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COMPARISON OF THE RESULTS OF CLASSICAL DIFFUSION AND QUANTUM  
CALCULATIONS OF VIBRATIONAL-TRANSLATIONAL RELAXATION OF  
DIATOMIC MOLECULES

M. N. Safaryan and O. V. Skrebkov

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INTRODUCTION

Starting with a numerical solution of the diffusion equation from [2], an investigation was performed in [1] of the vibrational relaxation of anharmonic oscillators in an inert gas medium, the relative effect of anharmonicity on the kinetics of the distribution function and the mean energy was determined, the dependence of the relaxation of the mean energy of the system on its deviation from equilibrium at each instant was shown, etc. The question arises of how far the results in [1] are applicable to quantum systems, and, more generally, what are the limits of applicability of the classical diffusion calculation. A quantitative answer to this question requires a step-by-step comparison with the corresponding quantum-mechanical calculation. We perform such a comparison in the present paper (cf. [3]).

We use the following notation:  $\epsilon$ , vibrational energy;  $\epsilon_i$ , energy corresponding to the  $i$ -th vibrational level;  $f(\epsilon, t)$  distribution function;  $f_i(t)$ , population of  $i$ -th level;  $f^0$  and  $f_i^0$ , equilibrium values at temperature  $T$ ;  $T$ , temperature of thermostat;  $T_0$ , initial vibrational temperature;  $\bar{\epsilon}(t)$ , mean energy;  $\epsilon_0$ , energy at zero time;  $\tau_1$ , vibrational relaxation time of harmonic oscillators;  $\omega_0$ ,  $\mu$ , and  $D$ , fundamental frequency, reduced mass, and dissociation energy of oscillator;  $N$ , number of levels of quantum oscillator;  $\xi_0$ , adiabaticity parameter;  $\xi_0 = (\omega_0 \pi / \alpha) \sqrt{M / 2kT}$ , where  $M$  is the reduced mass of the oscillator and particles of the thermostat, and  $\alpha$  is the parameter of the intermolecular interaction potential;  $F(t)$ , force acting on oscillator in a collision;  $P_{ik}$ , probability of transition of oscillator from  $i$ -th to  $k$ -th level per unit time;  $\alpha = D/kT$ ;  $\alpha_0 = D/kT_0$ ;  $\omega_{ik} = (1/\hbar) |\epsilon_i - \epsilon_k|$ ,  $\tau = t/\tau_1$ ;  $\varphi = f/f^0$ ;  $\varphi_i = f_i/f_i^0$ ;  $x = \epsilon/D$ ;  $\theta = \hbar\omega/kT$ ;  $\theta_0 = \hbar\omega/kT_0$ .

1. Statement of the Problem. Initial Equations.

It is well known that classical and quantum-mechanical methods of calculation are equivalent if

$$\theta_{\max} = \hbar\omega_0/kT_{\min} \ll 1, \quad (1.1)$$

where  $T_{\min}$  is the smaller of the values of  $T$  and  $T_0$ . This condition is sufficient, but it may or may not be necessary for the determination of a number of kinetic characteristics. Actually, another quantity determining the possibility of applying the classical method of calculation to quantum systems is the time of the kinetic process. It is known that a Fokker-Planck type of equation for an initial distribution function with large spatial derivatives does not give a correct description at times which are very short in comparison with the relaxation time, but starting from a certain instant the size of the initial gradient is of no

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importance in determining the applicability of this equation. On the other hand, if we are not interested in the near-equilibrium state of the system for initially highly excited oscillators, but for  $T_0 \ll T$ , on the contrary, in earlier times, then instead of Eq. (1.1), we can take

$$\theta(t) \cong \hbar\omega_0/\bar{\varepsilon}(t) \ll 1, \quad \theta(t) < \theta_{\max}, \quad (1.2)$$

where  $\bar{\varepsilon}(t)$  is the mean energy of an oscillator at times of interest to us; the times for which (1.2) is satisfied can be estimated by using the approximate relation  $\varepsilon(t) = \bar{\varepsilon}_e - (\bar{\varepsilon}_e - \bar{\varepsilon}_0)e^{-t/\tau_v}$ , where  $\tau_v$  is the vibrational relaxation time of the oscillators and  $\bar{\varepsilon}_e$  is the equilibrium value of  $\bar{\varepsilon}(t)$ ;  $\bar{\varepsilon}_e = \bar{\varepsilon}$  as  $t \rightarrow \infty$ . This less stringent condition than (1.1) arises from the fact that the range of significant variation of the kinetic characteristics of  $\bar{\varepsilon}$ ,  $\bar{\varepsilon} \geq \varepsilon(t)$ ; i.e., the scale of the problem, depends on the time. These qualitative arguments favor a wider range of applicability of the classical method of calculation than follows from (1.1).

