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VIBRATIONAL QUASIEQUILIBRIUM DURING RAPID QUANTUM EXCHANGE

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Quasiequilibrium distributions of vibrational energy are found resulting from rapid (compared with the vibrational relaxation as a whole) vibration-vibration transitions in a system of harmonic or anharmonic oscillators. Cases of simultaneous changes in the states of two or three oscillators are considered. The quasiequilibrium distributions are Bose distributions with a nonzero chemical potential of the quasiparticles, which are linear combinations of the numbers of vibrational quanta. Equations are formulated to describe slow relaxation of the quasiequilibrium distribution in gases.

ONE of the paths of vibrational relaxation in gases consists in the exchange of vibrational quanta according to the scheme

$$A_{i+p_A}+B_k \rightleftarrows A_i+B_{k+p_B} \tag{1}$$

(i and k are the level indices of oscillators A and B, p_A and p_B are small integers). This exchange is especially efficient when the oscillator frequencies ω_A and ω_B exactly or approximately satisfy the resonance condition

$$p_A\omega_A = p_B\omega_B. \tag{1$'$}$$

Simultaneous changes in the states of three oscillators are possible in collisions of polyatomic molecules:

$$A_{i+p_A}+B_k+C_l \rightleftarrows A_i+B_{k+p_B}+C_{l+p_C}. \tag{2}$$

Maximum probability of the transition (2) exists when

$$p_A\omega_A = p_B\omega_B + p_C\omega_C. \tag{2$'$}$$

Numerous experiments and theoretical calculations have shown that, close to resonance conditions, the effective exchange time of vibrational quanta is considerably shorter than the time required for complete vibrational relaxation of a gas (see [1-5], for example). The simplest one-quantum exchange ($p_A = p_B$) occurs extremely rapidly in any one-component molecular gas or in mixtures of gases having close oscillator frequencies. As specific gaseous mixtures wherein nearly resonant exchange of vibrational quanta occurs we note the mixture, used in laser technology, of carbon dioxide and nitrogen (the asymmetric vibrations of CO_2 molecules and the vibrations of N_2 have the frequencies 2396 and 2360 cm^{-1}, respectively) and the mixture of fluorine and nitrogen (the doubled frequency of F_2 vibrations is 1850 cm^{-1}). The resonance condition (2′) is approximately fulfilled, for example, by three vibrational frequencies of CO_2 molecules.

In the present work we analyze the general laws governing vibrational relaxation in systems that fulfill (1′) or (2′) approximately. We are interested in laws which are based on the rapid exchange of vibrational quanta and which are otherwise identical for all gases. A similar problem has been solved in the special case of process (1) for $p_A = p_B = 1$.[6,7]

We shall first consider two groups of oscillators, A and B, that approximately satisfy (1′), and shall determine the role of transitions (1) in relaxation, assuming them to be much more rapid processes than the vibrational relaxation process of the gas as a whole. Oscillators A and B may belong to different molecules of the gaseous mixture or to identical polyatomic molecules.

The vibrational quantum exchange (1) alone cannot produce complete thermodynamic equilibrium, which requires that a definite combination of the numbers N_A and N_B of vibrational quanta[1] be conserved:

$$N \equiv N_A/p_A + N_B/p_B = \text{const.} \tag{3}$$

However, if (1) is a rapid process the establishment of complete thermodynamic equilibrium follows long after quasiequilibrium, which is manifested by equal rates of (1) in the direct and reverse directions. We shall call this a quasiequilibrium state of the system consisting of the oscillators A and B.

A second, considerably more prolonged, stage of relaxation occurs in the quasiequilibrium system. It will be shown that the existence of vibrational quasiequilibrium permits a great simplification in the quantitative description of relaxation. This simplification consists in the fact that in quasiequilibrium the complete system of differential equations describing changes in the populations of all the vibrational levels is reduced to a single differential equation for N, which is conserved in quantum exchange (1), and to algebraic equations expressing the relations of N with the quasiequilibrium distributions of vibrational level populations and with other properties of the state.

