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The Callen-Welton and Kubo formulas for nonequilibrium states

Yu. L. Klimontovich

M. V. Lomonosov Moscow State University

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A self-consistent formulation of the fluctuation-dissipation theorem (FDT) is given for a macroscopic system in which the interaction of the particle can be separated into a strong and a weak part. The properties of the system considered determine not only the susceptibility tensor and the spectral densities of the internal parameters but also the spectral densities of the generalized forces conjugate to the internal parameters under consideration. As the weak interaction we consider the interaction of atoms via the fluctuating electromagnetic field in the dipole approximation. A theory of nonequilibrium fluctuations is developed. For nonequilibrium states the fluctuation-dissipation relation holds only for individual transitions and includes a dependence on the nonequilibrium distribution function. The corresponding kinetic equations, which describe, in particular, the process of relaxation to the Gibbs distribution, are found. In this case a spectral distribution in accordance with the equilibrium FDT is established. As an example, the kinetic equation for a gas whose atoms interact only via field fluctuations is obtained from the general kinetic equation. The first-moment approximation for the averaged density matrix and mean field is considered. The kinetic equation obtained can be used to describe the kinetics of equilibrium and nonequilibrium coherent states, *e.g.*, in phase transitions and super-radiance in the atoms + field system.

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1. INTRODUCTION

We recall briefly the content of the well known Callen-Welton and Kubo formulas. This is necessary for the formulation of the problem of the present paper. We consider a macroscopic system with Hamiltonian

$$\hat H=\hat H_0+\hat H_1, \quad \hat H_1=-\sum_i X_i F_i(t), \tag{1.1}$$

where $\hat H_0$ is the Hamiltonian of a macroscopic system consisting of N particles interacting arbitrarily strongly, F_i are external forces, and X_i are the corresponding internal parameters.

The Callen-Welton formula establishes a connection between the dissipative (antihermitian) part of the susceptibility tensor $\alpha_{ij}(\omega)$ and the spectral density of the fluctuations of X_i in the absence of external forces, when $\langle X_i\rangle=0$. The susceptibility tensor defines the relationship between the mean response $\langle X_i\rangle$ and the external force. In the notation of the book by Landau and Lifshitz [see Eq. (125.10) in Ref. 1], this formula has the form

$$(X_iX_j)_\omega=\frac{i\hbar}{2}(\alpha_{ij}^*-\alpha_{ji})\,\mathrm{cth}\frac{\hbar\omega}{2kT}. \tag{1.2}$$

The relationship expressed by this formula is called the fluctuation-dissipation theorem (FDT). The inverse relationship is called the Kubo formula.[1-4]

The formula (1.2) is established by comparing the expressions for the susceptibility tensor and the spectral density of the fluctuations of X_i. The first of these is obtained by averaging formula (125.9) from Ref. 1 over the distribution f_n. The antihermitian part of this tensor has the form

$$i(\alpha_{ij}^*(\omega)-\alpha_{ji}(\omega))=\frac{2\pi}{\hbar}\sum_{nm}(X_i)_{nm}(X_j)_{mn}\delta(\omega-\omega_{nm})(f_m-f_n), \quad (1.3)$$

where $(X_i)_{nm}$ is a matrix element for the system with Hamiltonian $\hat{H}_0$. The expression for the spectral density is obtained by averaging the formula (125.5) from Ref. 1. After symmetrization in the states n and m,

$$(X_iX_j)_\omega=\pi\sum_{nm}(X_i)_{nm}(X_j)_{mn}\delta(\omega-\omega_{nm})(f_m+f_n). \quad (1.4)$$

To obtain the Callen-Welton formula from (1.3) and (1.4) we must use the equality

$$\delta(\omega-\omega_{nm})\frac{f_m+f_n}{f_m-f_n}=\delta(\omega-\omega_{nm})\,\mathrm{cth}\frac{\hbar\omega}{2kT}, \quad (1.5)$$

which is valid when f_n is the Gibbs canonical distribution for the system with Hamiltonian $\hat{H}_0$.

In the formulas cited, only the temporal dispersion is taken into account. The generalization of these formulas to the case of spatial dispersion is well known (see, e.g., Sec. 9 in the book by Silin and Rukhadze[5] and Appendix I in the book by Levin and Rytov[6]).

The purpose of this paper is to generalize the fluctuation-dissipation relations to nonequilibrium states, when the function f_n is not a Gibbs distribution but satisfies a certain kinetic equation. The establishment of the form of this kinetic equation is one of the problems of the present work.

It will be shown in the paper that, under certain conditions, the expressions (1.3) and (1.4) also remain valid for nonequilibrium states. In this case, however, the Callen-Welton formula does not hold, since the equality (1.5) is fulfilled only for an equilibrium state. The fluctuation-dissipation relation is preserved for individual transitions $n \to m$. In fact, by comparing the expressions under the summation signs in the formulas, we obtain the relation

$$(X_iX_j)_\omega^{nm}=\frac{i\hbar}{2}(\alpha_{ij}^*-\alpha_{ji})_{nm}\frac{f_m+f_n}{f_m-f_n}. \quad (1.6)$$

This expression is also valid for an inverted population. In this case, naturally, both factors in the right-hand side change sign.

