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GENERAL THEORY OF VAN DER WAALS' FORCES

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1. INTRODUCTION

It is well known that there are attractive forces, called van der Waals' forces, between any two neutral atoms or molecules which are at a distance R which is large compared to the dimensions of the systems themselves. These forces have a long range character: they fall off with distance according to a power law and not exponentially.

From their origin the van der Waals' forces have electromagnetic character. They are obtained, as was first shown by F. London,¹ in second order perturbation theory applied to the electrostatic interaction of two dipoles; the energy of attraction is then proportional to R^{-6} . However, such a treatment is possible only so long as the distance R is small compared with the wavelength λ corresponding to transitions between the ground and excited states of the atoms. For $R \gtrsim \lambda$ effects of retardation become important. The interaction of atoms when retardation is taken into account was studied by Casimir and Polder² as an effect in fourth-order perturbation theory in the interaction of

an atom with the electromagnetic field. (The calculations were repeated by Dzyaloshinskii³ using the modern invariant Feynman technique.) In the limiting case when $R \gg \lambda$, the interaction energy is proportional to R^{-7} .

The appearance of attractive forces between neutral atoms naturally leads to the appearance of similar forces between any two macroscopic bodies whose surfaces are brought to very small distances from one another. However, the calculation of these forces, simply starting from the interaction of individual atoms (as has usually been done), is actually impossible. It would be valid only for sufficiently rarefied bodies such as gases, a case which actually, of course, cannot be achieved. On the other hand, in condensed bodies the atoms of the neighborhood cause an essential change in the properties of the electronic shells, and the presence of a medium between the interacting atoms affects the electromagnetic field through which the interaction is established.

However, in contrast to such a "microscopic" approach to this problem, one can also attack it from a

completely different, purely macroscopic point of view, in which the interacting bodies are treated as continuous media. The validity of such an approach is related to the fact that the distances between the surfaces of the bodies are assumed to be small, but still large compared with interatomic distances inside the bodies.

The fundamental idea of the theory is that the interaction between bodies is treated as being established through a fluctuating electromagnetic field. By virtue of thermodynamic fluctuations, such a field is always present inside any material medium and also extends beyond its boundaries. A well-known case where such a field manifests itself is the thermal radiation of a body, but it should be emphasized that this radiation does not exhaust all the fluctuation field outside the body. This is seen most clearly from the fact that electromagnetic fluctuations persist even at absolute zero, when there is no thermal radiation; at this temperature the fluctuations have a purely quantum character.

In addition to the attractive forces between bodies which are close to one another, from this point of view we may also treat other effects in condensed bodies which are related to the van der Waals' forces, in particular, the properties of thin films of liquid on the surface of a solid.

In all of these effects, from the point of view of thermodynamics there appears one general feature: all of them are associated with the nonadditivity of the free energy of a system of bodies when van der Waals' forces are taken into account. In fact, in all these cases the free energy is not simply proportional to the volume of the system, but depends for a fixed volume on parameters which characterize the mutual arrangement of the bodies. (For example, it may depend on the distance between the solid bodies or on the thickness of a film.) It is just this nonadditivity, which is related to the long-range character of the van der Waals' forces, which gives a qualitatively new effect, distinguishing the contribution of these forces to thermodynamic quantities from the very much greater additive parts of these quantities. This nonadditivity can also be understood easily by noting the connection between the van der Waals' forces and fluctuations of the electromagnetic field. In fact, every change of electrical properties of the medium in a certain region leads, by virtue of the Maxwell equations, to a change in the fluctuation field outside this region, too. Therefore, that part of the free energy which is associated with electromagnetic fluctuations is not determined solely by the properties of the material at a given point, i.e., it is non-additive.

We should now make more definite what we mean when, in speaking of fluctuations of the electromagnetic field, we consider the set of spectral components with wave length large compared to atomic dimensions. (We shall refer to them as "long-wave" fluctuations.) What we mean is that those fluctuations are important

whose wave lengths are of the order of magnitude of the characteristic dimensions of the inhomogeneities in the system. (For example, for a film, of the order of its thickness; for the case of attraction of bodies, of the order of the distance between the bodies.) All properties of long-range fluctuations and also their contribution to all thermodynamic quantities are expressed entirely in terms of the complex dielectric constant of the body.

It turns out that it is possible to construct a general macroscopic theory of van der Waals' forces which is free of any limitations except the one that all the characteristic dimensions of the bodies must be large compared with atomic separations. Such a theory is applicable, in principle, at any temperature to any bodies, independent of their molecular constitution (ionic or molecular crystals, amorphous bodies or liquids, metals, dielectrics, etc.). Since the theory starts from the exact equations of the electromagnetic field, it automatically includes retardation effects.

A theory of the van der Waals' attractive forces between bodies, based on these principles, was first constructed by E. M. Lifshitz.⁴ By applying the methods of present-day quantum field theory, it has been possible to find general formulas for computing the van der Waals' part of the thermodynamic quantities for an arbitrary inhomogeneous medium (I. E. Dzyaloshinskii and L. P. Pitaevskii⁵). This has made it possible to extend Lifshitz's theory to the case of bodies separated by a liquid layer, and also to the study of the properties of liquid films (I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskii⁶).

We begin our presentation with a brief summary of the methods of quantum field theory in statistical physics (Sec. 2). These methods make it possible to extend the whole theory of van der Waals' forces in the most natural and general fashion. The further presentation is arranged so that the reader who is interested only in the results of the theory can omit Secs. 2, 3, and 4a.

2. METHODS OF QUANTUM FIELD THEORY IN STATISTICAL PHYSICS

A characteristic feature of present day quantum field theory is the extensive use of the Feynman diagram technique, which makes it possible to give a very pictorial presentation of the structure and character of any approximation.

We know that in quantum field theory physical quantities are expressed in perturbation series in powers of the coupling constant (for example, in powers of the charge e of the electron). Any term in the perturbation series can be described by an appropriate diagram, and its computation on the basis of this diagram is done according to the rules of the Feynman technique. To each internal line of the diagram there is associated a so-called free particle Green's func-

tion G_0 , or a free photon Green's function D_0 ; to each intersection of lines on the diagram (vertex) there is associated a definite interaction operator (in quantum electrodynamics this is the Dirac matrix γ_μ multiplied by the electron charge), and finally an integration is carried out over the four-dimensional coordinates of each vertex in the diagram.

The advantages of the diagram technique are most clearly seen in the solution of problems in which one cannot limit oneself to a finite number of terms in the perturbation series, but must sum infinite sequences of so-called "principal diagrams." The possibility of summing infinite series makes the diagram technique especially attractive for quantum statistics, where the usual methods enable one to describe with great difficulty only the first two or three terms in the perturbation series.

The application of the methods of quantum field theory to problems of statistical physics at finite temperatures is based on the work of Matsubara,⁷ who showed that the computation of the free energy can be carried out according to the rules of the Feynman diagram technique. Any term of the series in the thermodynamic perturbation theory, as in field theory, is described by the corresponding Feynman diagram, and its calculation is done by analogous rules: each line of the diagram is associated with a "temperature" Green's function for the free particle \mathcal{G}_0 , and each vertex of the diagram is associated with an interaction operator. The only difference is that the Green's function \mathcal{G}_0 in the Matsubara technique depends not on the time t , but on a fictitious "imaginary time" τ , which varies over a finite range from zero to the reciprocal of the temperature, $1/T$.^{*} Correspondingly, in place of an integration over the time from $-\infty$ to ∞ , at each vertex of the diagram one carries out an integration with respect to τ between the limits from 0 to $1/T$.

We here give a brief presentation of Matsubara's argument. Let us consider for example a system of charged particles interacting with the electromagnetic field. The Hamiltonian of such a system has the form

$$H = H_0 + H_{\text{int}},$$

where H_0 is the Hamiltonian of the free particles and photons, which depends quadratically on the operators of the respective fields $\psi(\mathbf{r})$ and $A_\alpha(\mathbf{r})$ in the Schrödinger representation, while H_{int} is the interaction operator:

$$H_{\text{int}} = - \int A_\alpha(\mathbf{r}) j_\alpha(\mathbf{r}) d^3\mathbf{r},$$

$j_\alpha(\mathbf{r})$ is the current operator for the particles,[†] which

^{*}In Secs. 2, 3, and 4a we use a system of units in which $\hbar = c = 1$; the temperature is measured in energy units.

[†]Here and in the following Greek indices $\alpha, \beta = 0, 1, 2, 3$ number the components of 4-vectors and tensors, while Latin indices $i, k, \dots = 1, 2, 3$ number the components of vectors and tensors in three-dimensional space.

is some quadratic function of the particle operators $\psi(\mathbf{r})$.

The thermodynamic properties of the system are determined by the statistical matrix

$$\varrho = \exp\left(-\frac{H}{T}\right),$$

through which the free energy F is expressed by means of the relation

$$F = -T \ln \text{Sp } \varrho.$$

In computing the average value of any quantity (in this case, the average value of ρ), one uses in field theory the equations of motion for the field operators. The fundamental idea of Matsubara consists in a shift from the time t to an "imaginary time" τ , preserving the formal similarity with the usual equations of motion. To do this, let us first go over to the "interaction representation," which is the analogue of the usual quantum mechanical interaction representation, by using the formulas

$$\begin{aligned} A_\alpha(\mathbf{r}, \tau) &= e^{\tau H_0} A_\alpha(\mathbf{r}) e^{-\tau H_0}, & \psi(\mathbf{r}, \tau) &= e^{\tau H_0} \psi(\mathbf{r}) e^{-\tau H_0}, \\ \bar{\psi}(\mathbf{r}, \tau) &= e^{\tau H_0} \bar{\psi}(\mathbf{r}) e^{-\tau H_0}, & j_\alpha(\mathbf{r}, \tau) &= e^{\tau H_0} j_\alpha(\mathbf{r}) e^{-\tau H_0}, \\ H_{\text{int}}(\tau) &= e^{\tau H_0} H_{\text{int}} e^{-\tau H_0}. \end{aligned}$$

Obviously

$$H_{\text{int}}(\tau) = - \int A_\alpha(\mathbf{r}, \tau) j_\alpha(\mathbf{r}, \tau) d^3\mathbf{r}.$$

Let us also introduce the matrix

$$\varrho(\tau) = \exp(-\tau H)$$

and let us represent it in the form

$$\varrho(\tau) = \exp(-\tau H_0) \mathfrak{S}(\tau).$$

The matrix $\mathfrak{S}(\tau)$ thus defined is the analogue of the S-matrix in field theory. It satisfies the equation

$$- \frac{\partial \mathfrak{S}(\tau)}{\partial \tau} = H_{\text{int}}(\tau) \mathfrak{S}(\tau), \quad \mathfrak{S}(0) = 1,$$

which is obtained from the corresponding equation of field theory by replacing t by $i\tau$. Its solution is

$$\mathfrak{S}(\tau) = T_\tau \exp\left\{- \int_0^\tau H_{\text{int}}(\tau) d\tau\right\},$$

where T_τ is the time-ordering operator which orders the operators H in order of increasing "time" τ .

