kT} e^{-\varepsilon/kT}(\alpha_0 + \eta t) +$$
$$+ \frac{\eta}{kT} e^{-\varepsilon/kT} \sum_{\nu=1} \frac{1}{\nu} L_\nu\left(\frac{\varepsilon_0}{kT}\right) L_\nu\left(\frac{\varepsilon}{kT}\right)(1 - e^{-\nu t/\tau_1}), \tag{15}$$

where $L_\nu(x)$ are the Laguerre polynomials and $\alpha_\nu = \int\limits_0^\infty f(\varepsilon, t=0) L_\nu\left(\frac{\varepsilon}{kT}\right) d\varepsilon.$

The solution (15) describes the approach to a Boltzmann distribution of the initial particles (existing at t = 0) and the particles produced by the source.

For $t \gg \tau_1$ the solution (15) can be rewritten in the form

$$f(\varepsilon, t) = \frac{1}{kT} \exp(-\varepsilon/kT)\left(\int\limits_0^\infty f(\varepsilon, 0)\,d\varepsilon + \eta t\right) + \frac{\eta}{kT}\exp(-\varepsilon/kT) \sum_{\nu=1} \frac{1}{\nu} L_\nu(\varepsilon/kT) L_\nu(\varepsilon_0/kT). \tag{16}$$

We see from (16) that when $t \gg \tau_1$ the solution of (14) becomes quasistationary and can be represented as a combination of two terms. The first describes the particles which are characterized by an equilibrium Boltzmann distribution at time t. The second term describes a stationary but nonequilibrium distribution of particles which have not yet reached equilibrium. This second term, sometimes called the excitation function, depends on the strength of the source of particles.

Hence in general the quasistationary distribution can be represented as an equilibrium distribution function (with a variable number of particles) and an excitation function which is independent of the initial conditions but which is determined by the instantaneous value of an external parameter (in this case the strength of the source). In this sense the quasistationary distribution gives a condensed description of relaxation in which the initial conditions are forgotten and the distribution function is synchronized with the external parameters. Finding quasistationary distributions is a much simpler problem than obtaining the general solution. Moreover, the quasistationary distributions play the dominant role in kinetics in physical chemistry.

Rotational Relaxation in Single-Component Systems. Up to now we have only considered the rotational relaxation of rotators which are a weak impurity in a monatomic gas. An analysis of rotational relaxation in a single-component system requires a treatment of both RT processes and RR exchange in molecular collisions, where by RR exchange we mean an exchange of rotational energy. There are very few calculations of RR exchange probabilities in the literature (see [23, 24]). The values of the probabilities [23, 24] and diffusion coefficients [25] which have been obtained are not suitable for the solution of the gas-kinetic equations. But the effect of RR exchange on the process of rotational relaxation can be understood as follows. For the low rotational levels the probabilities of RR and RT exchange are comparable. Since, however, the rate of approach to a Boltzmann distribution is large for the low levels, RR exchange changes almost nothing in the kinetics. For the upper rotational levels the probability of RR exchange is larger than the probability of RT exchange. However RR exchange is ineffectual overall, since there are only a small number of particles in the upper levels and collisions between them are improbable. RR exchange is most important in the intermediate energy range (thermal and above). Here RR exchange can lead to the establishment of a Trinor distribution of rotational levels [1]. Also RR exchange can be important for the synchronization of the rotational distributions in different vibrational levels. In exothermal chemical reactions such as in the mixture $H_2 + F_2$, rotationally excited HF molecules occur in various vibrational levels. Rapid RR exchange can synchronize the nonequilibrium rotational distribution until vibrational relaxation occurs [26].

Polyatomic Molecules. The equation for the population densities (2) or the diffusion equations (5) and (6) are valid for linear molecules or spherical top molecules whose rotational energies depend only on a single quantum number. For symmetric or slightly asymmetric top molecules the rotational energy depends on two quantum numbers: j and K (the quantum number K characterizes the component of the angular momentum of the molecule along the symmetry axis of the top). In this case rotational relaxation must be described by a distribution function dependent on the quantum numbers j and K. In the diffusion approximation this process can be thought of as a two-dimensional diffusion of particles with respect to levels j and K (with different diffusion coefficients). Rotational relaxation has not been considered in this formulation. The possibility of creating population inversions in the K levels was discussed in [27]. An experimental study of rotational relaxation of water molecules (asymmetric top) was carried out in [28].

