SURVEY

VIBRATIONAL NONEQUILIBRIUM IN GASES

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§ 1. Introduction

The development of laser physics, laser chemistry, and laser engineering has stimulated interest in studying the state of incomplete statistical equilibrium. The present survey is devoted to vibrational kinetics in gases, i.e., to that division of the kinetic theory of gases which describes the state of incomplete statistical equilibrium due to the nonequilibrium energy distribution over the vibrational degrees of freedom. The vibrational relaxation processes which shape the equilibrium or nonequilibrium vibrational distributions proceed considerably more slowly than the equilibrium build-up processes in the translational and rotational degrees of freedom, and considerably more rapidly than the chemical reactions. In a first approximation this permits considering vibrational relaxation to be isolated in the background of the already terminated rapid processes of equilibrium build-up in the translational and rotational degrees of freedom and the chemical reactions which still have not started. The comparative slowness of the vibrational relaxation governs its exceptional role in the production of molecular media with a population inversion and in the shaping of the quasistationary distribution which permits active interference during the chemical reaction.

The history of the development of vibrational kinetics goes back several decades. The beginning of its first stage refers to the late 1920's and is associated with ultra-acoustic investigations. Namely, in those years Hertzfeld and Rice [1] assumed that anomalous absorption and dispersion of ultrasonic waves in polyatomic gases, which had repeatedly been observed earlier, are explained by the slow exchange of energy between the translational and vibrational degrees of freedom during molecular collisions. The Hertzfeld and Rice ideas were later developed by Kneser [2], Rutgers [3], Landau and Teller [4], Leontovich [5], et al., whereupon a relaxation theory of sound propagation in gases was produced [6]. The Einstein paper [7] in 1920 was the prototype of this theory.

The second stage in the development of vibrational kinetics is associated with the study of shock waves. Bethe and Teller [8] and Zel'dovich [9] were the first to turn attention to the role of vibrational relaxation in shock broadening.

The interest in shock-wave investigation grew abruptly in connection with the development of rocketry in the forties and fifties, which contributed to the appearance and perfection of shock-tube techniques. The application of shock tubes disclosed new possibilities for the study of vibrational relaxation under conditions which differed radically from the conditions in ultrasonic fields. As a rule, ultra-acoustic measurements encompassed the room-temperature range. Shock tubes permitted the study of vibrational relaxation in the temperature range from thousands to tens of thousands of degrees. This was naturally a stimulus for new theoretical investigations. A whole series of results was obtained: The computation of transition probabilities during molecular collisions was perfected, vibrational–translational and vibrational–vibrational energy exchange processes in pure gases and mixtures were studied, the role of excited-molecule sources was examined, a relaxation theory of thermal dissociation was created, etc. The results of these investigations are generalized in the surveys [10-12] and monographs [13-18].

The third stage in the development of vibrational kinetics is related to successes in laser physics. The sixties were marked by the explosive development of laser engineering. The use of molecular gases as the active lasing medium permitted obtaining high generation powers in a broad spectrum range from the near infrared to the submillimeter domain. Laser development caused the further development of vibrational kinetics which was particularly associated with a detailed analysis of the vibrational level populations, the investigation of relaxation in substantially nonequilibrium conditions in both diatomic and polyatomic gases, and taking account of the influence of different physical factors on the process. On the basis of the representations developed, for vibrational kinetics, the mechanism of laser operation at vibrational–rotational transitions was successfully conceived, population inversions for some of them were successfully estimated, and funda-

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mental dependences on the external parameters were successfully constructed. The results of these investigations are elucidated in the survey [19] (see [20] as well).

The development of vibrational kinetics also stimulated the study of physical processes in gasdynamics, chemical kinetics, and physics of the atmosphere. It has become perfectly clear at this time that the production of chemical kinetics at the molecular level is impossible without an analysis of the states of incomplete statistical equilibrium which occur during chemical reactions. A study of molecular chemical kinetics additionally stimulated the development of laser engineering, by disclosing new possibilities for purposeful action on chemical reactions. Presently, the most prospective method for such action is activation of molecules by selective heating of certain vibrational degrees of freedom because of absorption of laser radiation. Namely, by this means a number of interesting experimental and theoretical results have been obtained [21-32].

The survey performed has shown how interest in studying vibrational kinetics, which initially occurred in molecular acoustics, has gradually enclosed the most diverse regions of physics, chemistry, and engineering. At this time the study of vibrational nonequilibrium is an inherent part of molecular kinetics, thermophysics, physics of the atmosphere, molecular acoustics, physical gasdynamics, chemical kinetics, etc. There are tens and hundreds of papers in each of these areas; however, survey papers where the theoretical principles of vibrational kinetics, including the attainments of recent years, would be elucidated from a single aspect are almost absent. The purpose of this survey is to fill this gap, and it is devoted to elucidating the general regularities of vibrational kinetics, i.e., to the discussion of possible types of **distributions in the vibrational degrees** of freedom.