In order to find out the maximum value of  $\theta$  and the specific times for which the results of the classical description of the process can be used, it is necessary, as already noted, to perform a step-by-step comparison with the corresponding quantum-mechanical calculation. The classical and quantum-mechanical calculations of the kinetics of the process to be compared must be based on equivalent assumptions of the nature of the interaction of the oscillators with the thermostat) the initial equations which satisfy this requirement are written down below.

In the classical description of the kinetics of the process an equation of the diffusion type from [2] was used in the form (cf. [1, 2] for more details)

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial \varepsilon} \left\{ B f^0 \frac{\partial \Phi}{\partial \varepsilon} \right\}, \quad \frac{\partial f}{\partial t} = 2\eta_1 kT \mu \frac{\partial}{\partial \varepsilon} \left\{ \left[ \sum_{n=1}^{\infty} (n\omega)^2 |r_n|^2 \mathcal{F}_n \right] f^0 \frac{\partial \Phi}{\partial \varepsilon} \right\}, \quad (1.3)$$

where

$$\eta_1 = \frac{1}{2\tau_0} \frac{|F_{r.o}|^2}{\mu kT} \equiv (\tau_1)_{cl}^{-1}; \quad \mathcal{F}_n(\varepsilon, \xi_0) = \frac{\langle |F_n|^2 \rangle}{\langle |F_{h.o}|^2 \rangle}; \quad (1.4)$$

$F_n$  and  $F_{h.o.}$  are the Fourier components of the force for frequencies  $\omega$  and  $\omega_0$ , respectively, the  $r_n$  are the Fourier components of the unperturbed vibrational motion  $r(t)$  of the oscillator, the symbol  $\langle \dots \rangle$  denotes an average over all the impact parameters, and  $\tau_0$  is the mean free time of the molecules.

The quantum-mechanical calculation requires solving the balance equations

$$\frac{df_i}{dt} = -f_i \left( \sum_{k=i-1}^0 P_{ik} + \sum_{k=i+1}^N P_{ik} \right) + \sum_{k=0}^{i-1} f_k P_{ki} + \sum_{k=i+1}^N f_k P_{ki}, \quad i = 1, 2, \dots \quad (1.5)$$

In the problem under consideration, the  $P_{ik}$  are the semiclassical values obtained by treating the translational motion classically and the vibrational motion quantum mechanically. These values are obtained in first-order perturbation theory for an intermolecular interaction potential which is linear in  $r$  (cf. [4]) and can be written in the form

$$P_{ik} = \frac{1}{\tau_0} \langle p_{ik} \rangle, \quad \langle p_{ik} \rangle = |r_{ik}|^2 \frac{1}{\hbar^2} \langle |F_{ik}|^2 \rangle,$$

where the  $r_{ik}$  are the matrix elements of the unperturbed oscillator, the  $F_{ik}$  are the Fourier components of the force for the frequency  $\omega_{ik}$ , and the value of  $F(t)$  is the same as in (1.4).

By analogy with (1.3), we write  $P_{ik}$  in the form

$$P_{ik} = \frac{1}{\tau_0} \langle p_{10} \rangle \frac{2\mu\omega_0}{\hbar} |r_{ik}|^2 \mathcal{F}_{ik}, \quad \mathcal{F}_{ik} = \frac{\langle |F_{ik}|^2 \rangle}{\langle |F_{10}|^2 \rangle}. \quad (1.6)$$

Equations (1.5) taking account of (1.6) are the quantum-mechanical analog of Eqs. (1.3) and (1.4). The assumptions on which the calculations of the diffusion coefficient  $B$  and the probabilities  $P_{ik}$  are based agree completely. The results of the calculation of the kinetics

of the process obtained in [1] must be compared with the solution of Eqs. (1.5) and (1.6).

