Contribution of van der Waals forces to the free energy of condensed media

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Generating functions are found for the Green functions for a photon in an inhomogeneous medium of general form, for electrons in an inhomogeneous electron liquid, and also for the inverse permittivity tensor. Similar relations, of very general character, are satisfied also by other Green functions for inhomogeneous systems under stationary conditions. Use of the relations found for the Green function of a photon in a medium enables one actually to sum in general form, for arbitrary inhomogeneous media, the diagram series for the contribution of van der Waals forces to the free energy, and to reduce the result to a form convenient for applications. It is shown that the expression obtained earlier [Yu. S. Barash and V. L. Ginzburg, JETP Lett. **15**, 403 (1972)] for the free energy due to van der Waals interactions between bodies has a very broad range of applicability.

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1. INTRODUCTION

The contribution of van der Waals forces to the free energy of an inhomogeneous condensed medium, in the general case, was first considered by Dzyaloshinskiĭ and Pitaevskiĭ.[1,2] The diagram series found in Ref. 1 for the free energy could not be summed directly. But in order to find general expressions for the contributions of van der Waals forces to the stress tensor of an inhomogeneous condensed medium and to its chemical potential, it was sufficient to find a formula merely for the variation of the contribution of van der Waals forces to the free energy in a small change of the permittivity of the medium. Dzyaloshinskiĭ and Pitaevskiĭ found that this formula has the form

$$\delta F=-\frac{T}{4\pi\hbar c^2}\sum_{n=0}^{\infty}{}' \omega_n^2\int d\mathbf{r}_1\, d\mathbf{r}_2 \mathscr{D}_{ik}(\omega_n,\mathbf{r}_1,\mathbf{r}_2)\,\delta\varepsilon_{ki}(i\omega_n,\mathbf{r}_2,\mathbf{r}_1), \qquad \omega_n=2\pi Tn/\hbar. \tag{1.1}$$

Here and below, a prime on the summation sign means that the term with $n=0$ is taken with weight one half. In (1.1), the components of the temperature Green function of a photon in the medium satisfy the following equations:

$$\mathrm{rot}_{ik}\,\mathrm{rot}_{kl}\,\mathscr{D}_{ln}(\omega_n,\mathbf{r},\mathbf{r}')+\frac{\omega_n^2}{c^2}\int d\mathbf{r}_1\,\varepsilon_{il}(i\omega_n,\mathbf{r},\mathbf{r}_1)\mathscr{D}_{ln}(\omega_n,\mathbf{r}_1,\mathbf{r}') = -4\pi\hbar\delta_{in}\delta(\mathbf{r}-\mathbf{r}'). \tag{1.2}$$

The relations (1.1) and (1.2) are written here for the case of an inhomogeneous anisotropic medium, with allowance both for its frequency dispersion and for its spatial. In this form, allowance for spatial dispersion is possible, for example, for a plasma in the random-phase approximation.[3]

The general expressions that result from formula (1.1), after the calculations carried out in Ref. 1, for the contributions of van der Waals forces to the stress tensor and chemical potential of the medium make it possible, in principle, to calculate, in specific problems, the van der Waals parts of any thermodynamic quantities of the body. For such calculations, it would be possible also to use the expression (1.1) itself directly; but usually this method of solving problems is found to be more cumbersome, because of the necessity for carrying out in (1.1), in each specific case, an integration over the spatial coordinates in the inhomogeneous medium. But in the expression mentioned for the stress tensor, the necessity for such integration does not arise, at least when one neglects the spatial dispersion.

The question whether there exists a general expression for the contribution of van der Waals forces to the free energy, convenient for use in the solution of specific problems, is of interest not only from the methodological point of view but also for applications. Thus, for example, it is found that the van der Waals force of interaction between macroscopic bodies can be conveniently found by use of a general expression for the free energy (this has been clarified in the example of transparent media[4]). On the other hand, for a comparatively long time the contribution of van der Waals forces to the stress tensor of a condensed medium was studied better theoretically than was the analogous contribution to the free energy. Consideration of this last quantity is conveniently begun with the following remark. It is well known that the energy of the electromagnetic field in the presence of charged particles contains the energy of interaction between these particles. Similarly, the energy of the fluctuational electromagnetic field in a condensed medium should contain, in addition to the energy of thermal radiation, also the energy of such interaction between the particles as has a fluctuational origin. This is precisely the van der Waals interaction, if we consider the long-wave components of the fluctuational field. In the case of transparent media, the energy of the equilibrium fluctuational electromagnetic field is obviously described by the Planck expression with allowance for the zero-point oscillations:

$$E_{rad}=\sum_\alpha\left(\frac{\hbar\omega_\alpha}{2}+\frac{\hbar\omega_\alpha}{\exp(\hbar\omega_\alpha/T)-1}\right). \tag{1.3}$$

Here ω_α are the eigenfrequencies of the electromag-

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netic field in the medium.

Since the frequencies ω_α are found by solving a boundary problem for the macroscopic Maxwell equations, it is clear that the expression (1.3) gives the energy of the fluctuational field in a transparent medium in the form of a functional of the permittivity. In inhomogeneous media, the spectrum of characteristic oscillations of the electromagnetic field contains frequencies substantially dependent on the inhomogeneity parameters. In particular, in a system of two bodies there are characteristic frequencies dependent on the macroscopic distance l between these bodies. The dependence, resulting from formula (1.3), of the energy (and of the corresponding free energy) of the fluctuational field on distance leads to the appearance of a force acting on the bodies. Thus it is seen that formula (1.3), valid for the case of transparent media, contains, in accordance with what was said above, not only the energy of thermal radiation but also the energy of van der Waals interaction. As a result, with neglect of absorption, the problem of van der Waals forces between bodies reduces to finding the spectrum of characteristic waves in the system, i.e., it turns out to be comparatively simple (it is true that clarification of this question has occupied much time[4,5]; see also Ref. 3).

For the theory of van der Waals forces, the passage to consideration of absorbing media is very important. The point is that the fluctuational mechanism that leads to van der Waals interaction between bodies is usually importantly related to the spontaneous occurrence of fluctuational polarization in the bodies (the only exception is the limiting case of large distances $l \gg \lambda_0$, where λ_0 is a characteristic wavelength for the absorption spectrum of the bodies). As is clear from the fluctuation-dissipation relation, this process is described by means of the anti-Hermitian part of the permittivity and therefore is directly dependent on absorption in the media. In consequence of its fluctuational origin, the free energy of the equilibrium longwave electromagnetic field in the medium is a functional of the permittivity even with allowance for absorption. This fact is in general not self-evident. Thus, for example, it is known that the energy of a nonequilibrium longwave electromagnetic field in an absorbing medium is in general not expressible in terms of a single permittivity alone. At the same time, in the special case of a transparent medium such an expression for the energy of a nonequilibrium field exists.[6]

An expression for the contribution of van der Waals forces to the free energy, with allowance for absorption, was found, in the form of a functional of the permittivity, earlier[7] (see also Ref. 3). In Ref. 7, the fact was used that the general expression for the free energy of the fluctuational field in a medium must be applicable, in particular, to a description of electromagnetic fluctuations in electric circuits. By starting initially from a treatment of an elementary RCL circuit and then passing to a general dielectric description of inhomogeneous absorbing media, the following expression was obtained[7] for the free energy of van der Waals interaction (for simplicity of writing, we suppose that the system under consideration consists of two macroscopic bodies located at a distance l from each other):

$$\Delta F = T \sum_{n=0}^{\infty}{}' \int \rho(\beta)\, d\beta \ln D(\beta, i\omega_n, l). \tag{1.4}$$

