

The description of relaxation by the methods of classical statistics and mechanics has a number of advantages, the chief one of which is obviously the opportunity of using in place of a large number of balance equations for individual levels a single transport equation for a distribution function over vibrational energy and, in a number of cases, the additional opportunity for more general and clearer consideration of the various factors characterizing intra- and intermolecular interactions. A version of the classical theory for vibrational relaxation during weak interaction of molecules with a gas is diffusion theory in which a Fokker-Planck diffusion equation serves as the transport equation. In particular, a detailed study of the influence of anharmonicity at various values of the adiabaticity parameter ξ_0 on the kinetic characteristics of the process was carried out [2] within the limits of this theory on the basis of a solution of the diffusion equation from [1]; earlier [3], vibrational relaxation in a light inert-gas medium was considered in the diffusion approximation (for harmonic and anharmonic oscillators) which corresponds to relaxation for nonadiabatic interaction in a uniform temperature field ($\xi_0 \rightarrow 0$) as shown in [1]. The possibility of describing vibrational kinetics within the framework of diffusion theory involves two basic problems: 1) the possibility of approximating the transport equation for classical oscillators with a Fokker-Planck equation, and 2) the possibility of describing the relaxation of quantum oscillators by classical methods or the correspondence of classical and quantum theory of relaxation for weak interaction of molecules with a medium. The first of these problems is considered here.

§1. General Form of Conditions

According to [4], the linear integrodifferential equation which is taken as the starting point in the theory for relaxation of molecules in a medium consisting of particles in a uniform temperature field leads to a differential equation of second order in divergent form when boundary effects are neglected:

$$\partial f / \partial t = -\text{div } j; \quad (1.1)$$

$$-j = \frac{1}{2} B_{2n} f^0 \frac{\partial \varphi}{\partial \varepsilon} + \sum_{n=2} \left\{ \frac{1}{(2n)!} B_{2n} f^0 \frac{\partial^{2n-1} \varphi}{\partial \varepsilon^{2n-1}} + \sum_{m=1}^{n-1} D_{n,2m} \times \right. \\ \left. \times \left(\frac{d^{2m-1}}{d\varepsilon^{2m-1}} (B_{2n} f^0) \frac{\partial^{2n-2m} \varphi}{\partial \varepsilon^{2n-2m}} - \frac{d^{2m}}{d\varepsilon^{2m}} (B_{2n} f^0) \frac{\partial^{2n-2m-1} \varphi}{\partial \varepsilon^{2n-2m-1}} \right) \right\} \equiv \sum_{n=1} j_n, \quad (1.2)$$

where $f(\varepsilon, t)$ is the distribution function over vibrational energy ε ; $f^0(\varepsilon)$ is its equilibrium value when $t \rightarrow \infty$; $\varphi = f/f^0$; B_{2n} is a conversion moment of second order, for which we assume here

$$B_{2n} = \frac{\langle (\Delta \varepsilon)^{2n} \rangle}{\tau} \cong \frac{\langle (\Delta \varepsilon)^{2n} \rangle}{\tau_0}, \quad (1.3)$$

$\Delta \varepsilon$ is the change in ε per collision; the angle brackets denote averaging over all collision parameters; τ_0 is the mean free time of the molecules; $D_{n,2m}$ are certain coefficients [4] of which we use $D_{2,2} = 1/4!$, $D_{3,2} = 2/6!$, $D_{3,4} = -3/6!$, and $|D_{n,2n-2}/D_{n+1,2n}| \approx 10$.

If only the first term is kept in Eq. (1.2), Eq. (1.1) transforms into the Fokker-Planck equation used in [1-3]:

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial \varepsilon} j_1, \quad \frac{\partial f}{\partial t} = \frac{\partial}{\partial \varepsilon} \left\{ B f^0 \frac{\partial \varphi}{\partial \varepsilon} \right\}, \quad B = \frac{1}{2} B_2. \quad (1.4)$$

The conditions for approximation of Eq. (1.2) by a Fokker-Planck term* are discussed briefly in general terms in [4].

In this paper, we confine ourselves to the first three terms in Eq. (1.2), $j \approx j_1 + j_2 + j_3$, and we assume

$$|j_1| \gg |j_2|, \quad |j_1| \gg |j_3|. \quad (1.5)$$

for the desired approximation conditions.