For a weak interaction the terms taking account of transitions  $i \rightarrow k$  with  $k \neq i \pm 1$  are not controlling, and for an adiabatic interaction ( $\xi_0 \gg 1$ ) they can be completely neglected. On the other hand, when  $\xi_0 \gg 1$  one should expect the greatest difference between the classical and quantum-mechanical calculations, since in this case, as a rule,  $\theta > 1$ . One-quantum transitions imply neglecting all terms with  $n > 1$  in the diffusion coefficient  $B$  in the classical equations (1.3). For  $\theta \ll 1$  the system of equations which follows from (1.5) taking account of (1.6) for  $P_{ik} = 0$  must go over into the corresponding differential equation when  $i \neq k \pm 1$ . This transition gives a relation between  $P_{10}$  and  $\eta_1$ . Using  $f_{i+1}^0/f_i^0 = P_{i+1,i}/P_{i,i+1}$  and the approximation  $\omega_{i+1,i} \simeq \omega_{i,i-1} = \omega_i$ , we have the following from (1.5) for  $k = i \pm 1$ :

$$\frac{1}{\omega_i} f_i^0 \frac{d\varphi_i}{dt} = \frac{\Delta_{i+1,i}}{\hbar\omega_{i+1}} \left\{ B(\varepsilon_i) \frac{f_i^0}{\omega_i} \frac{\Delta_{i,i-1}\varphi}{\hbar\omega_i} \right\}, \Delta_{i+1,i} A_i = A_{i+1} - A_i; \quad (1.7)$$

$$B(\varepsilon_i) = P_{i,i-1} (\hbar\omega_i)^2. \quad (1.8)$$

For  $\theta \ll 1$  we have

$$\frac{\Delta_{i+1,i}}{\hbar\omega_{i+1}} \rightarrow \frac{\partial}{\partial \varepsilon}, \frac{f_i^0}{\omega_i} \rightarrow f^0(\varepsilon_i) G$$

$$\left( G = \int \frac{e^{-\varepsilon/\hbar T}}{\omega(\varepsilon)} d\varepsilon / \sum_i e^{-\varepsilon_i/\hbar T} \right),$$

and (1.7) goes over into the equation

$$f^0 \frac{\partial \varphi}{\partial t} = \frac{\partial}{\partial \varepsilon} \left\{ (\hbar\omega)^2 P_{i,i-1} f^0 \frac{\partial \varphi}{\partial \varepsilon} \right\} (\varepsilon = \varepsilon_i) \quad (1.9)$$

A comparison of (1.9) and (1.3), where  $n = 1$ , shows that

$$\eta_1 = \frac{\hbar\omega_0}{kT} P_{10} \equiv \frac{\theta}{1 - \exp(-\theta)} \frac{1}{(\tau_1)_{qu}},$$

where  $(\tau_1)_{qu}$  is the vibrational relaxation time of the quantum harmonic oscillators.

The quantity  $\tau_1$  in our calculations serves as a time scale of the kinetic process; in the classical calculation it corresponds to the relaxation time of the classical harmonic oscillators  $(\tau_1)_{cl} = \eta_1^{-1}$  and in the quantum-mechanical calculation to the relaxation time of quantum harmonic oscillators  $(\tau_1)_{qu}$ . From now on we omit the subscripts cl and qu. The quantities  $(\tau_1)_{cl}$  and  $(\tau_1)_{qu}$  agree if  $\theta/2 \ll 1$ , which follows from  $1 - (1 - \exp(-\theta))/\theta \ll 1$ .

Quantities characterizing the relative effect of anharmonicity of the vibrations were investigated in [1]. Anharmonicity is important for relatively high values of  $T$  and  $T_0$  (or  $\varepsilon_0$ ); processes in which  $\alpha = D/kT \leq 50$  were considered in [1], and for the most part this condition is retained here. We note that for thermostat temperatures corresponding to  $\alpha \leq 50$ ,  $\theta \leq 4$  for all diatomic molecules, while for  $O_2$ ,  $N_2$ ,  $NO$ ,  $CO$ ,  $Br_2$ ,  $I_2$ , and  $Cl_2$ ,  $\theta \leq 1$ .

## 2. Comparison of Calculated Results for One-Quantum Transitions ( $\xi_0 \gg 1$ ).

We present below the results of a specific comparison of the solutions of Eq. (1.3), in which only terms with  $n = 1$  are taken into account, and system (1.5) for  $k = i \pm 1$ . From now on we use the same values for  $F_n$  and  $F(t)$  as in [1, 2]; a molecule is also modeled by a Morse oscillator.

Relaxation of Distribution Function. We consider first an initial Boltzmann distribution with temperature  $T_0$ ,

$$f(x, 0) = C \frac{\exp(-a_0 x)}{\sqrt{1-x}}, \quad (2.1)$$

where the constant  $C$  is determined from the normalization condition.

