DIFFUSION EQUATION IN THE THEORY OF VIBRATIONAL RELAXATION OF DIATOMIC MOLECULES

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A kinetic equation is obtained for the distribution function of anharmonic oscillators with respect to the vibrational energy; it enables one in the diffusion approximation to describe the vibrational relaxation of diatomic molecules in a medium of inert gas when there is a weak interaction between the oscillators and a thermal bath. The main difference from the equation for harmonic oscillators is in the appearance in the diffusion coefficient of an adiabaticity function that characterizes the variation of the adiabaticity factor because of the anharmonicity of the vibrations. It follows from the form of this function that the greatest difference between the relaxation of anharmonic and harmonic oscillators is to be expected in the case of adiabatic interaction of oscillators with particles of the inert gas.

For the description of vibrational kinetics in systems with the excitation of fairly high vibrational levels, the diffusion approximation is very convenient, for it enables one to use instead of a large number of balance equations for the individual vibrational levels a kinetic equation of the type of the Fokker–Planck diffusion equation for the distribution function of the molecules with respect to the vibrational energy.

Such an equation is well known in the case of approximation of a molecule by a harmonic oscillator, but with increasing degree of excitation this approximation becomes too crude.

For anharmonic oscillators, the diffusion equation is in practice known only in the case of a nonadiabatic interaction (see [1]). In [2] this equation is given for a narrow range of energies near the dissociation energy, which is of no interest for the relaxation problem. In [3] a general method of obtaining an equation for a formally introduced distribution function with respect to the vibrational levels of molecules was developed; the results of [3] are basically of interest when one is considering processes in a one-component system.

The absence of a suitable equation is due to the complexity of the calculation of the diffusion coefficient of anharmonic oscillators in the space of the vibrational energy. In the present paper this problem is solved for Morse oscillators under the well-known assumptions used to calculate the probability of excitation of the n-th vibrational level of an oscillator in the first order of perturbation theory [4, 5].

1. Statement of the Problem

We consider a system of diatomic oscillator molecules in an inert gas medium (thermal bath) with temperature T. For the description of the kinetics of the process we use the distribution function $f(\varepsilon, t)$ with respect to the vibrational energy ε. This is justified either if the relaxation affects an appreciable number of levels $n \gg 1$ or the temperature T is sufficiently high $(h\nu_0/kT) < 1$, so that $\exp(-h\nu_0/kT) \approx 1 - h\nu_0/kT$ (ν_0 is the ground frequency of the vibrations of the oscillator). A diffusion equation of the Fokker–Planck type is used for $f(\varepsilon, t)$ under the assumption that there is equilibrium with respect to the rotational (and translational) degrees of freedom of the molecules; this equation has the form [6]

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial \varepsilon}\left\{Bf^\circ\left(\frac{\partial f}{\partial \varepsilon} - f\frac{\partial \ln f^\circ}{\partial \varepsilon}\right)\right\} \tag{1.1}$$

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$$B = \langle (\Delta\varepsilon)^2 \rangle / 2\tau_0 \tag{1.2}$$

Here $f^0(\varepsilon)$ is the equilibrium distribution function at temperature T; $\langle(\Delta\varepsilon)^2\rangle$ is the square of the change in the energy of the oscillator as a result of a collision averaged over all collisions; τ_0 is the mean free time of the oscillators in the gas.

The use of the diffusion approximation presupposes a weak interaction of the oscillators with the particles of the thermal bath: $\Delta\varepsilon \sim \sqrt{2\tau_0 B} \ll \varepsilon^*$, where ε^* is the region of appreciable variation of $f(\varepsilon, t)$ in the considered kinetic process.

The problem is to calculate the diffusion coefficient B. In general form for a three-dimensional collision and an arbitrary intermolecular potential such problems are very difficult to solve; in the best case (see [3]) the result can be reduced to a multiple integral, and to estimate this one must make severe simplifications, which are in practice equivalent to an initial simplified treatment of the collision dynamics; in particular, in [3] such an estimate was made under conditions analogous to those used in Landau–Teller theory.

In this paper we adopt a slightly different approach to the calculation of B – we attempt to determine not the absolute value of the diffusion coefficient of anharmonic oscillators but only its dependence on the energy ε, i.e., it is sufficient to calculate B to within some semiempirical factor that does not depend on the internal state of the molecule and is similar to a coefficient of friction in phenomenological diffusion theory.