The function $D(\beta, \omega, l)$ that occurs here has the form

$$D(\beta, \omega, l) = \prod_\alpha \frac{\Omega_\alpha^2(\beta, \omega, l) - \omega^2}{\Omega_\alpha^2(\beta, \omega, \infty) - \omega^2} = \prod_\alpha \Delta_\alpha(\beta, \omega, l), \tag{1.5}$$

where the quantities $\Omega_\alpha(\beta, \omega, l)$ are eigenfrequencies for certain auxiliary macroscopic Maxwell equations [see equation (2.2) of (2.3) below]. The variables β on which the eigenfrequencies $\Omega_\alpha(\beta, \omega, l)$ depend run through a continuous spectrum of values. In a homogeneous medium, the components of the wave vector play the role of the variables β. In inhomogeneous media, the specific choice of the variables β depends on the character of the inhomogeneities. The function $\rho(\beta)$ under the integral sign in formula (1.4) is the density of states, so that for a homogeneous medium this quantity is $V/(2\pi)^3$ (V is the volume of the system). The roots of the equation

$$D(\beta, \omega, l) = 0 \tag{1.6}$$

are the eigenfrequencies in the system under consideration, and they depend on the distance between the bodies.[3,7] In this sense, the free energy of van der Waals interaction is found, even with allowance for absorption, to be connected with the spectrum of characteristic waves in the system.

An RCL circuit is an example of an inhomogeneous absorbing system with frequency dispersion; thus it contains all the traits of the system being studied that are most important for the theory. Nevertheless, after derivation[7] of formula (1.4) it remained not completely clear what its range of applicability and its relation to the result (1.1) were. It is to this question that the present paper is devoted. A path to its solution was marked out earlier,[3] but some essential points were omitted. Furthermore, the formulation presented in Ref. 3 of the auxiliary-problem method is applicable only for nonmagnetoactive media. In the present paper, a more general approach is used, which permits us to consider magnetoactive absorbing media as well.

It is shown in the paper that there exists a very general representation for the Green function of a photon in a medium, in the form of the variational derivative, with respect to the permittivity, of the function $D(\beta, \omega)$ that occurs in (2.6). Similar representations exist also for other Green functions. By means of this representation for the Green function, it is possible actually to sum the diagram series for the contribution of van der Waals forces to the free energy, for the general case of inhomogeneous dispersive media, and to reduce the result to a form convenient for applications. It is further shown that the expression (1.4) for the free energy can be obtained also with the approach used here. Hence it follows that the expression (1.4) has a broad range of applicability, as did other general results, known earlier, of the theory of van der Waals forces.

2. A REPRESENTATION FOR GREEN FUNCTIONS

In this section, we consider a new and very general representation for the Green function of a photon in a medium. Other Green functions as well satisfy similar relations.

We consider an arbitrary inhomogeneous, anisotropic medium with frequency and spatial dispersion. The equations for the retarded Green function of a photon in such a medium have the form (see, for example, Ref. 8, §75)

$$\mathrm{rot}_{ik}\,\mathrm{rot}_{kl}\,\mathcal{D}_{ln}(\omega,\mathbf{r},\mathbf{r}')-\frac{\omega^2}{c^2}\int d\mathbf{r}_1\,\varepsilon_{il}(\omega,\mathbf{r},\mathbf{r}_1)\mathcal{D}_{ln}(\omega,\mathbf{r}_1,\mathbf{r}')=-4\pi\hbar\delta_{in}\delta(\mathbf{r}-\mathbf{r}'). \tag{2.1}$$

We now introduce two systems of eigenfunctions, $\{\Phi^+_{\Omega_\alpha}(\omega,\mathbf{r})\}$ and $\{\Phi^-_{\Omega_\alpha}(\omega,\mathbf{r})\}$, of the following auxiliary integrodifferential equations (macroscopic Maxwell equations for characteristic waves in the auxiliary systems):

$$\mathrm{rot}\,\mathrm{rot}\,\Phi^+_{\Omega_\alpha}(\omega,\mathbf{r})=\frac{\Omega_\alpha^2(\omega)}{c^2}\int d\mathbf{r}'\hat{\varepsilon}(\omega,\mathbf{r},\mathbf{r}')\Phi^+_{\Omega_\alpha}(\omega,\mathbf{r}'), \tag{2.2}$$

$$\mathrm{rot}\,\mathrm{rot}\,\Phi^-_{\Omega_\alpha}(\omega,\mathbf{r})=\frac{\Omega_\alpha^2(\omega)}{c^2}\int d\mathbf{r}'\,\Phi^-_{\Omega_\alpha}(\omega,\mathbf{r}')\hat{\varepsilon}(\omega,\mathbf{r}',\mathbf{r}). \tag{2.3}$$

The caret on the permittivity here indicates its matrix character. The permittivity in Eqs. (2.2) and (2.3) is independent of the frequency Ω, which corresponds to a Fourier transformation of the fields in an auxiliary system with respect to time. At the same time, the permittivity in the auxiliary equations depends on the frequency ω as a parameter, and this dependence is such that at all frequencies Ω, the permittivity of the auxiliary system is exactly equal to the permittivity of the real medium [for which equations (2.1) were written] at frequency ω.

It is easy to show that the eigenfrequencies $\Omega_\alpha(\omega)$ for equations (2.2) and (2.3) are the same. For the eigenfunctions of these equations, we shall use below the notation

$$\Phi_\alpha^\pm(\omega,\mathbf{r})\equiv\Phi^\pm_{\Omega_\alpha}(\omega,\mathbf{r}).$$

In the case of nonmagnetoactive media, when the permittivity is symmetric with respect to simultaneous interchange of the matrix indices and of the coordinates $\mathbf{r}$, $\mathbf{r}'$, equations (2.2) and (2.3) coincide, and then $\Phi_\alpha^+(\omega,\mathbf{r})=\Phi_\alpha^-(\omega,\mathbf{r})$. In the case of nonabsorptive but magnetoactive media, when the permittivity is Hermitian, equations (2.2) and (2.3) are complex-conjugate, and then $\Phi_\alpha^+(\omega,\mathbf{r})=[\Phi_\alpha^-(\omega,\mathbf{r})]^*$. But in the general case of a magnetoactive, absorptive medium, the solutions of equations (2.2) and (2.3) must be considered independent. We shall also suppose that the medium is placed in a sufficiently large cavity, with ideally conducting walls.

It is evident from equations (2.2) and (2.3) that the functions $\Phi_\alpha^+(\omega,\mathbf{r})$ and $\Phi_\alpha^-(\omega,\mathbf{r})$ satisfy the conditions

$$\mathrm{div}\left\{\int d\mathbf{r}'\,\hat{\varepsilon}(\omega,\mathbf{r},\mathbf{r}')\Phi_\alpha^+(\omega,\mathbf{r}')\right\}=0,\quad \mathrm{div}\left\{\int d\mathbf{r}'\,\Phi_\alpha^-(\omega,\mathbf{r}')\hat{\varepsilon}(\omega,\mathbf{r}',\mathbf{r})\right\}=0. \tag{2.4}$$

It is assumed below that the systems of functions $\{\Phi_\alpha^\pm(\omega,\mathbf{r})\}$ are complete, in the large cavity being considered, for the classes of fields $\mathbf{E}_\varepsilon^\pm(\omega,\mathbf{r})$, respectively, satisfying the conditions (2.4). This assumption has been proved at least in the simplest cases and justifies itself over a broad range of problems.