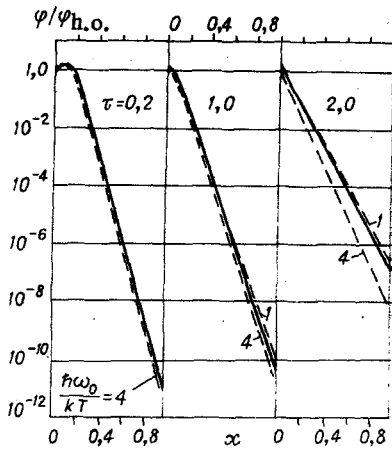


Fig. 1

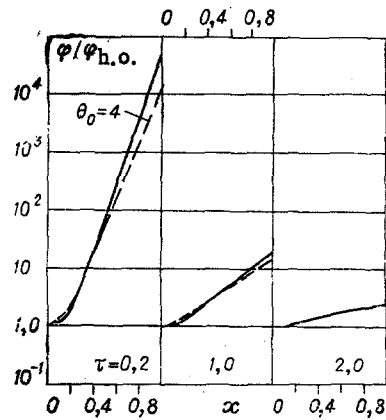


Fig. 2

A comparison\* of the solution  $\varphi$  of Eq. (1.3) for  $n = 1$  and solution  $\varphi_i$  of (1.4) with  $k = i \pm 1$  for the deactivation process ( $\alpha_0 = 7$ ,  $\alpha = 40$ ) for various values of  $\theta$  showed that for  $\theta \leq 1$ ,  $\varphi$  and  $\varphi_i$  agree within 10-20%. For  $\theta = 4$ ,  $\varphi$  and  $\varphi_i$  differ at most by about a factor of 3 at early times ( $\tau \leq 0.2$ ), but for  $\tau \geq 1$  the difference becomes negligible.

The values of  $(\varphi/\varphi_{h.o.})_{qu}$  and  $(\varphi/\varphi_{h.o.})_{cl}$  ( $\varphi/\varphi_{h.o.} \cong f/f_{h.o.}$ ) characterizing the relative effect of anharmonicity in the quantum ( $\theta = 1$  and 4) and classical cases are shown in Fig. 1 for the thermal deactivation process:  $\alpha_0 = 7$ ,  $\alpha = 40$ , and  $\xi_0 = 30$ . The solid curves are for the classical calculation and the open curves for the quantum calculation. For systems satisfying the condition  $\theta \leq 1$  the calculated values of  $\varphi/\varphi_{h.o.}$ , where  $\varphi_{h.o.}$  is the distribution function of harmonic oscillators relative to the equilibrium value, are practically the same as the corresponding results of the quantum treatment. For systems with a large vibrational quantum ( $\theta = 4$ ) the latter applies only to times less than the relaxation time ( $\tau < 1$ ). For  $\tau \geq 1$ ,  $(\varphi/\varphi_{h.o.})_{qu}$  and  $(\varphi/\varphi_{h.o.})_{cl}$  differ by as much as two orders of magnitude at the upper levels as a result of the difference between  $(\varphi_{h.o.})_{qu}$  and  $(\varphi_{h.o.})_{cl}$ . There are known analytic solutions for the last two quantities.

Generalizing these results one can say that in the initial stage of the deactivation process ( $\tau < 1$ ) the ratio  $(\varphi/\varphi_{h.o.})$  is insensitive to the value of  $\hbar\omega_0/kT$ . At later stages of the process which are closer to equilibrium ( $\tau \geq 1$ ), this applies to the value of  $\varphi$ , the classical analog of  $\varphi_i = f_i/f_i^0$ .

The results of the classical and quantum-mechanical calculations of  $\varphi/\varphi_{h.o.}$  and  $\varphi$  agree for the excitation of vibrations ( $T > T_0$ ) as well as for deactivation over the whole relaxation process if  $\theta_0 \leq 1$ . Figure 2 shows  $(\varphi/\varphi_{h.o.})_{cl}$  and  $(\varphi/\varphi_{h.o.})_{qu}$  during the excitation of vibrations ( $\alpha_0 = 40$ ,  $\alpha = 10$ , and  $\xi_0 = 20$ ). The solid curves denote the classical calculation and the quantum calculation for  $\theta_0 = 1$ ; the dashed curves denote the quantum calculation for  $\theta_0 = 4$ . It is clear that these quantities practically coincide during the whole relaxation process; their difference at the upper levels ( $x > 0.6$ ) in the initial stage of the process can be ignored because of the low population of these levels at the beginning of the excitation process. A comparison of  $\varphi$  and  $\varphi_i$  for the excitation process for  $\theta_0 = 4$  showed that they agree only for times  $\tau \geq 1$ .