1. QUASIEQUILIBRIUM DISTRIBUTION

We shall calculate the quasiequilibrium energy distribution of groups of the oscillators A and B, which may be either harmonic or anharmonic. For our problem we shall assume that the translational and vibrational motions of the oscillators (molecules) are characterized by a common temperature T. The distribution function can be calculated most simply as follows. The given quasiequilibrium statistical system includes, besides energy and mass, one additive integral of the mo-

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[1] The n-th vibrational level of an oscillator is populated by n vibrational quanta.

tion (3). We shall consider any p_A quanta of the A oscillators, or p_B quanta of the B oscillators, as a single quasiparticle. In this representation the integral of the motion (3) is interpreted as the conservation law of the total number N of quasiparticles. We then immediately write the distribution of the oscillators with respect to energy and the number of quasiparticles (the Bose grand canonical distribution):

$$W_{N,i}=\Omega^{-1}\exp\left[(N\mu-\varepsilon_{N,i})/kT\right], \tag{4}$$

where μ is the chemical potential of the quasiparticles, $\epsilon_{N,i}$ are the energy levels of the oscillator system for a given value of N, and Ω^{-1} is a normalization constant. The distribution (4) applies to any subsystem, including a single oscillator.

The energy and the number of quasiparticles of a single oscillator are interdependent. For example, an oscillator A populated with n/p_A quasiparticles is thereby populated with n quanta and its energy is ϵ_n^A (n is the index of the vibrational level). Thus the distribution function for a single oscillator is

$$W_n{}^L=\Omega_L{}^{-1}\exp\left[(n\mu/p_L-\varepsilon_n{}^L)/kT\right],$$
$$\Omega_L=\sum_n\exp[(n\mu/p_L-\varepsilon_n{}^L)/kT],\qquad L=A,B. \tag{5}$$

The distribution function (4) of the system obviously is the product of the functions (5) for all the oscillators. The relations of the chemical potential to the total vibrational energy ϵ and to the total number N of quasiparticles are given by

$$\varepsilon=kT^2\sum_{L=A,B}R_L\frac{\partial}{\partial T}(\ln\Omega_L)_{\mu/kT},\quad N=kT\sum_{L=A,B}R_L\frac{\partial}{\partial\mu}\ln\Omega_L. \tag{6}$$

Here R_L is the number of all oscillators L. In thermodynamic equilibrium the chemical potential of the quasiparticles is zero.

In the case of harmonic oscillators Eq. (5) represents Boltzmann distributions:

$$W_n{}^L=W_0{}^L\exp(-\varepsilon_n{}^L/kT_L),\qquad L=A,B. \tag{7}$$

The temperatures T_L of these distributions satisfy

$$\frac{p_A\omega_A}{T_A}-\frac{p_B\omega_B}{T_B}=\frac{p_A\omega_A-p_B\omega_B}{T} \tag{8}$$

and the following relation to the chemical potential:

$$\mu/p_L=\hbar\omega_L(1-T/T_L),\qquad L=A,B. \tag{9}$$

At exact resonance, $p_A\omega_A = p_B\omega_B$, the two groups of oscillators have an identical vibrational temperature ($T_A = T_B$).

The major contribution to the dependence of the chemical potential and vibrational temperature on the total vibrational energy usually comes from the lowest oscillator levels, where anharmonicity is small. Therefore (9) can be applied quite accurately to real molecules.[2)] In this approximation the distributions of anharmonic oscillator populations are given by

$$W_n{}^L=W_0{}^L\exp\left[\frac{\hbar\omega_L n}{k}\left(\frac{1}{T}-\frac{1}{T_L}\right)-\frac{\varepsilon_n{}^L}{kT}\right],\qquad L=A,B. \tag{10}$$

Here T_L is the temperature of the Boltzmann distribution at which the oscillator energy equals its actual quasiequilibrium value.

When the number of quanta is conserved ($p_A = p_B = 1$), Eqs. (5) and (8) are converted into the familiar distribution given in [6,7]. For the case of $2p_A = p_B = 2$, Eq. (8) was obtained in [9].

The distribution (5) is inapplicable to the upper vibrational levels of molecules, where the rate of quantum exchange (1) is much slower than the rates of other processes that lead to changes in vibrational level populations. The corresponding energy limit of the quasiequilibrium distribution for the case $p_A = p_B = 1$ was determined in [10,8]. For other values of p_A and p_B the limit of the quasiequilibrium distribution can be obtained as in [8].