For the statistical matrix $\rho = \rho(1/T)$ we obtain the obvious formula

$$\left. \begin{aligned} \varrho &= \exp\left(-\frac{H_0}{T}\right) \mathfrak{S}, \\ \mathfrak{S} &\equiv \mathfrak{S}\left(\frac{1}{T}\right) = T_\tau \exp\left\{- \int_0^{\frac{1}{T}} H_{\text{int}}(\tau) d\tau\right\}, \end{aligned} \right\} \quad (2.1)$$

from which we have for the free energy:

$$F = F_0 - T \ln \text{Sp} \{e^{(F_0 - H_0)/T} \mathfrak{S}\}, \quad (2.2)$$

where F_0 is the free energy of the noninteracting particles,

$$F_0 = -T \ln \text{Sp } e^{-H_0/T}.$$

Formula (2.2) can be written as

$$F = F_0 - T \ln \langle \mathfrak{S} \rangle, \tag{2.3}$$

where we understand by the symbol $\langle \dots \rangle$ the Gibbs average over free particle states

$$\langle \dots \rangle = \text{Sp} \{ e^{(F_0 - H_0)/T} \dots \}.$$

Expanding the expression for \mathfrak{S} in powers of H_{int} , averaging each term in the series and, finally, taking its logarithm, we obtain the perturbation series of thermodynamic theory for the free energy. This averaging reduces to computing the average values of ordered products of various numbers of operators for the electromagnetic field and the particles, for example:

$$\langle T_{\tau} \{ A_{\alpha}(\mathbf{r}_1, \tau_1) A_{\beta}(\mathbf{r}_2, \tau_2) \psi(\mathbf{r}_3, \tau_3) \bar{\psi}(\mathbf{r}_4, \tau_4) \} \rangle. \tag{2.4}$$

Expressions of this same type occur in quantum field theory.

The Feynman diagram technique is based on the following two properties of the equations of field theory: first, on the possibility of representing all quantities of the theory (S-matrix etc.) as averages of ordered products (T-products) of various numbers of field operators; and secondly, on Wick's theorem, according to which the average of a T-product of any number of operators for free particles is expressed in terms of products of all possible averages over pairs of these operators. The pair averages are described by the above-mentioned Green's functions for the free particles. Thus the average of any number of quantities is expressed in terms of these Green's functions.

Formulas (2.1), (2.2), and (2.4) show that the first property also holds in the thermodynamic theory. It also turns out that in this case Wick's theorem remains valid, but here it becomes a statement which is exact only as the total number of particles N tends to infinity (for a given density): more precisely, Wick's theorem is valid to terms of order $1/N$. Applying Wick's theorem to expressions of the type (2.4) we obtain, for example:

$$\begin{aligned} &\langle T_{\tau} \{ A_{\alpha}(\mathbf{r}_1, \tau_1) A_{\beta}(\mathbf{r}_2, \tau_2) \psi(\mathbf{r}_3, \tau_3) \bar{\psi}(\mathbf{r}_4, \tau_4) \} \rangle \\ &= \langle T_{\tau} \{ A_{\alpha}(\mathbf{r}_1, \tau_1) A_{\beta}(\mathbf{r}_2, \tau_2) \} \rangle \langle T_{\tau} \{ \psi(\mathbf{r}_3, \tau_3) \bar{\psi}(\mathbf{r}_4, \tau_4) \} \rangle, \end{aligned}$$

$$\begin{aligned} &\langle T_{\tau} \{ A_{\alpha}(\mathbf{r}_1, \tau_1) A_{\beta}(\mathbf{r}_2, \tau_2) A_{\gamma}(\mathbf{r}_3, \tau_3) A_{\delta}(\mathbf{r}_4, \tau_4) \} \rangle \\ &= \langle T_{\tau} \{ A_{\alpha}(\mathbf{r}_1, \tau_1) A_{\beta}(\mathbf{r}_2, \tau_2) \} \rangle \langle T_{\tau} \{ A_{\gamma}(\mathbf{r}_3, \tau_3) A_{\delta}(\mathbf{r}_4, \tau_4) \} \rangle \\ &+ \langle T_{\tau} \{ A_{\alpha}(\mathbf{r}_1, \tau_1) A_{\gamma}(\mathbf{r}_3, \tau_3) \} \rangle \langle T_{\tau} \{ A_{\beta}(\mathbf{r}_2, \tau_2) A_{\delta}(\mathbf{r}_4, \tau_4) \} \rangle \\ &+ \langle T_{\tau} \{ A_{\alpha}(\mathbf{r}_1, \tau_1) A_{\delta}(\mathbf{r}_4, \tau_4) \} \rangle \langle T_{\tau} \{ A_{\beta}(\mathbf{r}_2, \tau_2) A_{\gamma}(\mathbf{r}_3, \tau_3) \} \rangle \end{aligned}$$

etc. It is clear that the technique thus developed is completely analogous to the field theory technique, with the one difference that the zeroth order Green's functions for the free particles and photons are replaced by the temperature Green's functions for the free particles

$$\mathfrak{S}^0 = -\langle T_{\tau} \{ \psi(\mathbf{r}_1, \tau_1) \bar{\psi}(\mathbf{r}_2, \tau_2) \} \rangle \tag{2.4a}$$

and the photons

$$\mathfrak{D}_{\alpha\beta}^0 = -\langle T_{\tau} \{ A_{\alpha}(\mathbf{r}_1, \tau_1) A_{\beta}(\mathbf{r}_2, \tau_2) \} \rangle, \tag{2.4b}$$

and in place of an integration over the time between infinite limits, there appears an integration with respect to the "imaginary time" τ between the limits zero and $1/T$.

The Feynman diagrams which describe the corrections to the free energy have the form of closed loops. For the case of interaction of particles with the electromagnetic field the diagram for second order is shown in Fig. 1a, the diagrams for fourth order in Fig. 1b, 1c, and 1d. (The solid lines show the Green's function of the particle, the dashed lines the Green's function of the photon.) We note that in the corrections for any order of perturbation theory one should include only connected diagrams of that order, i.e., diagrams which do not split up into parts which are not connected by any lines. (The order of a diagram is obviously equal to the number of vertices in the diagram.) For example, the diagram of Fig. 2 should not be included in the sixth order corrections. This property is related to the fact that the expression for the free energy has the form $\ln \langle \dots \rangle$. It can be shown that in taking the logarithm all the unconnected diagrams cancel one another.

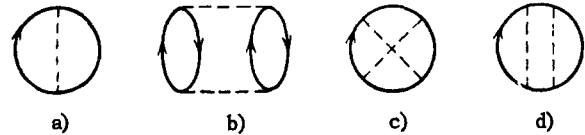


FIG. 1

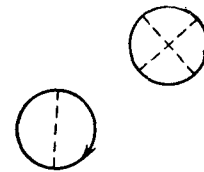


FIG. 2

The perturbation series for the free energy, however, has an unpleasant property. It turns out that the diagrams appear in it with a coefficient which depends essentially on the order n , namely with the coefficient $1/n$. (A coefficient of the form a^n , with a constant a which is common to diagrams of all orders, would obviously be unimportant, since a can for example be included formally in the charge.) This property of the series for the free energy makes it practically unsuitable for problems where the coupling constant is not small and where one has to sum infinite sequences of diagrams. Fortunately, it is present only in diagrams which have the form of closed loops, whereas for diagrams which have external lines the coefficients

do not depend essentially on the order of approximation in perturbation theory.

Among these latter diagrams, the most important are diagrams with two free ends, for example, diagrams of the type of Fig. 3. The sum of all possible coupled diagrams with two external photon lines is called the total temperature Green's function of the photon. It

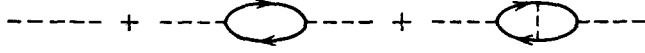


FIG. 3

obviously depends on eight variables: the space coordinates and the "times" τ of the free ends. It is not difficult to write an analytic expression for it in terms of the operators in the interaction representation [cf. (2.4b)]:

$$\mathfrak{D}_{\alpha\beta}(\mathbf{r}_1, \tau_1; \mathbf{r}_2, \tau_2) = - \frac{\langle T_{\tau} \{ A_{\alpha}(\mathbf{r}_1, \tau_1) A_{\beta}(\mathbf{r}_2, \tau_2) \mathcal{E} \} \rangle}{\langle \mathcal{E} \rangle}.$$

Analogous formulas also apply for the Green's functions of the particles. We also give a very useful formula which expresses the total temperature Green's function of the photon in terms of the operators in the Schrödinger representation:

$$\begin{aligned} \mathfrak{D}_{\alpha\beta}(\mathbf{r}_1, \tau_1; \mathbf{r}_2, \tau_2) &= \begin{cases} - \text{Sp} \{ e^{(F-H)/T} e^{H(\tau_1-\tau_2)} A_{\alpha}(\mathbf{r}_1) e^{-H(\tau_1-\tau_2)} A_{\beta}(\mathbf{r}_2) \}, & \tau_1 > \tau_2, \\ - \text{Sp} \{ e^{(F-H)/T} e^{-H(\tau_1-\tau_2)} A_{\beta}(\mathbf{r}_2) e^{H(\tau_1-\tau_2)} A_{\alpha}(\mathbf{r}_1) \}, & \tau_1 < \tau_2. \end{cases} \end{aligned} \quad (2.5)$$

The formula for the Green's function of the free photon is obtained from this by the substitution $H \rightarrow H_0$, $F \rightarrow F_0$.

From formula (2.5) it is immediately clear that \mathfrak{D} is a function of the difference $\tau_1 - \tau_2 = \tau$ ($\mathfrak{D}_{\alpha\beta} = \mathfrak{D}_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2, \tau)$). In the case of systems which are uniform over space, the coordinates will also appear only in the form of a difference $\mathbf{r}_1 - \mathbf{r}_2$.

The total temperature Green's function is related to the free energy by very simple and convenient formulas. Knowing it is sufficient to determine all the thermal properties of the system. However, its actual calculation by the Matsubara technique is still quite difficult. The point is that the success of field theory methods is related to a very high degree to the automatic procedure in computations which is achieved by expanding all quantities in Fourier integrals over all the coordinates and times. However, in Matsubara's method this automatic procedure does not exist because of the finite interval of variation of τ : \mathfrak{G}^0 and \mathfrak{D}^0 are discontinuous functions of the variable τ , and all the integrals with respect to τ actually split up into integrals over a very large number of regions, the number of which increases very rapidly ($\sim 2^n$) with increasing order of approximation.

The Matsubara technique can be improved considerably if one uses certain general properties of temperature Green's functions (Abrikosov, Gor'kov,

Dzyaloshinskii,⁸ Fradkin⁹). As already pointed out, the Green's function depends only on the difference $\tau_1 - \tau_2$, and as such is given in the interval from $-1/T$ to $1/T$. It is therefore useful to expand it in a Fourier series in the variable $\tau = \tau_1 - \tau_2$:*

$$\begin{aligned} \mathfrak{G}(\tau) &= T \sum_{\mathbf{n}} e^{-i\xi_{\mathbf{n}}\tau} \mathfrak{G}(\xi_{\mathbf{n}}), \\ \mathfrak{G}(\xi_{\mathbf{n}}) &= \frac{1}{2} \int_{-1/T}^{1/T} e^{i\xi_{\mathbf{n}}\tau} \mathfrak{G}(\tau) d\tau, \quad \xi_{\mathbf{n}} = \pi n T \end{aligned} \quad (2.6)$$

[and similarly for $\mathfrak{D}(\tau)$].

The following property of \mathfrak{G} is very important for transformations of the perturbation series. From expression (2.5) for \mathfrak{D} it follows that the photon Green's function for negative values of τ is related with \mathfrak{D} for $\tau > 0$ by the simple relation

$$\mathfrak{D}(\tau) = \mathfrak{D}\left(\tau + \frac{1}{T}\right), \quad \tau < 0. \quad (2.7a)$$

Such a connection results obviously also for the Green's function of bosons. For fermions we have, in place of (2.7a)

$$\mathfrak{G}(\tau) = -\mathfrak{G}\left(\tau + \frac{1}{T}\right), \quad \tau < 0. \quad (2.7b)$$

Formulas (2.7a) and (2.7b) are easily derived if one realizes that one can change the order of the operators under the trace cyclically in (2.5) and in the analogous formula for fermions. Relations (2.7a) and (2.7b) are obviously also valid for the free Green's functions.

If furthermore we consider that an even number of fermion lines enter at each vertex of the Feynman diagram, it is easy to see that all of the integrals

$\int_0^{1/T} \dots d\tau$ in the perturbation series can be replaced by $\frac{1}{2} \int_{-1/T}^{1/T} \dots d\tau$, after which the transformation is easily carried out. Relations (2.7a) and (2.7b) also have the consequence that, in the Fourier expansion for the boson (and photon) Green's function, there are only components with "frequencies" $\xi_{\mathbf{n}} = 2\pi n T$, while in the expansion for the fermion function there are only components with $\xi_{\mathbf{n}} = (2n+1)\pi T$.