We remark that the presence of the function $\delta(\omega-\omega_{nm})$ in formulas (1.3) and (1.4) corresponds to the condition for an infinitesimally narrow resonance. In its turn, this demonstrates the presence in these formulas of an undetermined time parameter, defining the real width of the resonances. We shall denote this undetermined parameter by τ_{cor} (the correlation time). Naturally, in the generalization of the Callen-Welton formula to nonequilibrium states the value of this as-yet undetermined time parameter becomes important. This question will be discussed in Sec. 4.

The parameter τ_{cor} may also turn out to be important in the equilibrium state. Indeed, the equality (1.5) is fulfilled only in the zeroth approximation in the frequencies

$$1/\tau_{\mathrm{cor}}, \quad kT/\hbar.$$

When the resonance has a finite width this condition ceases to be fulfilled at sufficiently low temperatures, which could be, e.g., tenths of a degree.

In all the preceding formulas the matrix element $(X_i)_{nm}$ is determined by wavefunctions that are eigenfunctions of the Hamiltonian $\hat{H}_0$. It is not possible to find these eigenfunctions in the general case, and, therefore, the FDT is applied in practice to simpler systems, when it is possible to use small parameters, e.g., the plasma parameter or density parameters, in the calculations. In these cases the FDT has also been used for nonequilibrium states. The theory of fluctuations of laser radiation[7-9] and the theory of nonequilibrium fluctuations in a dilute plasma[5,10,11] can serve as examples. In both cases the distribution functions appearing in the fluctuation-dissipation relations satisfy appropriate kinetic equations for the single-particle distribution functions.

To solve the problem of the derivation of the kinetic equations for the many-particle distribution functions occurring in the formulas (1.3), (1.4), and (1.6), it is necessary to use a different interpretation of the Callen-Welton and Kubo formulas, in which the susceptibility tensor determines the response not to external forces but to internal fluctuation forces. This possibility has been discussed in the literature (cf. Secs. 124 and 125 in Ref. 1); however, it has not been developed to completion, inasmuch as the question of the nature of these random forces has remained open. Naturally, they should be determined by the structure of the actual system under consideration. Thus, before proceeding to the derivation of the kinetic equation for the many-particle distribution function f_n, it is necessary to give a self-consistent formulation of the FDT in which the properties of the system under consideration determine not only the tensor α_{ij} and the spectral density of the fluctuations of X_i but also the spectral density of the random forces F_i.

The problem of constructing the kinetic equation for the distribution function for the states of macroscopic systems has attracted the attention of many investigators for a long time. Of the recent work we note the paper by Kukharenko.[12] Unlike in the latter work, here we separate not the weak interaction with surrounding bodies but the weak interaction of the particles of the actual system under consideration. For definiteness we shall assume that the weak (in the dipole approximation) interaction via the fluctuating electromagnetic field is included in $\hat{H}_1$. Below, the system with Hamiltonian $\hat{H}_0$ will be called the basic system, while the system with the full Hamiltonian $\hat{H}_0+\hat{H}_1$ will be called the extended system.

2. FLUCTUATIONS OF THE DENSITY MATRIX

For the basic system the density matrix $f_{nm}(t)$ gives a complete statistical description. In the classical theory the corresponding quantity is the distribution function $f_N(x,t)$, satisfying the Liouville equation. The two-time distribution function $f_N(x, t; x', t')$ also satisfies this equation, since the variables x' and t' appear as parameters. Here, x is the set of coordinates and momenta of the basic system.

To determine the two-time distribution function it is necessary to solve the Liouville equation with the initial condition

$$f_N(x, t; x', t')|_{t=t'} = \delta(x-x') f_N(x, t), \quad \int f_N(x, t)\, dx = 1. \tag{2.1}$$

We introduce notation for the deviation of the two-time function from the product of the distribution functions at each of the times:

$$\langle \delta f_N \delta f_N \rangle_{x, t; x', t'} = f_N(x, t; x', t') - f_N(x, t) f_N(x', t'). \tag{2.2}$$

When the times coincide, taking (2.1) into account, from this we find

$$\langle \delta f_N \delta f_N \rangle_{x, x', t} = \delta(x-x') f_N(x, t) - f_N(x, t) f_N(x', t). \tag{2.3}$$

The usefulness of the notation introduced is revealed when we go over to the extended system, when the description by means of the function f_N (or f_{nm}) is no longer complete, since the state in this case is determined not only by the particle variables but also by the field variables, so that $f_N(x, t)$ is a random function.

Because of this, for the extended system it will be possible to interpret the expressions in the left-hand sides of the equalities (2.2) and (2.3) as, respectively, the two-time correlator and one-time correlator of the fluctuations of the distribution function. Here, the f_N in the right-hand sides of the equalities must be understood as the corresponding averaged functions. Henceforth, $\langle f_N \rangle \equiv f_N$. The symbol $\langle \cdots \rangle$ denotes averaging over the ensemble of extended systems.