4. Rotational Nonequilibrium Processes in Physical Chemistry

Rotational Relaxation of the Products of a Chemical Reaction. A nonequilibrium rotational distribution in hydrogen halides formed in reactions of halogen atoms with water molecules was observed in [29]. This was one of the first experiments studying a nonequilibrium distribution function of rotational energies. Subsequently reactions involving halogen atoms have been studied repeatedly, since they are widely used to create population inversions in chemical lasers.

In experiments [29] on infrared luminescence of HCl, the existence of a biomodal distribution of molecules over the rotational levels was observed. Equation (3) for the RT transition probabilities was used to explain these experiments. Equation (5) can be solved analytically with the probabilities given by (3). For an initial distribution in the form of a delta-function, the solution (as already noted) has the form

$$f(\varepsilon, t) = NG(\varepsilon, \varepsilon_0, t). \tag{17}$$

The function NG (see (9)) is the sum of two parts: the first term is initially equal to $N\delta(\varepsilon-\varepsilon_0)$ and the second is initially zero. As time increases, the first term decreases, which means that the number of particles with energies near ε_0 decreases, and the second term increases and approaches the equilibrium distribution $\frac{N}{kT}\exp(-\varepsilon/kT)$. Thus the relaxation of the initial delta-function distribution can be thought of as a slow spreading of the delta-function component with the rapid formation of a Boltzmann distribution of those particles which have reached the region of thermal energies. This type of relaxation implies that the distribution function of the rotational energies (17) will be biomodal for particular times and temperatures [10, 30].

It is important that during the spreading of the delta-function distribution an inversion of the rotational levels can be maintained over a certain time. The time of existence of the inversion is small, but it can be significantly increased. This can be done by using a molecular system with a constant source of rotationally excited particles. The rotational distribution function is determined in this case from the solution of (5), where a term is added to the right-hand side which takes into account the source. If $q(\varepsilon, t)$ is the number of particles produced with energy ε per unit time and per unit volume, the solution of (5) with the addition of the source has the form

$$f(\varepsilon, t) = \int_0^\infty G(\varepsilon, \varepsilon', t)\varphi(\varepsilon')\,d\varepsilon' + \int_0^t dt' \int_0^\infty G(\varepsilon, \varepsilon', t-t')\,q(\varepsilon', t')\,d\varepsilon'.$$

For $q(\varepsilon, t) = Kt\delta(\varepsilon-\varepsilon_0)$ (this corresponds to nonbranching chain reactions) the time of existence of the inversion, according to the data of [31] (see also [27]), is given by ($\varepsilon_0 \gg kT$):

$$t_{\text{inv}} \sim \sqrt{2}\, e^{\varepsilon_0/kT}\, \tau_{RT}.$$

Estimates of the maximum inversions attainable in specific cases are given in [31, 27].

Loss of Rotational Equilibrium in a Radiating Gas. The interpretation of the molecular spectra of nonequilibrium gases (upper atmosphere, interstellar clouds, reacting gases) requires both a knowledge of the optical transition probabilities and information on the distribution functions of the radiating components. If, as is generally true, the distribution function of the translation energies is Maxwellian, then the energy distribution of the internal (rotational) degrees of freedom can differ significantly from equilibrium, and this will naturally affect the radiation intensity.

Under normal conditions (normal temperature and pressure) the radiation does not significantly distort the equilibrium distribution functions because the collision mechanism of energy exchange between the different degrees of freedom is so effective that it can reestablish the equilibrium lost due to radiation. Indeed, the probability of spontaneous emission from the first rotational level of CO is $A_{10} = 1.8 \cdot 10^{-7}$ sec^{-1}, and the inverse rotational relaxation time of CO in H_2 at normal pressures is $\tau_{RT}^{-1} \sim 10^8$ sec^{-1}. However, the situation changes radically when we consider rarefied gases such as dense interstellar clouds which are concentrations of molecular hydrogen (with concentrations of 10^4 cm^{-3}) containing small amounts of C, C$^+$, CO, CO$^+$, CH, etc. The temperature in the outer regions of the cloud is about 30°K and that of the inner regions is ∿10°K [32]. The relative content of CO in these clouds is much larger than that of other diatomic molecules or carbon-containing impurities and on average is equal to $0.6 \cdot 10^{-5}$. Therefore the most important cooling mechanism in these clouds will be the spontaneous emission of CO in rotational bands. At these densities and temperatures the inverse relaxation time is 10^{-7} sec^{-1} which is comparable to the probability of spontaneous emission.