In some cases of departure of the system from equilibrium conditions where the first term in Eq. (1.2) is much greater than the succeeding terms, it can be reduced to relations for the conversion moments.

In the near-equilibrium stage, $t > \tau_r$ (τ_r is the relaxation time); also for systems with insignificant deviation from equilibrium, by assuming the validity of the inequality

$$\left| \frac{\partial^l \varphi}{\partial \varepsilon^l} \frac{d^{2n-l}}{d\varepsilon^{2n-l}} (B_{2n} f^0) \right| \gg \left| \frac{\partial^{l+1} \varphi}{\partial \varepsilon^{l+1}} \frac{d^{2n-l-1}}{d\varepsilon^{2n-l-1}} (B_{2n} f^0) \right| \quad (1.6)$$

terms with $\partial^l \varphi / \partial \varepsilon^l$, $l \geq 2$, can be neglected in Eq. (1.2) and the first relation in Eqs. (1.5) is written in the form

$$B_2 f^0 \gg \frac{1}{12} \left| \frac{d^2}{d\varepsilon^2} (B_4 f^0) \right|. \quad (1.7)$$

The relation (1.6) is particularly realized for an initial Boltzmann distribution with temperature T_0 at the time t such that $|1 - T_0/T| e^{-t/\tau_r} \ll 1$.

Using $f^0 \sim e^{-\varepsilon/kT}$, Eq. (1.7) takes the form

$$\bar{B}_2 \gg \frac{1}{12} \bar{B}_4 - 2 \frac{d\bar{B}_4}{dy} + \frac{d^2 \bar{B}_4}{dy^2}; \quad \bar{B}_{2n} = \frac{B_{2n}}{(kT)^{2n}} \frac{\omega_0}{\omega(\varepsilon)}, \quad y = \frac{\varepsilon}{kT}, \quad (1.8)$$

where $\omega(\varepsilon)$ is the vibrational frequency of a molecular oscillator having an energy ε ; T is the temperature of the uniform temperature field.

In the essentially nonequilibrium stage ($t \ll \tau_r$), relaxation of the distribution is such that one can set $\partial^l \varphi / \partial y^l \approx \partial \varphi / \partial y$ (in particular, this is satisfied for an initial Boltzmann distribution with $T_0 \gg T$) and the condition equivalent to (1.8) is written

$$\bar{B}_2 \gg \frac{1}{12} \left| \bar{B}_4 - 3 \frac{d\bar{B}_4}{dy} + \frac{d^2 \bar{B}_4}{dy^2} \right|. \quad (1.9)$$

The condition (1.9), like the condition (1.8), does not depend on the width (or properties) of the initial distribution but only on the properties of the conversion moments for a given temperature T of the uniform temperature field; this is a consequence of the fact that (1.9) was actually obtained for a rather broad distribution.

Let the initial distribution have a Gaussian shape,

$$f(\varepsilon, 0) = A \exp \left\{ -\frac{p}{(kT)^2} (\varepsilon - \varepsilon_0)^2 \right\}, \quad \int f(\varepsilon, 0) d\varepsilon = 1, \quad (1.10)$$

then the desired condition corresponds to (1.9) when $p \gg 1$ and $p|y - y_0| \ll 1$ for $t \ll \tau_r$. Additional consideration is required when $p \gg 1$ since, as is well known, the Fokker-Planck equation does not describe the initial time for relaxation of a distribution with a maximally small dispersion. Very rapid "smearing" after $t \approx t_0$, $t_0 \sim 5\tau_0$ ($B\tau_p > 1$), of the initial distribution makes it possible to use this equation from the time $t \geq t_0$ [5]. For times $t \geq t_0$, $t \ll \tau_r$ ($t_0 \ll \tau_r$), approximation conditions like (1.9) must be satisfied. Expansion of Eq. (1.2) also makes possible the evaluation of the upper value of the parameter p (or the lower value of T_0 , $T_0 \ll T$, for a Boltzmann distribution), i.e., the minimum width of the initial distribution for which the diffusion approximation is applicable also for times $0 \leq t < t_0$; several such estimates are given below.

*Note that here the term containing B_2 is understood to be the Fokker-Planck term; actually, it includes the two terms (with $\langle \Delta \rangle$ and $\langle \Delta^2 \rangle$) which appears in the usual Fokker-Planck equation.