We shall give the corresponding definitions for a quantum system. The equality analogous to (2.3) has the form

$$\langle \delta f_{nm}(t) \delta f^*_{n_1 m_1}(t) \rangle = \delta_{n n_1} f_{m_1 m} - f_{nm} f_{m_1 n_1}. \tag{2.4}$$

If the density matrix is nonequilibrium but diagonal this definition is simplified and, after symmetrization, takes the form

$$\langle \delta f_{nm}(t) \delta f^*_{n_1 m_1}(t) \rangle = {}^1/_2 \delta_{n n_1} \delta_{m m_1} (f_m + f_n) - \delta_{nm} \delta_{n_1 m_1} f_n f_{n_1}. \tag{2.5}$$

We shall regard this expression as the initial condition to the equation for the corresponding two-time function:

$$\left(\frac{\partial}{\partial t} + i\omega_{nm} \right) \langle \delta f_{nm}(t) \delta f_{n_1 m_1}(t') \rangle = 0. \tag{2.6}$$

Jumping ahead, we shall assume that for the extended system the relaxation time of the function $\langle f_n(t) \rangle \equiv f_n(t)$ is long compared with the characteristic times for the two-time correlator (with τ_{cor}). In the zeroth approximation with respect to these times (the "collisionless" approximation in the calculation of the fluctuations), using Eq. (2.6) we find the following expression for the spectral density of the fluctuations of the distribution function:

$$(\delta f_{nm} \delta f_{n_1 m_1})_\omega = \pi \delta(\omega - \omega_{nm}) \delta_{n n_1} \delta_{m m_1} (f_m + f_n), \quad \omega \neq 0. \tag{2.7}$$

This spectral density depends implicitly, through the distribution functions, on the time. The condition $\omega \neq 0$ allows us to omit the term with $\delta(\omega)$.

We note that the spectral density (1.4) of the fluctuations can now be represented in the form

$$(X_i X_j)_\omega = \sum_{nm} \sum_{n_1 m_1} (X_i)_{nm} (X_j^*)_{n_1 m_1} (\delta f_{nm} \delta f_{n_1 m_1})_\omega, \tag{2.8}$$

i.e., as a quantum-mechanical average with the spectral density (2.7). Naturally, the formula (2.7) is more general than the formula (1.4).

In place of Eq. (2.6) with the initial condition (2.5) we can write the corresponding Lagevin equation, which is the Liouville equation (in the classical theory) or the corresponding density-matrix equation with a random source. The intensity of the random source can be determined, e.g., by comparing the results obtained by the two methods.

We note once again that, for the basic system, the formulas (2.5) and (2.7) are exact, i.e., they give a complete description. However, for the extended system they can be regarded as the sources in the corresponding equations for the correlators or spectral densities of the fluctuations. To emphasize this circumstance, below we shall use the index "sou."

3. FLUCTUATIONS IN THE EXTENDED SYSTEM

To make the account less formal, we shall assume at once that the Hamiltonian $\hat{H}_1$ is determined by the interaction of the atoms via the electromagnetic field in the dipole approximation, i.e.,

$$\hat{H}_1 = -\int \mathbf{P}^m(\mathbf{R}, t) \mathbf{E}^m(\mathbf{R}, t)\, d\mathbf{R}. \tag{3.1}$$

Here $\mathbf{P}^m$ and $\mathbf{E}^m$ are the vectors of the polarization and intensity of the field. The superscript m indicates that these are microscopic characteristics. The matrix elements of $\hat{H}_1$ are defined by the expression

$$(H_1)_{nm} = -\int \mathbf{D}_{nm}(\mathbf{R}) E^m(\mathbf{R}, t)\, d\mathbf{R}. \tag{3.2}$$

Here we have used the notation

$$\mathbf{D}_{nm}(\mathbf{R}) = \int \Psi_n^*(x) \sum_{1 \leqslant i \leqslant N} e\mathbf{r}_i \delta(\mathbf{R} - \mathbf{R}_i) \Psi_m(x) \frac{dx}{V^{2N}}, \tag{3.3}$$

where V is the volume of the system, and $x = (r_1, \ldots, r_N, R_1, \ldots, R_N)$.

The equation for the density matrix of the extended system has the following form:

$$\left(\frac{\partial}{\partial t} + i\omega_{nm} \right) f_{nm} = -\frac{i}{\hbar} \sum_{n_1} \left((H_1)_{n n_1} f_{n_1 m} - f_{n n_1} (H_1)_{n_1 m} \right). \tag{3.4}$$

In order to separate out the relaxation process determined by the weak interaction we suppose that

$$\langle f_{nm}(t) \rangle = \delta_{nm} \langle f_n(t) \rangle = \delta_{nm} f_n, \quad \langle \mathbf{P}^m \rangle = 0, \quad \langle \mathbf{E}^m \rangle = 0. \tag{3.5}$$

A kinetic equation will be obtained for the function $f_n(t)$. Naturally, a kinetic stage of evolution also exists for the nondiagonal elements of the density matrix, but when the interaction $\hat{H}_1$ is small the contribution of the nondiagonal elements to the collision integral is small. In this approximation the dissipative matrix in the equation for the function $\langle f_{nm} \rangle$ is expressed in terms of the transition probabilities that determine the collision integral $I_n(t)$.