The existing calculations of the dynamics of vibration excitation enable one to assume that factors such as the steric factor, which takes into account the three-dimensionality of a collision, the influence of the long-range part of the intermolecular interaction potential, and various others change essentially the absolute value of the excitation probability and have little influence on the dependence of this quantity on the degree of excitation. Thus, it is here assumed that the dependence of B on ε is basically determined by the short-range intermolecular forces. Accordingly, B will be calculated below for the simplest case of a one-dimensional interaction of the oscillator with an atom of the thermal bath on the basis of a potential of exponential form. Then, in the diffusion equation, we preserve the dependence B (ε) that is obtained and the absolute value of B is found through the vibrational relaxation time of the harmonic oscillators, which is calculated, as is well known, under more general assumptions about the character of the interaction.

2. Determination of B as a Function of ε

The variation of the oscillator energy $\Delta\varepsilon$ ($\Delta\varepsilon \ll \varepsilon$) under the influence of a perturbing force F (t) due to a collision of the oscillator with an atom of the inert gas can be expressed in the first perturbation order in the form

$$\Delta\varepsilon = -\int_{-\infty}^{\infty} \dot{r}(t) F(t)\, dt, \qquad \dot{r} = \frac{dr}{dt} \tag{2.1}$$

where r (t) is the coordinate of the vibrational motion of the oscillator in the absence of the perturbing force.

The force F (t) in the case of interaction with a potential of the form $W(z) = W_0 \exp(-\alpha z)$ for a collision that is one-dimensional along r (see [4, 5] for more details) is

$$F(t) = {}^1/_2\, \lambda\alpha Mv^2\, \mathrm{sch}^2(\alpha vt/2) \tag{2.2}$$

Here v is the relative velocity of the atom; M is the reduced mass of the atom and oscillator; λ is a parameter that depends on the ratio of the masses of the atoms of the oscillator, and $\alpha r_e > 1$, $|\alpha(r - r_e)| < 1$.

As anharmonic oscillator we take a Morse oscillator with potential function

$$V(r) = D\,(1 - \exp(-\beta(r - r_e)))^2 \tag{2.3}$$

where D is the dissociation energy and r_e is the equilibrium distance.

The potential (2.3) enables one to obtain the exact dependence r (t). However, for r (t) we first take an approximate expression (weak anharmonicity), which especially simplifies the calculation of $\Delta\varepsilon$, and we then make the calculation more precise and consider how this approximation affects the final results for $\langle(\Delta\varepsilon)^2\rangle$.

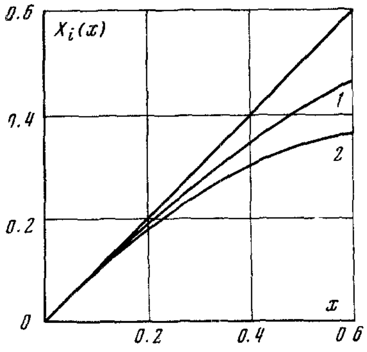

Fig. 1

We assume

$$r(t) - r_e = r_0(\varepsilon)\cos(\omega(\varepsilon)t + \varphi) \tag{2.4}$$

Here φ is the initial phase of the vibrations and $\omega(\varepsilon)$ corresponds to the cyclic frequency of vibrations of the Morse oscillator with energy ε:

$$\omega = \omega_0\sqrt{1-x}, \quad \omega_0 = \beta\sqrt{2D/\mu}, \quad x = \varepsilon/D \tag{2.5}$$

μ is the reduced mass of the oscillator, and the oscillation amplitude $r_0(\varepsilon)$ is determined from the condition

$$\langle\mu\dot{r}^2/2\rangle_\varepsilon + V(r) = \varepsilon \tag{2.6}$$

where the angular brackets denote the mean value for given ε.

From (2.6) with allowance for (2.3)

$$\langle\mu\dot{r}^2/2\rangle_\varepsilon = D\sqrt{1-x}(1-\sqrt{1-x})$$

Hence, with allowance for (2.4)

$$r_0(\varepsilon) = \frac{1}{\beta}\left\{\frac{2(1-\sqrt{1-x})}{\sqrt{1-x}}\right\}^{1/2} \tag{2.7}$$

In the zeroth approximation for $x \ll 1$, Eq. (2.4) with (2.5) and (2.7) describes a harmonic vibration with constant frequency ω_0.