Making a Fourier transformation with respect to the coordinates[†] and the "time" τ in all the terms of perturbation series for the Green's function (or for the free energy), one can easily show that the procedure thus obtained is completely equivalent to the diagram technique of quantum field theory in the impulse approximation. Each line of the diagram corresponds

*The Fourier components $\mathfrak{G}(\xi_{\mathbf{n}})$ should be distinguished from the function $\mathfrak{G}(\tau)$ itself by still another index; we do not do this in order to abbreviate the notation.

†This is of course possible only in the case of bodies which are uniform in space.

to a free particle Green's function $\mathcal{G}^0(\mathbf{p}, \xi_n)$, and each vertex to a δ function which expresses the conservation laws $\Sigma \mathbf{p} = 0, \Sigma \xi_n = 0$. Integration and summation is carried out over all the momenta and "frequencies" corresponding to each of the lines. Formally, the expression for the corrections coming from any diagram in this theory can be obtained from expressions which would correspond to this diagram in field theory by making the substitutions

$$\omega \rightarrow i\xi_n, \int_{-\infty}^{\infty} \dots d\omega \rightarrow -2\pi iT \sum_n.$$

The close connection of the theory presented here with the technique of quantum field theory makes it possible to apply many of the results of that theory to the present case. As in field theory, the temperature Green's functions satisfy an integral equation of the type of the Dyson equation.

For example, let us consider diagrams of various orders for the Green's function of a photon. In addition to the diagram in Fig. 3, there are also diagrams of the type of Fig. 4 and other more complicated ones. The whole aggregate of diagrams can be pictured by the method described in Fig. 5, where the shaded loop denotes a sum of all graphs which do not break up into parts and which are connected to one another only by a single photon line. Such a summation of diagrams is obviously possible only because the coefficient in front of the diagram does not depend essentially on its order (in the sense indicated above with respect to the series for the free energy).

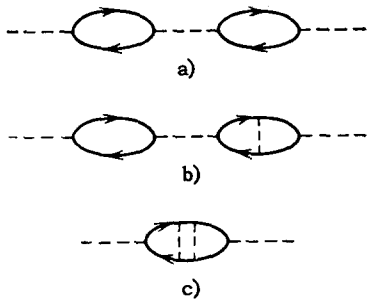


FIG. 4

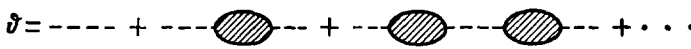


FIG. 5

Thus, to calculate the total Green's function of the photon one must sum the series which is shown schematically in Fig. 5. It has the form (for the case of a spatially inhomogeneous system)

$$\begin{aligned} \mathcal{D}_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2; \xi_n) &= \mathcal{D}_{\alpha\beta}^0(\mathbf{r}_1, \mathbf{r}_2; \xi_n) + \int \mathcal{D}_{\alpha\gamma}(\mathbf{r}_1, \mathbf{r}_3; \xi_n) \Pi_{\gamma\delta}(\mathbf{r}_3, \mathbf{r}_4; \xi_n) \\ &\times \mathcal{D}_{\delta\beta}^0(\mathbf{r}_4, \mathbf{r}_2; \xi_n) d\mathbf{r}_3 d\mathbf{r}_4 \\ &+ \int \mathcal{D}_{\alpha\gamma}^0(\mathbf{r}_1, \mathbf{r}_3; \xi_n) \Pi_{\gamma\delta}(\mathbf{r}_3, \mathbf{r}_4; \xi_n) \mathcal{D}_{\delta\mu}^0(\mathbf{r}_4, \mathbf{r}_5; \xi_n) \\ &\times \Pi_{\mu\nu}(\mathbf{r}_5, \mathbf{r}_6; \xi_n) \mathcal{D}_{\nu\beta}^0(\mathbf{r}_6, \mathbf{r}_2; \xi_n) d\mathbf{r}_3 d\mathbf{r}_4 d\mathbf{r}_5 d\mathbf{r}_6 + \dots \end{aligned} \quad (2.8)$$

Here $\Pi_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2; \xi_n)$ is the so-called polarization operator of the system, which is equal to the sum of the graphs shown in Fig. 5 by the shaded loops. Rewriting (2.8) as follows:

$$\begin{aligned} \mathcal{D}_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2; \xi_n) &= \mathcal{D}_{\alpha\beta}^0(\mathbf{r}_1, \mathbf{r}_2; \xi_n) \\ &+ \int d\mathbf{r}_3 d\mathbf{r}_4 \mathcal{D}_{\alpha\gamma}^0(\mathbf{r}_1, \mathbf{r}_3; \xi_n) \Pi_{\gamma\delta}(\mathbf{r}_3, \mathbf{r}_4; \xi_n) \left\{ \mathcal{D}_{\delta\beta}^0(\mathbf{r}_4, \mathbf{r}_2; \xi_n) \right. \\ &+ \int d\mathbf{r}_5 d\mathbf{r}_6 \mathcal{D}_{\delta\mu}^0(\mathbf{r}_4, \mathbf{r}_5; \xi_n) \Pi_{\mu\nu}(\mathbf{r}_5, \mathbf{r}_6; \xi_n) \mathcal{D}_{\nu\beta}^0(\mathbf{r}_6, \mathbf{r}_2; \xi_n) \\ &+ \int d\mathbf{r}_5 d\mathbf{r}_6 d\mathbf{r}_7 d\mathbf{r}_8 \mathcal{D}_{\delta\mu}^0(\mathbf{r}_4, \mathbf{r}_5; \xi_n) \Pi_{\mu\nu}(\mathbf{r}_5, \mathbf{r}_6; \xi_n) \mathcal{D}_{\nu\lambda}^0(\mathbf{r}_6, \mathbf{r}_7; \xi_n) \\ &\left. \times \Pi_{\lambda\alpha}(\mathbf{r}_7, \mathbf{r}_8; \xi_n) \mathcal{D}_{\delta\beta}^0(\mathbf{r}_8, \mathbf{r}_2; \xi_n) + \dots \right\}, \end{aligned}$$

it is easy to show that it is an integral equation for \mathcal{D} , of the form

$$\mathcal{D}_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2; \xi_n) = \mathcal{D}_{\alpha\beta}^0(\mathbf{r}_1, \mathbf{r}_2; \xi_n) + \int \mathcal{D}_{\alpha\gamma}^0(\mathbf{r}_1, \mathbf{r}_3; \xi_n) \Pi_{\gamma\delta}(\mathbf{r}_3, \mathbf{r}_4; \xi_n) \mathcal{D}_{\delta\beta}^0(\mathbf{r}_4, \mathbf{r}_2; \xi_n) d\mathbf{r}_3 d\mathbf{r}_4. \quad (2.9)$$

The summation process is shown graphically in Fig. 6.

In the general case it is not possible to write a closed equation for the polarization operator. Nevertheless, the Dyson equation is very useful in various specific problems, since it frequently is possible to find approximate equations for the polarization operator which enable one to go beyond perturbation theory.

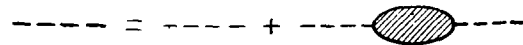


FIG. 6

In the case of long-wave photons, which is of interest to us, the polarization operator, as we shall see later, can be expressed in terms of the dielectric constant of the body.

3. THE ENERGY OF A CONDENSED BODY ASSOCIATED WITH LONG-WAVE ELECTROMAGNETIC FLUCTUATIONS

Let us proceed now to solve our main problem — the computation of the additional terms in the energy of a condensed body which come from long-wave fluctuations of the electromagnetic field. To do this we separate out of the total Hamiltonian of the system a part describing the energy of interaction of the particles with the electromagnetic field with wave lengths much greater than interatomic distances ($\lambda \gg a$), and we treat it as a perturbation*

$$H = H_0 + H_{\text{int}} = H_0 - \int A_\alpha(\mathbf{r}) j_\alpha(\mathbf{r}) d^3\mathbf{r}.$$

The interaction of the particles (electrons and nuclei) with the short-wave field we assign to the unperturbed Hamiltonian. From these we get the short range interatomic forces which keep the body in its condensed

*The separation of the long-wave part means mathematically that the integral in this formula is cut off somehow at small distances. However, we shall not introduce this cutoff explicitly since the answer does not depend on it.

state. We also include in the unperturbed Hamiltonian the energy of the long-wave electromagnetic field in vacuum.

Let us now calculate the corresponding corrections to the free energy. As is easily seen, the results presented in the preceding section are not entirely applicable in our case. The point is that to establish the Matsubara technique it was very important to make use of Wick's theorem, according to which the average value of a product of a large number of operators can be expressed as a product of various pair averages. But Wick's theorem is valid only if the Gibbs average is taken over states of noninteracting particles. In our case, the latter is valid only with respect to the operators of the long-wave electromagnetic field, while the averaging of the operators for the particles occurs over their states in the condensed body and therefore the average values of the products of the operators will no longer reduce to pair averages.

For this reason we proceed as follows: In the perturbation series for the free energy (or for the Green's function of the long-wave photons) the particle operators appear only in combinations of the form

$$\langle T_{\tau} \{ \bar{\psi}(\mathbf{r}_1, \tau_1) \psi(\mathbf{r}_1, \tau_1) \bar{\psi}(\mathbf{r}_2, \tau_2) \psi(\mathbf{r}_2, \tau_2) \} \rangle$$

$$\langle T_{\tau} \{ \bar{\psi}(\mathbf{r}_1, \tau_1) \psi(\mathbf{r}_1, \tau_1) \bar{\psi}(\mathbf{r}_2, \tau_2) \psi(\mathbf{r}_2, \tau_2) \} \rangle$$

$$\times \bar{\psi}(\mathbf{r}_3, \tau_3) \psi(\mathbf{r}_3, \tau_3) \bar{\psi}(\mathbf{r}_4, \tau_4) \psi(\mathbf{r}_4, \tau_4) \rangle$$

etc., i.e., the number of operators under the averaging sign is always a multiple of four, where they always appear in pairs of the type $\bar{\psi}(\mathbf{r}_1, \tau_1) \psi(\mathbf{r}_1, \tau_1)$. We remove from the average value of the product of eight operators the quantity

$$\langle T_{\tau} \{ \bar{\psi}(\mathbf{r}_1, \tau_1) \psi(\mathbf{r}_1, \tau_1) \bar{\psi}(\mathbf{r}_2, \tau_2) \psi(\mathbf{r}_2, \tau_2) \} \rangle$$

$$\times \langle T_{\tau} \{ \bar{\psi}(\mathbf{r}_3, \tau_3) \psi(\mathbf{r}_3, \tau_3) \bar{\psi}(\mathbf{r}_4, \tau_4) \psi(\mathbf{r}_4, \tau_4) \} \rangle$$

$$\times \langle T_{\tau} \{ \bar{\psi}(\mathbf{r}_1, \tau_1) \psi(\mathbf{r}_1, \tau_1) \bar{\psi}(\mathbf{r}_3, \tau_3) \psi(\mathbf{r}_3, \tau_3) \} \rangle$$

$$\times \langle T_{\tau} \{ \bar{\psi}(\mathbf{r}_2, \tau_2) \psi(\mathbf{r}_2, \tau_2) \bar{\psi}(\mathbf{r}_4, \tau_4) \psi(\mathbf{r}_4, \tau_4) \} \rangle$$

$$+ \langle T_{\tau} \{ \bar{\psi}(\mathbf{r}_1, \tau_1) \psi(\mathbf{r}_1, \tau_1) \bar{\psi}(\mathbf{r}_4, \tau_4) \psi(\mathbf{r}_4, \tau_4) \} \rangle$$

$$\times \langle T_{\tau} \{ \bar{\psi}(\mathbf{r}_2, \tau_2) \psi(\mathbf{r}_2, \tau_2) \bar{\psi}(\mathbf{r}_3, \tau_3) \psi(\mathbf{r}_3, \tau_3) \} \rangle$$

(i.e., the value which would be obtained if the average were carried out only to all possible four-term averages of this type), and we call this difference an irreducible quadrilateral and denote it by a shaded square. Furthermore, from the average value of twelve oper-

ators, we subtract the quantity obtained when we split it up into all possible combinations of four and of eight operators. The remaining quantity we call an irreducible hexagon (the shaded hexagons in Figs. 7 and 8) etc.