§ 2. Kinetic Equations

The description of vibrational relaxation kinetics is performed in the terminology of populations of the vibrational levels of molecules, i.e., in the terminology of the density of numbers of molecules in a given vibrational state. It is hence considered that the molecules in this vibrational state have an equilibrium distribution in the translational and rotational energies with respect to which the average is taken. Kinetic equations analogous to the Boltzmann kinetic gas equation are written (and not derived) for the populations from considerations of the balance of the numbers of particles at each vibrational level. For the most typical case of a binary mixture of diatomic molecules with chemical reactions and pumping, these equations have the form

$$\frac{dx_n}{dt} = I_{VT}(x_m, x_n) + I_{VV}(x_m, x_n) + I_{VV'}(y_m, x_n) + I_{\mathrm{p}} + I_\sigma, \tag{2.1}$$

$$n = 0, 1, 2, \ldots, k$$

and analogous equations for dy_n/dt. Here x_n and y_n are the populations of the n-th vibrational levels of the molecules A and B, the number k denotes the last discrete vibrational level of the molecule A, and the I are collision operators describing the change in the number of molecules at the n-th vibrational level because of the collisions accompanied by vibrational–translational (VT) energy exchange (I_{VT}), vibrational–vibrational exchange with molecules of this same species (I_{VV}, VV exchange), and with molecules of another species ($I_{VV'}$, VV' exchange), as well as because of the chemical reactions I_r and pumping I_p.

The collision operators I_{VT}, I_{VV} and $I_{VV'}$, have an identical structure of the type

$$I(x_m, x_n) = \sum_m \mathscr{P}^A_{mn} x_m - \sum_n \mathscr{P}^A_{nm} x_n, \tag{2.2}$$

where $\mathscr{P}^A_{mn}$ is the number of elementary acts per unit time at which the vibrational transition m–n occurs in the molecule A.

The first member in (2.2) describes the change in the number of molecules at the n-th vibrational level because of collisions for which molecule transitions occur to the level n from all the remaining vibrational levels, and the second member describes the inverse process, i.e., the drift of molecules from the level n to all the remaining vibrational levels because of transitions.

For VT exchange

$$\mathscr{P}^A_{mn} = Z^0_{AA} N_A P^{AA}_{mn} + Z^0_{AB} N_B P^{AB}_{mn}, \tag{2.3}$$

where $Z^0_{AA,AB}$ is the number of collisions per unit time of the molecule A with the molecules A or B for a unit concentration of the components A or B, respectively; $N_A = \sum_{n=0}^{k} x_n$, $N_B = \sum_{n=0}^{k} y_n$, $P^{AA,AB}_{mn}$ are the probabilities of the vibrational m–n transition in the molecule A during collisions with the molecule A or B referred to single collision.

The probabilities of the direct and reverse transitions P^{AA}_{mn} and P^{AA}_{nm} (or P^{AB}_{mn} and P^{AB}_{nm}) are connected by the detailed equilibrium relation

$$P^{AA,AB}_{mn} \exp(-\varepsilon^A_m/kT) = P^{AA,AB}_{nm} \exp(-\varepsilon^A_n/kT), \tag{2.4}$$

where ε^A_m, ε^A_n are energies of vibrational levels of the molecules A. An analogous relationship for the vibrational transition probabilities of the molecules B has the form

$$P^{BB,BA}_{mn} \exp(-\varepsilon^B_m/kT)\, P^{BB,BA}_{nm} \exp(-\varepsilon^B_n/kT). \tag{2.5}$$

The T in the relationships (2.4) and (2.5) is the temperature of the translational degrees of freedom (the gas temperature).

For VV exchange

$$\mathcal{P}^A_{mn} = Z^0_{AA} \sum_{s,l} Q^{sl}_{mn}(A,\ A)\, x_s, \tag{2.6}$$

where $Q^{sl}_{mn}(A, A)$ is the probability of VV exchange referred to one collision at which the colliding molecules A in the vibrational states m and s go over into the states n and l, respectively, after collision.

The probability of the VV exchange is also connected by the detailed equilibrium relationship

$$Q^{sl}_{mn}(A,\ A) \exp\left(-\frac{\varepsilon^A_s + \varepsilon^A_m}{kT}\right) = Q^{ls}_{nm}(A,\ A) \exp\left(-\frac{\varepsilon^A_l + \varepsilon^A_n}{kT}\right). \tag{2.7}$$

The relationship for the probabilities of VV exchange of the molecules B is obtained from (2.7) by replacing A by B.

For VV' exchange

$$\mathcal{P}^A_{mn} = Z^0_{AB} \sum_{s,l} Q'^{sl}_{mn}(A,\ B)\, y_s, \tag{2.8}$$

where $Q'^{sl}_{mn}(A, B)$ is the probability of VV' exchange referred to one collision between a molecule A and a molecule B for which the molecule makes the transition from the vibrational state m to the state n while the molecule B goes from the state s to the state l.