For an initial inverse distribution of the form

$$f(x, 0) = C \exp(-p(x - x_m)^2), \quad p \gg 1 \quad (2.2)$$

the classical treatment also adequately describes the relaxation of the distribution function in energy regions where the excited energy levels have substantial populations. In the initial stage of the process this is  $x \simeq x_m$ . Figure 3 shows  $\varphi(x, \tau)$  in the thermal deactivation of the initial inverse distribution (2.2),  $\alpha = 40$ ,  $x_m = 0.35$ , and  $\xi_0 = 30$ .

\*For the distribution functions the comparison was performed for  $\epsilon = \epsilon_i = \hbar\omega_0 i(1 - i/2N)$ .

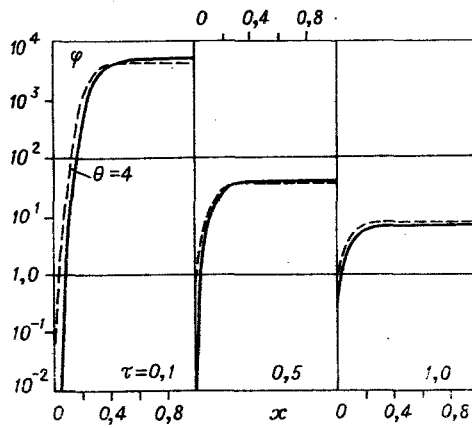


Fig. 3

Relaxation of the Mean Vibrational Energy. The relative effect of anharmonicity on the characteristic relaxation time of the mean energy of the oscillators is characterized by a quantity  $g$  [1] given by

$$g(\tau) = \tau / \ln [(\bar{\epsilon}_0 - \bar{\epsilon}_p) / (\bar{\epsilon}(\tau) - \bar{\epsilon}_p)].$$

A quantitative comparison of  $g_{cl}$  and  $g_{qu}$  showed that for systems satisfying the condition  $\theta$  or  $\theta_0 \leq 1$ , the classical result for  $g$  agrees rather closely with the quantum value:  $(g_{cl} - g_{qu})/g_{qu} < 0.1$ . For systems with a large vibrational quantum the difference between  $g_{cl}$  and  $g_{qu}$  can be more substantial: For  $\theta = 4$  it amounts to a factor of 1.5 increase in the effect of anharmonicity. For the deactivation of vibrations, however, the latter applies only for times  $\tau > 1$ ; for the initial stage ( $\tau \leq 0.5$ ) for  $\theta = 4$  and for sufficiently high  $T_0$  ( $\alpha_0 \simeq 10$ ) the values of  $g_{cl}$  and  $g_{qu}$  agree within  $\simeq 10\%$ . This is in qualitative agreement with (1.2).

The practically interesting and experimentally measurable quantity is the ratio of the characteristic times of excitation  $\tau_a$  and deactivation  $\tau_d$  of vibrations. The classical and quantum values of  $\tau_a/\tau_d$  for  $\theta$  or  $\theta_0 = 4$  differ by no more than 15-20%.

### 3. Finite-Difference Diffusion Equation when Other Than One-Quantum Transitions Are Taken into Account

Equation (1.7) for  $\xi_0 \gg 1$  is actually a finite-difference diffusion equation without restrictions on the value of  $\theta$ ; it is equivalent to the system of quantum equations (1.5) for  $P_{ik} = 0$  if  $n = |i - k| > 1$ .