We shall average Eq. (3.4). Under the condition (3.5) we obtain the following equation for the distribution function $f_n(t)$:

$$\frac{\partial f_n(t)}{\partial t}=\frac{2}{\hbar}\sum_m\int \operatorname{Im}\langle\delta f_{nm}(t)\delta\mathbf{E}(\mathbf{R},t)\rangle\mathbf{D}_{nm}(\mathbf{R})\,d\mathbf{R}\equiv I_n(t). \tag{3.6}$$

We see that to calculate the collision integral it is necessary to find the correlator of the fluctuations δf_{nm} and $\delta\mathbf{E}$. The deviation of δf_{nm} from $\delta f_{nm}^{\text{sou}}$ as a consequence of the small interaction $\hat{H}_1$ is determined in the linear approximation in $\delta\mathbf{E}$ by the equation [compare with Eq. (35.1) in Ref. 10]

$$\left(\frac{\partial}{\partial t}+\Delta+i\omega_{nm}\right)(\delta f_{nm}-\delta f_{nm}^{\text{sou}})=\frac{i}{\hbar}(f_m-f_n)\int\mathbf{D}_{nm}(\mathbf{R})\delta\mathbf{E}(\mathbf{R},t)\,d\mathbf{R},\quad \Delta\to 0. \tag{3.7}$$

The Fourier components of the fluctuation of the polarization vector are related to the function δf_{nm}. Using this relationship, we obtain an equation for δP_i:

$$\delta P_i(\mathbf{R},\omega)=\int\alpha_{ij}(\mathbf{R},\mathbf{R}',\omega)\delta E_j(\mathbf{R}',\omega)\,d\mathbf{R}'+\delta P_i^{\text{sou}}(\mathbf{R},\omega). \tag{3.8}$$

The polarizability tensor and function δP_i^{sou} that appear in this are determined by the expressions

$$\alpha_{ij}(\mathbf{R},\mathbf{R}',\omega)=\sum_{nm}(D_i(\mathbf{R}))_{mn}(D_j(\mathbf{R}'))_{nm}\frac{f_n-f_m}{\hbar(\omega+i\Delta-\omega_{nm})}, \tag{3.9}$$

$$\delta\mathbf{P}^{\text{sou}}(\mathbf{R},\omega)=\sum_{nm}\mathbf{D}_{nm}(\mathbf{R})\delta f_{nm}^{\text{sou}}(\omega). \tag{3.10}$$

In the case of a homogeneous and isotropic medium the dielectric permittivity tensor ε_{ij} is expressed in terms of the functions $\varepsilon^{\parallel}$ and $\varepsilon^{\perp}$,[5,10,11] which, for the system under consideration, are determined by the expressions

$$\varepsilon^{\parallel}(\omega,\mathbf{k})=1+\frac{4\pi}{\hbar V}\sum_{nm}|\mathbf{D}_{nm}^{\parallel}(-\mathbf{k})|^2\frac{f_n-f_m}{\omega+i\Delta-\omega_{nm}}, \tag{3.11}$$

$$\varepsilon^{\perp}(\omega,\mathbf{k})=1+\frac{2\pi}{\hbar V}\sum_{nm}|\mathbf{D}_{nm}^{\perp}(-\mathbf{k})|^2\frac{f_n-f_m}{\omega+i\Delta-\omega_{nm}}. \tag{3.12}$$

Here $\mathbf{D}_{nm}^{\parallel}$ and $\mathbf{D}_{nm}^{\perp}$ are the longitudinal and transverse components (with respect to the wave vector) of the vector $\mathbf{D}_{nm}(-\mathbf{k})$.

We find the spectral density of the fluctuations $\delta\mathbf{P}^{\text{sou}}$ with the aid of the formulas (3.10) and (2.7):

$$(\delta\mathbf{P}\delta\mathbf{P})_{\omega\mathbf{k}}^{\text{sou}}=\frac{\pi}{V}\sum_{nm}|\mathbf{D}_{mn}(-\mathbf{k})|^2\delta(\omega-\omega_{nm})(f_m+f_n). \tag{3.13}$$

This expression corresponds to the formula (1.6). The superscript "sou" is justified by the fact that induced fluctuations of the polarization vector also exist in the extended system [cf. Eq. (3.8)].

In the equilibrium state, using the expressions (3.10)–(3.13) we can obtain two Callen-Welton formulas, connecting the functions

$$(\delta\mathbf{P}^{\parallel}\delta\mathbf{P}^{\parallel})_{\omega,\mathbf{k}}^{\text{sou}},\quad \operatorname{Im}\varepsilon^{\parallel}(\omega,\mathbf{k});\quad (\delta\mathbf{P}^{\perp}\delta\mathbf{P}^{\perp})_{\omega,\mathbf{k}}^{\text{sou}},\quad \operatorname{Im}\varepsilon^{\perp}(\omega,\mathbf{k}).$$

For nonequilibrium states the corresponding relations hold only for individual transitions $n\to m$.