Rotational distribution functions in radiating gases were calculated in [33, 34], where the nonequilibrium distribution function is found by solving the Fokker–Planck equation

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial \varepsilon}\left[\frac{\overline{\Delta^2}}{2\tau_0}\left(\frac{\partial f}{\partial \varepsilon} + \frac{f}{kT}\right)\right] + \frac{\partial}{\partial \varepsilon}\left[2\beta B_e \rho(\omega)\frac{\partial f}{\partial \varepsilon} + \frac{3A_{10}}{B_e}\varepsilon^2 f\right]. \tag{18}$$

The first term on the right-hand side of (18) describes the collisional exchange of energy, as in (4). The second term characterizes the effects of external electromagnetic radiation (with spectral energy density $\rho(\omega)$ and spontaneous emission on the distribution function. In (18) $\beta = 2\pi\mu^2/3\hbar^2$, where μ is the dipole moment and B_e is the rotational constant of the rigid rotators modelling the CO molecule.

The stationary distribution is obtained from (18) for $\rho(\omega) = 0$ and $\overline{\Delta^2}/2\tau_0$ = const and has the form

$$f(\varepsilon) = \frac{N}{B_e} C \exp\left[-\frac{\varepsilon}{kT} - \frac{A_{10}\tau kT}{B_e}\left(\frac{\varepsilon}{kT}\right)^3\right], \tag{19}$$

where $\tau = 2\tau_0 \dfrac{(kT)^2}{\overline{\Delta^2}}$.

We see from (19) that self-radiation distorts the equilibrium distribution and leads to the depletion of the upper rotational levels. We note that in a gas of radiating oscillators spontaneous emission does not distort the equilibrium form of the distribution, but only leads to a lowering of the vibrational temperature of the oscillators in comparison to the temperature of the heat reservoir [1].

Rotational Nonequilibrium in Expanding Gas Jets. Successes in the creation of gasdynamical lasers using vibrational–rotational transitions has led naturally to the question of the creation of inversions of the rotational levels in expanding gas jets. In a series of experiments carried out from the early 1970s [28, 36, 37] it has been established that the rotational energy distribution in an ultrasonic jet of expanding gas is a nonequilibrium distribution. Although population inversions of the rotational levels were not observed in these experiments, the study of rotational relaxation through the rotational distribution in an ultrasonic expansion of gas has been demonstrated as an important technique and has obtained a wide following.

A distinct advantage of this method is the possibility of studying rapid rotational relaxation processes under stationary conditions. The rapid decrease of density in the jet with increasing distance from the nozzle section, and consequently the decrease in the frequency of collisions, leads to a slowing of the relaxation processes such that the rotational energy distribution cannot follow the decreasing translational temperature. By observing experimentally the change of state of the gas from thermodynamic equilibrium in the precombustion chamber of the nozzle to a nonequilibrium state at a certain distance away, we can obtain information on the rotational relaxation rates constants. In actual experiments [38] electron and molecular beam methods are used to measure the gas density, population densities of the rotational levels, and the translational velocity distribution function of the molecules on the axis of the free gas jet, which is expanding in a vacuum.

Applied to rotational relaxation, one of the fundamental experimental results in jets is that for low enough impact temperatures the effective rotational temperature of the molecules is higher for the upper rotational levels than for the lower levels. Repopulation of the upper rotational levels and depopulation of the lower ones in expanding jets is explained qualitatively by the hypothesis that the rotational distribution is not able to follow the rapidly varying temperature of the translational degrees of freedom. Because of the differing rotational relaxation rates of the upper and lower levels, the degree of freezing of the rotational energies is different. The rotational distribution of the upper levels is closer to the equilibrium distribution in the chamber than that of the lower levels.

Numerical solutions of the gas-kinetic equations (2) for the population densities of the rotational levels in expanding jets [37, 38] (see also [39, 40]) have confirmed the repopulation of the rotational levels and agree well with experiment. However in the opinion of the author of [37] "this description cannot be considered to be a theoretical model, but a compact summary of the experimental data." This conclusion is based primarily on the fact that the experimental data can be described satisfactorily by different expressions for the rate constants if the free parameters are chosen appropriately.