Further definition of the conditions (1.5), (1.8), and (1.9) requires knowledge of the conversion moments B_{2n} .

§2. Calculation of the Conversion Moments B_{2n}

Calculation of the quantity $\Delta \varepsilon$ is achieved here using a model of an "oscillator with external force"; i.e., it is assumed that the change in vibrational energy of a molecule after a collision is equivalent to the change in energy of an oscillator through the action of an external force $F(t)$ arising as the result of interaction of colliding particles.

We have

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

where $r(t) = dr/dt$ and $r(t)$ is the trajectory of the vibrational motion of the oscillator; $F(t)$ is the component of the force along the axis of the molecule; $F(t)$ is assumed an even function of t in the following.

We designate ω_0 and μ as the fundamental vibrational frequency and reduced mass of the oscillator; $r_*(t) = r(t)$ in the absence of an external force; r_e is the equilibrium value of $r_*(t)$.

We first consider the case of a harmonic oscillator,

$$r_* - r_e = r_0 \sin(\omega_0 t + \varphi_0), \quad r_0 = \frac{1}{\omega_0} \sqrt{\frac{2\varepsilon}{\mu}}. \quad (2.2)$$

As is well known [6], $\dot{r}(t)$ for this model can be represented in the form

$$\dot{r}(t) = \text{Re} \left\{ e^{i\omega_0 t} \left[\int_{-\infty}^t \frac{1}{\mu} F(t) e^{i\omega_0 t} dt + \omega_0 r_0 \cos \varphi_0 + i\omega_0 r_0 \sin \varphi_0 \right] \right\}. \quad (2.3)$$

Using Eq. (2.3), we have from Eq. (2.1)

$$\Delta \varepsilon = \frac{1}{\mu} \int_{-\infty}^{\infty} F(t) e^{i\omega_0 t} dt \int_{-\infty}^t F(z) e^{-i\omega_0 z} dz + \omega_0 r_0 \cos \varphi_0 \int_{-\infty}^{\infty} F(t) e^{i\omega_0 t} dt = \frac{1}{2\mu} |F_1|^2 + \omega_0 r_0 \cos \varphi_0 F_1; \quad (2.4)$$

$$F_1 = \int_{-\infty}^{\infty} F(t) e^{i\omega_0 t} dt = \int_{-\infty}^{\infty} F(t) \cos \omega_0 t dt. \quad (2.5)$$

Equations (2.4) and (2.5) agree with values of $\Delta \varepsilon$ obtained by somewhat different means in [6] under identical conditions.

Using Eq. (2.4), we have

$$(\Delta \varepsilon)^{2n} = \sum_{s=0}^{2n} \binom{2n}{s} (\omega_0 r_0)^s \cos^s \varphi_0 \left(\frac{1}{2\mu} |F_1|^2 \right)^{2n-s} F_1^s. \quad (2.6)$$

Using Eq. (2.2) and averaging over all random values of the initial phase φ_0 of the vibrations of the oscillators and over collisions, we obtain from Eq. (2.6)

$$\bar{B}_{2n} = \sum_{s=0}^n \frac{(2n)! 2^s}{(2s)! (2n-2s)! s!} y^s \left(\frac{1}{2\mu kT} |F_1|^2 \right)^{2n-s} \quad (2.7)$$

the angle brackets here and below [as in Eq. (1.3)] denote averaging over all collision parameters but per unit time.

The quantity

$$\xi_1 = \frac{\left\langle \left(\frac{1}{2\mu kT} |F_1|^2 \right)^2 \right\rangle}{\left\langle \frac{1}{2\mu kT} |F_1|^2 \right\rangle} \ll 1 \quad (2.8)$$

is taken as a parameter which characterizes weak interaction of oscillators with a medium, and also

$$\zeta_k = \frac{\left\langle \left(\frac{1}{2\mu kT} |F_1|^2 \right)^{k+1} \right\rangle}{\left\langle \left(\frac{1}{2\mu kT} |F_1|^2 \right)^k \right\rangle}, \quad k > 1, \quad \zeta_0 = \tau \left\langle \frac{1}{2\mu kT} |F_1|^2 \right\rangle. \quad (2.9)$$