2. RELAXATION OF THE QUASIEQUILIBRIUM DISTRIBUTION

The system (5), (6) of algebraic equations determine the quasiequilibrium state of the oscillators for given values of the translational motion temperature and one additional parameter, such as the number of quasiparticles or the chemical potential. To describe the process of complete vibrational relaxation we must add an equation describing the slow change in the number N of quasiparticles, which occurs in vibration-translation transitions

$$A_i+M\rightleftarrows A_{i+1}+M \tag{11}$$

(M is any particle) and is described in the harmonic approximation by the differential equation

$$\frac{dN}{dt}=\sum_{L=A,\,B}\frac{R_L\,[E^L_{(T)}-E^L_{(T_L)}]}{\hbar\omega_L p_L\tau_L(T)},\quad \frac{E^L_{(x)}}{\hbar\omega_L}\equiv\frac{1}{\exp(\hbar\omega_L/kx)-1}. \tag{11'}$$

Here $\tau_L(T)$ is the ordinary (unassociated with vibrational quantum exchange) vibrational relaxation time of oscillators of the group L in the given gaseous mixture. If in this system processes besides (11) lead to essential changes of N, these additional processes must be taken into account by adding the appropriate terms to the right-hand side of (11′).

3. SIMULTANEOUS CHANGES IN THE STATES OF THREE OSCILLATORS

We now turn to the transitions (2) which satisfy (2′) either exactly or approximately. Assuming that these are the most rapid transitions, we shall consider the quasiequilibrium to which they lead. In (2), two linearly independent combinations of the numbers of vibrational quanta are conserved:[3)]

$$P_B\equiv N_A/p_A+N_B/p_B=\text{const},$$
$$P_C\equiv N_A/p_A+N_C/p_C=\text{const}. \tag{12}$$

The two integrals of the motion (12) in the quasiequilibrium state of the system correspond to the chemical potentials μ_A and μ_C, respectively. In other respects the procedure for constructing the distribution func-

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[2)] In [8] anharmonicity is taken into account more exactly.

[3)] For P_B and P_C we may choose any two independent conserved linear combinations of the numbers N_A, N_B, and N_C, such as $2N_A/p_A + N_B/p_B + N_C/p_C$ and $N_A/p_A + N_B/p_B$.

tions of the system and subsystems is entirely analogous to that described in Sec. 1.

The distributions of the entire vibrational system (W) and of a single oscillator in each group are represented by

$$\begin{gathered}W_i = \Omega^{-1}\exp\left[(P_B\mu_B + P_C\mu_C - \varepsilon_{P_B,\,P_C,\,i})\,/\,kT\right],\\ W_n{}^A = W_0{}^A\exp\{[n(\mu_B+\mu_C)\,/\,p_A - \varepsilon_n{}^A]\,/\,kT\},\\ W_n{}^L = W_0{}^L\exp\left[(n\mu_L\,/\,p_L - \varepsilon_n{}^L)\,/\,kT\right],\ L = B,\ C.\end{gathered} \tag{13}$$

The relation of the chemical potentials to the total vibrational energy and to the numbers P_B, P_C is similar to (6) and can be obtained easily from (13). The relations for the temperatures of the oscillators are

$$\frac{p_A\omega_A}{T_A} - \frac{p_B\omega_B}{T_B} - \frac{p_C\omega_C}{T_C} = \frac{p_A\omega_A - (p_B\omega_B + p_C\omega_C)}{T},$$

$$\frac{\mu_L}{p_L} = \frac{\hbar\omega_L}{k}\left(1 - \frac{T}{T_L}\right), \qquad L = B, C.$$

For all three groups of oscillators Eq. (10) is also valid.

Relaxation of the quasiequilibrium state is described by two differential equations that take into account the slow change of the numbers P_B and P_C of quasiparticles. If these changes result only from the vibration-translation interaction (11), we have, analogously to (11′),

$$\frac{dP_L}{dt} = \frac{R_A\,[E^A_{(T)} - E^A_{(T_A)}]}{\hbar\omega_A p_A \tau_A(T)} + \frac{R_L\,[E^L_{(T)} - E^L_{(T_L)}]}{\hbar\omega_L p_L \tau_L(T)}, \quad L = B,\ C.$$

4. THE CASE OF SEVERAL RAPID PROCESSES OF VIBRATIONAL QUANTUM EXCHANGE

A. The relations (3)–(10) are extended directly to the case of three or more oscillator groups (A, B, C, ...) that satisfy resonance conditions such as (1′). Specifically, if in addition to (1) we have a rapid exchange of vibrational quanta between oscillators B and C according to

$$B_{i+p_B} + C_k \rightleftarrows B_i + C_{k+p_C},$$

the conserved quantity is

$$N = N_A\,/\,p_A + N_B\,/\,p_B + N_C\,/\,p_C. \tag{14}$$

However, it is important to emphasize that here the direct transfer of quanta from A to C, and the reverse, should either not occur at all (resulting, for example, from low relative concentrations of the oscillators A and C), or that it should not violate (14). Otherwise no integrals of the motion could be formed from the numbers of vibrational quanta, and the quasiequilibrium of all rapid vibrational quantum exchange processes would be the same thing as complete thermodynamic equilibrium. Thus a rapid exchange of vibrational quanta which is not subject to quasiparticle conservation as given by (3) and (14) leads to the equally rapid establishment of complete thermodynamic equilibrium independently of the slow transitions (11).