Like the probabilities of the VV process, the probabilities of VV' exchange are connected by the detailed equilibrium relationship

$$Q'^{sl}_{mn}(A,\ B) \exp\left(-\frac{\varepsilon^B_s + \varepsilon^A_m}{kT}\right) = Q'^{ls}_{nm}(A,\ B) \exp\left(-\frac{\varepsilon^B_l + \varepsilon^A_n}{kT}\right). \tag{2.9}$$

Let us emphasize that the collision operators I_{VV} and $I_{VV'}$ in (2.1) are nonlinear operators. Specific numerical values for the probabilities of VT, VV, and VV' exchange during the collisions of different molecules are presented in the surveys [33, 34] (see the survey [35], also).

The form of the operators I_r and I_p is determined by the specific reaction mechanism and the specific kind of pumping. For example, in the case of pumping by resonant laser radiation absorbed during the vibrational transition 0−n with the probability W_{0n}

$$I_p = W_{0n} x_0 - W_{n0} x_n. \tag{2.10}$$

The second member in (2.10) describes the induced radiation during the transition n−0. The absorption W_{0n} and stimulated radiation W_{n0} probabilities (the Einstein coefficients if W_{0n} and W_{n0} refer to unit spectrum density of the radiation) are related by the relationship

$$g_0 W_{0n} = g_n W_{n0}, \tag{2.11}$$

where g_0 and g_n are the statistical weights of the levels. In the absence of degeneration $g_0 = g_n = 1$, hence $W_{0n} = W_{n0}$. The absorption probability W_{0n} is proportional to the number of photons for first-order processes, hence

$$W_{0n} = \frac{\sigma_{0n} I}{\hbar\omega_{0n}}, \tag{2.12}$$

where σ_{0n} is the radiation-absorption cross section at the transition 0−n, I is the radiation intensity, and $\hbar\omega_{0n} = \varepsilon^A_n - \varepsilon^A_0$. If the induced transition occurs between the vibrational−rotational levels (v, j − v_1, j_1), then (2.11) takes the form

$$g(j) \frac{W_{vv_1}}{n(j)} = g(j_1) \frac{W_{v_1 v}}{n(j_1)}, \tag{2.13}$$

where n(j) and g(j) are the population and statistical weight of the rotational level j. Under rapid rotational relaxation conditions

$$n(j) = g(j)\exp(-\varepsilon_j/kT)\,Z_{\mathrm{rot}}^{-1}, \tag{2.14}$$

where ε_j is the energy of the rotational level, and Z_{rot} is the rotational statistical sum.

Only induced radiation and absorption processes are taken into account in (2.10). At low pressures the spontaneous radiation processes also turn out to be substantial. The corresponding contribution to the right side of (2.1) has the form

$$\sum_{m>n} A_{mn}x_m - \sum_{m<n} A_{nm}x_n, \tag{2.15}$$

where A_{mn} are the probabilities of spontaneous radiation transitions $m-n$ $(m>n)$.

The expression governing the increment of particles in the case of pumping by electron impact is analogous in form

$$I_{\mathrm{p}} = N_e\sum_{m\neq n} K_{mn}x_m - N_e\sum_{m\neq n} K_{nm}x_n, \tag{2.16}$$

where N_e is the electron concentration and K_{mn} is the probability of the vibrational transition $m-n$ under electron impact.

As before, the probabilities of the direct and reverse transitions K_{mn} and K_{nm} are connected by the detailed equilibrium relationship. However, in contradiction to (2.5), the ratio K_{mn}/K_{nm} is not determined by the gas temperature but by the electron temperature (or its analog if the electron distribution is not Maxwellian). Specific data about the probabilities of vibrational excitation of molecules by electron impact are contained in the survey [24]. The form of the operator I_{r} describing the change in the number of particles in chemical reactions is determined by the specific reaction mechanism. For example, in the case of a dissociation reaction occurring by means of molecule transitions from a discrete vibrational state to a continuous state (and reverse processes) induced by collisions,

$$I_{\mathrm{r}} = \sum_{n=0}^{k} K_{dn}N_A^2 - \sum_{n=0}^{k} K_{nd}x_n, \tag{2.17}$$

where $K_{dn}N_A^2$ and $K_{nd}x_n$ is the number of recombination and dissociation elementary acts (per unit time) which accompanied the molecule transition from the continuous spectrum at the n-th vibrational level, and conversely. The recombination K_{dn} and dissociation K_{nd} probabilities (or the rate constants if K_{dn} and K_{nd} refer to unit concentration of collision partners) are related by the effective mass law, which is a variant of the detailed equilibrium relationships.

A chemical reaction changes the number of particles in a system, hence, the system (2.1) must generally be supplemented by the balance equations for the concentration of atoms and other reaction products. Corresponding changes must also be introduced into (2.3) to take account of VT exchange during collisions with atoms and other reaction products. This latter consideration will not include chemical reactions, hence, these questions remain outside the limits of the present survey (see [37, 38] for more details).