The index α, on which the eigenfrequencies $\Omega_\alpha(\omega)$ of the auxiliary problem depend, denotes in general both discrete variables (used for enumeration of the branches of the oscillations) and variables that traverse a continuous or quasicontinuous spectrum of values (for example, components of a wave vector). For what follows, it is convenient to separate out the continuous variables. We shall denote them by the letter β, reserving the index α solely for discrete variables. We shall then write the eigenfrequencies of the auxiliary problem in the form $\Omega_\alpha(\beta,\omega)$, and when it is necessary we shall go over from summation over the variable β to integration,

$$\sum_\alpha\to\sum_\alpha\int\rho(\beta)\,d\beta,$$

where $\rho(\beta)$ is the density of states.

It can be proved (see Appendix) that the Green function $\mathcal{D}_{ik}(\omega,\mathbf{r},\mathbf{r}')$ satisfies the following relation:

$$\mathcal{D}_{ik}(\omega,\mathbf{r},\mathbf{r}')=\frac{4\pi\hbar c^2}{\omega^2}\left\{\int\rho(\beta)\,d\beta\,\frac{\delta\ln D(\beta,\omega)}{\delta\varepsilon_{kl}(\omega,\mathbf{r}',\mathbf{r})}+\varepsilon_{ik}^{-1}(\omega,\mathbf{r},\mathbf{r}')\right\}, \tag{2.5}$$

where we have introduced the notation

$$D(\beta,\omega)=\prod_\alpha\frac{\Omega_\alpha^2(\beta,\omega)-\omega^2}{\Omega_{0\alpha}^2(\omega)}. \tag{2.6}$$

The index α here enumerates all the branches of the characteristic oscillations in the auxiliary system, with allowance for the multiplicity of their degeneracy. The quantities $\Omega_{0\alpha}$ that occur in formula (2.6) are independent of the dielectric properties of the medium (but may, for example, be functions of the frequency ω). Therefore after the taking of the variational derivative, the quantities $\Omega_{0\alpha}(\omega)$ no longer occur in the expression (2.5). Introduction of the frequencies $\Omega_{0\alpha}(\omega)$ makes it possible to determine the function $D(\beta,\omega)$ as a dimensionless quantity. Furthermore, if in the system considered the number of branches of the characteristic oscillations is infinite (as often happens), then the quantities $\Omega_{0\alpha}(\omega)$ also insure convergence of the infinite product that occurs in the expression (2.6). Otherwise, the specific choice of the quantities $\Omega_{0\alpha}(\omega)$ is dependent on considerations of convenience.

The representation of the Green function in the form (2.5) is the principal result to which the present section of the paper is devoted. For the case under consideration, longwave photons, equations (2.1) are linear, because the permittivity, with good accuracy, is functionally independent of the Green function of the longwave photons. It can be shown also that the relation (2.5) retains its form in those cases in which the functional dependence of the permittivity (or of the polarization operator) on the Green function of a photon is taken into account. Equation (2.1) is then nonlinear, while the auxiliary equations (2.2) and (2.3) should remain linear as before, but dependent on the Green function of the photon as a functional parameter (in consequence of the dependence of the polarization operator on this parameter).

The relation (2.5) can be further transformed, if we bring in the expression for the inverse permittivity $\varepsilon_{ik}^{-1}(\omega, \mathbf{r}, \mathbf{r}')$, to a form similar to the representation considered for the Green function. For this purpose, we introduce the susceptibility $\chi_{il}(\omega, \mathbf{r}, \mathbf{r}')$ of the medium:

$$\varepsilon_{il}(\omega, \mathbf{r}, \mathbf{r}')=\delta_{il}\delta(\mathbf{r}-\mathbf{r}')+4\pi\chi_{il}(\omega, \mathbf{r}, \mathbf{r}'). \quad (2.7)$$

The quantity $\varepsilon_{il}(\omega, \mathbf{r}, \mathbf{r}')$ obviously satisfies the following relation:

$$\varepsilon_{il}^{-1}(\omega, \mathbf{r}, \mathbf{r}')+4\pi\int d\mathbf{r}_1\, \varepsilon_{ik}^{-1}(\omega, \mathbf{r}, \mathbf{r}_1)\chi_{kl}(\omega, \mathbf{r}_1, \mathbf{r}')=\delta_{il}\delta(\mathbf{r}-\mathbf{r}'). \quad (2.8)$$

We now denote by $\varphi_\alpha^{\pm}(\omega, \mathbf{r})$ and $\mu_\alpha(\omega)$ the eigenfunctions and eigenvalues of the auxiliary integral equations

$$\int d\mathbf{r}'\, \hat{\chi}(\omega, \mathbf{r}, \mathbf{r}')\varphi_\alpha^{+}(\omega, \mathbf{r}')=\mu_\alpha(\omega)\varphi_\alpha^{+}(\omega, \mathbf{r}), \quad (2.9)$$

$$\int d\mathbf{r}'\, \varphi_\alpha^{-}(\omega, \mathbf{r}')\hat{\chi}(\omega, \mathbf{r}', \mathbf{r})=\mu_\alpha(\omega)\varphi_\alpha^{-}(\omega, \mathbf{r}). \quad (2.10)$$

It can be shown (see the Appendix) that the inverse permittivity satisfies the following relation:

$$\varepsilon_{ik}^{-1}(\omega, \mathbf{r}, \mathbf{r}')=\int \rho(\beta)d\beta\frac{\delta \ln D^{(e)}(\beta, \omega)}{\delta\varepsilon_{ki}(\omega, \mathbf{r}', \mathbf{r})}, \quad (2.11)$$

where we have introduced the notation

$$D^{(e)}(\beta, \omega)=\prod_\gamma \frac{1+4\pi\mu_\gamma(\beta, \omega)}{\mu_0}. \quad (2.12)$$

The variables α in formulas (2.9) and (2.10) denote discrete variables γ and the variables β that occur separately in the expressions (2.11) and (2.12). The quantity μ_0 in (2.12) is independent of the dielectric properties of the medium. Therefore after the taking of the variational derivative, the quantity μ_0 no longer occurs in the expression (2.11); otherwise its choice is dependent on considerations of convenience.

With the aid of the relation (2.11), the representation (2.5) for the Green function of a photon can be written in the following compact form:

$$\mathscr{D}_{ik}(\omega, \mathbf{r}, \mathbf{r}')=\frac{\delta}{\delta\varepsilon_{ki}(\omega, \mathbf{r}', \mathbf{r})}\left\{\frac{4\pi\hbar c^2}{\omega^2}\int \rho(\beta)d\beta \ln(D(\beta, \omega)D^{(e)}(\beta, \omega))\right\}. \quad (2.13)$$

From a comparison of equations (2.1) and (2.2) and the definition (2.6) it is evident that the roots of the equation

$$D(\beta, \omega)=0 \quad (2.14)$$

are the frequencies of those characteristic waves in the inhomogeneous medium under consideration, with permittivity $\varepsilon_{ik}(\omega, \mathbf{r}, \mathbf{r}')$, for which the electric induction is nonzero. But from the relations (2.7) and (2.9) and the definition (2.12) it is evident that the roots of the equation

$$D^{(e)}(\beta, \omega)=0 \quad (2.15)$$

are the characteristic frequencies for those electric fields in the medium for which the electric induction is zero (in the case of a homogeneous isotropic medium, for longitudinal fields). Thus as follows from the relation (2.13) found here, the generating function for the Green function of a photon in the medium turns out to be directly related to the spectrum of all characteristic waves in the system.

The quantities $\omega^2\mathscr{D}_{ik}(\omega, \mathbf{r}, \mathbf{r}')$ and $\varepsilon_{ik}^{-1}(\omega, \mathbf{r}, \mathbf{r}')$, as is well known, are analytic functions in the upper part of the complex plane for the frequency ω. If this property is possessed also by the permittivity $\varepsilon_{ki}(\omega, \mathbf{r}, \mathbf{r}')$, then it follows from (2.5) that the function $D(\beta, \omega)$ is also analytic in the upper part of the complex plane for the frequency ω and furthermore takes no zero values there. The last fact is related to the fact that in an equilibrium system, only attenuating characteristic waves can exist.