This equation corresponds to taking account of only the term with  $n = 1$  in the coefficient  $B$ ; from the direct analogy of  $r_{ik}$  with  $r_n$  and  $F_{ik}$  with  $F_n$  [cf. (1.6) with the terms of the sum in (1.3)], it can be seen that the successive terms correspond to the contribution of multiquantum transitions to the coefficient  $B$ . These terms are smaller than the first, but taking them into account for interactions which are not adiabatic or only weakly so ( $\xi_0 \leq 5$ ) has an appreciable effect on the relaxation of the distribution function of highly excited oscillators. On the other hand, under certain assumptions an equation can be derived which is similar to (1.7) and takes account of multiquantum transitions. We reduce (1.5) to the form

$$f_i^0 \frac{d\varphi_i}{dt} = \sum_{n=1}^{N-i} P_{i+n,i} \omega_{i+n,i}^2 \frac{f_{i+n}^0}{\omega_{i+n,i}} \frac{\Delta_{i+n,i} \Psi}{\omega_{i+n,i}} - \sum_{n=1}^i P_{i,i-n} \omega_{i,i-n}^2 \frac{f_i^0}{\omega_{i,i-n}} \frac{\Delta_{i,i-n} \Psi}{\omega_{i,i-n}}, \quad (3.1)$$

$$\Delta_{sp} = \varphi_s - \varphi_p, \quad n = |i - k|,$$

by using the assumptions

$$n \ll N, \quad \omega_{i+n,i} \simeq n\omega_{i+1,i} \quad (3.2)$$

$$\frac{f_{i+n}^0}{\hbar\omega_{i+n,i}} \frac{\Delta_{i+n,i} \Psi}{\hbar\omega_{i+n,i}} \simeq \frac{f_{i+1}^0}{\hbar\omega_{i+1,i}} \frac{\Delta_{i+1,i} \Psi}{\hbar\omega_{i+1,i}} \quad (3.3)$$

$$\frac{f_i^0}{\hbar\omega_{i,i-n}} \frac{\Delta_{i,i-n} \Psi}{\hbar\omega_{i,i-n}} \simeq \frac{f_i^0}{\hbar\omega_{i,i-1}} \frac{\Delta_{i,i-1} \Psi}{\hbar\omega_{i,i-1}}$$

By using (3.3), Eq. (3.1) can be transformed into an equation of the (1.7) type, in which Eq. (1.8) for the diffusion coefficient is replaced by

$$B(\varepsilon_i) \cong (\hbar\omega_{i,i-1})^2 \sum_n n^2 P_{i,i-n}. \quad (3.4)$$

When (3.4) is used, Eq. (1.7) goes over into (1.3) in the limit  $\theta \ll 1$ . For any values of  $\theta$ , Eq. (1.7) is a finite-difference diffusion equation with  $B$  given by (3.4). The accuracy with which this equation takes account of multiquantum transitions depends on the value of  $\theta$ , and calculations show that for (1.7) to be applicable with  $B$  given by (3.4), the restrictions (3.2) must be supplemented by the condition  $\theta \leq 1$ .

Equation (1.7) with  $B$  given by (3.4) agrees formally with (1.5) for  $k = i \pm 1$  if the probability of one-quantum transitions is taken as the effective value

$$(P_{i,i-1})_{\text{eff}} = \sum_n n^2 P_{i,i-n}, \quad (3.5)$$

permitting multiquantum transitions to be taken into account approximately in the one-quantum calculational scheme.\*

Later we shall compare the solution of (1.5) with that of (1.7) combined with (3.4) [or the solution of (1.5) and that of (1.5) combined with (3.5)] and estimate the effect of multiquantum transitions for various values of  $\xi_0$  following from the exact solution of Eqs. (1.5).

The ratio of the distribution function for the deactivation of distribution (2.1) calculated by taking account of multiquantum transitions ( $f_{n \geq 1}$ ) and the distribution function calculated by assuming only one-quantum transitions ( $f_{n=1}$ ) ( $\alpha_0 = 7$ ,  $\alpha = 40$ ,  $N = 80$ , and  $\xi_0 = 2$ ) is denoted by  $\Phi(x, \tau)$  and plotted in Fig. 4. The solid curves were calculated by Eqs. (1.5) and the open curves by Eqs. (1.7) combined with (3.4). For  $\theta = 1$  the solution which takes account of the effect of multiquantum transitions by the approximate model — (1.7) combined with (3.4) or (1.5) with  $|k - i| = 1$  combined with (3.5) — is in good agreement with the corresponding exact solution of Eqs. (1.5) for  $|k - i| \geq 1$ . A similar conclusion holds for  $\xi_0 = 0$  and 4; the corresponding graphs are omitted.