It is now not difficult to see that the perturbation series will be described by diagrams of the type of Fig. 7 (for the free energy) and Fig. 8 (for the Green's function of the long-wave photons). The shaded loops show the quantity obtained from the average value of four particle operators. The fact that

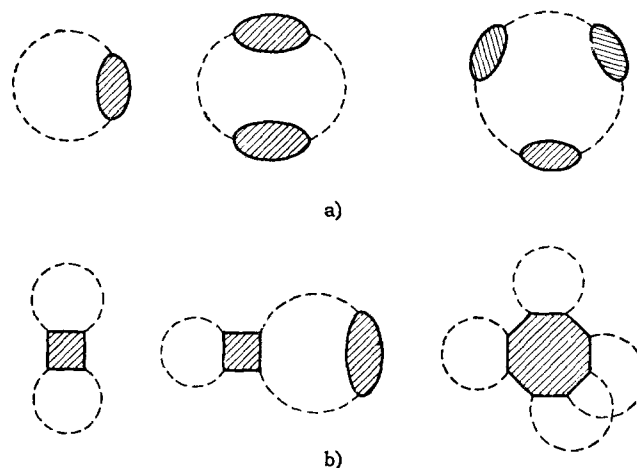


FIG. 7

we have used for it the symbol which was applied in the previous section for the polarization operator will be justified by the later results.

Physically it is immediately clear that diagrams containing irreducible quadrilaterals, hexagons, etc. are negligibly small in number since they take into account various nonlinear processes of the type of the scattering of light by light. This statement can also be proved in the following fashion: Since we have included in H_{int} only the interaction with long-wave photons, we should assume that all the integrals over the momenta of the virtual photons are cut off at some value k_0 which is much smaller than the reciprocal of the interatomic distances $1/a$. It is therefore obvious that each long-wave photon line over which an integration is carried out gives a small quantity of the order of $k_0 a$. The only diagrams in which the integration over photon momenta is not carried out are the dia-

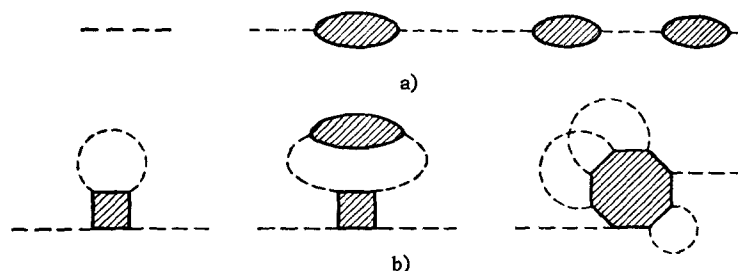


FIG. 8

grams of Figs. 7a and 8a. (One should realize that the Green's function of the photon in zeroth approximation depends only on the coordinate difference.)

Thus, in the approximation where $k_0 a \ll 1$, only the diagrams of the type of Fig. 7a give a correction to the free energy. The corresponding expression for the free energy is

$$\begin{aligned}
 F = F_0 - \frac{1}{2} T \sum_{n=-\infty}^{\infty} \left\{ \int \Pi_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2; \xi_n) \mathfrak{D}_{\beta\alpha}^0(\mathbf{r}_2, \mathbf{r}_1; \xi_n) d\mathbf{r}_1 d\mathbf{r}_2 \right. \\
 + \frac{1}{2} \int \Pi_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2; \xi_n) \mathfrak{D}_{\beta\gamma}^0(\mathbf{r}_2, \mathbf{r}_3; \xi_n) \Pi_{\gamma\delta}^0(\mathbf{r}_3, \mathbf{r}_4; \xi_n) \\
 \times \mathfrak{D}_{\delta\alpha}^0(\mathbf{r}_4, \mathbf{r}_1; \xi_n) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 + \dots \\
 + \frac{1}{m} \int \Pi_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2; \xi_n) \mathfrak{D}_{\beta\gamma}^0(\mathbf{r}_2, \mathbf{r}_3; \xi_n) \\
 \left. \dots \Pi_{\mu\nu}(\mathbf{r}_{2m-1}, \mathbf{r}_{2m}; \xi_n) \mathfrak{D}_{\nu\alpha}^0(\mathbf{r}_{2m}, \mathbf{r}_1; \xi_n) d\mathbf{r}_1 \dots d\mathbf{r}_{2m} + \dots \right\}, \quad (3.1)
 \end{aligned}$$

where $\Pi_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2; \xi_n)$ is the quantity indicated on the diagram by the shaded loop. One should also note the coefficients in front of the integrals (1/m for the m-th term), which represent the contributions of the various diagrams.

Including in this same approximation for the photon Green's function only the contribution of the diagram in Fig. 8a by the same procedure as was used in the preceding section for obtaining the Dyson equation, we obtain for it an equation which coincides formally with (2.9); however, in our approximation the polarization operator Π which was derived in the preceding section does not include the contribution of virtual photon lines and is a fixed function, depending only on the properties of the body.

The fact that the wave lengths of electromagnetic waves which are of interest to us are large compared with interatomic distances enables us to express the polarization operator (and with it the photon Green's function and the free energy of the system) in terms of only the macroscopic characteristics of the body. The only quantity which characterizes the interaction of the condensed body with long-wave radiation is its dielectric constant.*

The dielectric constant ϵ in the case of absorbing media is an integral operator acting on functions depending on the ordinary time variable t . Because of this it is difficult to take over directly the concept of a dielectric constant into a theory which operates with an imaginary "time" τ . We shall therefore use the connection obtained by Abrikosov, Gor'kov, and Dzyaloshinskii⁸ (cf. also Landau¹⁰) between the temperature Green's functions and the Green's functions of field theory.

It turns out that the temperature Green's function of the photon $\mathfrak{D}_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2; \xi_n)$ is related simply to the

*Here and throughout the following we shall completely neglect magnetic properties of matter, since in the frequency ranges of importance to us they play no role whatsoever.

so-called retarded Green's function of the electromagnetic field $D_{\alpha\beta}^R(\mathbf{r}_1, \mathbf{r}_2; t)$ defined as:

$$D_{\alpha\beta}^R(\mathbf{r}_1, \mathbf{r}_2; t_1 - t_2) = \begin{cases} -i \text{Sp} \{ e^{(F-H)/T} [A_\alpha(\mathbf{r}_1, t_1) A_\beta(\mathbf{r}_2, t_2) \\ - A_\beta(\mathbf{r}_2, t_2) A_\alpha(\mathbf{r}_1, t_1)] \}, & t_1 > t_2, \\ 0, & t_1 < t_2. \end{cases} \quad (3.2)$$

[Here $A_\alpha(\mathbf{r}, t)$ are Heisenberg operators.] Calculations analogous to those carried out in the paper of Abrikosov et al.⁸ for the case of a homogeneous body lead to the conclusion that $\mathfrak{D}_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2; \xi_n)$ is expressed in terms of the Fourier component of the function D^R . If we define

$$D_{\alpha\beta}^R(\mathbf{r}_1, \mathbf{r}_2; \omega) = \int_{-\infty}^{\infty} e^{i\omega t} D_{\alpha\beta}^R(\mathbf{r}_1, \mathbf{r}_2; t) dt,$$

then for $\xi_n > 0$ we have the relation

$$\mathfrak{D}_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2; \xi_n) = D_{\alpha\beta}^R(\mathbf{r}_1, \mathbf{r}_2; i\xi_n). \quad (3.3)$$

The value of $\mathfrak{D}_{\alpha\beta}$ for $\xi_n < 0$ can be obtained from the formula for the complex conjugate quantity $\mathfrak{D}_{\alpha\beta}^*$ which follows directly from the definition of the temperature Green's function (2.5) and the hermiticity of the operators for the electromagnetic field:

$$\mathfrak{D}_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2; \xi_n) = \mathfrak{D}_{\beta\alpha}^*(\mathbf{r}_2, \mathbf{r}_1; -\xi_n). \quad (3.4)$$

We now give the equation for the retarded function D^R . An important point here is the gauging of the vector potentials. The tensor $D_{\alpha\beta}^R$ (or $\mathfrak{D}_{\alpha\beta}$) has altogether ten different independent components. However, there remains a considerable arbitrariness associated with gauge invariance. In fact, the quantities $D_{\alpha\beta}^R$, which are formed from the components of the vector potential, do not themselves have physical significance, but rather only the six corresponding quantities which are formed from the components of the electric field intensity. Thus there are only six physical conditions imposed on the ten quantities, so that we have four arbitrary functions at our disposal. This arbitrariness can be used to make the components D_{00}^R and D_{0i}^R equal to zero. This choice obviously corresponds to a gauging with zero scalar potential. In this case the Heisenberg operators \mathbf{E} and \mathbf{H} are related to \mathbf{A} by the formulas*

$$\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{H} = \text{rot } \mathbf{A}.$$

In order to express D_{ik}^R in terms of $\epsilon(\omega)$ we proceed as follows: Let us imagine that our system, consisting of a body and electromagnetic radiation in equilibrium, is placed in an external field produced by an external current $\mathbf{j}^{\text{ext}}(\mathbf{r}, t)$. If we limit ourselves to the case of low frequencies, we can write the equations for the average values, i.e., the Gibbs averages of the electric and magnetic field intensities $\langle \mathbf{E}(\mathbf{r}, t) \rangle$

*rot $\mathbf{A} = \text{curl } \mathbf{A}$.

and $\langle \mathbf{H}(\mathbf{r}, t) \rangle$. These equations naturally coincide with the usual Maxwell equations in a medium with dielectric constant ϵ , and (in time Fourier components) have the form

$$\begin{aligned} \text{rot} \langle \mathbf{H}(\mathbf{r}, \omega) \rangle &= 4\pi \mathbf{j}^{\text{ext}}(\mathbf{r}, \omega) - i\epsilon(\omega) \omega \langle \mathbf{E}(\mathbf{r}, \omega) \rangle, \\ \text{rot} \langle \mathbf{E}(\mathbf{r}, \omega) \rangle &= i\omega \langle \mathbf{H}(\mathbf{r}, \omega) \rangle. \end{aligned}$$

The averaged vector potential $\langle \mathbf{A} \rangle$ in the gauge chosen by us satisfies the equation

$$[(\mathbf{r}, \omega) \omega^2 \delta_{ik} - \text{rot}_{il} \text{rot}_{lk}] \langle A_k(\mathbf{r}, \omega) \rangle = -4\pi j_i^{\text{ext}}(\mathbf{r}, \omega), \quad (3.5)$$

whose solution can be written in the form

$$\langle A_i^{\text{ext}}(\mathbf{r}, \omega) \rangle = - \int \bar{D}_{ik}(\mathbf{r}, \mathbf{r}'; \omega) j_k^{\text{ext}}(\mathbf{r}', \omega) d^3r', \quad (3.6)$$

where \bar{D}_{ik} is the Green's function for equation (3.5). \bar{D}_{ik} , as we know, satisfies the equation

$$[\epsilon(\mathbf{r}, \omega) \omega^2 \delta_{il} - \text{rot}_{im} \text{rot}_{ml}] \bar{D}_{lk}(\mathbf{r}, \mathbf{r}', \omega) = 4\pi \delta_{lk} \delta(\mathbf{r} - \mathbf{r}'). \quad (3.7)$$

The symbol curl_{ik} here denotes the operator $e_{ikl}(\partial/\partial x_l)$, where e_{ikl} is the completely antisymmetric unit tensor.