Using Eqs. (2.8) and (2.9), Eq. (2.7) can be written in the form

$$\bar{B}_{2n} = \frac{2^n (2n-1)!!}{n!} \left(\frac{\varepsilon}{kT} \right)^n \left\langle \left(\frac{1}{2\mu kT} |F_1|^2 \right)^n \right\rangle \left[1 + \sum_{k=1}^n \frac{(2n)!!n!}{(2n-2k)!!(n-k)!2k!} \times \left(\frac{kT}{2\varepsilon} \right)^k \prod_{s=0}^{k-1} \zeta_{n+s} \right], \quad (2.10)$$

so that correct to terms of the order ζ_n/y , the conversion moment of second order for harmonic oscillators is

$$\bar{B}_{2n} \cong \frac{2^n (2n-1)!!}{n!} y^n \left\langle \left(\frac{1}{2\mu kT} |F_1|^2 \right)^n \right\rangle = \frac{1}{\tau} \frac{2^n (2n-1)!!}{n!} y^n \prod_{k=0}^{n-1} \zeta_k. \quad (2.11)$$

Equation (2.11) can also be obtained if one uses in place of Eq. (2.1)

$$\Delta\varepsilon = \int_{-\infty}^{\infty} F(t) r_*(t) dt, \quad (2.12)$$

which corresponds to the expression for $\Delta\varepsilon$ used in [1] for calculating the oscillator diffusion coefficient $B = (1/2)B_2$ [7].

We next obtain B_{2n} for anharmonic oscillators; let

$$r_*(t) = r(\varepsilon, \cos(\omega t + \varphi_0)), \quad \omega = \omega(\varepsilon), \quad (2.13)$$

then using Eq. (2.13), we have under the approximation (2.12) (see [1] also)

$$(\Delta\varepsilon)^{2n} = \left[\sum_{k=1}^n k\omega F_{k\omega} r_k \sin k\varphi_0 \right]^{2n},$$

$$F_{k\omega} = \int_{-\infty}^{\infty} F(t) \cos k\omega t dt, \quad r_k = \frac{1}{\pi} \int_{-\pi}^{\pi} r_*(z) \cos kz dz, \quad z = \omega t + \varphi_0.$$

Assuming

$$r_m r_k \left\langle \frac{1}{2\mu} F_{m\omega} F_{k\omega} \right\rangle \ll r_1^2 \left\langle \frac{1}{2\mu} |F_1|^2 \right\rangle \quad (m, k > 1), \quad (2.14)$$

to terms of the order of \dagger

$$\zeta_{\omega n} = \frac{\left\langle \left(\frac{1}{2\mu kT} |F_{1\omega}|^2 \right)^{n+1} \right\rangle}{\left\langle \left(\frac{1}{2\mu kT} |F_{1\omega}|^2 \right)^n \right\rangle} \quad (\zeta_{\omega 1} \ll 1) \quad (2.15)$$

we obtain for the anharmonic oscillators

$$\bar{B}_{2n} \cong \frac{(2n-1)!!}{n!} \frac{\omega_0}{\omega} \left(\frac{\mu\omega^2 r_1^2}{kT} \right)^n \left\langle \left(\frac{1}{2\mu kT} |F_{1\omega}|^2 \right)^n \right\rangle. \quad (2.16)$$

Equation (2.16) can be obtained from Eq. (2.12) by using Eq. (2.2) if ω_0 is replaced by $\omega(\varepsilon)$ and r_0 by r_1 in Eq. (2.2). Equation (2.16) corresponds to a calculation of B_{2n} in which the anharmonicity is taken into account in the approximation (2.14) and the interaction with the medium in the approximation $y \gg \zeta_{\omega 1}$, which makes it possible to use Eq. (2.12).

§3. Condition for Applicability of Diffusion Approximation

Using Eq. (2.11), we obtain from Eq. (1.8) the desired conditions for a process (or stage of a process) with slight deviation from equilibrium

$$\zeta_1 \ll 2y \ll 8/\zeta_1. \quad (3.1)$$

Somewhat weaker conditions may be valid in place of (3.1) in a limited energy range; in particular, $\zeta_1 \ll 4y$ is sufficient when $y \geq 1/8$ and $\zeta_1 \ll 8/y$ when $y \leq 10$.

\dagger It should be kept in mind that $\zeta_{\omega k}$ and $F_{1\omega}$ transform, respectively, into ζ^k and F_1 when $\omega = \omega_0$.