A series of calculations of nonequilibrium distribution functions in expanding gas jets were carried out in [41], where the nonequilibrium distribution functions of the rotational energies and translational velocities were determined from the solution of the Boltzmann gas-kinetic equations. (The solution can be obtained by assuming that the macroscopic parameters vary over a time τ much larger than the characteristic times of translational τ_0 and rotational τ_{RT} relaxation and under the condition that the rotational transition probabilities decrease rapidly with increasing energy transfer. For jets with steady-state (or slowly varying in time) hydrodynamical flow, the rotational distribution function has the form

$$N_j = \frac{B_e}{kT}\,(2j+1)\,e^{-\frac{B_e}{kT}j(j+1)}\left\{1 - 2\frac{\tau_{RT}}{\tau}\,\mathrm{sgn}\;\mathrm{grad}\,T\left[\left(\frac{B_e}{kT}\,j(j+1)\right)^2 - 2\right]\right\}, \qquad (20)$$

where $\tau = \left|\frac{T}{v\,\mathrm{grad}T}\right|$, and v and T are the velocity and temperature of the medium at point r.

Comparison of the distribution (20) with the equilibrium distribution of rotational energies at a temperature equal to the gas temperature of this radial distance shows that in the distribution (20) the lower levels are depopulated and the upper ones repopulated. In addition (and most importantly) for certain values of the ratio τ_{RT}/τ a population inversion is formed in the upper rotational levels.

The formation of a population inversion can be explained by the difference in relaxation times for the lower and upper levels. Since the relaxation time of the population densities is large for the upper levels, rotational relaxation under conditions of rapid cooling implies slow decrease of the population densities of the upper levels with the simultaneous rapid formation of the Boltzmann distribution corresponding to the particles of the medium at the lower levels (see the distribution (17) and its analysis). Therefore in the relaxation stage, the upper levels will be repopulated since their population densities will differ only slightly from the equilibrium values corresponding to a higher temperature (such as the temperature in the chamber) while the lower levels will be depopulated. In the low-temperature end of the distribution (i.e., the lower levels) there may be fewer molecules than in the neighboring high levels where there is a high-temperature distribution. Hence, the theory predicts the possibility of a population inversion of the rotational levels in expanding jets.

Rotational Relaxation in Shock Waves. A shock wave is considered in hydrodynamics as a surface of discontinuity, but physically it is actually a layer of finite thickness separating two states of thermodynamic equilibrium (before and after the wave). Over the extent of this layer there is a transition of the distribution functions from one equilibrium state to the other. If the translational and rotational relaxation times are of the same order of magnitude, the rotational distribution function evolves in the background of a non-Maxwellian velocity distribution (which also deteriorates). This explains the interest in rotational relaxation in shock waves.

The rotational distribution of N_2 in a shock wave propagating in pure nitrogen was studied in [42, 43, 35] using electron-beam induced fluorescence. It was shown in [42] that at small Mach numbers the rotational distribution is close to a Boltzmann distribution and the rotational temperature profile follows the density profile. For high Mach numbers the rotational distribution varies smoothly with increasing j from a Boltzmann distribution with a temperature equal to that in front of the shock wave to another with a temperature equal to that behind the shock wave, and the "rotational temperature" profile leads the density profile [42, 43].

Numerical calculations of the rotational distribution in a shock wave in N_2–Ar mixtures with probabilities of the form (3) were carried out in [9]. In the averaging of the transition probabilities over velocity, the Mott–Smith bimodal distribution [44] was used. The bimodal velocity distribution in a shock wave was written as a linear combination of equilibrium Maxwellian distribution functions [44] describing the equilibrium state of the gas behind and in front of the shock wave. The weighting factors in front of the Maxwellian distributions are functions of the distance from the center of the shock wave and were varied between zero and unity in such a way as to insure the correct asymptotic limit in front of and behind the shock wave front.

The observed growth of the population densities of the rotational levels with large j in the front part of the shock wave can be explained by the effect of hot molecules in the bimodal distribution insuring the effective occupation of the high rotational levels.

It is interesting to note that the general forms of the rotational distribution with low rotational temperatures for small j and high rotational temperatures for large j are identical both for rapid expansion and for rapid contraction. In analogy with the rapid expansion in a jet one also expects the formation of rotational inversions in shock waves. However this has not been discussed in the literature.

Rotational Relaxation upon the Absorption of Laser Infrared Radiation by Molecular Gases. Upon the absorption of intense infrared radiation in the vibrational–rotational transitions $v_0j_0 \to v_1j_1$, the system is observed to clear, which corresponds to a decrease in the absorption coefficient. Physically this can be explained by the absorption of infrared radiation with $W\tau_{RT} \gg 1$ (W is the probability of induced transitions under the action of the radiation) equalizing the population densities of the levels v_0j_0 and v_1j_1. The further absorption of infrared radiation in this transition (which determines the rate of vibrational excitation) is limited by the rate of inflow of molecules into the level v_0j_0 and the transition rate from the level v_1j_1 due to rotational relaxation.