On the other hand, $\langle \mathbf{A}^{\text{ext}} \rangle$ in the presence of external currents can be calculated using the apparatus of quantum field theory. The operator for the vector potential $\mathbf{A}^{\text{ext}}(\mathbf{r}, t)$ in this case is related to the operator $\mathbf{A}(\mathbf{r}, t)$ in the absence of external currents by the relation

$$\mathbf{A}^{\text{ext}}(\mathbf{r}, t) = S_{\text{ext}}^{-1}(t) \mathbf{A}(\mathbf{r}, t) S_{\text{ext}}(t),$$

where $S(t)$ is the S-matrix of field theory, which in our case has the form

$$S_{\text{ext}}(t) = T \exp \left\{ i \int_{-\infty}^t dt \int d\mathbf{r} \mathbf{j}^{\text{ext}}(\mathbf{r}, t) \mathbf{A}(\mathbf{r}, t) \right\}.$$

Here T is the ordering operator over the usual time.

To terms of first order in \mathbf{j}^{ext} the expression for $\langle \mathbf{A}^{\text{ext}} \rangle$ now has the form

$$\begin{aligned} \langle A_i^{\text{ext}}(\mathbf{r}, t) \rangle &= -i \int_{-\infty}^t dt' \int d\mathbf{r}' j_k^{\text{ext}}(\mathbf{r}', t') \langle (A_k(\mathbf{r}', t') A_i(\mathbf{r}, t) \\ &\quad - A_i(\mathbf{r}, t) A_k(\mathbf{r}', t')) \rangle. \end{aligned} \quad (3.8)$$

The right side of (3.8) can be expressed in terms of the retarded Green's function D_{ik}^R . According to the definition (3.2) we have

$$\langle A_i^{\text{ext}}(\mathbf{r}, t) \rangle = - \int_{-\infty}^{\infty} dt' \int d^3r' D_{ik}^R(\mathbf{r}, \mathbf{r}'; t-t') j_k^{\text{ext}}(\mathbf{r}', t').$$

Changing to time-Fourier components in this relation, we finally obtain

$$\langle A_i^{\text{ext}}(\mathbf{r}, \omega) \rangle = - \int d^3r' D_{ik}^R(\mathbf{r}, \mathbf{r}'; \omega) j_k^{\text{ext}}(\mathbf{r}', \omega). \quad (3.9)$$

Comparing (3.9) and (3.6) we see that, because of the arbitrariness of \mathbf{j}^{ext} , the function D_{ik}^R coincides with the Green's function of (3.5).

Thus D_{ik}^R satisfies Eq. (3.7). Replacing ω by $i\xi_n$ in (3.7), we find that the function $\mathfrak{D}_{ik}(\mathbf{r}, \mathbf{r}'; \xi_n)$ satisfies the equations

fies the equations

$$\{\epsilon(\mathbf{r}, i\xi_n) \xi_n^2 \delta_{il} + \text{rot}_{im} \text{rot}_{ml}\} \mathfrak{D}_{lk}(\mathbf{r}, \mathbf{r}'; \xi_n) = -4\pi \delta(\mathbf{r} - \mathbf{r}') \delta_{lk} \quad (3.10)$$

for $\xi_n > 0$.

The dielectric constant which appears in this equation for imaginary values of the frequency is related simply to the imaginary part of the dielectric constant for real frequencies, $\epsilon''(\omega)$ (see, for example, the book of Landau and Lifshitz,¹¹ Sec. 58):

$$\epsilon(i\xi_n) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{\omega \epsilon''(\omega)}{\omega^2 + \xi_n^2} d\omega. \quad (3.11)$$

Since $\epsilon'' > 0$ always, we see from this formula that $\epsilon(i\xi_n)$ is a real positive monotonically decreasing function of ξ_n .

Because $\epsilon(i\xi_n)$ is real, the Green's function \mathfrak{D}_{ik} (for $\xi_n > 0$) is also real. Its value for $\xi_n < 0$ is determined by the relation [cf. Eq. (3.4)]

$$\mathfrak{D}_{ik}(\mathbf{r}_1, \mathbf{r}_2; \xi_n) = \mathfrak{D}_{ki}(\mathbf{r}_2, \mathbf{r}_1; -\xi_n). \quad (3.12)$$

Using the Dyson equation (2.9) it is easy to show that the polarization operator

$$\Pi_{ik}(\mathbf{r}_1, \mathbf{r}_2; \xi_n) = \Pi_{ki}(\mathbf{r}_2, \mathbf{r}_1; -\xi_n) \quad (3.13)$$

satisfies the same relation.

Now we can express the polarization operator of the system in terms of $\epsilon(i\xi_n)$. To do this we operate on Eq. (2.9) (for our choice of the gauge the components of $\mathfrak{D}_{\alpha\beta}$ with $\alpha = 0$ or $\beta = 0$ are equal to zero) from the left with the operator

$$\xi_n^2 \delta_{ik} + \text{rot}_{il} \text{rot}_{lk}.$$

Making use of the fact that \mathfrak{D} satisfies Eq. (3.10), and \mathfrak{D}^0 the same equation with $\epsilon(i\xi_n) = 1$, we obtain:

$$\begin{aligned} \int \Pi_{il}(\mathbf{r}_1, \mathbf{r}'; \xi_n) \mathfrak{D}_{lk}(\mathbf{r}', \mathbf{r}_2; \xi_n) d^3r' \\ = \frac{\epsilon(\mathbf{r}_1, i\xi_n) - 1}{4\pi} \xi_n^2 \mathfrak{D}_{ik}(\mathbf{r}_1, \mathbf{r}_2; \xi_n), \end{aligned}$$

from which we immediately have (for $\xi_n > 0$):

$$\Pi_{ik}(\mathbf{r}_1, \mathbf{r}_2; \xi_n) = \frac{\epsilon(\mathbf{r}_1, i\xi_n) - 1}{4\pi} \xi_n^2 \delta_{ik} \delta(\mathbf{r}_1 - \mathbf{r}_2).$$

Determining the polarization operator for $\xi_n < 0$ from the relation (3.13), we finally have for all ξ_n ,

$$\Pi_{ik}(\mathbf{r}_1, \mathbf{r}_2; \xi_n) = \frac{\epsilon(\mathbf{r}_1, i|\xi_n|) - 1}{4\pi} \xi_n^2 \delta(\mathbf{r}_1 - \mathbf{r}_2). \quad (3.14)$$

The fact that the polarization operator is proportional to $\delta(\mathbf{r}_1 - \mathbf{r}_2)$ is associated with the neglect in the macroscopic theory of effects of space correlations. These effects are important in metals (especially in superconductors) at frequencies where an anomalous skin effect occurs. However, in the following we shall be interested in much higher frequencies (infrared and above) in which region there is no spatial dispersion.

Having expressions for the polarization operator in terms of the dielectric constant of the body, we

could in principle compute the corresponding correction to formula (3.1). [The Green's function of the free photon can be found directly from the definition (2.4b) or by solving equation (3.9) with $\epsilon = 1$.] But, as we have already remarked, the series (3.1) cannot be summed directly. Instead we determine the additional pressure (more precisely, the additional stress tensor) which arises as a result of interaction with the long wave fluctuating field.

For this purpose we imagine that the body is subjected to a small deformation with displacement vector $\mathbf{u}(\mathbf{r})$. Then the change in the free energy δF is equal to $\int \mathbf{f} \mathbf{u} dV$ where \mathbf{f} is the force per unit volume of the body in the deformation. The corresponding change of the unperturbed energy δF_0 is

$$-\int \mathbf{u} \text{grad } p_0 dV,$$

where $p_0(\rho, T)$ is the pressure, when we omit the corrections, at the given density and temperature T . From this displacement there arise corrections only in the polarization operator, since it alone depends on the properties of the medium:

$$\delta \Pi_{ik}(\mathbf{r}_1, \mathbf{r}_2; \xi_n) = \frac{1}{4\pi} \xi_n^2 \delta(\mathbf{r}_1 - \mathbf{r}_2) \delta \epsilon(\mathbf{r}, i|\xi_n|) \delta_{ik}.$$

Varying the series (3.1) we obtain

$$\begin{aligned} \delta F = \delta F_0 - \frac{T}{8\pi} \sum_{n=-\infty}^{\infty} \xi_n^2 \int d^3r \delta \epsilon(\mathbf{r}, i|\xi_n|) \left\{ \mathcal{D}_{ii}^0(\mathbf{r}, \mathbf{r}; \xi_n) \right. \\ + \int \mathcal{D}_{ik}^0(\mathbf{r}, \mathbf{r}_1; \xi_n) \Pi_{kl}(\mathbf{r}_1, \mathbf{r}_2; \xi_n) \mathcal{D}_{li}^0(\mathbf{r}_2, \mathbf{r}; \xi_n) d^3r_1 d^3r_2 \\ + \int \mathcal{D}_{ik}^0(\mathbf{r}, \mathbf{r}_1; \xi_n) \Pi_{kl}(\mathbf{r}_1, \mathbf{r}_2; \xi_n) \mathcal{D}_{lm}^0(\mathbf{r}_2, \mathbf{r}_3; \xi_n) \Pi_{mp}(\mathbf{r}_3, \mathbf{r}_4; \xi_n) \\ \left. \times \mathcal{D}_{pi}^0(\mathbf{r}_4, \mathbf{r}; \xi_n) d^3r_1 d^3r_2 d^3r_3 d^3r_4 + \dots \right\}. \end{aligned}$$

The series in curly brackets is just the series for the photon Green's function corresponding to the diagrams of Fig. 8a. Therefore

$$\delta F = \delta F_0 - \frac{T}{8\pi} \sum_{n=-\infty}^{\infty} \xi_n^2 \int \mathcal{D}_{ii}(\mathbf{r}, \mathbf{r}; \xi_n) \delta \epsilon(\mathbf{r}, i|\xi_n|) d^3r.$$

Using relation (3.12), we finally obtain:

$$\delta F = \delta F_0 - \frac{T}{4\pi} \sum_{n=0}^{\infty} \xi_n^2 \int \mathcal{D}_{ii}(\mathbf{r}, \mathbf{r}; \xi_n) \delta \epsilon(\mathbf{r}, i\xi_n) d^3r. \quad (3.15)$$

The prime on the summation symbol means that the term with $n = 0$ is given only a weight of $1/2$. We remind the reader that $\xi_n = 2\pi nT$.

The variation of ϵ is related to the displacement \mathbf{u} as follows:

$$\delta \epsilon = -\mathbf{u} \text{grad } \epsilon - \rho \frac{\partial \epsilon}{\partial \rho} \text{div } \mathbf{u}. \quad (3.16)$$

Substituting this in (3.15) and carrying out an integration by parts, we obtain for the force acting on unit volume of the body the formula

$$\begin{aligned} \mathbf{f} = -\text{grad } p_0 - \frac{T}{4\pi} \sum_{n=0}^{\infty} \xi_n^2 \mathcal{D}_{ii}(\mathbf{r}, \mathbf{r}; \xi_n) \text{grad } \epsilon \\ + \frac{T}{4\pi} \sum_{n=0}^{\infty} \xi_n^2 \text{grad} \left\{ \mathcal{D}_{ii}(\mathbf{r}, \mathbf{r}; \xi_n) \rho \frac{\partial \epsilon}{\partial \rho} \right\}. \end{aligned} \quad (3.17)$$

This formula enables us without difficulty to compute the correction to the chemical potential of the body. For this purpose we note that at chemical equilibrium $\mathbf{f} = 0$. Equating the expression (3.17) to zero and noting that for a fixed temperature we have the relations

$$\text{grad } \epsilon(\rho, T) = \frac{\partial \epsilon}{\partial \rho} \text{grad } \rho, \quad dp_0(\rho, T) = \rho d\xi_0(\rho, T) \quad (3.18)$$

[where $\xi_0(\rho, T)$ is the unperturbed chemical potential of the body, per unit mass], we obtain after a simple transformation:

$$\rho \text{grad } \xi = 0, \quad \xi(\rho, T) = \xi_0(\rho, T) - \frac{T}{4\pi} \sum_{n=0}^{\infty} \xi_n^2 \mathcal{D}_{ii}(\mathbf{r}, \mathbf{r}; \xi_n) \frac{\partial \epsilon}{\partial \rho}. \quad (3.19)$$

We know that the condition of equilibrium of any inhomogeneous body is the constancy throughout the body of the chemical potential; it is therefore clear that the expression (3.19) determines this potential (taken per unit mass).