In accordance with what has been said above, in the present self-consistent description of the fluctuations for equilibrium and nonequilibrium states we can also find expressions for the spectral densities of the fluctuations of the longitudinal and transverse fields:

$$(\delta\mathbf{E}^{\parallel}\delta\mathbf{E}^{\parallel})_{\omega,\mathbf{k}}=\frac{16\pi^3}{V}\sum_{nm}|\mathbf{D}_{nm}^{\parallel}(-\mathbf{k})|^2\frac{\delta(\omega-\omega_{nm})(f_m+f_n)}{|\varepsilon^{\parallel}(\omega,\mathbf{k})|^2}, \tag{3.14}$$

$$(\delta\mathbf{E}^{\perp}\delta\mathbf{E}^{\perp})_{\omega,\mathbf{k}}=\frac{16\pi^3}{V}\sum_{nm}|\mathbf{D}_{nm}^{\perp}(-\mathbf{k})|^2\frac{\omega^4\delta(\omega-\omega_{nm})(f_m+f_n)}{|\omega^2\varepsilon^{\perp}(\omega,\mathbf{k})-c^2\mathbf{k}^2|^2}. \tag{3.15}$$

In the equilibrium state, when f_n is the Gibbs distribution, well known expressions[5,10,11] follow from this; e.g.,

$$(\delta\mathbf{E}^{\perp}\delta\mathbf{E}^{\perp})_{\omega,\mathbf{k}}=\frac{8\pi\hbar\omega^4\operatorname{Im}\varepsilon^{\perp}(\omega,\mathbf{k})}{|\omega^2\varepsilon^{\perp}(\omega,\mathbf{k})-c^2\mathbf{k}^2|^2}\operatorname{cth}\frac{\hbar\omega}{2kT}. \tag{3.16}$$

Naturally, the concrete form of the function $\varepsilon^{\perp}$ appearing here is different for different systems.

4. KINETIC EQUATION FOR THE DISTRIBUTION FUNCTION $f_n(t)$

It follows from the definition (3.6) of the collision integral that the relaxation time of the distribution function $f_n(t)$ is determined by the weak interaction $\hat{H}_1$ and, because of this, is long compared with the characteristic times for the system with Hamiltonian $\hat{H}_0$. On this basis we can divide the fluctuations into fine-scale (fast) and coarse-scale (slow) fluctuations. Using the jargon of plasma theory, we may say that the formulas (3.11)–(3.15) apply to the "collisionless" regime. However, the fluctuations described by these formulas themselves determine the collision integral. Thus, to a certain degree the situation that obtains in the theory or gases and plasmas[10] is repeated here.

We note that, in its structure, Eq. (3.7) coincides with Eq. (33.24) in the author's book,[10] which determines the evolution of fluctuations of the phase density of the charged particles of a plasma. Because of this we can omit the computations, which are analogous to those performed in Secs. 34–37, 39, and 40 in Ref. 10, and write down immediately the final expressions for the collision integral.

The collision integral can be represented in the form of a sum of two contributions, determined by the fluctuations of the longitudinal and transverse fields, respectively:

$$I_n(t)=I_n^{\parallel}(t)+I_n^{\perp}(t). \tag{4.1}$$

The expressions for the collision integrals $I_n^{\parallel}$ and $I_n^{\perp}$ can be represented in the following form:

$$I_n^{\parallel}(t)=\frac{1}{(2\pi)^3\hbar^2}\sum_m\int d\omega d\mathbf{k}|D_{nm}^{\parallel}(-\mathbf{k})|^2\delta(\omega-\omega_{nm})\Big[(\delta\mathbf{E}^{\parallel}\delta\mathbf{E}^{\parallel})_{\omega,\mathbf{k}}(f_m-f_n)-\frac{4\pi\hbar\operatorname{Im}\varepsilon^{\parallel}(\omega,\mathbf{k})}{|\varepsilon^{\parallel}(\omega,\mathbf{k})|^2}(f_m+f_n)\Big], \tag{4.2}$$

$$I_n^{\perp}=\frac{1}{16\pi^3\hbar^2}\sum_m\int d\omega d\mathbf{k}|\mathbf{D}_{nm}^{\perp}(-\mathbf{k})|^2\delta(\omega-\omega_{nm})\Big[(\delta\mathbf{E}^{\perp}\delta\mathbf{E}^{\perp})_{\omega,\mathbf{k}}(f_m-f_n)-\frac{8\pi\hbar\omega^4\operatorname{Im}\varepsilon^{\perp}(\omega,\mathbf{k})}{|\omega^2\varepsilon^{\perp}(\omega,\mathbf{k})-c^2\mathbf{k}^2|^2}(f_m+f_n)\Big]. \tag{4.3}$$

These expressions must be supplemented by the formulas (3.11), (3.12), (3.14), and (3.15).

Thus, we have obtained the kinetic equation for the distribution function of the nonequilibrium states of a system of particles with arbitrarily strong interactions. Only the interaction $\hat{H}_1$ is assumed to be small. In the case under consideration, $\hat{H}_1$ is the interaction of the atoms via the fluctuating electromagnetic field. All information about the interaction not associated with $\hat{H}_1$ is contained in the matrix elements $\mathbf{D}_{nm}$.

Naturally, a different "Boltzmann" form of the expression for the collision integral is also possible. To go over to this form we must substitute into the formulas (4.2) and (4.3) expressions for the functions $\mathrm{Im}\,\varepsilon^{\parallel}$ and $\mathrm{Im}\,\varepsilon^{\perp}$, which follow from (3.11) and (3.12), and expressions for the spectral densities of the electromagnetic-field fluctuations. Taking into account here the conditions that the medium is homogeneous and isotropic, we obtain the expression

$$I_n=\frac{4}{9V\hbar^2}\sum_{mn_1m_1}\int d\omega d\mathbf{k}|\mathbf{D}_{nm}(-\mathbf{k})|^2|\mathbf{D}_{n_1m_1}(-\mathbf{k})|^2\delta(\omega-\omega_{nm})$$
$$\times\delta(E_n+E_{m_1}-E_{n_1}-E_m)\left[\frac{1}{|\varepsilon^{\parallel}(\omega,\mathbf{k})|^2}+\frac{2\omega^4}{|\omega^2\varepsilon^{\perp}(\omega,\mathbf{k})-c^2\mathbf{k}^2|^2}\right](f_mf_{n_1}-f_{m_1}f_n). \tag{4.4}$$

This collision integral vanishes when the Gibbs distribution is substituted into it. The collision integral (4.1)–(4.3) vanishes when we substitute the Gibbs distribution and the formulas for the spectral densities of the equilibrium fluctuations of the longitudinal and transverse fields into it.