With allowance for (2.3) and (2.4), we obtain from (2.1)

$$\Delta\varepsilon = 2M\pi\omega^2 r_0\lambda\,(\alpha\,\mathrm{sh}\,(\omega\pi/\alpha v))^{-1}\sin\varphi \tag{2.8}$$

Averaging now $(\Delta\varepsilon)^2$ with allowance for (2.8) over all values of φ and the Maxwellian distribution for the velocities of the atoms, which for a one-dimensional flux of particles has here the form

$$F_0(v) = (M/kT)\,v\exp(-Mv^2/2kT)$$

we obtain

$$\langle(\Delta\varepsilon^2)\rangle = 4\,kT\lambda^2\omega^2 r_0^2\,M\Phi(\xi) \tag{2.9}$$

$$\Phi(z) = z^2\int_0^\infty \exp(-y)\,\mathrm{csch}^2\left(\frac{z}{\sqrt{y}}\right)dy \tag{2.10}$$

$$\xi = \frac{\omega\pi}{\alpha}\sqrt{\frac{M}{2kT}} = \xi_0\sqrt{1-x}, \quad \xi_0 = \frac{\omega_0\pi}{\alpha}\sqrt{\frac{M}{2kT}} \tag{2.11}$$

Taking into account (2.5), (2.7), (2.9)-(2.11), for the diffusion coefficient $B = B_1$ we obtain in this approximation

$$B_1 = 8\frac{kTD}{\tau_0}\frac{M}{\mu}\lambda^2\sqrt{1-x}(1-\sqrt{1-x})\,\Phi(\xi) \tag{2.12}$$

We can expect that in the framework of the assumption of a weak interaction in a more general treatment of the collision dynamics (allowance for three-dimensionality, forces of attraction in the potential of the intermolecular interaction, etc.) the dependence of B on ε (or x) will not be strongly changed from (2.12). Accordingly,

$$B = b2\sqrt{1-x}(1-\sqrt{1-x})\,\Phi(\xi_0\sqrt{1-x}) \equiv bX_1(x)\,\Phi(\xi) \tag{2.13}$$

where b does not depend on x.

We now consider how the dependence of B on x changes if the exact value r(t) instead of (2.4) is used to calculate $\Delta\varepsilon$.

For the Morse oscillator, r(t) has the form

$$r - r_e = \beta^{-1}\ln[(1+\sqrt{x}\sin(\omega t+\varphi))/(1-x)] \tag{2.14}$$

and accordingly

$$\dot{r}=\frac{\omega}{\beta}\sqrt{x}\cos(\omega t+\varphi)\sum_{k=1}^{\infty}(-1)^{k-1}\left(\sqrt{x}\sin(\omega t+\varphi)\right)^{k-1},\quad x<1 \tag{2.15}$$

Retaining a few terms in the expansion (2.15) and making transformations, we obtain

$$\begin{aligned}\dot{r}(t)=\omega\sqrt{x}\,\{&(1+{}^1/_4x+{}^1/_8x^2+{}^5/_{64}x^3+\ldots)\cos(\omega t+\varphi)-{}^1/_2\sqrt{x}\,(1+{}^1/_2x+{}^3/_{16}x^2+\ldots)\sin 2(\omega t+\varphi)-\\ &-{}^1/_4x\,(1+{}^3/_4x+\ldots)\cos 3(\omega t+\varphi)+{}^1/_8x\sqrt{x}\sin 4(\omega t+\varphi)+{}^1/_{16}x^2\cos 5(\omega t+\varphi)+\ldots\}\end{aligned} \tag{2.16}$$

After integration of (2.1) with allowance for (2.2) and (2.16) and subsequent averaging of the value obtained for $(\Delta\varepsilon)^2$ with respect to φ and then with respect to v, we obtain for the dependence of B on x

$$\begin{aligned}B\cong b\,\{&x\,(1-{}^1/_2x-{}^3/_8x^2-{}^3/_{32}x^3)\,\Phi(\xi)+{}^1/_4x^2\,(1-{}^1/_8x^2)\,\Phi(2\xi)+\\ &+{}^1/_{16}x^3\,(1+{}^1/_2x)\,\Phi(3\xi)+{}^1/_{64}x^4\Phi(4\xi)+O(x^5,\Phi(5\xi))\}\equiv b\sum_n\alpha_n(x)\,\Phi(n\xi)\end{aligned} \tag{2.17}$$

where Φ (z) and ξ are determined by (2.10) and (2.11).

It can be seen from (2.17) that allowance for the exact expression for r (t) has led to the appearance in the diffusion coefficient of terms with Φ (nξ), n > 1, which in the language of quantum mechanics corresponds to the manifestation of multiquantum transitions of the anharmonic oscillator.