Let us now turn to a computation of the pressure. To do this we must change the expression for the force acting on unit volume of the body (3.17) to a form

$$f_i = -\frac{\partial \sigma_{ik}}{\partial x_k}, \quad (3.20)$$

where σ_{ik} is the stress tensor which we want to find. The computations required for this practically coincide step by step with the calculations made in electrodynamics for finding the Maxwell stress tensor. (Cf., for example, reference 11, Sec. 15.)

However we shall present them here briefly.

As a preliminary we introduce, in addition to the photon Green's function $\mathcal{D}_{ik}(\mathbf{r}, \mathbf{r}'; \xi_n)$, two other functions:

$$\left. \begin{aligned} \mathcal{D}_{ik}^E(\mathbf{r}, \mathbf{r}'; \xi_n) &= -\xi_n^2 \mathcal{D}_{ik}(\mathbf{r}, \mathbf{r}'; \xi_n), \\ \mathcal{D}_{ik}^H(\mathbf{r}, \mathbf{r}'; \xi_n) &= \text{rot}_{il} \text{rot}_{km} \mathcal{D}_{lm}(\mathbf{r}, \mathbf{r}'; \xi_n), \end{aligned} \right\} \quad (3.21)$$

which are made up of the operators for the electric and magnetic field according to the same rules by which \mathcal{D}_{ik} was made up from the operators for the vector potential.

We rewrite the expression for the force (3.17) in the new notation:*

$$\begin{aligned} f_i = -\frac{\partial p_0}{\partial x_i} + \frac{T}{4\pi} \sum' \frac{\partial}{\partial x_i} \left\{ \epsilon(\mathbf{r}, i\xi_n) \mathcal{D}_{kk}^E(\mathbf{r}, \mathbf{r}; \xi_n) \right. \\ \left. - \rho \frac{\partial \epsilon}{\partial \rho} \mathcal{D}_{kk}^E(\mathbf{r}, \mathbf{r}; \xi_n) \right\} - \frac{T}{4\pi} \sum' \epsilon(\mathbf{r}, i\xi_n) \frac{\partial}{\partial x_i} \mathcal{D}_{kk}^E(\mathbf{r}, \mathbf{r}; \xi_n). \end{aligned} \quad (3.22)$$

*For purposes of brevity we shall omit the arguments ξ_n and $i\xi_n$ of the functions \mathcal{D}_{ik} and ϵ in the intermediate formulas.

Consequently we have only to transform the last term in (3.22). We rewrite it (disregarding the summation and the factor $T/4\pi$) in the form

$$\varepsilon(\mathbf{r}') \frac{\partial}{\partial x_i} \mathfrak{D}_{hk}^E(\mathbf{r}, \mathbf{r}') + \varepsilon(\mathbf{r}) \frac{\partial}{\partial x'_i} \mathfrak{D}_{hk}^E(\mathbf{r}, \mathbf{r}'),$$

where we intend to set $\mathbf{r} = \mathbf{r}'$ at the end of the computation. Proceeding with further obvious transformations, we obtain

$$\begin{aligned} & \varepsilon(\mathbf{r}') \frac{\partial}{\partial x_i} \mathfrak{D}_{hk}^E(\mathbf{r}, \mathbf{r}') + \varepsilon(\mathbf{r}) \frac{\partial}{\partial x_i} \mathfrak{D}_{hk}^E(\mathbf{r}, \mathbf{r}') \\ &= 2 \frac{\partial \varepsilon(\mathbf{r}) \mathfrak{D}_{ik}^E(\mathbf{r}, \mathbf{r}')}{\partial x_h} - \frac{\partial}{\partial x_h} \varepsilon(\mathbf{r}) \mathfrak{D}_{ki}^E(\mathbf{r}, \mathbf{r}') \\ & - \frac{\partial}{\partial x_h} \varepsilon(\mathbf{r}') \mathfrak{D}_{ik}^E(\mathbf{r}, \mathbf{r}') + \varepsilon(\mathbf{r}') \left(\frac{\partial}{\partial x_i} \mathfrak{D}_{hk}^E(\mathbf{r}, \mathbf{r}') - \frac{\partial}{\partial x_h} \mathfrak{D}_{ik}^E(\mathbf{r}, \mathbf{r}') \right) \\ & + \varepsilon(\mathbf{r}) \left(\frac{\partial}{\partial x'_i} \mathfrak{D}_{hk}^E(\mathbf{r}, \mathbf{r}') - \frac{\partial}{\partial x'_h} \mathfrak{D}_{ki}^E(\mathbf{r}, \mathbf{r}') \right). \end{aligned} \quad (3.23)$$

From Eq. (3.10) for the Green's function we can obtain the identities

$$\begin{aligned} & \frac{\partial}{\partial x_h} \varepsilon(\mathbf{r}) \mathfrak{D}_{ki}^E(\mathbf{r}, \mathbf{r}') = 4\pi \frac{\partial}{\partial x_i} \delta(\mathbf{r} - \mathbf{r}'), \\ & \frac{\partial}{\partial x'_h} \varepsilon(\mathbf{r}') \mathfrak{D}_{ik}^E(\mathbf{r}, \mathbf{r}') = -4\pi \frac{\partial}{\partial x_i} \delta(\mathbf{r} - \mathbf{r}'), \\ & \varepsilon(\mathbf{r}') \left[\frac{\partial}{\partial x_h} \mathfrak{D}_{ik}^E(\mathbf{r}, \mathbf{r}') - \frac{\partial}{\partial x'_i} \mathfrak{D}_{hk}^E(\mathbf{r}, \mathbf{r}') \right] \\ &= -\frac{\partial}{\partial x'_h} \mathfrak{D}_{ki}^H(\mathbf{r}, \mathbf{r}') + \frac{\partial}{\partial x'_i} \mathfrak{D}_{hk}^H(\mathbf{r}, \mathbf{r}') - 8\pi \frac{\partial}{\partial x_i} \delta(\mathbf{r} - \mathbf{r}'), \\ & \varepsilon(\mathbf{r}) \left[\frac{\partial}{\partial x'_h} \mathfrak{D}_{ki}^E(\mathbf{r}, \mathbf{r}') - \frac{\partial}{\partial x'_i} \mathfrak{D}_{hk}^E(\mathbf{r}, \mathbf{r}') \right] \\ &= -\frac{\partial}{\partial x_h} \mathfrak{D}_{ik}^H(\mathbf{r}, \mathbf{r}') + \frac{\partial}{\partial x_i} \mathfrak{D}_{hk}^H(\mathbf{r}, \mathbf{r}') + 8\pi \frac{\partial}{\partial x_i} \delta(\mathbf{r} - \mathbf{r}'). \end{aligned}$$

Substituting them in (3.21) and setting $\mathbf{r} = \mathbf{r}'$, we find:

$$\begin{aligned} & \varepsilon(\mathbf{r}) \frac{\partial}{\partial x_i} \mathfrak{D}_{hk}^E(\mathbf{r}, \mathbf{r}) \\ &= 2 \frac{\partial}{\partial x_h} \varepsilon(\mathbf{r}) \mathfrak{D}_{ik}^E(\mathbf{r}, \mathbf{r}) + 2 \frac{\partial}{\partial x_h} \mathfrak{D}_{ik}^H(\mathbf{r}, \mathbf{r}) - \frac{\partial}{\partial x_i} \mathfrak{D}_{hk}^H(\mathbf{r}, \mathbf{r}). \end{aligned}$$

Substituting this in (3.22) we obtain finally that the force can be expressed in the form (3.20) with the stress tensor

$$\begin{aligned} \sigma_{ik} &= -p_0 \delta_{ik} \\ & - \frac{T}{2\pi} \sum_{n=0}^{\infty} \left\{ -\frac{1}{2} \delta_{ik} \left[\varepsilon(\mathbf{r}, i\xi_n) - \varrho \frac{\partial \varepsilon(\mathbf{r}, i\xi_n)}{\partial \varrho} \right] \mathfrak{D}_{ii}^E(\mathbf{r}, \mathbf{r}; \xi_n) \right. \\ & + \varepsilon(\mathbf{r}, i\xi_n) \mathfrak{D}_{ik}^E(\mathbf{r}, \mathbf{r}; \xi_n) \\ & \left. - \frac{1}{2} \delta_{ik} \mathfrak{D}_{ii}^H(\mathbf{r}, \mathbf{r}; \xi_n) + \mathfrak{D}_{ik}^H(\mathbf{r}, \mathbf{r}; \xi_n) \right\}. \end{aligned} \quad (3.24)$$

However, this formula still does not have a direct physical meaning, since the quantities $\mathfrak{D}_{ik}^E(\mathbf{r}, \mathbf{r}')$ and $\mathfrak{D}_{ik}^H(\mathbf{r}, \mathbf{r}')$ which appear in it go to infinity at $\mathbf{r} = \mathbf{r}'$. This is related to the fact that if we do not make an appropriate cut-off, there is an infinite contribution to σ_{ik} of fluctuations with small wave lengths, which have no relation to the inhomogeneity of the body in the sense that their contributions are the same both

in homogeneous and inhomogeneous bodies which, at a particular point, have the same value of ε . The contribution of long-wave fluctuations to the stress tensor of an inhomogeneous medium, in which we are interested, does not depend on the nature of the cut off, and is obtained by the appropriate subtraction in formula (3.24). Actually, the Green's function $\mathfrak{D}_{ik}^E(\mathbf{r}, \mathbf{r})$ (and similarly for \mathfrak{D}_{ik}^H) in this formula should be understood to be the limit of the difference

$$\lim_{\mathbf{r}' \rightarrow \mathbf{r}} [\mathfrak{D}_{ik}^E(\mathbf{r}, \mathbf{r}') - \overline{\mathfrak{D}}_{ik}^E(\mathbf{r}, \mathbf{r}')],$$

where $\overline{\mathfrak{D}}_{ik}^E$ is the Green's function of a homogeneous unbounded medium whose dielectric constant coincides with that for the inhomogeneous body at the point at which the stress tensor is computed. To avoid too complicated formulas, we shall, in the following, write formula (3.24) in its previous form, with the understanding that the subtraction we have indicated has already been carried out. Then $p_0(\rho, T)$ is the pressure in the unbounded homogeneous medium for given values of ρ and T .

The same remarks also apply to formula (3.19) for the chemical potential which, when we take account of (3.21), can be written in the form

$$\zeta(\varrho, T) = \zeta_0(\varrho, T) + \frac{T}{4\pi} \sum_{n=0}^{\infty} \frac{\partial \varepsilon(\mathbf{r}, i\xi_n)}{\partial \varrho} \mathfrak{D}_{ii}^E(\mathbf{r}, \mathbf{r}; \xi_n). \quad (3.25)$$

We note that among inhomogeneous media we also include systems which consist of several bodies each of which is homogeneous. In such a case in solving Eqs. (3.10) the components of \mathfrak{D}_{ik} must satisfy definite boundary conditions at the boundaries of the bodies. We remind the reader that in Eqs. (3.10) the independent variables are the coordinates \mathbf{r} , while the coordinates \mathbf{r}' play the role of parameters. Therefore we are dealing with boundary conditions on the variables \mathbf{r} . These conditions correspond to continuity of the tangential components of the electric and magnetic fields. Since to the point \mathbf{r} there corresponds [in the sense of the definition (3.2)] one of the indices i of the tensor \mathfrak{D}_{ik} , the tangential components of the tensors \mathfrak{D}_{ik}^E and \mathfrak{D}_{ik}^H must be continuous in this index.