The collision integral (4.4) also possesses the property

$$-k\sum_n I_n(t)\ln f_n(t)\geqslant 0, \tag{4.5}$$

which ensures that the entropy

$$S(t)=-k\sum_n f_n\ln f_n \tag{4.6}$$

for the system with Hamiltonian $\hat{H}_0$ does not decrease. The equality sign pertains to the equilibrium state. In this case, the expression (4.6) coincides with the Gibbs definition of the entropy.

We note once again that the equation obtained describes only those dissipative processes which are determined by the weak interaction that we have separated out. In accordance with this, the growth of the entropy (4.6) is also determined entirely by these dissipative processes.

In the zeroth approximation in $\hat{H}_1$, Eq. (3.4) coincides with the Liouville equation (equation for the density matrix) for the system with Hamiltonian $\hat{H}_0$. Naturally, in this approximation the entropy (4.6) remains constant.

Also of importance is the fact that, in determining the collision integral, only the correlations of the fine-scale fluctuations are taken into account. As in the theory of gases and plasmas, here too we can develop a kinetic theory of the coarse-scale fluctuations whose correlation times are determined by the weak interaction (see Chapters 4 and 11 in Ref. 10).

Finally, we shall make one more remark. The kinetic equation with the collision integral (4.1)–(4.3) [or (4.4)] leads to a conservation law for the average energy $\langle\hat{H}_0\rangle$ but not for the average energy $\langle\hat{H}_0+\hat{H}_1\rangle$ of the extended system. This shows that, in the approximation under consideration, the weak interaction $\hat{H}_1$ only determines the dissipative processes and does not make a contribution to the law of conservation of the average energy. The situation here is analogous to that which obtains in the kinetic theory of gases and plasmas.[10] Thus, e.g., in the Boltzmann kinetic equation the interaction of the atoms determines only the dissipative process, and the contribution of the interaction to the thermodynamic functions is not taken into account. For a more complete description of the contribution of the interaction, it is necessary, in the derivation of the kinetic equation, to take into account the temporal retardation.

The contribution of the interaction $\hat{H}_1$ is disregarded here not only in the expression for the average energy but also in the expressions for the other thermodynamic functions—in particular, in the expression (4.6) for the entropy. This is already clear from the fact that, in the equilibrium state, the formula (4.6) does not depend on $\hat{H}_1$. When the nonideality with respect to $\hat{H}_1$ is taken into account the expression for the entropy is changed (compare with the results of Sec. 14 in Ref. 10). Under the condition that the average energy $\langle\hat{H}_0\rangle$, and not the total energy $\langle\hat{H}_0+\hat{H}_1\rangle$, is conserved in the relaxation process, the fact that the entropy is a maximum in the final state, when f_n is the Gibbs distribution, can also be proved without use of the kinetic equation.

In fact, we shall compare the entropy values calculated from formula (4.6) for two distribution functions: the Gibbs distribution f_n and an arbitrary distribution f_n^1. For the latter we can take the nonequilibrium solution of the kinetic equation for any time t, i.e., the function $f_n^1=f_n(t)$. We shall compare the corresponding values of the entropy when the following two conditions are fulfilled:

$$\sum_n f_n=\sum_n f_n{}^1=1,\qquad \sum_n E_nf_n=\sum_n E_nf_n{}^1=\langle\hat{H}_0\rangle, \tag{4.7}$$

i.e., the normalization condition and the condition for conservation of the average energy in the process of evolution to the equilibrium state. Using the method proposed by Gibbs himself,[13] we can show that

$$S\geqslant S^1. \tag{4.8}$$

The equality sign holds only when the functions f_n and f_n^1 are equal, i.e., when the equilibrium state is reached.

We shall estimate the relaxation time for relaxation of the function $f_n(t)$ to the Gibbs distribution. We shall do this using the example of the equation for the logarithm of the distribution function. From the formulas (3.13)–(3.15) and the definition of the matrix element (3.3) it follows that, in the thermodynamic limit, under the condition that the correlation lengths of the quantum-mechanical distributions are finite, the squares of the moduli of the matrix elements, i.e., $|\mathbf{D}_{nm}|^2$, increases like N. Owing to this, the spectral densities (3.14) and (3.15) of the field fluctuations, and the polarizabilities $\alpha^{\parallel}$ and $\alpha^{\perp}$, are proportional to the concentration $n=N/V$.