When $W\tau_{RT} \gg 1$ the transition is always effective, therefore it can be assumed that the population densities of the rotational sublevels of the lower and upper vibrational states (n_0' and n_1') are approximately equal; $n_0' \cong n_1' = n'$. If we let N_0 and N_1 be the total population densities of the lower and upper vibrational states, then we can write the following system of relaxation equations for N_0 and N_1:

$$\frac{dN_0}{dt} = L_{RT}^{(0)}, \quad \frac{dN_1}{dt} = L_{RT}^{(1)}, \qquad (21)$$

where $L_{RT}^{(0,1)}$ are collision operators determining the rate of RT relaxation for the lower and upper vibrational levels. In estimating the maximum rate of vibrational excitation, the operators $L_{RT}^{(0,1)}$ are usually represented according to the strong collision model [45]:

$$L_{RT}^{(0)} = \frac{n' - qN_0}{\tau_{RT}}, \quad L_{RT}^{(1)} = \frac{n' - qN_1}{\tau_{RT}},$$

where q is the relative equilibrium fraction of molecules in the rotational sublevel and we assume that $q_{j_0} \approx q_{j_1} = q$.

Since $N_0 + N_1$ = const we have $n' = \frac{q}{2}(N_0 + N_1)$ and the system (21) can be rewritten as:

$$\frac{dN_0}{dt} = -\frac{q}{2\tau_{RT}}(N_0 - N_1), \quad \frac{dN_1}{dt} = \frac{q}{2\tau_{RT}}(N_0 - N_1). \tag{22}$$

We see from (22) that the rate of excitation of the upper vibrational level cannot exceed $q/2\tau_{RT}$.

For diatomic molecules the maximum value of q is reached at the level $j_{\max} = \sqrt{kT/2B_e}$. Typically $B_e \sim (0.1\text{-}10)\ \text{cm}^{-1}$ and T = 300°K, and we have $q_{\max} = 0.01\text{-}0.1$. The experimental values of q (especially for polyatomic molecules) are significantly higher than the theoretical ones and are of order unity [46]. A possible cause of the disagreement between theory and experiment is that the strong collision model underestimates the rate of rotational relaxation.

The rate of vibrational relaxation upon the absorption of infrared radiation was calculated in [31] in the diffusion approximation for the operators L_{RT} (K_{dif}), where it was shown that

$$K_{\text{dif}} / (q/2\tau_{RT}) \sim \frac{1}{q}.$$

This result contradicts the conclusion of [45] that vibrational heating is ineffective until the beginning of vibrational—translational relaxation. We note that this conclusion is only correct in the strong collision model. Hence the widely accepted view that the strong collision model predicts the largest rotational relaxation rate is incorrect. In the strong collision model the relaxation channels of the population densities of the discrete rotational sublevels are independent. In the other models the relaxation channels from discrete levels are coupled and there exist several paths for the relaxation of the population densities. This evidently also explains the faster relaxation in the other models.

5. Conclusion

As noted above, the study of nonequilibrium process, including rotational relaxation, began in the beginning of the present century and has attracted further interest in the succeeding decades. The fundamental causes stimulating the development of nonequilibrium kinetics have been the needs for the solutions of both basic and applied problems in the study of a nonequilibrium gas as a special state of matter. Examples are problems in nonequilibrium acoustics, physical gas dynamics, and laser physics. The solution of some problems has led to new ones; however the solution of the fundamental problems have left their mark. In molecular acoustics a new direction has been developed: acoustic spectroscopy [47]. Physical gas dynamics has introduced into practice a new method of studying high temperature processes: the method of shock tubes [48, 49]. The introduction of lasers in physics and chemistry has produced well-known consequences. At the present time the study of nonequilibrium processes, particularly rotational relaxation, is stimulated by the need to solve two fundamental problems. The first is the creation of lasers in the far-infrared region, including lasers using purely rotational transitions. The second is the development of the technology of controlled chemical reactions. Finally, besides the fundamental problems, there are many other problems whose solutions became possible only with the introduction of unique laser techniques of selective excitation and detection of discrete molecular states. These are listed and described in Sec. 3 in the context of rotational relaxation.

The physics of nonequilibrium gases is currently in the first stage of its development. As in any new field, it is difficult to estimate the importance of a particular effect and its possible practical applications. Nevertheless it is already clear that the study of nonequilibrium states is not a simple extension of the frontiers of physics. Progress in the study of nonequilibrium states implies the discovery of deeper properties of nature, which always leads to new practical applications.

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