3. EXPRESSION FOR THE FREE ENERGY

With the aid of the relation (2.5) obtained in the preceding section, we shall transform the expression (1.1) for the variation of the van der Waals part of the free energy. We find

$$\delta F=\delta\left\{T\sum_{n=0}^{\infty}{}'\left[\int \rho(\beta)d\beta \ln D(\beta, i\omega_n)+\mathrm{Sp}\ln(\varepsilon_{ik}(i\omega_n, \mathbf{r}, \mathbf{r}'))\right]\right\}. \quad (3.1)$$

Here the argument of the spur of the logarithm is the kernel of the integral operator that represents the permittivity of the inhomogeneous medium with allowance for spatial dispersion. The definition of a logarithmic function of an operator argument, as usual, involves the Taylor power series for this function.

The expression in curly brackets on the right side of the relation (3.1) obviously describes the contribution of van der Waals forces to the free energy of an inhomogeneous condensed medium to within a term independent of the properties of the medium. With the form of notation used, the finding of this term reduces to the finding of the quantities $\Omega_{0\alpha}(\omega)$ that occurred in the definition (2.6) of the function $D(\beta, \omega)$ and that have not yet been fixed in definite form. If we are interested in the total contribution to the free energy from the interaction of particles with the longwave fluctuational electromagnetic field, then the quantities $\Omega_{0\alpha}(\omega)$ should be defined on the basis of the requirement that the desired expression

$$F_{cl}=T\sum_{n=0}^{\infty}{}'\left\{\int \rho(\beta)d\beta \ln D(\beta, i\omega_n)+\mathrm{Sp}\ln(\varepsilon_{ik}(i\omega_n, \mathbf{r}, \mathbf{r}'))\right\}$$

$$=T\sum_{n=0}^{\infty}{}'\int \rho(\beta)d\beta \ln(D(\beta, i\omega_n)D^{(e)}(\beta, i\omega_n)) \quad (3.2)$$

shall vanish in the limit $\varepsilon_{ik}(i\omega_n, \mathbf{r}, \mathbf{r}')\to\delta_{ik}\delta(\mathbf{r}-\mathbf{r}')$. Then we have $\mu_0=1$ and

$$\Omega_{0\alpha}^2(i\omega_n)=\lim\,(\Omega_\alpha^2(\beta, i\omega_n)+\omega_n^2),\quad \varepsilon_{ik}(i\omega_n, \mathbf{r}, \mathbf{r}')\to\delta_{ik}\delta(\mathbf{r}-\mathbf{r}'). \quad (3.3)$$

When the condition (3.3) is satisfied, the expression (3.2) is a direct result of summation of the diagram series for the van der Waals part of the free energy, as defined by Dzyaloshinskiĭ and Pitaevskiĭ.[1] Since the relation (2.5) has a very general character, it is clear that the expressions (3.4) and (1.1) have the same range of applicability. From a comparison of these expressions it is also evident that the transformation carried out has enabled us, in the formula for the free energy, to avoid the necessity for performing an integration over spatial coordinates in the inhomogeneous medium. This is important in the use of the general formula for the free energy for solution of specific problems.

The expression (3.2) can usually be simplified if we are interested only in van der Waals forces between bodies, or in problems in which the only other thing of interest is the part of the free energy that is dependent on inhomogeneities. A contribution to the interaction force is made only by terms dependent on the distances between the bodies. Therefore it is sufficient to consider only the part ΔF of the free energy:

$$\Delta F = F_{fl}(l) - F_{fl}(\infty). \tag{3.4}$$

The expression $\mathrm{Sp}\ln[\varepsilon_{ik}(\omega, \mathbf{r}, \mathbf{r}')]$ is independent of the distance between the bodies and makes no contribution to the value of ΔF, provided the dimensions and the permittivities of the bodies do not change by any significant amount when the bodies are shifted with respect to each other. We also take into account that the function $D(\beta, \omega)$ can be factored with respect to the branches of the characteristic waves of the auxiliary problem. Then from (3.2) and (3.4) we arrive at the expression (1.4) found earlier[7] for the quantity ΔF; the function $D(\beta, \omega, l)$, defined in (1.5), is now related only to branches of the characteristic frequencies that are dependent on the distance between the bodies.

According to formulas (1.4) and (1.5), in order to find the free energy of van der Waals interaction it is sufficient to find the quantities $\Delta_\alpha(\beta, \omega, l)$ that occur in (1.5). From (1.5) it is evident also that these quantities can in turn be expressed in terms of characteristic frequencies $\Omega_\alpha(\beta, \omega, l)$ of the auxiliary problem. It is found, however, that in the expressions for the quantities $\Delta_\alpha(\beta, \omega, l)$, in which the frequencies $\Omega_\alpha(\beta, \omega, l)$ occur, on division of the numerator by the denominator a factor remains that is often difficult to calculate analytically. For this reason, in specific problems it is convenient to find the quantities $\Delta_\alpha(\beta, \omega, l)$ by a method that avoids direct calculation of the characteristic frequencies $\Omega_\alpha(\beta, \omega, l)$ for the auxiliary equations (2.2).

This can be done by at least two methods. For example, it is possible to use the fact that the denominators in the Green function, as is evident from (2.5) and (1.5) [see also the relation (A.6) in the Appendix], coincide, except for a factor, with the quantities $\Delta_\alpha(\beta, \omega, l)$. The factor mentioned can be fixed on the basis of the requirement $\Delta_\alpha(\beta, \omega, l) \to 1$ for $l \to \infty$. But usually the quantity

$$D(\beta, \omega, l) = \prod_\alpha \Delta_\alpha(\beta, \omega, l)$$

can be found also by a simpler method, without carrying out a complete calculation of the Green function.

In fact, assume that by solution of the boundary problem, we have found a dispersion equation, dependent on the distance between the bodies, for the characteristic electromagnetic waves in the system,

$$W(\beta, \omega, l) = 0, \tag{3.5}$$

this equation is so written that as $l \to \infty$

$$W(\beta, \omega, l) \to 1. \tag{3.6}$$

Since Eq. (1.6) has the same physical meaning as Eq. (3.5), and since furthermore it follows from (1.5) that for $l \to \infty$

$$D(\beta, \omega, l) \to 1, \tag{3.7}$$

it would be natural simply to identify the functions considered, i.e., to set

$$W(\beta, \omega, l) = D(\beta, \omega, l). \tag{3.8}$$

It might then be thought that the abstract mathematical possibility of constructing other functions [besides $W(\beta, \omega, l)$] that vanish at the same values of frequency as does the function $W(\beta, \omega, l)$, as was indeed found uniquely by direct solution of the boundary problem for the macroscopic Maxwell equations, has no physical meaning. It is furthermore clear that the factors that constitute the function $W(\beta, \omega, l)$ and that correspond to different branches of the characteristic waves also occur directly in the denominators of the Green functions. If this is so, the problem of finding the van der Waals part of the free energy ΔF reduces to finding the dispersion equation (3.5) and then using the relations (3.8) and (1.5). This method of solution of specific problems justifies itself in all known cases and proves to be very convenient (see, for example, Ref. 3 and the literature cited there).

At the same time, a more rigorous establishment of the validity of the relation (3.8) than that given above is desirable. In order to find certain sufficient conditions for the validity of this relation, we shall investigate the analytic properties of the functions being considered. We note that the quantity $D(\beta, \omega, l)$ has no singular points in the upper part of the complex plane for the frequency ω if the permittivity $\varepsilon_{ik}(\omega, \mathbf{r}, \mathbf{r}')$ possesses the same property (see the end of Sec. 2 of the paper). Therefore the presence of these analytical properties for the function $W(\beta, \omega, l)$ as well is important for validity of the relation (3.8).