Before analyzing the solution of the system (2.1) we list the main physical assumptions under which (2.1) is valid. It was assumed in writing the system (2.1) that the buildup of equilibrium in the translational and rotational degrees of freedom occurs more rapidly than any of the vibrational relaxation processes under consideration, including the pumping. This condition imposes a constraint on the intensity of the external pumping. Namely, the characteristic time associated with the pumping should be greater than the time of rotational relaxation. In the opposite case, rotational nonequilibrium must be taken into account, which results in a whole number of new effects (see [39], for instance).

It should also be stressed that writing (2.1) from considerations of the balance in the number of particles is not a derivation in the ordinary sense of this word. Balance considerations permit writing an equation just for the diagonal elements of the density matrix which have the meaning of vibrational level populations. The question of the nondiagonal density matrix elements and their corresponding coherent effects is not substantially worked out in the theory of vibrational relaxation. Moreover, (2.1) was written from the very beginning for single-particle distribution functions. The question of the reduction of multiparticle distribution functions to single-particle distribution functions, i.e., the question of the disintegration of correlation during vibrational relaxation, has hardly been discussed in the literature [40, 41].

Finally, the system (2.1) takes account of only binary collisions. The simultaneous collisions of three and more particles are not examined in (2.1). Therefore, (2.1) is not applicable to high density gases.

§ 3. Hierarchy of Quasiequilibrium Distributions

The equilibrium distribution in a relaxing system described by (2.1) with $I_p = I_r = 0$ is determined from the condition of an extremum of the thermodynamic potentials. If we limit ourselves to the consideration of vibrational relaxation under conditions of constant temperature of the translational degrees of freedom, then it is convenient to introduce the free energy of the vibrational degrees of freedom

$$F = E - TS, \quad \text{where} \quad E = \Sigma \varepsilon_n^A x_n + \Sigma \varepsilon_n^B y_n, \qquad S = -k\Sigma x_n (\ln x_n - 1) - k\Sigma y_n (\ln y_n - 1) \tag{3.1}$$

corresponding to the energy and entropy of the vibrational degrees of freedom of the molecules A and B per unit volume.

Taking account of (2.1), the following expression can be obtained from (3.1) for the production of the free energy:

$$\begin{aligned} \frac{dF}{dt} = \frac{1}{2} kT \sum_{m,n} \overline{\mathscr{P}}^A_{mn} \left(\ln \frac{x'_n}{x'_m} \right) (x'_n - x'_n) + \\ + \frac{1}{4} kTZ^0_{AA} \sum_{m,n,s,l} \overline{Q}^{sl}_{mn}(A,\ A) \left(\ln \frac{x'_n x'_l}{x'_m x'_s} \right) (x'_m x'_s - x'_n x'_l) + \\ + \frac{1}{2} kT \sum_{m,n} \overline{\mathscr{P}}^B_{mn} \left(\ln \frac{y'_n}{y'_m} \right) (y'_m - y'_n) + \\ + \frac{1}{4} kTZ^0_{BB} \sum_{m,n,s,l} \overline{Q}^{sl}_{mn}(B,\ B) \left(\ln \frac{y'_n y'_l}{y'_m y'_s} \right) (y'_m y'_s - y'_n y'_l) + \\ + \frac{1}{2} kTZ^0_{AB} \sum_{m,n,s,l} \overline{Q}'^{sl}_{mn}(A,\ B) \left(\ln \frac{x'_n y'_l}{x'_m y'_s} \right) (x'_m y'_s - x'_n y'_l), \end{aligned} \tag{3.2}$$

$$\text{where } \overline{\mathscr{P}}^{A,B}_{mn} = \mathscr{P}^{A,B}_{mn} \exp(-\varepsilon_m^{A,B}/kT);$$

$$\overline{Q}^{sl}_{mn}(A,\ A) = Q^{sl}_{mn}(A,\ A) \exp\left(-\frac{\varepsilon^A_m + \varepsilon^A_s}{kT}\right);$$

$$\overline{Q}'^{sl}_{mn}(A,\ B) = Q'^{sl}_{mn}(A,\ B) \exp\left(-\frac{\varepsilon^A_m + \varepsilon^B_s}{kT}\right);$$

$$x'_m = x_m \exp(\varepsilon^A_n/kT); \quad y'_m = y_m \exp(\varepsilon^B_m/kT).$$

Each member in the right side of (3.2) has the form $(\ln a/b)(b - a)$, hence, in conformity with the deductions of phenomenological thermodynamics

$$\frac{dF}{dt} \leqslant 0, \tag{3.3}$$

and the extremal value of the thermodynamic potential is determined by the distribution satisfying the system of equations

$$\{b - a = 0\}. \tag{3.4}$$

A unique solution corresponding to the extremum of the free energy is the equilibrium solution determined from the conditions $x'_m = x'_n$ and $y'_m = y'_n$, i.e.,

$$x_m = x_0 \exp(-\varepsilon^A_m/kT), \quad y_m = y_0 \exp(-\varepsilon^B_m/kT). \tag{3.5}$$