A comparison of the exact and approximate methods of taking account of the effect of multiquantum transitions for  $\xi_0 \leq 1$  and  $\theta \leq 1$  in calculating the relaxation of an initial Boltzmann distribution (cf. Fig. 4) shows that the results can be transferred to the relaxation of an initial inverse distribution of the type (2.2). It should be noted here that the results of this comparison are only weakly dependent on the characteristic width of the inverse distribution  $\delta = 1/\sqrt{2p}$  in the range  $0.025 \leq \delta \leq 0.15$  investigated. Figure 5 shows  $\Psi_i(\tau) = f(x_i, \tau)/f(x_m, \tau)$  for  $\xi_0 = 2$  and  $\theta = 1$  for the deactivation of distribution (2.2) with  $x_m = 0.506$  ( $m = 24$ ),  $\alpha = 40$ , and various values of  $\delta$ : 1)  $\delta = 0.15$ ,  $p = 22.2$ ; 2)  $\delta = 0.1$ ,  $p = 50$ ; 3)  $\delta = 0.5 \cdot 10^{-1}$ ,  $p = 200$ ; 4)  $\delta = 0.25 \cdot 10^{-1}$ ,  $p = 800$ . These values characterize the change of the relative population with time for three fixed values of  $x_i$ :  $x_i < x_m$ ,  $x_i = x_m$ ,  $x_i > x_m$  ( $16 \leq i \leq 32$ ); a)  $x_i = 0.358$ ,  $i = 16$ ; b)  $x_i = x_m = 0.506$ ,  $i = m = 24$ ; c)  $x_i = 0.635$ ,  $i = 32$ . In this energy range the effect of multiquantum transitions is relatively small (cf. Fig. 4), and the diffusion model — (1.7) combined with (3.4) (dashed-dot curves) — correctly takes this effect into account. The solid curves correspond to the exact calculation and the dashed curves to the one-quantum calculation. Figure 5 also illustrates the dependence of the kinetics of the deactivation of the inverse distribution (2.2) on its width: For large  $\delta$

\*The method of approximating the effect of multiquantum transitions in the one-quantum calculational scheme by replacing  $P_{i,i-1}$  by  $(P_{i,i-1})_{\text{eff}}$  was used also in [5] to treat the distribution of atoms over excited states. Problems of the diffusion description of the kinetics of a low-temperature plasma have been discussed in many papers (cf. L. M. Biberman et al., "The theory of a nonequilibrium low-temperature plasma," in: The MHD Method of Obtaining Electrical Energy [in Russian], Énergiya, Moscow (1968)).

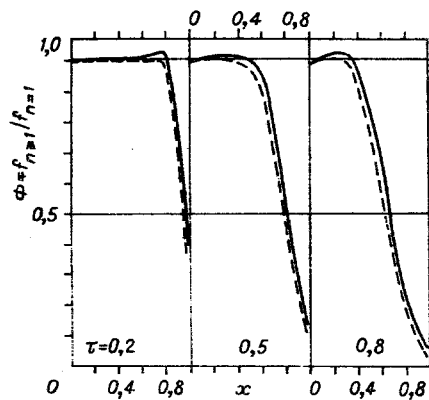


Fig. 4

the distribution is compressed and, consequently, the peak is increased, while for small  $\delta$  the peak is simply eroded.

We note that for  $\xi_0 \leq 1$ , quite a different picture is observed in a comparison of  $\phi(x, \tau)$  and  $\Psi_i(\tau)$  found from the exact [system (1.5)] and approximate [Eq. (1.7) combined with (3.4)] calculations if  $\theta = 4$  ( $\alpha = 40$  and  $N = 20$ ). In this case ( $\theta = 4$ ) the effect of multi-quantum transitions is taken into account by the diffusion model [(1.7) combined with (3.4)] approximately correctly only for highly excited states of the oscillators ( $x_i \geq 0.7$ ); in the rest of the range of excitation energies the values of  $(f_{n \geq 1} - f_{n=1})$  obtained in the exact and approximate calculations have different signs.

Figure 6 illustrates the effect of multi-quantum transitions on the relaxation of the distribution function in the deactivation process for  $\theta = 1$ ,  $N = 80$ ,  $\alpha_0 = 7$ , and  $\alpha = 40$  for various values of the adiabaticity parameter  $\xi_0$  calculated with the diffusion equation (1.7) combined with (3.4). The figure shows  $\Phi_i(\tau)$  found from a numerical solution of system (1.5) for  $k = i \pm 1$  with the probabilities (3.5), or (1.7) combined with (3.4), which is equivalent. Calculations show that the corresponding quantity  $\phi(x, \tau)$  obtained in the classical approximation, i.e., the ratio of  $f(x, \tau)$  calculated with  $B = \sum_n B_n$  to  $f(x, \tau)$  calculated with  $B = B_1$ , practically agrees with the results shown in Fig. 6.