We now introduce into consideration a new function $W(\beta, \omega, \Omega, l)$ such that the roots of the equation

$$W(\beta, \omega, \Omega, l) = 0 \tag{3.9}$$

are eigenfrequencies $\Omega_\alpha(\beta, \omega, l)$ for the auxiliary equations (2.2). From a comparison of equations (2.2) and (2.1) it is evident that the value of $W(\beta, \omega, \Omega, l)$ can be obtained directly from the expression for the function $W(\beta, \omega, l) \equiv W(\beta, \omega, \omega, l)$, if in the latter we replace the frequency ω, which is not an argument of the permittivity, by the frequency Ω. Here the dependence of the permittivity on the frequency ω must be left unchanged. Consideration of the analytic properties of the quantity $W(\beta, \omega, \Omega, l)$ as a function of the frequency Ω, instead of investigation of the properties of the function $W(\beta, \omega, l)$ in the complex plane for the frequency ω, enables us to avoid assumptions about the character of the singularities in the permittivity. These assumptions are unimportant for the problem under consideration. We shall now show how it is possible to arrive at formula (3.8) by starting from certain assumptions about the analytic properties of the function $W(\beta, \omega, \Omega, l)$.

We assume that the quantity $W(\beta, \omega, \Omega, l)$ is a meromorphic function of the variable Ω; that is, in any finite part of the complex plane for this variable there are no singular points except poles. At the same time, the function $W(\beta, \omega, \Omega, l)$ may have an essential singularity at the infinitely distant point, Furthermore, let the function $W(\beta, \omega, \Omega, l)$ approach unity sufficiently rapidly when $\Omega \to \pm\infty$. We now consider the following integral:

$$I_1=\int_{-\infty}^{+\infty} d\Omega \ln W(\beta,\omega,\Omega,l)\frac{\partial}{\partial\Omega}\ln(\Omega^2-\omega^2-i\eta), \quad \eta\to+0. \qquad (3.10)$$

We close the contour of integration in the integral in (3.10) with a large semicircle C_R, with radius $R = |\Omega|$, in the upper part of the complex plane for the variable Ω. From physical considerations it is clear that the dependence of the function $W(\beta, \omega, \Omega, l)$ on the distance between the bodies must show up significantly only in the frequency range $\Omega \lesssim l/c$. For this reason, the result of integration over a sufficiently large semicircle C_R will not depend on the distance l. We shall assume that in the limit as $R \to +\infty$ the contribution from integration over the large semicircle is finite, and we shall write it in the form $2\pi i \ln I_2(\beta, \omega)$.

In the upper half-plane, by means of small circles C_α and $C_\alpha^{(\infty)}$, we now separate out small neighborhoods of the zeroes $\Omega_\alpha(\beta, \omega, l)$ and poles $\Omega_\alpha^{(\infty)}(\beta, \omega)$, respectively, of the function $W(\beta, \omega, \Omega, l)$. We shall suppose that the poles of this function are independent of the distance between the bodies and that all the integration contours used are oriented counterclockwise. As a result, by means of the theory of residues, we arrive at the following relation:

$$I_1+2\pi i\ln I_2(\beta,\omega)-\sum_\alpha\int_{C_\alpha} d\Omega\ln W(\beta,\omega,\Omega,l)\frac{\partial}{\partial\Omega}\ln(\Omega^2-\omega^2-i\eta)$$
$$-\sum_\alpha\int_{C_\alpha^{(\infty)}} d\Omega\ln W(\beta,\omega,\Omega,l)\frac{\partial}{\partial\Omega}\ln(\Omega^2-\omega^2-i\eta)=2\pi i\ln W(\beta,\omega,\omega,l). \qquad (3.11)$$

We now note that the quantity $W(\beta, \omega, \Omega, l)$ is an even function of the frequency Ω. This follows from the fact that in equations (2.2) only the quantity Ω^2 occurs. Then the integrand in (3.10) turns out to be an odd function, and therefore $I_1 = 0$. We shall furthermore find the values of the integrals over the small circles C_α and $C_\alpha^{(\infty)}$. For this purpose, we integrate by parts in each of them and use the argument principle. As a result, we get from (3.11)

$$W(\beta,\omega,\omega,l)=\prod_\alpha(\Omega_\alpha^2(\beta,\omega,l)-\omega^2)I_2(\beta,\omega)\Big/\prod_\alpha(\Omega_\alpha^{(\infty)2}(\beta,\omega)-\omega^2). \qquad (3.12)$$

The value of $I_2(\beta, \omega)$ can now be found by use of the condition (3.6):

$$I_2(\beta,\omega)=\prod_\alpha(\Omega_\alpha^{(\infty)2}(\beta,\omega)-\omega^2)\Big/\prod_\alpha(\Omega_\alpha^2(\beta,\omega,\infty)-\omega^2), \qquad (3.13)$$

It is evident from (3.13) that if the equality $\Omega_\alpha(\beta, \omega, \infty) = \Omega^{(\infty)}(\beta, \omega)$ is satisfied for all the eigenfrequencies $\Omega_\alpha(\beta, \omega, l)$, then the integral over the large circle C_R must vanish for $R \to +\infty$. From (3.12), (3.13), and the definition (1.5) for the function (1.5) for the function $D(\beta, \omega, l)$, the relation (3.8) follows.

The conditions used above in the derivation of formulas (3.11)–(3.13) are sufficient, but not necessary, for validity of the equality (3.8). Therefore the treatment carried out is useful only for those specific problems for which the assumptions made above are justified. But in consideration of specific examples of the question of the nature of the singularities of the function $W(\beta, \omega, \Omega, l)$ in the complex plane for the variable Ω, the following fact is clarified. It is found that the nature of the singularities of the function under consideration depends substantially on whether the system is bounded by ideally conducting walls at a sufficiently large distance from the bodies. If the system is bounded, then for a physically correct formulation of the problem, the function $W(\beta, \omega, \Omega, l)$ is mermorphic in the variable Ω. Then the other assumptions made above, in the formal proof of the equality (3.8), are also satisfied. But if in the problem we pass to the "thermodynamic" limit of a spatially unbounded system, branch points appear in the function $W(\beta, \omega, \Omega, l)$ at finite values of Ω. The sufficient conditions used above for proof of the equality (3.8) are then obviously not satisfied. Nevertheless the equality (3.8) is found to be valid even in the limit of a spatially unbounded system. From the physical point of view, this last is entirely natural, since it is clear that the forces in any meaningful problem cannot depend to a significant degree on the presence of the distant walls of the resonator. As regards the formal derivation of the relation (3.8) carried out above, it follows from what has been said that the assumption regarding the meromorphic character of the function $W(\beta, \omega, \Omega, l)$ in general is of a special character. It is justified for a class of certain spatially bounded systems, whereas the relation (3.8) is valid also for a broad range of systems not bounded in space. But to get rid of this assumption and find necessary conditions for satisfaction of the relation (3.8) in a general treatment is impossible because of the complication of the mathematical side of the problem that arises.