Meanwhile, the structure of (3.2) is such that we can speak of relative extremums. Indeed, three characteristic time scales corresponding to

$$\begin{gathered} VT \text{ exchange } \tau_{VT} \sim (\mathscr{P}^A_{01})^{-1}, \quad (\mathscr{P}^B_{01})^{-1}; \\ VV' \text{ exchange } \tau_{VV'} \sim [Z^0_{AB} N_B Q'^{01}_{10}(A,\ B)]^{-1}, \quad [Z^0_{AB} N_A Q'^{01}_{10}(A,\ B)]^{-1}; \\ VV \text{ exchange } \tau_{VV} \sim [Z^0_{AA} N_A Q^{01}_{10}(A,\ A)]^{-1}, \quad [Z^0_{BB} N_B Q^{01}_{10}(B,\ B)]^{-1} \end{gathered} \tag{3.6}$$

figure in (2.1) [(as well as in (3.2)]. As a rule

$$\tau_{VV} \ll \tau_{VV'} \ll \tau_{VT}. \tag{3.7}$$

The inequality (3.7) permits consideration of the system (2.1) in different time scales. One process predominates during each such scale (the preceding scale is considered terminated at each instant and only its result is important for later, while the next has not yet started). Each of the processes listed introduced its contribution to the production of the free energy. For example, the first and third members in (3.2) describe the VT exchange contribution, the second and fourth the VV exchange contribution, and the fifth the VV' process contribution. The disappearance of the corresponding member in dF/dt determines the state of incomplete statistical equilibrium in which the process under consideration and the preceding processes have already terminated, while the next has still not started. Therefore, a representation of the hierarchy of quasiequilibrium distributions occurs.

Quasiequilibrium distributions formed in each of the components by the fastest VV exchange processes are at the lowest steps of this hierarchy. The distribution being formed under the effect of VV' exchange occupies an intermediate position. Finally, the Boltzmann equilibrium distribution in which the VT exchange results will close this hierarchy.

Let us examine each of these distributions individually.

1. Processes of VV exchange result in a distribution which is determined from the solution of the system of equations

$$x'_m x'_s = x'_n x'_l, \quad m,\ s,\ n,\ l = 0,\ 1,\ 2,\ \ldots \tag{3.8}$$

If (3.8) is written in a form analogous to the conservation law

$$\ln x'_m + \ln x'_s = \ln x'_n + \ln x'_l, \tag{3.9}$$

then it becomes clear that the system (3.9) will be satisfied by ln x'_n, which is a linear combination of quantities being conserved during the collision (integrator invariants). Such quantities are the number of particles and the number of vibrational quanta in single-quantum VV exchange. In fact, in the single-quantum exchange occurring by the vibrational transition scheme m, s$-$n, l, where n = m ± 1, l = s ± 1, the total number of vibrational quanta (as the total number of particles) is conserved; i.e., the number of vibrational quanta of each molecule and one are the integrator invariants. Therefore,

$$\ln x'_n = C + C_1 n \tag{3.10}$$

or, after replacement of the primed by the unprimed quantities according to (3.2),

$$x_n = x_0 \exp(-\gamma n - \varepsilon_n^A/kT). \tag{3.11}$$

The unknown constants C and C_1 (or x_0 and γ) are determined by the total number of particles and the total number of vibrational quanta in the system being conserved during VV exchange.

The distribution (3.11) is known as the Treanor distribution and was first obtained in [42] (see [43, 44] also). It is convenient to express the constant γ in terms of the "temperature" of the first vibrational level T_1 determined by using the relationship

$$x_1 = x_0 \exp(-\varepsilon_1^A/kT). \tag{3.12}$$

In this case

$$\gamma = \frac{\varepsilon_1^A}{kT_1} - \frac{\varepsilon_1^A}{kT} \tag{3.13}$$

and the distribution (3.11) can be written in the form

$$x_n = x_0 \exp\left(-\frac{n\varepsilon_1^A}{kT_1} + \frac{n\varepsilon_1^A - \varepsilon_n^A}{kT}\right). \tag{3.14}$$

For $T_1 > T$ the constant $\gamma < 0$; hence, for large n the population of the vibrational levels described by the distribution (3.11) will be above the equilibrium distribution. The physical reason for the repopulation of the upper vibrational levels because of VV exchange can be conceived if it is taken into account that the dynamic equilibrium between the vibrational levels maintaining the Boltzmann distribution is spoiled with the reduction of the translational temperature relative to the vibrational ($T_1 > T$). The transition of a large quantum from the low vibrational levels into a smaller quantum of the upper levels hence turns out to be a more probable result of VV exchange than the converse. A relative increase in the particle flux at the upper levels in comparison to a reverse particle flux at the lower level will result in the stationary state corresponding to the equality of the forward and reverse fluxes being achieved for large (as compared to the equilibrium) values of the upper level population. Even the formation of population inversions is hence possible. The level n_0, starting with which a population inversion is observed in the Treanor distribution, is determined from the condition

$$\frac{d}{dn}(\gamma n + \varepsilon_n^A/kT) = 0. \tag{3.15}$$

If the zero level of the vibrational energy ε_0^A is taken as origin, then we can write

$$\varepsilon_n^A = \varepsilon_1^A n + \Delta\varepsilon n(n-1), \tag{3.16}$$

where $\Delta\varepsilon = x_l\omega_l$ is the anharmonicity constant. Taking account of (3.16), there follows from (3.15)

$$n_0 = \frac{\varepsilon_1^A}{2\Delta\varepsilon}\frac{T}{T_1} + \frac{1}{2}. \tag{3.17}$$

For example, for CO ($\varepsilon_i^A = 2168\ \text{cm}^{-1}$, $\Delta\varepsilon = 13\ \text{cm}^{-1}$) $n \approx 12$ when $T = 350°\text{K}$ and $T_1 = 2500°\text{K}$.