Formula (3.24) coincides in appearance precisely with the usual formula for the Maxwell stresses in an electromagnetic field, where the quadratic combinations of components of electric and magnetic fields are replaced by the corresponding functions D_{ik}^E and D_{ik}^H . However, this analogy should not be given any too profound significance. The point is that there is serious reason to think that the concept of a stress tensor for a variable electromagnetic field in an absorbing medium has no meaning in general. In formula (3.24), however, we are dealing not with an arbitrary electromagnetic field, but with the thermodynamic equilibrium fluctuation field in the medium.

Formulas (3.24) and (3.25), which were obtained by Dzyaloshinskii and Pitaevskii,⁵ in principle solve the

problem of computing the van der Waals' part of the thermodynamic quantities for a body, reducing it in each specific case to the solution of Eqs. (3.10) for the Green's function \mathfrak{D}_{ik} .

4. MOLECULAR FORCES BETWEEN SOLIDS

a) Derivation of the general formula. Let us apply the general theory developed above to computing the van der Waals' forces which act between solid bodies whose surfaces are brought to very short distances from one another. When this is done, the gap separating the bodies may still be filled with some liquid. In the following we shall denote by indices 1 and 2 quantities referring to the two solid bodies, and by index 3 quantities referring to the medium which fills the gap.

Although we shall assume that the gap is plane parallel, it should be kept in mind that in actuality for correct formulation of the problem of the force of interaction between bodies, we must regard at least one of them as having finite dimensions and as being surrounded on all sides by medium 3, so that we can determine the total force acting on it; in view of the very rapid fall-off of molecular forces with distance, this resulting force actually can be ascribed completely to the forces acting through the narrow gap separating the two bodies.

The total force acting on body 2 can be computed as the total flux of momentum flowing into the body from the medium 3 which surrounds it; i.e., it can be written in the form of an integral $\oint \sigma_{ik} df_k$ over the surface surrounding it. Here it should be kept in mind that medium 3 is in thermodynamic equilibrium, one of the conditions for which consists in the constancy of its chemical potential: $\xi = \text{const}$, where ξ is given by formula (3.25). Since corrections to the density of the medium associated with long wave fluctuations of the field are small, we may assume that the density ρ is constant along medium 3, while the change in chemical potential $\xi_0(\rho, T)$ coincides [by virtue of (3.18)] with the change of the quantity $p_0(\rho, T)/\rho$. Therefore the condition $\xi = \text{const}$ can be written as

$$p_0(\rho, T) + \frac{T}{4\pi} \sum_{n=0}^{\infty} \epsilon \frac{\partial \epsilon_n}{\partial \rho} \mathfrak{D}_{il}^E(\mathbf{r}, \mathbf{r}) = \text{const.} \quad (4.1)$$

In view of this condition the part (3.24) of the total stress tensor is a constant uniform pressure through the liquid and gives no contribution to the total force acting on the body. Dropping this constant part, i.e., subtracting from σ_{ik} the left side of Eq. (4.1) multiplied by δ_{ik} , we come to the conclusion that to determine the required force it is actually sufficient to write the stress tensor in medium 3 in the form

$$\sigma'_{ik} = -\frac{T}{2\pi} \sum_{n=0}^{\infty} \left\{ \epsilon_n \left[\mathfrak{D}_{ik}^E(\mathbf{r}, \mathbf{r}) - \frac{1}{2} \delta_{ik} \mathfrak{D}_{il}^E(\mathbf{r}, \mathbf{r}) \right] + \mathfrak{D}_{ik}^H(\mathbf{r}, \mathbf{r}) - \frac{1}{2} \delta_{ik} \mathfrak{D}_{il}^H(\mathbf{r}, \mathbf{r}) \right\}. \quad (4.2)$$

We direct the x axis perpendicular to the plane of the gap, whose width we denote by l (so that the surfaces of the bodies 1 and 2 are the planes $x = 0$ and $x = l$). Then, by virtue of what has been said above, the force F acting on unit area of the surface of body 2 is equal to

$$F(l) = \sigma'_{xx}(l) = \frac{T}{4\pi} \sum_{n=0}^{\infty} \left\{ \epsilon_n \left[\mathfrak{D}_{yy}^E(l, l; \xi_n) + \mathfrak{D}_{zz}^E(l, l; \xi_n) - \mathfrak{D}_{xx}^E(l, l; \xi_n) \right] + \mathfrak{D}_{yy}^H(l, l; \xi_n) + \mathfrak{D}_{zz}^H(l, l; \xi_n) - \mathfrak{D}_{xx}^H(l, l; \xi_n) \right\}. \quad (4.3)$$

A positive force corresponds to an attraction of the bodies, a negative force to a repulsion.

The Green's function $\mathfrak{D}_{ik}(\mathbf{r}, \mathbf{r}')$, because of the homogeneity of the problem along the y and z directions, depends only on the differences $y - y'$ and $z - z'$. We make a Fourier transformation with respect to these variables:

$$\mathfrak{D}_{ik}(x, x', \mathbf{q}; \xi_n) = \int \int e^{-iq_y(y-y') - iq_z(z-z')} \mathfrak{D}_{ik}(\mathbf{r}, \mathbf{r}'; \xi_n) d(y-y') d(z-z')$$

and draw the y axis along the vector \mathbf{q} . Equations (3.9) for the Green's function take the form:

$$\begin{aligned} \left(\omega^2 - \frac{d^2}{dx^2} \right) \mathfrak{D}_{zz}(x, x') &= -4\pi\delta(x - x'), \\ \left(\omega^2 - q^2 - \frac{d^2}{dx^2} \right) \mathfrak{D}_{yy}(x, x') + iq \frac{d}{dx} \mathfrak{D}_{xy}(x, x') &= -4\pi\delta(x - x'), \\ \omega^2 \mathfrak{D}_{xy}(x, x') + iq \frac{d}{dx} \mathfrak{D}_{yy}(x, x') &= 0, \\ \omega^2 \mathfrak{D}_{xx}(x, x') + iq \frac{d}{dx} \mathfrak{D}_{xy}(x, x') &= -4\pi\delta(x - x'), \\ \left(\omega^2 - q^2 - \frac{d^2}{dx^2} \right) \mathfrak{D}_{xy}(x, x') + iq \frac{d}{dx} \mathfrak{D}_{xx}(x, x') &= 0, \end{aligned}$$

where $w = \sqrt{\epsilon \xi_n^2 + q^2}$, and x' plays the role of a parameter (the components of the Green's function \mathfrak{D}_{xz} and \mathfrak{D}_{yz} are equal to zero, since the equations for them are homogeneous).

The solution of this system reduces to the solution of just two equations:

$$\left. \begin{aligned} \left(\omega^2 - \frac{d^2}{dx^2} \right) \mathfrak{D}_{zz}(x, x') &= -4\pi\delta(x - x'), \\ \left(\omega^2 - \frac{d^2}{dx^2} \right) \mathfrak{D}_{yy}(x, x') &= -\frac{4\pi\omega^2}{\epsilon \xi_n^2} \delta(x - x'), \end{aligned} \right\} \quad (4.4)$$

after which \mathfrak{D}_{xy} and \mathfrak{D}_{xx} are determined by

$$\begin{aligned} \mathfrak{D}_{xy}(x, x') &= -\frac{iq}{\omega^2} \frac{d}{dx} \mathfrak{D}_{yy}(x, x'), \quad \mathfrak{D}_{xx}(x, x') \\ &= -\frac{iq}{\omega^2} \frac{d}{dx} \mathfrak{D}_{xy}(x, x') - \frac{4\pi}{\omega^2} \delta(x - x'). \end{aligned} \quad (4.5)$$

The boundary conditions corresponding to continuity of the tangential components of the electric and magnetic field stresses reduce to the requirement that the quantities \mathfrak{D}_{yk}^E , \mathfrak{D}_{zk}^E , \mathfrak{D}_{yk}^H , and \mathfrak{D}_{zk}^H be continuous, or, what is the same thing, that the quantities

$$\mathfrak{D}_{yk}, \quad \mathfrak{D}_{zk}, \quad \text{rot}_{y'l} \mathfrak{D}_{lk}, \quad \text{rot}_{z'l} \mathfrak{D}_{lk}$$

be continuous. Using the first of the equalities (4.5), we find that at the boundary of separation the quantities

$$\mathfrak{D}_{zz}, \quad \frac{d}{dx} \mathfrak{D}_{zz}, \quad \mathfrak{D}_{yy}, \quad \frac{\varepsilon}{w^2} \frac{d}{dx} \mathfrak{D}_{yy} \quad (4.6)$$

must be continuous.

Since we are interested only in the Green's function in the region of the gap 3, we can immediately restrict ourselves to the case of $0 < x' < l$. In the region $0 < x < l$ the functions \mathfrak{D}_{yy} and \mathfrak{D}_{zz} are determined by Eqs. (4.4) with $\varepsilon = \varepsilon_3$, $w = w_3 = \sqrt{\varepsilon_3 \xi_n^2 + q^2}$. In regions 1 ($x < 0$) and 2 ($x > l$) they satisfy the same equation with the right sides omitted (since now we always have $x \neq x'$) with ε_1 , w_1 and ε_2 , w_2 , respectively, in place of ε , w .

The subtraction which was mentioned at the end of Sec. 3 reduces to the following: we should subtract from all the functions \mathfrak{D}_{ik} in the region of the gap their values for $\varepsilon_1 = \varepsilon_2 = \varepsilon_3$ and $w_1 = w_2 = w_3$. As a result, in particular, we can immediately omit the term with the δ function in the second of the relations (4.5), so that the functions \mathfrak{D}_{xy} and \mathfrak{D}_{xx} in the region of the gap are given by the formulas:

$$\mathfrak{D}_{xy} = -\frac{iq}{w_3^2} \frac{d}{dx} \mathfrak{D}_{yy}, \quad \mathfrak{D}_{xx} = -\frac{iq}{w_3^2} \frac{d\mathfrak{D}_{xy}}{dx} \quad (4.7)$$

Before we go on to solving the equations, let us make one further remark. The general solution of Eqs. (4.4) has the form $f^+(x-x') + f^-(x-x')$. Using (4.4), (4.7), and the definition of the functions \mathfrak{D}_{ik}^E and \mathfrak{D}_{ik}^H , one can show that the parts of the Green's functions which depend on the sum $x+x'$ give no contribution to the expression (4.3) for the force F . We shall not spend time on this here since this result is obvious beforehand from physical considerations: setting $x = x'$ in the solution of the form $f^+(x+x')$, we would obtain a flux of momentum in the gap which would depend on the coordinates, in contradiction to the conservation law. In the following we shall therefore as a rule present only the expression for the part of the Green's functions \mathfrak{D}_{ik}^+ which depends only on $x-x'$.