In accordance with this, the dependence of the collision integrals (4.2) and (4.3) on the number of particles is determined, in the thermodynamic limit, by the dependence of the quantity $|\mathbf{D}_{nm}|^2$ on the number of particles. Since the square of the matrix element increases like N, $I_n \propto N$. We define the relaxation time by the relation $I_n = \tau_p^{-1} f_n$, and therefore $\tau_p^{-1} \propto N$. It follows from this that the time derivative of the logarithm of the distribution function, calculated per particle, is determined entirely by the particle concentration.

The relaxation time, proportional to $|\mathbf{D}_{nm}|^4/V^2 \sim n^2$, characterizes the establishment of local equilibrium in the kinetic stage. The time of establishment of complete equilibrium is determined by the "hydrodynamic" stage of the relaxation process and depends, naturally, on the size of the system.

5. KINETIC EQUATION FOR THE SINGLE-PARTICLE DISTRIBUTION FUNCTION OF THE ATOMS

The kinetic equation with the collision integral (4.1)–(4.3) can serve as the starting point for the derivation of the kinetic equations for simpler distribution functions, e.g., for the distribution functions of the states of the individual atoms. We shall consider an atomic gas, the particles of which interact only through the fluctuating electromagnetic field. Under this condition the eigenfunctions of the system of atoms can be represented in the form

$$\Psi_n(x) = \prod_{1 \le i \le N} \Psi_{n_i}(\mathbf{r}_i) \exp\left(i \frac{\mathbf{R}_i \mathbf{P}_i}{\hbar}\right). \tag{5.1}$$

Here, n_i are the quantum numbers characterizing the internal states of the individual atoms, and $\mathbf{P}_i$ are the momenta of the atoms. Under this condition, e.g., the expressions for the permittivity $\varepsilon^\perp$ and the spectral density of the fluctuations $\delta\mathbf{E}^\perp$ take the form

$$\varepsilon^\perp(\omega, \mathbf{k}) = 1 + \frac{2\pi N}{\hbar V} \sum_{nm} \int \frac{V}{(2\pi\hbar)^3} d\mathbf{P} |\mathbf{d}_{nm}{}^\perp|^2 \times \frac{f_n(\mathbf{P} + {}^1\!/_2\hbar\mathbf{k}) - f_m(\mathbf{P} - {}^1\!/_2\hbar\mathbf{k})}{\omega + i\Delta - \mathbf{kV} - \omega_{nm}}, \quad \Delta \to 0; \tag{5.2}$$

$$(\delta\mathbf{E}^\perp \delta\mathbf{E}^\perp)_{\omega,\mathbf{k}} = \frac{16\pi^3 N}{V} \sum_{nm} \int \frac{V}{(2\pi\hbar)^3} d\mathbf{P} \delta(\omega - \mathbf{kV} - \omega_{nm}) \times \frac{\omega^4 |\mathbf{d}_{nm}{}^\perp|^2}{|\omega^2 \varepsilon^\perp(\omega, \mathbf{k}) - c^2 k^2|^2} \left(f_n\left(\mathbf{P} + \frac{1}{2}\hbar\mathbf{k}\right) + f_m\left(\mathbf{P} - \frac{1}{2}\hbar\mathbf{k}\right)\right). \tag{5.3}$$

Here, n and m are the quantum numbers of the states of single atoms.

The corresponding collision integral is determined by the expression

$$I_n(\mathbf{P}, t) = \frac{1}{16\pi^3\hbar^2} \sum_m \int d\omega\, d\mathbf{k} |\mathbf{d}_{nm}{}^\perp|^2 \delta(\omega - \mathbf{kV} - \omega_{nm}) \times \Big[(\delta\mathbf{E}^\perp \delta\mathbf{E}^\perp)_{\omega,\mathbf{k}} \left(f_m\left(\mathbf{P} - \frac{1}{2}\hbar\mathbf{k}\right) - f_n\left(\mathbf{P} + \frac{1}{2}\hbar\mathbf{k}\right)\right) - \frac{8\pi\hbar\omega^4 \operatorname{Im} \varepsilon^\perp(\omega, \mathbf{k})}{|\omega^2 \varepsilon^\perp(\omega, \mathbf{k}) - c^2 \mathbf{k}^2|^2} \left(f_m\left(\mathbf{P} - \frac{1}{2}\hbar\mathbf{k}\right) + f_n\left(\mathbf{P} + \frac{1}{2}\hbar\mathbf{k}\right)\right)\Big]. \tag{5.4}$$

The kinetic equation obtained for the distribution function $f_n(\mathbf{P}, t)$ of the states of the atoms and the corresponding equation for the nondiagonal density matrix can be used to solve various problems in the kinetic theory of electromagnetic processes in gases—in particular in the theory of lasers and the theory of the broadening of the spectral emission lines of atoms (cf., e.g., Refs. 14 and 15).