For a quantitative comparison of (2.17) and (2.13) we note that Φ (z) ≪ 1 when z ≫1 and Φ (z) ≈ 1 when z ≪1, so that

$$B\cong b\sum_n\alpha_n(x)\equiv bX_3(x),\quad n\xi\ll 1 \tag{2.18}$$

$$B\cong b\,\alpha_1(x)\,\Phi(\xi)=bX_2(x)\,\Phi(\xi),\ \xi\gg 1 \tag{2.19}$$

The comparison shows that when nξ ≪ 1 Eq. (2.13) is identical with (2.17), i.e., $X_3 \approx X_1$ [to within the terms taken into account in (2.17)] and that X_1 (x) $\gtrsim$ X_2 (x) when ξ ≫1; for intermediate values of ξ, the dependence of B on x is between (2.19) and (2.13). To elucidate this, Fig. 1 shows the dependences X_1 (x) and X_2 (x) (curves 1 and 2); the straight line corresponds to a harmonic oscillator for which

$$B=bx\Phi(\xi_0) \tag{2.20}$$

What we have said illustrates the degree of approximation of weak anharmonicity [(2.4) with (2.5) and (2.7)] in the calculation of $\langle(\Delta\varepsilon)^2\rangle$. This approximation is fully justified in the description of vibrational relaxation in the region of the excitation energies usually realized (x $\lesssim$ 1/3).

3. Diffusion Equation

The kinetic equation (1.1) for f (ε, t) with allowance for (2.13) can be written as

$$a\frac{\partial f}{\partial t}=b_1\Phi(\xi_0)\frac{\partial}{\partial x}\left\{2\sqrt{1-x}\,(1-\sqrt{1-x})\,\frac{\Phi(\xi)}{\Phi(\xi_0)}\left(\frac{\partial f}{\partial x}-f\frac{\partial\ln f^{\circ}}{\partial x}\right)\right\},\quad b_1=b\,(kTD)^{-1} \tag{3.1}$$

We now remember that for harmonic oscillators with allowance for (2.20) the equation has the form

$$a\frac{\partial f}{\partial t}=b_1\Phi(\xi_0)\frac{\partial}{\partial x}\left\{x\left(\frac{\partial f}{\partial x}+af\right)\right\},\quad a=\frac{D}{kT} \tag{3.2}$$

Eq. (3.1) goes over into (3.2) in the limit x ≪ 1.

The solution of (3.2) is well known; multiplying (3.2) by x and integrating the result with respect to dx, we obtain the usual relaxation equation for the average energy, from which it follows that $b_1\Phi$ (ξ_0) is uniquely related to the relaxation time τ_1 [$b_1\Phi(\xi_0)=(\tau_1)^{-1}$].

Therefore, the required diffusion equation is

$$\begin{gathered}a\frac{\partial f}{\partial\tau}=\frac{\partial}{\partial x}\left\{2\sqrt{1-x}\,(1-\sqrt{1-x})\,F(x,\xi_0)\left(\frac{\partial f}{\partial x}-f\frac{\partial\ln f^{\circ}}{\partial x}\right)\right\}\\ F(x,\ \xi_0)=\Phi(\xi(x))\,/\,\Phi(\xi_0),\quad \tau=t\,/\,\tau_1\end{gathered} \tag{3.3}$$

where τ_1 is the vibrational relaxation time of the harmonic oscillators.

Let us consider in more detail the quantities in (3.3).

The parameter $\xi(x)$ has a simple physical meaning; it is the adiabaticity parameter that characterizes the ratio of the interaction time to the period of the oscillator vibration with energy ε.

The adiabaticity factor, $\Phi(\xi)$, here determines the dependence of $\langle(\Delta\varepsilon)^2\rangle$ on the adiabaticity parameter.

Finally, the function $F(x, \xi_0)$, which may be called the adiabaticity function, characterizes the relative variation of the adiabaticity factor due to the anharmonicity of the vibrations.