The situation described above applies, in particular, to a system of two thick plates, separated by a plane gap filled with a liquid.[1)] It is easy to show that in the case of the system shown in Fig. 1a, when the thick

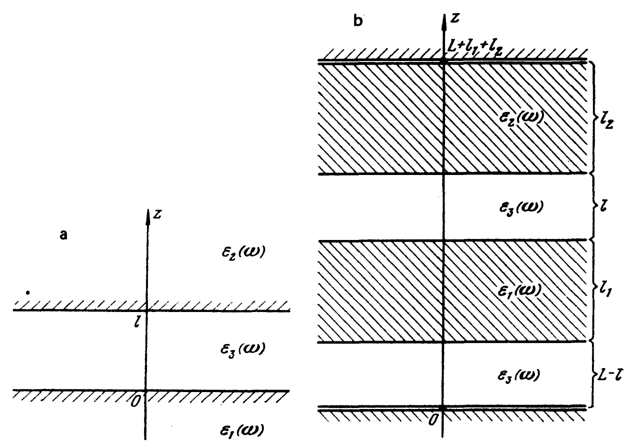

FIG. 1. Figure 1b shows a system consisting of two crystalline plates with permittivities $\varepsilon_1(\omega)$, $\varepsilon_2(\omega)$ and thicknesses l_1, l_2 respectively. The system is bounded by ideally conducting planes at $z = 0$ and $z = L + l_1 + l_2$. The gaps are assumed to be filled with a liquid with permittivity $\varepsilon_3(\omega)$ and total thickness L. In the limit $l_{1,2}/l \to \infty$, $L/l \to \infty$ the thick plates can obviously be represented as two half-planes, as is shown in Fig. 1a. But then the analytic properties of the function $W(\beta, \omega, \Omega, l)$ change significantly.

plates are represented as half-planes, the function $W(q, \omega, \Omega, l)$ has branch points $\Omega_p^{\pm}(\omega, q) = \pm cq/\varepsilon_p^{1/2}(\omega)$ ($p = 1, 2, 3$; here q is the value of the component of the wave vector parallel to the plane of the gap). These branch points are caused by the dependence of the function $W(q, \omega, \Omega, l)$ on the quantities

$$\rho_p(\omega, \Omega, q) = [q^2 - \Omega^2\varepsilon_p(\omega)/c^2]^{1/2}, \quad p = 1, 2, 3. \tag{3.14}$$

At the same time, if we take into account the finite thickness of the plates and place the whole system between ideally conducting walls (see Fig. 1b), then the function $W(q, \omega, \Omega, l, l_1, l_2, L)$ corresponding to this case is found to be meromorphic and also satisfies the other conditions used in the derivation of formulas (3.11)–(3.13).

4. CONCLUSIONS

The representation found in this article for the Green function of a photon in a medium, in the form (2.13), has a very general character. Similar relations can be obtained also for other Green functions (see also the Appendix). Use of formula (2.13) makes it possible actually to sum, in the general case, for arbitrary inhomogeneous media, the diagram series for the part of the free energy of a condensed medium due to interaction of the particles with the longwave equilibrium fluctuational electromagnetic field. As a result, the expression for the free energy is described by the relations (3.2) and (3.3). In the application to problems concerning van der Waals forces between bodies, the expression for the free energy can usually be simplified further and reduced to formulas (1.4) and (1.5), found earlier.[7] The approach developed here enables us to explain the broad range of applicability of these relations and their relation to the results of Dzyaloshinskiĭ and Pitaevskiĭ.[1] It should also be noted that formulas (3.2) and (3.3) describe also the free energy of an inhomogeneous plasma in the random-phase approximation. It is important that in the solution of specific problems one can use, besides formulas (1.4) and (1.5), also the relation (3.8). As a result it is found that it is simpler to find the van der Waals forces between bodies by using the general expression for the free energy rather than for the stress tensor.

APPENDIX

The eigenfunctions and eigenfrequencies of the auxiliary equations (2.2) and (2.3) possess some very useful properties. To derive the first of them, we multiply both sides of (2.2) scalarly by $\Phi_\alpha^-(\omega, \mathbf{r})$ and both sides of (2.3) by $\Phi_\alpha^+(\omega, \mathbf{r})$. We then perform a volume integration in both equations, using integration by parts and the boundary conditions on the ideally conducting walls of the large cavity. Then after some simple calculations we find that for the nondegenerate modes, the eigenfunctions of the auxiliary problem satisfy the following orthogonality relation:

$$\int d\mathbf{r}d\mathbf{r}'\Phi_{\alpha'}^-(\omega, \mathbf{r})\hat{\varepsilon}(\omega, \mathbf{r}, \mathbf{r}')\Phi_\alpha^+(\omega, \mathbf{r}') = \delta_{\alpha\alpha'}N_\alpha(\omega). \tag{A.1}$$

Here the normalization function $N_\alpha(\omega)$ has the dimensions of energy. For degenerate modes, the orthogonalization (A.1) can be carried out by appropriate choice of the independent eigenfields; this also will everywhere be assumed done.

We shall now find an expression for the variation $\delta\Omega_\alpha$ of an eigenfrequency of the auxiliary problem. For this purpose we vary all the quantities in equation (2.2) with a small variation of the permittivity. The latter may be produced either by changes of the physical parameters that describe the condensed medium or by change of the frequency ω. We then multiply both sides of the resulting relation scalarly by $\Phi_\alpha^-(\omega, \mathbf{r})$ and integrate all terms over the volume of the large cavity. We furthermore transform the term on the left side of this relation, integrating by parts and using the boundary conditions on the ideally conducting walls of the large cavity and Eq. (2.3). As a result we get

$$\delta\Omega_\alpha(\omega) = -\frac{\Omega_\alpha(\omega)}{2N_\alpha(\omega)}\int d\mathbf{r}_1 d\mathbf{r}_2 \Phi_\alpha^-(\omega, \mathbf{r}_1)\delta\varepsilon(\omega, \mathbf{r}_1, \mathbf{r}_2)\Phi_\alpha^+(\omega, \mathbf{r}_2). \tag{A.2}$$

Below, we shall need also the following relation:

$$\int d\mathbf{r}\Phi_{\alpha,i}^-(\omega, \mathbf{r})\,\mathrm{rot}_{ik}\,\mathrm{rot}_{km}\,\varepsilon_{mj}^{-1}(\omega, \mathbf{r}, \mathbf{r}') = \frac{\Omega_\alpha^2(\omega)}{c^2}\Phi_{\alpha,j}^-(\omega, \mathbf{r}'). \tag{A.3}$$

The correctness of formula (A.3) can be shown by performing an integration by parts in its left member and then using Eq. (2.3) and also the boundary conditions for the fields on the walls of the large cavity.

It follows from Eqs. (2.1) that the retarded Green function of a photon in the medium satisfies the conditions

$$\frac{\partial}{\partial x_i}\left\{\int d\mathbf{r}_1\varepsilon_{il}(\omega, \mathbf{r}, \mathbf{r}_1)\mathscr{D}_{lk}(\omega, \mathbf{r}_1, \mathbf{r}')\right\} = \frac{4\pi\hbar c^2}{\omega^2}\frac{\partial}{\partial x_k}\delta(\mathbf{r}-\mathbf{r}'). \tag{A.4}$$

Hence, in accordance with formulas (2.4) and the discussion of them, it is clear that the expression for the Green function can be represented in the form of the following expansion:

$$\frac{\omega^2}{4\pi\hbar c^2}\mathscr{D}_{lk}(\omega, \mathbf{r}, \mathbf{r}') = \sum_\alpha a_\alpha(\omega)\Phi_{\alpha,l}^+(\omega, \mathbf{r})\Phi_{\alpha,k}^-(\omega, \mathbf{r}') + \varepsilon_{lk}^{-1}(\omega, \mathbf{r}, \mathbf{r}'). \tag{A.5}$$

We now substitute this expansion in (2.1) and use the relation (2.2). We then multiply both sides of the resulting equation scalarly by $\Phi_{\alpha'}^-(\omega, \mathbf{r})$ and perform an integration over $d\mathbf{r}$. We then find explicit expressions for the coefficients $a_\alpha(\omega)$ by using the relations (A.3) and the orthogonality condition (A.1). As a result, we get the following expression for the Green function:

$$\mathscr{D}_{lk}(\omega, \mathbf{r}, \mathbf{r}') = -\frac{4\pi\hbar c^2}{\omega^2}\left\{\sum_\alpha \frac{\Omega_\alpha^2(\omega)}{\Omega_\alpha^2(\omega)-\omega^2} \times \frac{\Phi_{\alpha,l}^+(\omega, \mathbf{r})\Phi_{\alpha,k}^-(\omega, \mathbf{r}')}{N_\alpha(\omega)} - \varepsilon_{lk}^{-1}(\omega, \mathbf{r}, \mathbf{r}')\right\}. \tag{A.6}$$

It can be shown that in the special case of a homogeneous and isotropic medium, the relation (A.6) corresponds to the well known result.