Relaxation of this kind is possible, in principle, for two groups of oscillators (A, B) when one quantum of oscillator A can be "converted" rapidly to either one or two quanta of oscillator B:

$$A_{i+1} + B_k \rightleftarrows A_i + B_{k+1};\ A_{i+1} + B_k \rightleftarrows A_i + B_{k+2},\ i,\ k = 0, 1, 2\ldots \tag{15}$$

Overall quasiequilibrium of all processes (15) is possible only in the case of thermodynamic equilibrium:

$$T_A = T_B = T. \tag{16}$$

Some comment is required regarding an investigation[9] where for the quasiequilibrium of the processes (15) a relation different from (16) was obtained between the temperatures T_A, T_B, and T. This relation in [9] was derived from the time independence of the populations W_n^A of oscillators A for the quasiequilibrium stage of processes (15). The relation is correct but must be supplemented by an additional relation arising out of the constancy of the populations W_n^B of oscillators in the second group; the only solution will then be (16).

Time independence of vibrational level populations in the rapid exchange processes (15) for $T_A \neq T_B \neq T$ is possible if the system exists not in quasiequilibrium, but in a stationary state for which a necessary condition is the presence of at least one external source of vibrational energy (such as the pumping of energy by a laser, or chemical reactions leading to the production or loss of vibrationally excited molecules).

The character of the stationary distribution of the populations depends on the ratio of the effective times τ_1 and τ_2 determining the intensity of the source and of the exchange processes (15), respectively. If $\tau_1 \gg \tau_2$, then T_A, T_B, and T are equal in the stationary regime. If $\tau_1 \lesssim \tau_2$, the stationary populations of the vibrational levels depend strongly on the intensity of the source. Then the relation between the temperatures[4)] also depends, as a general rule, on the intensity of the sources. It can be shown that in the special case where the sources are coupled directly to only one group of oscillators there exists a relation between the temperatures that does not explicitly contain parameters which characterize the intensity of the sources. The form of this relation depends on which one of the two oscillator groups is coupled to the sources. The relation between the temperature that was obtained in [9] is valid when the sources are coupled to oscillators B.

B. The quasiequilibrium, considered in Sec. 3, with two chemical potentials can, when an additional rapid exchange process is "switched on," be converted into a different distribution with one or two chemical potentials. Instead of considering all the possible variants, we shall now mention only the case where, in addition to (2), rapid quantum exchange takes place between oscillators B and C as follows:

$$B_{i+p_{B'}} + C_k \rightleftarrows B_i + C_{k+p_{C'}}.$$

It is easily seen that only one combination of numbers of vibrational quanta is now conserved:

$$\frac{N_A}{p_A} + \frac{N_B}{p_B + p_C p_B'/p_C'} + \frac{N_C}{p_C + p_B p_C'/p_B'} = \text{const},$$

which does not differ essentially from (14).

We note, in conclusion, that the foregoing equations for quasiequilibrium energy distribution were obtained subject to the formal requirement of sufficiently rapid vibrational quantum exchange. The question as to the

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[4)] The temperatures T_A and T_B are significant if the time τ_1 of the source is still much greater than the effective time of quantum exchange between identical oscillators.

fulfillment of this condition should be answerable by solving concrete problems where molecular parameters and the temperature dependence of vibrational relaxation times are taken into account. The probability of resonant vibrational quantum exchange processes is ordinarily diminished rapidly by an increase in the number of quanta Σp_L participating in exchange (by a factor of several tens when Σp_L is changed by unity). Therefore, of all the possible resonance transitions and the corresponding quasiequilibrium distributions, the most interesting cases (with not too low probability) from a practical point of view are $\omega_A = \omega_B$, $\omega_A = 2\omega_B$, $\omega_A = 3\omega_B$, $\omega_A = \omega_B + \omega_C$, $2\omega_A = \omega_B + \omega_C$, and $\omega_A = 2\omega_B + \omega_C$.

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