To particularize F, one must calculate the integral (2.10). The calculation simplifies in two limiting cases: $z \ll 1$ and $z \gg 1$. For a nonadiabatic interaction, $\xi \ll 1$, we have $\Phi(\xi) = 1$; in the opposite case $\xi \gg 1$ of an adiabatic interaction the result of the calculation gives the well-known Landau–Teller dependence:

$$\Phi(\xi) \cong 8\sqrt{{}^{1}/_{3}\pi}\,\xi^{7/6}\exp(-3\xi^{2/3}) \tag{3.4}$$

For intermediate values of ξ one must calculate $\Phi(\xi)$ numerically and the result for $0 \leq \xi \leq 20$ (with relative error ±20%) is given in [2] and can be represented in the form

$$\Phi(\xi) \approx {}^{1}/_{2}\,[3 - \exp(-{}^{2}/_{3}\,\xi)]\exp(-{}^{2}/_{3}\,\xi) \tag{3.5}$$

Accordingly, $F = 1$ for $\xi \ll 1$ and (3.3) goes over into an equation that describes vibrational relaxation in the case of a nonadiabatic interaction; the solution of this equation was investigated in [1]. In this case, (3.3) is also identical with the diffusion equation obtained for Morse oscillators [7] in the framework of the phenomenological diffusion theory of Kramers, which assumes that the coefficient of friction is independent of the vibrational energy. Here, the role of the coefficient of friction is played by $1/\tau_1$.

In the more common case $\xi_0 \gg 1$, the vibrational relaxation in the region of low energies can be described by writing Eq. (3.3) approximately with allowance for (3.4) in the form

$$a\,\frac{\partial f}{\partial \tau} \cong \frac{\partial}{\partial x}\left\{x\exp(\xi_0{}^{2/3}x)\left(\frac{\partial f}{\partial x} + af\right)\right\} \tag{3.6}$$

It follows from Eqs. (3.3), (3.6), and (3.2) that the difference between the relaxation of the distribution function of anharmonic and harmonic oscillators depends on ξ_0. When $\xi_0 \ll 1$, it is due to the difference in the diffusion coefficient between $2(1-\sqrt{1-x})$ and x and is manifested basically when $x \sim 1$. When $\xi_0 \gg 1$, the difference is characterized by the strongest dependence on x with the form $\exp(\xi_0^{2/3}x)$. Therefore, in the case of an adiabatic interaction, the relaxation of the distribution function of anharmonic oscillators may be very different from the relaxation of harmonic oscillators in the region of low energies (even for $x \ll 1$); in the same case of interaction one will observe the greatest difference between the relaxation time of the mean energy and τ_1 and between the form of the relaxation equation for the energy and the ordinary exponential form.

It is of interest to make a detailed investigation of the kinetics of the process of deactivation (and excitation) of vibrations as a function of the parameter ξ_0 by either the numerical or approximate analytic solution of Eq. (3.3) and also the equation that is obtained when instead of (2.13) one uses the more general dependence (2.17) [in the latter the function $F_n(x, \xi_0) = \Phi(n\xi)/\Phi(n\xi_0)$ appears as well as $F(x, \xi_0)$]. It is important that to determine the influence of anharmonicity on the kinetics of the process it is not necessary to particularize τ_1. It is helpful to remember that τ_1 can be expressed in terms of the probability of excitation of the first vibrational level of a harmonic oscillator, whose value can be determined experimentally (or computationally).

Finally we note that the condition of weak interaction, on which the diffusion approximation is based, is satisfied better, the more adiabatic is the collision, i.e., the larger is ξ_0, and for any interaction it presupposes $\tau_1 \gg \tau_0$.

LITERATURE CITED

1. M. H. Safaryan and N. M. Pruchkina, "Vibrational relaxation of anharmonic oscillators," Teor. Eksp. Khim., 6, No. 3 (1970);
2. J. Keck and G. Carrier, "Diffusion theory of nonequilibrium dissociation and recombination," J. Chem. Phys. 43, No. 7 (1965).
3. C. A. Brau, "Classical theory of vibrational relaxation of anharmonic oscillators," Physica (The Hague), 58, No. 4 (1972).

4. E. V. Stupochenko, S. A. Losev and A. I. Osipov, Relaxation Processes in Shock Waves [in Russian], Nauka, Moscow (1965).
5. E. E. Nikitin, Theory of Elementary Atomic-Molecular Processes in Gases, Khimiya, Moscow (1970).
6. M. H. Safaryan and E. V. Stupochenko, "Vibrational relaxation of diatomic molecules in a light inert gas," Prikl. Mekh. i Tekh. Fiz., No. 4 (1964).
7. T. A. Bak and K. Andersen, "Dissociation of diatomic molecules considered as diffusion in phase space," Danske videnskabernes Selskab., Mat.-fys. Medd., 33, No. 7 (1961).