For $T_1 < T$ the parameter $\gamma > 0$, hence in conformity with (3.11), a lag in the population from the equilibrium Boltzmann distribution will be observed starting with a certain n.

The case $T_1 > T(\gamma < 0)$ is observed during energy pumping in the vibrational degrees of freedom of molecules or during rapid expansion of a molecular gas; the opposite case $T_1 < T(\gamma > 0)$ is realized in the relaxation zone behind a shock front.

At low levels of the vibrational excitation, the nonequidistant vibrational levels can be neglected and a harmonic oscillator model can be considered. In this case $\varepsilon_n^A = n\varepsilon_1^A$ and the distribution (3.11) goes over into a Boltzmann distribution with the vibrational temperature $T_1 \neq T$.

Let us emphasize that the separation between the vibrational and translational temperatures during gas expansion underlies the operating principle of the gasdynamic laser [45-49].

The Treanor distribution (3.11) is a new kind of distribution in gas systems. It is formed under the effect of VV exchange processes and hence is valid in the domain of vibrational levels where VV exchange processes predominate over the VT relaxation processes [50].

2. The VV' exchange processes form a distribution satisfying the system of equations

$$x'_m y'_s = x'_n y'_l, \tag{3.18}$$

which must be considered in combination with the distribution (3.11) and an analogous distribution for y_n since τ_{VV} is less or even much less than $\tau_{VV'}$. This latter condition assures that the formation of the Treanor distributions will precede VV' exchange. If we limit ourselves to single-quantum VV' exchange, i.e., consider that $n = m \pm 1$, $l = s \mp 1$, then the solution of the system (3.18) for the Treanor distribution functions x_m and y_s results in the condition

$$\gamma_A = \gamma_B, \tag{3.19}$$

which can be written in the form

$$\frac{\varepsilon_1^A}{kT_1^A} - \frac{\varepsilon_1^B}{kT_1^B} = \frac{\varepsilon_1^A - \varepsilon_1^B}{kT}. \tag{3.20}$$

The relationship (3.20) relates the "temperature" of the first vibrational levels of the components $A(T_1^A)$ and $B(T_1^B)$ to the gas temperature. An analogous relationship for the "temperatures" of the n-th level is discussed in [51]. The vibrational temperature of the n-th level of the component A is determined from the relationship

$$x_n = x_0 \exp(-\varepsilon_n^A/kT_n^A)$$

and analogously for the component B.

Therefore, VV exchange in each of the components results in a Treanor distribution without altering the store of vibrational quanta in the components. Single-quantum VV' exchange processes synchronize the store of vibrational quanta in both components in correspondence with (3.20) without changing the total number of vibrational quanta in the system.

The harmonic oscillator model is applicable at low vibrational excitation levels. In this case the situation is simplified. The VV exchange processes result in the buildup of a Boltzmann distribution with its own vibrational temperature in each of the components; single-quantum VV' exchange relates these temperatures according to (3.20). Extension of (3.20) to the case of multiquantum VV' exchange is contained in [52, 53].

It follows from (3.20) that for sufficiently small T the vibrational temperature of the component with the smaller vibrational quantum will be above the vibrational temperature of the second component. This fact was observed experimentally. An excess of the vibrational temperature of CO ($\varepsilon_1^{CO} = 3090°\text{K}$) over N_2 ($\varepsilon_1^{N_2} = 3353°\text{K}$) [54] was detected during expansion of a mixture of CO and N_2 in a nozzle.

The VV' exchange processes can result in a number of interesting thermal effects. For instance, let the whole vibrational energy of a binary mixture of gases A and B be concentrated at the initial instant in the component B ($\varepsilon_1^A > \varepsilon_1^B$). In this case, part of the vibrational energy of the component B will go over into the vibrational energy of the component A, according to (3.20), in the single quantum VV' exchange process. Since $\varepsilon_1^A > \varepsilon_1^B$ and the number of quanta is conserved, this process will be accompanied by energy absorption of the translational degrees of freedom, which will result in a lowering of the translational temperature. According to estimates [55], the reduction in gas temperature for an equal concentration of components will be ≈ 30°K in a binary CO and N_2 mixture with the initial conditions: $T = 270$°K is the translational temperature, $T_1^{N_2} \approx 0$, and $T_1^{CO} \approx 3000$°K is the vibrational temperature.