We correspondingly obtain from Eq. (1.10) conditions for the essentially nonequilibrium stage of relaxation of a sufficiently broad initial distribution:

$$\zeta_1 \ll y \ll 1/\zeta_1 \quad (3.2)$$

$\zeta_1 \ll 2y$ for $y \leq 2/3$; $y \ll 8/\zeta_1$ for $4 \leq y \leq 15$; $y \ll 4/\zeta_1$ for $y \gg 1$ ($y \geq 20$).

For a comparatively narrow initial distribution, an estimate of a condition such as (3.2) can be obtained for $t \ll t_0$ by substituting the initial value of φ in Eq. (1.2); we find as a result that for a Boltzmann distribution with $T_0 \ll T$ the right-hand inequality in (3.2) should be replaced by $yT/T_0 = \varepsilon/kT_0 \ll 1/\zeta_1$ and for a distribution of the form (1.10) with $p \gg 1$ in the region $|y - y_0| \leq 1/p$, the right-hand inequality should correspondingly be replaced by $-y_0 p \ll 1/\zeta_1$, $y_0 > 1$. Consequently, the weaker the interaction ($\zeta_1 \ll 1$), the better the diffusion approximation describes relaxation of a distribution with small dispersion.

The conditions (3.1) and (3.2) follow from the first relation in Eq. (1.5). It can be shown that the second inequality in (1.5) is satisfied automatically; considering the expression for j_s in the approximation $\zeta_1 \ll 1$, $\zeta_n \sim \zeta_1$, we find $|j_2| > |j_3|$ with the exception of values of y for which the right sides of Eqs. (1.8) and (1.9) go to zero. For those values of y [$y = 2 \pm \sqrt{2}$ for Eq. (1.8) and $y = 3 \pm \sqrt{7}$ for Eq. (1.9)], instead of (3.1) and (3.2), the weaker condition $\zeta_1^2 \ll y^2 \ll 1/\zeta_1^2$ follow from $|j_1| \gg |j_3|$.

The use of the exact value of \bar{B}_{2n} from Eq. (2.10) instead of Eq. (2.11) leads to no marked change in the conditions (3.1) and (3.2) when $\zeta_1 \ll 1$ ($\zeta_n \sim \zeta_1$). This means that within the limitations of the diffusion approximation, it is sufficient to calculate the coefficient $B = (\frac{1}{2})B_2$ by means of the simple equation (2.12). It is also noteworthy that Eqs. (1.1) and (1.2), strictly speaking, are valid in the region $\varepsilon \gg |\Delta\varepsilon|$ or (on the average) $y \gg \langle \Delta/kT \rangle 1/\tau \sim \zeta_0$ so that the condition $y > \zeta_1 \geq \zeta_0$ is necessary.

The conditions above were obtained for harmonic oscillators. For anharmonic oscillators, a similar discussion using Eq. (2.16) leads, on the whole, to replacement of the parameter ζ_1 by $\zeta_{\omega_1}(\omega/\omega_0)^2 \approx \zeta_{\omega_1} (d \ln \zeta_{\omega_0} \zeta_{\omega_1} / dy \leq 1)$ in the conditions given above. There is some difference in the energy region close to the dissociation energy but this difference is not fundamental; this energy region requires special consideration and it is particularly necessary to calculate the coefficient B_{2n} with an accuracy similar to the accuracy used in the calculation of B_2 in [1]. The result will be physically distinguished from Eq. (2.16) by the consideration of multiquantum transitions.

We consider what ensures the weak interaction condition $\zeta_1 \ll 1$, $\zeta_{\omega_1} \ll 1$ during a vibrational-translational exchange. For this purpose, we use as an example similar to that used in [1] a well-known expression for $F(t)$,

$$F(t) = -\frac{1}{4} \alpha M v^2 \operatorname{sch}^2 \frac{\alpha v t}{2}, \quad (3.3)$$

where α is a parameter of exponential form for the intermolecular potential; $M = 2m\mu/(4\mu + m)$; m and v are, respectively, the mass and relative velocity of the particles in the uniform temperature field. Equation (3.3) for F assumes: 1) The change $\Delta\varepsilon$ in oscillator energy as the result of a collision has no effect on the trajectory of particles in the uniform temperature field; 2) the intermolecular interaction potential depends linearly on the vibrational coordinate $r(t)$; 3) collinear collisions make the main contribution to $\Delta\varepsilon$. The last two assumptions are not important under the approximations (2.12) and (2.14), but the first can be written in the form [compare (3.1), (3.2)]

$$\langle (\Delta\varepsilon)^2 \rangle \simeq \tau B_2 \ll (kT)^2, \text{ i.e., } y \zeta_{\omega_0} \ll 1$$

[(3.3) overestimates the value of ζ in the case of a slightly adiabatic interaction].