6. THE REGION OF TRANSPARENCY

In the collision integral (4.3) we shall separate out the contribution from the region of transparency, in which the values of ω and $\mathbf{k}$ are related by a dispersion equation. If we confine ourselves to taking only the temporal dispersion into account, the contribution of the region of transparency to the expression (4.3) will be determined by the expression

$$I_n{}^\perp = \frac{1}{3\hbar^2} \sum_m |\mathbf{D}_{nm}(0)|^2 \left[(\delta\mathbf{E}^\perp \delta\mathbf{E}^\perp)_{\omega_{nm}} (f_m - f_n) - \frac{2\hbar\omega_{nm}{}^3}{c^3} (f_n + f_m) \right]. \tag{6.1}$$

This expression can be simplified if we introduce notation for the coefficients of the induced and spontaneous emission

$$B_m{}^n = \frac{4\pi^2 |\mathbf{D}_{nm}(0)|^2}{3\hbar^2} \qquad A\ {}^n = \frac{4|\mathbf{D}_{nm}(0)|^2 \omega_{nm}{}^3 (\operatorname{Re} \varepsilon)^{1/2}}{3\hbar c^3} \tag{6.2}$$

of the system of atoms. From (6.2), with the replacement

$$|\mathbf{D}_{nm}(0)|^2 \to |\mathbf{d}_{nm}|^2, \tag{6.3}$$

the expressions for the Einstein coefficients characterizing the emission from individual atoms follow.

We note that in the formula (6.2) for the coefficient of spontaneous emission and in the corresponding formula for the Einstein coefficient, the properties of the medium are taken into account through the refractive index $(\operatorname{Re}\varepsilon)^{1/2}$. Naturally, for a gas this factor does not play an important role, since the refractive index is close to unity. The position changes substantially for a system of strongly interacting particles. The role of this factor is especially great for near-critical states.

7. THE FIRST-MOMENT APPROXIMATION– EQUATIONS WITH A SELF-CONSISTENT FIELD

It has already been noted above that, when the interaction of the atoms via the field is taken into account, i.e., for the extended system, there is no closed equation for the density matrix, and, therefore, when the corresponding operator equation (3.4) is averaged, a chain of coupled equations arises. For this system of equations we shall consider the first-moment approximation, i.e., we shall consider the equations for the functions $\langle f_{nm} \rangle$ and $\mathbf{E} = \langle \mathbf{E}^m \rangle$ with neglect of correlations of the fluctuations. In this approximation, from (3.4) we find the following equation for the averaged density matrix:

$$\left(\frac{\partial}{\partial t} + i\omega_{nm}\right) \langle f_{nm}(t) \rangle = -\frac{i}{\hbar} \sum_{n_1} \int [\mathbf{D}_{nn_1}(\mathbf{R}) \langle f_{n_1 m}(t) \rangle - \langle f_{nn_1}(t) \rangle \mathbf{D}_{n_1 m}(\mathbf{R})] \mathbf{E}(\mathbf{R}, t) d\mathbf{R}. \tag{7.1}$$

The mean polarization vector is connected with the averaged density matrix by the relation

$$\mathbf{P}(\mathbf{R}, t) = \sum_{nm} \mathbf{D}_{mn}(\mathbf{R}) \langle f_{nm}(t) \rangle, \tag{7.2}$$

while the charge density and current density are connected with the polarization vector in the dipole approximation by the usual relations. As a result, together with the Maxwell equations, we obtain a closed system of equations for the first moments.

As in plasma theory, the first-moment approximation is valid when the characteristic times of the processes under consideration are much shorter than the relaxation times determined by the collision integrals (4.2), (4.3). For example, one of the characteristic parameters is the lifetime of the radiation (photons) in the volume occupied by the system.

With the self-consistent field the system has the particular solution

$$\langle f_{nm}\rangle=\delta_{nm}f_n,\quad \mathbf{P}=0,\quad \mathbf{E}=0. \tag{7.3}$$

The equations of the approximation linear in the deviations from this particular solution determine, in particular, the wave properties of the system. The values of ω and $\mathbf{k}$ for the waves are related by the usual dispersion equations, in which the functions $\varepsilon^{\parallel}$ and $\varepsilon^{\perp}$ are determined by the formulas (3.11) and (3.12). Now, however, f_n in them is the particular solution (7.3) of the equations with the self-consistent field.

The account in the present work touches upon only an extremely small fraction of the problems of the kinetic theory of electromagnetic processes in systems with strong interaction. Of these, the most interesting are problems in the kinetic theory of equilibrium and nonequilibrium coherent states, e.g., the kinetics of phase transitions in the atoms-field system, super-radiance, etc. Of course, the derivation of the corresponding kinetic equations for chemically reacting systems is of interest.

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Effective pressure on the Fermi surface of zinc

A. G. Budarin, V. A. Ventsel', and A. V. Rudnev

Institute of High Pressure Physics, USSR Academy of Sciences

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Apparatus is described for the measurements of the influence of pressure up to 140 bar on the frequencies of the oscillations in the de Haas–van Alphen effect in zinc in pulsed magnetic fields up to 100 kOe. The pressure dependence of the areas of the extremal sections of the Fermi surface serves as a confirmation of the correctness of the model proposed by Rubin and Stark (The de Haas–van Alphen Spectrum of Zinc, Preprint, University of Chicago) for all the sections observed in experiment.

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The Fermi surface (FS) of zinc was investigated in detail both theoretically[1,2] and experimentally,[3-10] but to this day it cannot be said that its form has been finally established. In fact, on the one hand, the form of the FS agrees well with the model of almost free electrons,[1] but the presence of *d* states in the conduction band can lead to nonlocality of the potential and consequently to a strong deviation of the FS from the form proposed in Ref. 1 in some parts of the Brillouin zone (BZ).[2] The interpretation of the observed oscillations in the de Haas–van Alphen effect is made difficult by the complexity of the "bare" form of the FS and by the