Let us emphasize that the maximum $|\Delta T|$ will be observed with the lapse of time $\sim \tau_{VV'}$. Because of the VT exchange, the ΔT will later tend to zero. Therefore, an experimental study of the time dependence of ΔT will, in principle, permit determination of the probabilities of VV' and VT exchange.

An interesting thermal effect occurs also when powerful CO_2 laser radiation passes through the atmosphere [56]. Generally speaking, gas heating caused by radiation absorption occurs during laser radiation propagation in the atmosphere. However, at the initial instants after the beginning of absorption, gas cooling rather than heating can take place. The physical reason for this is the following. Radiation of a CO_2 laser is absorbed in an atmosphere of CO_2 molecules, where the CO_2 molecules make the transition from the level 10°0 to the level 00°1. The level 00°1 of CO_2 is in resonance with the first vibrational level of N_2, hence, the VV' exchange results in intensive pumping of energy from CO_2 into N_2. The excess vibrational energy of CO_2 and N_2 makes the transition because of VT exchange into thermal energy (into the energy of translational and rotational degrees of freedom), which results in heating of the gas. On the other hand, the VT exchange probability for the CO_2 10°0 level is high compared to the analogous probability for the N_2 vibrational level. Hence, destruction of the CO_2 10°0 level because of resonance radiation absorption will be considerably more rapidly compensated by fluxes of particles because of VT exchange than the N_2 excess vibrational energy will be resorbed because of the slow VT exchange of the N_2 molecule. In this connection, energy evacuation from the translational degrees of freedom and its storage in the vibrational degrees of freedom of the CO_2 and N_2 will occur in the initial times after absorption, which indeed results in cooling of the gas. Let us note that the lifetime of the cooling effect is determined by the VT exchange probability and is around 10^{-2} sec at ~ 1 tech. atm pressure, while the degree of cooling at room temperature is on the order of 1°. An experimental study of the time dependence of ΔT can be the source of information on the VT exchange probabilities.

3. The VT exchange processes result in a buildup of the total statistical equilibrium in the system. Their role is to equilibrate all the "temperatures" in the system. Indeed, VT exchange forms a distribution subject to the equations

$$x'_m = x'_n. \tag{3.21}$$

For $\gamma = 0$, i.e., an equilibrium Boltzmann distribution with a temperature equal to the temperature of the translational degrees of freedom, the distribution (3.11) satisfies the system (3.21). Radiation transition must be taken into account in addition to VT exchange for heteronuclear molecules. In this case the probabilities $\mathscr{P}^A_{mn}$ in the collision operator I_{VT} in (2.1) must be written in the form

$$\tilde{\mathscr{P}}_{mn} = \mathscr{P}^A_{mn} + (A_{mn} + B_{mn}\rho), \quad \tilde{\mathscr{P}}_{nm} = \mathscr{P}^A_{nm} + B_{nm}\rho, \quad m > n, \tag{3.22}$$

where $\mathscr{P}^A_{mn}$ is defined by (2.3). The A_{mn} and B_{mn} in (3.22) are Einstein coefficients, and ρ is the radiation energy density. In isolated systems in which there is no energy and material exchange with the surrounding sphere, ρ is the Planck distribution function under equilibrium conditions. If the relation between the Einstein coefficients A_{mn} and B_{mn} and the relationship (2.4) are taken into account, then we can write

$$\tilde{\mathscr{P}}_{mn}\exp(-\varepsilon^A_m/kT) = \tilde{\mathscr{P}}_{nm}\exp(-\varepsilon^A_n/kT) \tag{3.23}$$

and an analogous relationship for the component B. It follows automatically from (3.23) that the particle distribution in the vibrational levels in the equilibrium state is described by a Boltzmann distribution function. Therefore, radiation transitions in isolated systems do not spoil the Boltzmann distribution [57].

The structure of the distribution hierarchy is determined by the relationship between the different relaxation times. The nature of these relationships depends strongly on the mixture composition (especially in mixtures of polyatomic gases) and on the vibrational-level range under consideration. Nevertheless, the approach elucidated, based on extraction of the fast and slow processes, turns out to be valid independently of the specific form of the inequality (3.7).

§ 4. Stationary Distributions

The hierarchy of quasiequilibrium distributions is observed in the evolution of the system from the initial nonequilibrium state. In this case, the system passes through a sequence of quasiequilibrium distributions during the buildup of the total statistical equilibrium. One type of distribution is replaced by another with time and with the change in time scale. This course of the distribution can be delayed if an external effect, optical or electrical pumping, for instance, fixes the nonequilibrium population of some excited level. A representation of a stationary distribution being formed under the effect of an external source* occurs by such a means. The molecule distribution over the vibrational levels in the energy range beyond the limits of source action reflects the solidified hierarchy in which one type of distribution is replaced by another, but in the space of vibrational energies rather than in time. Thus, for instance, regions where single-quantum VV exchange, VT processes, and transient modes predominate can be extracted in a stationary distribution in a single-component system of anharmonic oscillators.