The relation (2.5) follows from formula (A.6) by use of the definition (2.6) for the function $D(\beta, \omega)$ and of the expression (A.2) for the variation of the eigenfrequencies of the auxiliary problem.

The method of obtaining the relation (2.11) is completely analogous to the derivation of formula (2.5) given above. In this case, the orthogonality relation for the functions $\varphi_\alpha^+(\omega, \mathbf{r})$ and $\varphi_\alpha^-(\omega, \mathbf{r})$ has the form

$$\frac{1}{\mu_\alpha(\omega)}\int d\mathbf{r}d\mathbf{r}'\varphi_{\alpha'}^-(\omega,\mathbf{r}')\chi(\omega,\mathbf{r}',\mathbf{r})\varphi_\alpha^+(\omega,\mathbf{r}) = \int d\mathbf{r}\varphi_{\alpha'}^-(\omega,\mathbf{r})\varphi_\alpha^+(\omega,\mathbf{r}) = \delta_{\alpha\alpha'}N_\alpha^{(\varepsilon)}(\omega). \tag{A.7}$$

The expression for the variation $\delta\mu_\alpha(\omega)$ of the eigenvalues is written as follows:

$$\delta\mu_\alpha(\omega) = \frac{1}{N_\alpha^{(\varepsilon)}(\omega)}\int d\mathbf{r}d\mathbf{r}'\varphi_\alpha^-(\omega,\mathbf{r})\delta\hat{\chi}(\omega,\mathbf{r},\mathbf{r}')\varphi_\alpha^+(\omega,\mathbf{r}'). \tag{A.8}$$

Then from the expansion for the inverse permittivity,

$$\varepsilon_{ik}^{-1}(\omega,\mathbf{r},\mathbf{r}') = \sum_\alpha \frac{1}{1+4\pi\mu_\alpha(\omega)}\cdot\frac{\varphi_{\alpha,i}^+(\omega,\mathbf{r})\varphi_{\alpha,k}^-(\omega,\mathbf{r}')}{N_\alpha^{(\varepsilon)}(\omega)} \tag{A.9}$$

and from formulas (A.8) and (2.12) we arrive at the relation (2.11).

Starting from formula (A.2), one can also find a general expression for the variation $\delta\omega_\alpha(\beta)$ of the real (not the auxiliary) system. In fact, let the eigenfrequency $\omega_\alpha(\beta)$ correspond to the eigenfrequency $\Omega_\alpha(\beta,\omega)$ of the auxiliary problem. Since the frequency $\omega_\alpha(\beta)$ is a root of Eq. (2.14), it follows from the relation (2.6) that $\Omega_\alpha^2[\beta,\omega_\alpha(\beta)] = \omega_\alpha^2(\beta)$. Then for the variation of the quantities under consideration in a small change of the physical characteristics of the medium, we get the relation

$$\delta\{\Omega_\alpha(\beta,\omega_\alpha)\}_{\omega_\alpha=\mathrm{const}} + \frac{\partial\Omega_\alpha(\beta,\omega_\alpha)}{\partial\omega_\alpha}\delta\omega_\alpha = \delta\omega_\alpha. \tag{A.10}$$

For simplicity of the notation, here and below we do not write the arguments of the function $\omega_\alpha(\beta)$ explicitly.

We now take into account that for $\omega=\omega_\alpha$, the eigenfunctions of the auxiliary equations (2.2) [or (2.3)] coincide with the eigenfields $\mathbf{E}_\alpha^+(\beta,\mathbf{r})$ in a medium with permittivity $\varepsilon_{ik}(\omega_\alpha,\mathbf{r},\mathbf{r}',\mathbf{B}_0)$ [or with the fields $\mathbf{E}_\alpha^-(\beta,\mathbf{r})$ in a medium with permittivity $\varepsilon_{ik}(\omega_\alpha,\mathbf{r},\mathbf{r}',-\mathbf{B}_0)$; here $\mathbf{B}_0$ is a magnetic field due to the magnetoactive properties of the medium]. Then it follows from (A.10) and (A.2) that

$$\delta\omega_\alpha = -\frac{\omega_\alpha}{2N_\alpha(\beta,\omega_\alpha)(1-\partial\Omega_\alpha(\beta,\omega_\alpha)/\partial\omega_\alpha)} \times\int d\mathbf{r}_1 d\mathbf{r}_2 E_{\alpha,i}^-(\beta,\mathbf{r}_1)\delta\varepsilon_{ij}(\omega_\alpha,\mathbf{r}_1,\mathbf{r}_2)E_{\alpha,j}^+(\beta,\mathbf{r}_2). \tag{A.11}$$

A formula for the variation $\delta\omega_\alpha$ of the eigenfrequency is necessary, for example, in order to find an expression for the variation δF_α of the free energy of the characteristic electromagnetic wave $\mathbf{E}_\alpha(\beta,\mathbf{r})$ in a transparent medium during an adiabatically slow change of the permittivity. This problem has been considered by Pitaevskiĭ.[10] In a linear transparent medium, the number of photons of a given mode is an adiabatic invariant. Therefore we have, in analogy to the expression for the adiabatic variation of the energy of an oscillator,

$$\delta F_\alpha/F_\alpha = \delta\omega_\alpha/\omega_\alpha. \tag{A.12}$$

The expression for the free energy of a characteristic electromagnetic wave in a medium, with neglect of absorption, can be written in the form (see, for example, Ref. 11)

$$F_\alpha = \frac{1}{16\pi}\int d\mathbf{r}_1 d\mathbf{r}_2\frac{1}{\omega_\alpha}\frac{d(\omega_\alpha^2\varepsilon_{ij}(\omega_\alpha,\mathbf{r}_1,\mathbf{r}_2))}{d\omega_\alpha}E_{\alpha,j}(\mathbf{r}_2)E_{\alpha,i}^*(\mathbf{r}_1) = \frac{1}{8\pi}N_\alpha(\omega_\alpha)\left(1-\frac{\partial\Omega_\alpha(\omega_\alpha)}{\partial\omega_\alpha}\right). \tag{A.13}$$

Here formulas (A.1) and (A.2) have been used in passage to the last expression. From (A.12), (A.13), and (A.11) we now get, for nonabsorbing media, Pitaevskiĭ's result

$$\delta F_\alpha(\beta) = -\frac{1}{16\pi}\int d\mathbf{r}_1 d\mathbf{r}_2 E_{\alpha,i}^*(\beta,\mathbf{r}_1)\delta\varepsilon_{ij}(\omega_\alpha,\mathbf{r}_1,\mathbf{r}_2)E_{\alpha,j}(\beta,\mathbf{r}_2). \tag{A.14}$$

In Pitaevskiĭ's paper,[10] the formula for the variation $\delta\omega_\alpha$ of the eigenfrequency in a transparent medium was obtained by consideration of nonattenuating electromagnetic oscillations in the simplest LC circuit. Here we have obtained the expression (A.11) as a general result of the electrodynamics of continuous media. Then the broad range of applicability of formula (A.14) also becomes clearer.