After averaging the quantity $(|F_1|^2)^k$ over v and using Eqs. (3.3) and (2.5), we have

$$\left\langle \left(\frac{1}{2\mu kT} |F_1|^2 \right)^k \right\rangle \simeq \frac{1}{\tau_0} \frac{M}{\mu} I_k(\xi_0), \quad \zeta_k = \frac{M}{\mu} \frac{I_{k+1}}{I_k}; \quad (3.4)$$

$$I_k(\xi_0) = \xi_0^{2k} \int_0^\infty e^{-y} \operatorname{csch}^{2k} \left(\frac{\xi_0}{\sqrt{y}} \right) dy, \quad \xi_0 = \frac{\pi \omega_0}{\alpha} \left(\frac{M}{2kT} \right)^{1/2}, \quad (3.5)$$

where ξ_0 is the adiabaticity parameter and I_k , when $k = 1$, converts into the adiabaticity factor $\Phi(\xi_0)$ [1].

The integral $I_k(\xi_0)$ was calculated in explicit form for the limiting cases $\xi_0 \ll 1$ and $\xi_0 \gg 1$. For the nonadiabatic interaction $\xi_0 \ll 1$, we obtain

$$I_k(\xi_0) \simeq k! \left(1 - \frac{\xi_0^2}{3} + \dots \right) \simeq k! \quad (3.6)$$

For the adiabatic interaction $\xi_0 \gg 1$, we obtain, by using the method of steepest descent,*

$$I_k(\xi_0) \simeq 2(2\xi_0)^{2k} (k\xi_0)^{1/3} \exp(-3(k\xi_0)^{2/3}) \quad (3.7)$$

[in practice, Eq. (3.7) provides sufficient accuracy for evaluation under the condition $4k \cdot \exp(-2(\xi_0^2/k)^{1/3}) < 1$]. When $2 \leq k\xi_0 \leq 20$, one can use the following approximation for $I_k(\xi_0)$:

$$I_k(\xi_0) \simeq \frac{3}{2} \frac{1}{k^2} (2\xi_0)^{2k-2} \exp\left(-\frac{2}{3} k\xi_0\right). \quad (3.8)$$

By replacing ω_0 by ω and ξ_0 by ξ ($\xi = \xi_0\omega/\omega_0$) in Eqs. (3.4)-(3.8), we obtain the values of $\langle (|F_{1\omega}|^2)^k \rangle$ and $\zeta_{\omega k}$ for anharmonic oscillators.

We have from Eqs. (3.4)-(3.8)

$$\zeta_1 \simeq \zeta_{\omega 1} = 2M/\mu, \quad \zeta_n \simeq \zeta_{\omega n} = (n+1)M/\mu; \quad (3.9)$$

$$\zeta_{\omega 1} \simeq 5(M/\mu)\xi^2 \exp(-1.8\xi^{2/3}), \quad (3.10)$$

$$\zeta_{\omega n} \simeq \frac{M}{\mu} (2\xi)^2 \exp\left(-2\left(\frac{\xi^2}{n}\right)^{1/3}\right), \quad \xi = \xi_0 \frac{\omega}{\omega_0} \gg 1;$$

$$\zeta_{\omega n} \simeq \frac{M}{\mu} \left(\frac{2n}{n+1}\right)^2 \xi^2 \exp\left(-\frac{2}{3} \xi\right), \quad 2 \leq n\xi \leq 20. \quad (3.11)$$

Setting $\omega = \omega_0$ and $\xi = \xi_0$ in Eqs. (3.10) and (3.11), we obtain ζ_n .