Single-quantum VV exchange plays the dominant part in the collision of molecules in the lower vibrational levels. Hence, if the ratio between the populations of the zero and first vibrational levels is fixed, for example, then the populations at the following low vibrational levels under stationary conditions will be determined by the Treanor distribution (3.11) or (3.14).

The VT exchange plays the main role in the collision of molecules at the upper vibrational levels. The VT exchange processes result in the buildup of a Boltzmann distribution with a vibrational temperature equal to the temperature of the translation degrees of freedom at the upper levels. Meanwhile, the absolute population of the upper vibrational levels will be above the equilibrium value [for $T_1 > T$, see (3.12)] since the Boltzmann distribution should merge with the Treanor distribution or one similar in the domain of intermediate vibrational energies, which exceeds the equilibrium distribution for $T_1 > T$.

The distribution function has the most complex form at intermediate vibrational levels since it is impossible to extract the dominant process in this range. It is nevertheless clear that the Treanor distribution function should go more or less smoothly over into the Boltzmann function in the intermediate range of vibrational energies. Analytical expressions for the transition distribution function have been obtained in [30, 44, 61-63]. Let us emphasize that the distribution function in the intermediate energy range takes on the shape of a plateau for a sufficiently large store of mean vibrational energy [64-68].

The existence of stationary or quasistationary distributions for different pumping methods discloses the possibility of stimulating chemical reactions if they go through the vibrational excited state. Such stimulation can be accomplished by IR laser radiation, for example, by a singly-directed effect in the quasistationary reaction stage. This method of controlling chemical reactions was first proposed in [27], and developed in [31, 32] and other papers.

Another type of distribution occurs in the region where external pumping acts. Optical or electrical pumping, which transfers a molecule from the m-th into the n-th state, for instance, tends to equalize the populations of the m-th and n-th levels. In the limit case of very intense pumping, a columnar distribution with equally probable molecule distribution over the 0−n vibrational levels is formed according to the scheme of single-step transitions 0−1−2−...−n at the 0−n levels [69, 31]. A population inversion at levels near n can occur in addition to equalization of the populations of the m-th and n-th levels under intense single-step pumping m−n. Equalization of the populations constrains the rate of energy insertion during pumping. This question is investigated in detail in [39].

Energy pumping, associated with the effect of positive or negative sources of vibrationally excited particles, can also result in the formation of quasistationary distributions. The negative source will hence diminish the population and the positive will increase the population as compared to the instantaneous equilibrium value. Let us note that the range of perturbations in the distribution function will be greater in the case of the positive source, hence the occurrence of an absolute inversion is possible.

Systems with positive and negative sources of vibrationally excited particles model two large classes of chemical reactions. The formation of products in vibrationally excited states is characteristic for the first type of reaction (for exchange reactions between halogen atoms and hydrogen halide molecules, for example). The second type of reaction is characterized by the fact that the reaction proceeds through the vibrationally

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*The problem of constructing a statistical theory of gas systems with particle sources on the basis of the Boltzmann kinetic equation was first posed in [58-60].

excited state; i.e., it is accompanied by the disappearance of excited particles (thermal dissociation reaction, for example). Theoretical computations of distributions occurring in these reactions are performed in [70-73, 37, 38].

Stationary vibrational-energy distributions also occur upon spoilage of the Maxwell velocity distribution [74-76]. It is interesting to note that a Boltzmann distribution over the vibrational levels with a different temperature than the translational is built up in a non-Maxwell thermostat during the vibrational relaxation of harmonic oscillators if the translational temperature is determined in terms of the root-mean-square velocity [77].

The representation of stationary or quasistationary distributions turns out to be valid only within definite limits. The pumping constant in polyatomic molecules can result in the occurrence of self-oscillation modes. Thus, a stationary regime does not occur for stationary pumping in an asymmetric CO_2 mode under specific conditions since the rate of disintegration of a quantum of asymmetric vibrations into three quanta of a deformed mode depends nonlinearly on the number of quanta of the deformed mode [78]. Hence, the rate of energy transfer from the asymmetric to the deformation vibrations grows strongly with the growth in excitation of the deformation mode. An increase in the rate of disintegration of the asymmetric vibrations increases the number of deformation vibration quanta and, therefore, increases the rate of disintegration of the deformation quanta still more. An instability appears which results in almost complete destruction of the asymmetric mode. If a sufficiently rapid elimination of energy from the deformation mode is assured, then the state of the destructive instability can go over into the self-oscillation regime. The effect mentioned can result in a peak generation regime in CO_2-based lasers [79, 80]. Instability of the nonequilibrium state of the molecular gas can also be observed for a VT exchange if there is a strong dependence of the VT exchange probability on the gas temperature [81].

Conclusions

The stationary and quasistationary distribution functions of the vibrational energy considered in this survey include all the basic types of vibrational distributions and have a sufficiently general nature. This generality is determined primarily by the fact that the stationary or quasistationary modes are, as a rule, compulsory of any nonequilibrium process. The clarification of the governing role of the quasistationary stage during a nonequilibrium process is the main result in the area of vibrational kinetics in recent years, which discloses extensive possibilities for controlling nonequilibrium processes.

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