Relations of the type (2.5) and (2.11) can actually be obtained for any Green functions. In closing, we shall consider by way of example the retarded Green function $G_{ij}(\omega,\mathbf{r}_1,\mathbf{r}_2)$ for an inhomogeneous anisotropic electron liquid. This quantity, as is well known, satisfies the following relation (see, for example, Ref. 8, § 62):

$$\left(\omega+\mu+\frac{\Delta_1}{2m}\right)G_{ij}(\omega,\mathbf{r}_1,\mathbf{r}_2) - \int d\mathbf{r}'\Sigma_{ik}(\omega,\mathbf{r}_1,\mathbf{r}')G_{kj}(\omega,\mathbf{r}',\mathbf{r}_2) = \delta_{ij}\delta(\mathbf{r}_1-\mathbf{r}_2), \tag{A.15}$$

where $\Sigma_{ik}(\omega,\mathbf{r}_1,\mathbf{r}')$ is the self-energy function, and where the indices i,j,k now correspond to spin variables. Equation (A.15) is nonlinear, since the self-energy function and the chemical potential depend functionally on the Green function of the electrons.

We now introduce the following auxiliary equations:

$$\left(\Omega_\nu(\omega)+\frac{\Delta}{2m}\right)\chi_{\nu,i}^+(\omega,\mathbf{r}) = \int d\mathbf{r}'\Sigma_{ik}(\omega,\mathbf{r},\mathbf{r}')\chi_{\nu,k}^+(\omega,\mathbf{r}'), \tag{A.16}$$

$$\left(\Omega_\nu(\omega)+\frac{\Delta}{2m}\right)\chi_{\nu,i}^-(\omega,\mathbf{r}) = \int d\mathbf{r}'\chi_{\nu,k}^-(\omega,\mathbf{r}')\Sigma_{ki}(\omega,\mathbf{r}',\mathbf{r}). \tag{A.17}$$

The self-energy function and therefore the solutions of the linear equations (A.16) and (A.17) depend on the Green function of the electrons as a functional parameter (which has not been written explicitly). The characteristic of Eqs. (A.16) and (A.17) is that the self-energy function that occurs in them is independent of the frequency Ω, which corresponds to a Fourier expansion of the solutions of these equations with respect to time. At the same time the self-energy function depends on the frequency ω as a parameter, and this dependence is such that at all frequencies Ω the self-energy function is taken for the electron liquid under consideration at frequency ω.

The advantage of introducing the auxiliary equations (A.16) and (A.17) is that their solutions possess very useful properties. In fact, by starting from Eqs. (A.16) and (A.17) and proceeding in analogy to the derivation of formulas (A.1), (A.7) and (A.2), (A.8), it is easy to obtain the orthogonality relation

$$\int d\mathbf{r}\chi_{\nu,i}^+(\omega,\mathbf{r})\chi_{\nu',i}^-(\omega,\mathbf{r}) = \delta_{\nu,\nu'}N_\nu^{(\Sigma)}(\omega) \tag{A.18}$$

and the expression for the variation $\delta\Omega_\nu(\omega)$ of the eigenfrequency

$$\delta\Omega_\nu(\omega) = \frac{1}{N_\nu^{(\Sigma)}(\omega)}\int d\mathbf{r}_1 d\mathbf{r}_2\chi_{\nu,i}^-(\omega,\mathbf{r}_1)\delta\Sigma_{ik}(\omega,\mathbf{r}_1,\mathbf{r}_2)\chi_{\nu,k}^+(\omega,\mathbf{r}_2). \tag{A.19}$$

The following desired representation for the Green function is then obtained:

$$G_{ij}(\omega, \mathbf{r}_1, \mathbf{r}_2)=\sum_\nu \frac{\chi^+_{\nu,i}(\omega, \mathbf{r}_1)\chi^-_{\nu,j}(\omega, \mathbf{r}_2)}{(\omega+\mu-\Omega_\nu(\omega))N^{(\Sigma)}_\nu(\omega)}=-\frac{\delta\left(\int\rho(\zeta)d\zeta\ln D^{(\Sigma)}(\zeta, \omega)\right)}{\delta\Sigma_{ji}(\omega, \mathbf{r}_2, \mathbf{r}_1)}. \tag{A.20}$$

The quantity $D^{(\Sigma)}(\zeta, \omega)$ that occurs here has the form

$$D^{(\Sigma)}(\zeta, \omega)=\prod_k \frac{\Omega_k(\zeta, \omega)-\omega-\mu}{\Omega^{(\Sigma)}_0}. \tag{A.21}$$

The quantity $\Omega_0^{(\Sigma)}$ is independent of the properties of the electron liquid, and after taking of the variation derivation it no longer occurs in the expression (A.20). The variables ν here denote both discrete variables k and continuous (or quasicontinuous) variables ζ, which occur separately in the writing of formulas (A.20) and (A.21).

It is evident from a comparison of the relations (A.15) and (A.16) that the roots of the equation

$$D^{(\Sigma)}(\zeta, \omega)=0 \tag{A.22}$$

give the energy spectrum of the electron liquid. Thus, as follows from (A.20), the generating function for the Green function $G_{ij}(\omega, \mathbf{r}_1, \mathbf{r}_2)$ turns out to be directly related to the spectrum of excitations of the electron liquid.

[1)] The difference between the analytic properties of functions from the dispersion equations for systems of plates bounded and unbounded in space were discussed earlier by Schram.[9] We note that the system of plates bounded in space investigated by him differs from the system considered here and shown in Fig. 1b. Furthermore, Schram considered only the case of a transparent medium, the permittivity of which has no singular points in the complex frequency plane except poles on the real axis.

[1]I. E. Dzyaloshinskiĭ and L. P. Pitaevskiĭ, Zh. Eksp. Teor. Fiz. **36**, 1797 (1959) [Sov. Phys. JETP **9**, 1282 (1959)].

[2]I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskiĭ, Usp. Fiz. Nauk **73**, 381 (1961) [Sov. Phys. Usp. **4**, 153 (1961)].

[3]Yu. S. Barash and V. L. Ginzburg, Usp. Fiz. Nauk **116**, 5 (1975) [Sov. Phys. Usp. **18**, 305 (1975)].

[4]N. G. Van Kampen, B. R. A. Nijboer, and K. Schram, Phys. Lett. **26A**, 307 (1968).

[5]H. B. G. Casimir, Proc. Kon. Ned. Ak. Wetenschap. **51**, 793 (1948).

[6]Yu. S. Barash and V. L. Ginzburg, Usp. Fiz. Nauk **118**, 523 (1976) [Sov. Phys. Usp. **19**, 263 (1976)].

[7]Yu. S. Barash and V. L. Ginzburg, Pis'ma Zh. Eksp. Teor. Fiz. **15**, 567 (1972) [JETP Lett. **15**, 403 (1972)].

[8]E. M. Lifshitz and L. P. Pitaevskiĭ, Statisticheskaya fizika (Statistical Physics), Part 2. M.: Nauka, 1978 (transl., Pergamon Press, 1980).

[9]K. Schram, Phys. Lett. **43A**, 282 (1973).

[10]L. P. Pitaevskiĭ, Zh. Eksp. Teor. Fiz. **39**, 1450 (1960) [Sov. Phys. JETP **12**, 1008 (1961)].

[11]Yu. S. Barash, Izv. Vyssh. Uchebn. Zaved., Radiofiz. **21**, 736 (1978) [Radiophys. and Quant. Electron. **21**, 521 (1978)].

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