Equations (3.9)-(3.11) show that the condition for a weak interaction, $\zeta_1 < 1$, $\zeta_{\omega 1} < 1$, is satisfied if one of the following relations is realized: $\xi = \xi_0\omega/\omega_0 \gg 1$, M/μ arbitrary or $\xi_0\omega/\omega_0 \geq 2$, $M/\mu \sim 1$, $2M/\mu < 1$, $\xi_0 \geq 0$; Eqs. (3.10) and (3.11) make it possible to define conditions (1.8) and (1.9) somewhat better than Eqs. (3.1) and (3.2) do when $\varepsilon \gg 1$ but the difference is not basic.

Thus, in order to evaluate the possibility of using the classical diffusion equation (1.4), it is necessary to compare the diffusion coefficient with the conversion moment of fourth order, i.e., B_2 with B_4 . For applicability of Eq. (1.4) in the case of an oscillator excited by a force $F(t)$, it is necessary that the parameter $\zeta_{\omega 1}$ in Eq. (2.15) be small in comparison with unity; the energy region of applicability is limited by the condition $\zeta_{\omega 1} < \varepsilon/kT < 1/\zeta_{\omega 1}$. The condition for the smallness of $\zeta_{\omega 1}$ is realized if the interaction is adiabatic or the ratio between the masses of molecules and medium is the same as that for Brownian particles. Calculation of $\langle (\Delta\varepsilon)^2 \rangle$ by means of Eq. (2.12) and the applicability of Eq. (1.4) are of the same degree of approximation.

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*In Eq. (3.7) the ratio of the masses of the atomic oscillators is assumed to be unity; it is necessary to introduce the appropriate factor for a heterogeneous molecule.

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DECAY OF A PLASMA PRODUCED BY A PULSED BEAM OF ACCELERATED ELECTRONS IN
AN He-Ne MIXTURE AT HIGH PRESSURE

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Increased interest has recently been shown in the low-temperature plasma produced by the action of electron beams on dense gases. This interest is due to the possibility of investigating plasma-chemical reactions in highly nonequilibrium conditions [1] and also to the prospect of introducing new methods of pumping gas lasers: by recombination [2], charge transfer [3], the formation of complex compounds [4, 5], etc. The plasma in question is characterized by high rates of reactions involving charged and neutral particles, which largely accounts for the difficulty of investigating such a plasma experimentally. For instance, problems of determining the kind of ions predominating in the plasma, the mechanism of recombination decay, the nature of the luminescence on individual spectral transitions, etc., become nontrivial. In this paper we investigate the decay of a plasma in neon and in an He-Ne mixture at high gas pressure.

§1. Experimental method

The kinetics of recombination processes were investigated by the photoelectric method of recording the spectrum and measuring the decay of electron density in the plasma. The experimental apparatus is shown schematically in Fig. 1. A beam of fast electrons from the accelerator 1 was injected into the gas cuvette through a window sealed with titanium foil 20 μ thick. The beam-current density was 25 A/cm², the length of the current pulse at the base was $1.5 \cdot 10^{-7}$ sec, and the electron energy was 200 keV. The time for recombination decay of the plasma greatly exceeded the duration of the beam current and, hence, the electron beam, ionizing the gas in the cuvette, determined the initial density of electrons and ions (n_0).

The photoelectric system for recording of the emission spectrum consisted of an MDR-3 grating monochromator 4, an FEU-38 photomultiplier 3, and an S8-2 dual-beam recording oscilloscope 2. The resolving time of the spectrum recording channel was 25 nsec.

An electric field was applied to the plasma by connecting a capacitor bank 6, charged from a voltage supply 5, to the anode 7 of the gas cuvette. The anode was a disk 4 cm in diameter. The cathode 8 was a brass grid with 0.2×0.2 -mm² mesh. The interelectrode distance was 4.5 cm. There were two reasons for applying a voltage to the plasma: for stabilization of the electron temperature and for determination of the variation of the electron concentration with time from the current across the gap. In the absence of the field the electron temperature is determined by the balance between the processes leading to heating and to cooling of the electrons [6-8]. The electrons are cooled by elastic and inelastic collisions with gas atoms. Fast electrons can be produced by ionization of the gas by the beam electrons, deexcitation of metastables by electron impact, production of electrons in metastable-metastable collisions, and so on. In the considered conditions (electron concentration $n > 10^{14}$ cm⁻³, gas pressure ~ 1 atm) the excess of electron temperature over the gas

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