It can be seen from Fig. 6 that taking account of multi-quantum transitions leads to a decrease in  $f_i(\tau)$  (acceleration of the deactivation process) for high excitation energies. As might be expected, the overall effect of multi-quantum transitions increases with a decrease in  $\xi_0$ , and the energy range of this effect is broadened. But the maximum effect of multi-quantum transitions for small  $\xi_0$  (up to several orders of magnitude for  $f_i$  at the upper levels) is observed for  $\tau \geq 1$ , i.e., at times for which the populations of excited vibrational states are small. As a result, the transitions  $i \rightarrow i \pm n$  ( $n > 1$ ) have little effect on the relaxation of the average energy. It should be noted that the estimate of the effect of multi-quantum transitions given above is valid within the framework of the calculational model, i.e., first-order perturbation theory calculation of the interaction. It is known that such a calculation gives somewhat too low values of the multi-quantum transition probabilities, and, therefore, our results are somewhat of an underestimate.

The physical parameter determining the vibrational kinetics is the adiabaticity parameter  $\xi_0$ , and the conditions for the applicability of the diffusion description depend on the parameter  $\theta$ . For real systems in the range  $\theta \leq 1$  the nature of the interaction can vary from adiabatic ( $\xi_0 \gg 1$ ) to nonadiabatic ( $\xi_0 \ll 1$ ).

As a result of the calculations performed we note that to estimate the applicability of the diffusion description of the vibrational kinetics of anharmonic oscillators it is necessary to replace the condition "much less than unity" in (1.1) by "less than and of the order of unity." In an adiabatic interaction ( $\xi_0 > 5$ ) the results of the classical calculation for the relative values of the distribution function with respect to the value for harmonic oscillators for times  $t < \tau_1$  and to the equilibrium value for  $t > \tau_1$  can be carried over to quantum systems practically without restrictions on the value of  $\hbar\omega_0/kT$ . The transfer of the results of the classical calculation of the kinetics to quantum systems must be performed in the time scale of  $\tau_1$ ,  $(\tau_1)_{cl} \neq (\tau_1)_{qu}$ ; the energy  $\epsilon_i$  is measured from the zero level. For  $\xi_0 \leq 5$

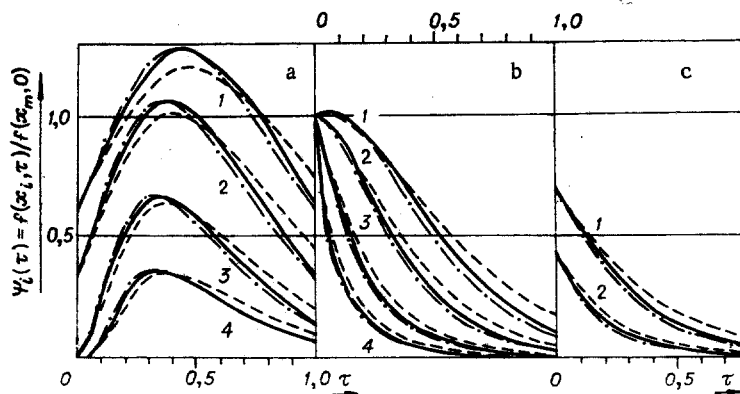


Fig. 5

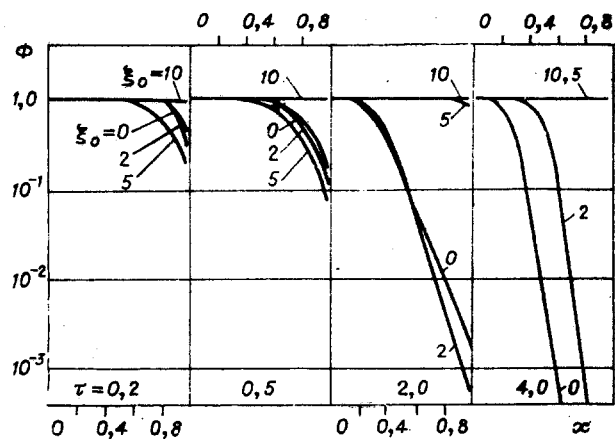


Fig. 6

the effect of multiquantum transitions can be taken into account with adequate accuracy in the diffusion calculation over the whole range of  $\epsilon$  if  $\hbar\omega_0/kT \leq 1$ .

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