Let us proceed now to find the function \mathfrak{D}_{zz} . It satisfies the equations

$$\begin{aligned} \left(w_3^2 - \frac{d^2}{dx^2} \right) \mathfrak{D}_{zz}(x, x') &= -4\pi\delta(x-x'), & 0 < x < l, \\ \left(w_1^2 - \frac{d^2}{dx^2} \right) \mathfrak{D}_{zz}(x, x') &= 0, & x < 0, \\ \left(w_2^2 - \frac{d^2}{dx^2} \right) \mathfrak{D}_{zz}(x, x') &= 0, & x > l. \end{aligned}$$

From these we find

$$\begin{aligned} \mathfrak{D}_{zz} &= Ae^{w_1 x}, & x < 0, \\ \mathfrak{D}_{zz} &= Be^{-w_2 x}, & x > l, \\ \mathfrak{D}_{zz} &= C_1 e^{w_3 x} + C_2 e^{-w_3 x} - \frac{2\pi}{w_3} e^{-w_3|x-x'|}, & 0 < x < l. \end{aligned}$$

Determining the constants A , B , C_1 , C_2 , from the boundary conditions of continuity of \mathfrak{D}_{zz} and $d\mathfrak{D}_{zz}/dx$, we find for \mathfrak{D}_{zz}^+ :

$$\mathfrak{D}_{zz}^+ = \frac{4\pi}{w_3 \Delta} \text{ch } w_3(x-x') - \frac{2\pi}{w_3} e^{-w_3|x-x'|}, \quad 0 < x < l,$$

where

$$\Delta = 1 - e^{2w_3 l} \frac{(w_1 + w_3)(w_2 + w_3)}{(w_1 - w_3)(w_2 - w_3)}. \quad (4.8)$$

Subtracting the value of \mathfrak{D}_{zz}^+ for $w_1 = w_2 = w_3$ (so that $1/\Delta$ goes to zero), we finally obtain

$$\mathfrak{D}_{zz}^+ = \frac{4\pi}{w_3 \Delta} \text{ch } w_3(x-x'). \quad (4.9)^*$$

Similarly, solving the equation for \mathfrak{D}_{yy} , we find (after the subtraction)

$$\mathfrak{D}_{yy}^+ = \frac{4\pi w_3}{\xi_n^2 \varepsilon_3 \Delta} \text{ch } w_3(x-x'), \quad (4.10)$$

$$\bar{\Delta} = 1 - e^{2w_3 l} \frac{(\varepsilon_1 w_3 + \varepsilon_3 w_1)(\varepsilon_2 w_3 + \varepsilon_3 w_2)}{(\varepsilon_1 w_3 - \varepsilon_3 w_1)(\varepsilon_2 w_3 - \varepsilon_3 w_2)} \quad (4.11)$$

and using relation (4.7):

$$\left. \begin{aligned} \mathfrak{D}_{xy}^+ &= -\frac{4\pi iq}{\xi_n^2 \varepsilon_3 \Delta} \text{sh } w_3(x-x'), \\ \mathfrak{D}_{xx}^+ &= -\frac{4\pi q^2}{\xi_n^2 \varepsilon_3 w_3 \Delta} \text{ch } w_3(x-x'). \end{aligned} \right\} \quad (4.12)$$

Now computing the quantities $\mathfrak{D}_{ik}^E(x, x'; \mathbf{q}; \xi_n)$ and $\mathfrak{D}_{ik}^H(x, x'; \mathbf{q}; \xi_n)$ and substituting them in formula (4.3), we obtain

$$F(l) = -\frac{T}{2\pi} \sum_{n=0}^{\infty} \int_0^{\infty} q dq w_3 \left(\frac{1}{\Delta} + \frac{1}{\bar{\Delta}} \right).$$

Transforming to a new integration variable p using the substitution $q = \xi_n \sqrt{\varepsilon_3(p^2 - 1)}$ and changing to the usual system of units, we arrive at the final expression for the force F acting on unit area of each of the two bodies (media 1 and 2), separated by a gap of width l , filled with medium 3 (cf. Fig. 9):

$$\begin{aligned} F(l) &= \frac{kT}{\pi c^3} \sum_{n=0}^{\infty} \varepsilon_3^{3/2} \xi_n^3 \int_1^{\infty} p^2 \left\{ \left[\frac{(s_1 + p)(s_2 + p)}{(s_1 - p)(s_2 - p)} \exp\left(\frac{2p\xi_n l \sqrt{\varepsilon_3}}{c}\right) - 1 \right]^{-1} \right. \\ &\quad \left. + \left[\frac{(s_1 + p\varepsilon_1/\varepsilon_3)(s_2 + p\varepsilon_2/\varepsilon_3)}{(s_1 - p\varepsilon_1/\varepsilon_3)(s_2 - p\varepsilon_2/\varepsilon_3)} \exp\left(\frac{2p\xi_n l \sqrt{\varepsilon_3}}{c}\right) - 1 \right]^{-1} \right\} dp, \end{aligned} \quad (4.13)$$

where

$$s_1 = \sqrt{(\varepsilon_1/\varepsilon_3) - 1 + p^2}, \quad s_2 = \sqrt{(\varepsilon_2/\varepsilon_3) - 1 + p^2}, \quad \xi_n = 2\pi n k T / \hbar;$$

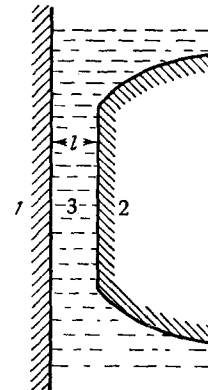


FIG. 9

*sh = sinh, ch = cosh.

$\epsilon_1, \epsilon_2, \epsilon_3$ are functions of the imaginary frequency $\omega = i\xi_n$ ($\epsilon = \epsilon(i\xi_n)$), and k is the Boltzmann constant. The summation is carried out over integer values of n , and the prime on the summation sign means that the term with $n = 0$ is taken with a weight of $1/2$. Positive values of F correspond to attraction, and negative values to repulsion of the bodies.

This formula (for $\epsilon_3 = 1$, i.e., for bodies which are separated by an empty gap) was first obtained by Lifshitz⁴ by a different procedure without using the methods of quantum field theory. However, the use of these methods is necessary for its generalization to the case of a gap filled with an arbitrary medium (Dzyaloshinskii, Lifshitz, and Pitaevskii⁶).

b) Discussion of the general formula and limiting cases.* The general formula (4.13) contains the functions $\epsilon(\omega)$ — the dielectric constants as functions of the frequency ω of the field — for both of the solid bodies (ϵ_1 and ϵ_2) and for the liquid medium which fills the space between them (ϵ_3). We recall that $\epsilon(\omega)$ is a complex quantity [$\epsilon = \epsilon'(\omega) + i\epsilon''(\omega)$] whose imaginary part is always positive and determines the dissipation of the energy of an electromagnetic wave propagating in the medium. The function $\epsilon(\omega)$ is related to the index of refraction n and the absorption coefficient κ of the medium by the well-known relation $\sqrt{\epsilon} = n + i\kappa$. As is well known, by formally treating the function $\epsilon(\omega)$ as a function of the complex variable ω , one can establish definite integral relations between $\epsilon'(\omega)$ and $\epsilon''(\omega)$, the so-called Kramers-Kronig formulas.

A partial consequence of these formulas is the relation (3.11), which determines the values of the function ϵ of the pure imaginary argument $\omega = i\xi$ in terms of the values of the function $\epsilon''(\omega)$ of the real argument ω ; $\epsilon(i\xi)$ is a real quantity which decreases monotonically from the value ϵ_0 (the static value of the dielectric constant) for $\xi = 0$ to unity for $\xi \rightarrow \infty$. It is precisely these functions $\epsilon(i\xi)$ which appear in formula (4.13). We may therefore say that the only macroscopic characteristics of bodies which determine their forces of molecular interaction are essentially the imaginary parts $\epsilon''(\omega)$ of their dielectric constants.†

Before proceeding to discuss the formulas which we have obtained, we must make the following general remark. If two bodies are separated by an empty gap, the electromagnetic forces computed by us are the

*Most of the results presented in sections 4b, c, and d are due to E. M. Lifshitz.⁴

†Formula (4.13) was derived on the assumption that all media are isotropic. Therefore its application to crystals implies that it is possible to neglect the anisotropy of their dielectric constant. Although this is completely permissible in most cases, it should be kept in mind that anisotropy of bodies leads in general to still another physical phenomenon—the appearance of moments which tend to turn the bodies with respect to one another.

only forces of interaction between the bodies. But if the gap is filled with some medium, then in this medium there are also possible fluctuations associated with other oscillations, aside from electromagnetic (for example, sound vibrations), which can also give a contribution to the interaction. However, as will be shown in Sec. 5b on the example of the forces in films, the contribution of these nonelectromagnetic forces is small in the majority of cases.

If both bodies are identical ($\epsilon_1 = \epsilon_2$), then the integrand in each of the terms of the sum in (4.13) is always positive,* and for given p and ξ_n falls off monotonically with increasing l . From this it follows that $F > 0$ and $dF/dl < 0$, i.e., identical bodies attract one another for any layer thickness between them, and the force of attraction decreases monotonically with increasing distance.† This assertion is also valid for two different bodies separated by an empty space ($\epsilon_3 = 1$). But if the bodies are different and the space between them is filled with liquid, then the interaction between them can be either an attraction or a repulsion (cf. below).

The general formula (4.13) is very complicated. However, it can be simplified considerably by noting that the effect of the temperature on the interaction of the bodies turns out to be usually completely unimportant.‡

The point is that because of the presence of the exponential in the integrands in (4.13), the main contribution to the sum comes only from those terms for which $\xi_n \sim c/l$ or $n \sim c\hbar/lkT$. In the case where $lkT/c\hbar \ll 1$, the important terms will be those with large values of n , and we can in (4.13) change from summation to integration with respect to the variable $dn = (\hbar/2\pi kT) d\xi$. Then the temperature drops out of the formula and we obtain the following result:

$$F = \frac{\hbar}{2\pi^2 c^3} \int_0^\infty \int_1^\infty p^2 \xi^3 \epsilon_3^{3/2} \left\{ \left[\frac{(s_1+p)(s_2+p)}{(s_1-p)(s_2-p)} \exp\left(\frac{2p\xi}{c} l \sqrt{\epsilon_3}\right) - 1 \right]^{-1} + \left[\frac{(s_1+p \epsilon_1/\epsilon_3)(s_2+p \epsilon_2/\epsilon_3)}{(s_1-p \epsilon_1/\epsilon_3)(s_2-p \epsilon_2/\epsilon_3)} \exp\left(\frac{2p\xi}{c} l \sqrt{\epsilon_3}\right) - 1 \right]^{-1} \right\} dp d\xi. \quad (4.14)$$

According to what we have said above, this formula is applicable for distances $l \ll c\hbar/kT$; at room temperature this already gives distances approximately up to 10^{-4} cm.

Formula (4.14) is still complicated. It permits of further essential simplification in two important limiting cases.

*This can easily be seen by noting that for $s = \sqrt{\epsilon - 1 + p^2}$ (where $p \geq 1$), the inequality $\epsilon p > s > p$ holds for $\epsilon > 1$, and $\epsilon p < s < p$ for $\epsilon < 1$.

†Such an assertion was already made previously by Hamaker¹² on the basis of the assumption of additivity of the molecular forces (which is actually not the case).

‡When we speak of the influence of temperature, we are disregarding the temperature dependence which is associated simply with the dependence of the dielectric constant itself on temperature.

Let us first consider the limiting case of "small" separations, by which we mean separations which are small compared with the wave lengths λ_0 which are characteristic for the absorption spectra of the bodies. The temperatures with which one may be concerned for condensed bodies are in all cases small compared with the values of $\hbar\omega$ which are important here (for example, in the visible region of the spectrum), so that the inequality $kT/\hbar c \ll 1$ is surely satisfied.

Because of the presence of the exponential factor $\exp(2p\xi l\sqrt{\epsilon_3}/c)$ in the denominators of the integrand, the main contribution to the integral over p comes from those values of p such that $p\xi l/c \sim 1$. In this case $p \gg 1$, and therefore in determining the main terms we may set $s_1 \approx s_2 \approx p$. In this approximation the first term in the curly brackets in (4.14) goes to zero. The second term, after we introduce the integration variable $x = 2lp\xi\sqrt{\epsilon_3}/c$, gives

$$F = \frac{\hbar}{16\pi^2 l^3} \int_0^\infty \int_0^\infty x^2 \left[\frac{(\epsilon_1 + \epsilon_2)(\epsilon_2 + \epsilon_3)}{(\epsilon_1 - \epsilon_3)(\epsilon_2 - \epsilon_3)} e^x - 1 \right]^{-1} dx d\xi \quad (4.15)$$

(in this same approximation the lower limit of integration with respect to x is set equal to zero).

In this case the force turns out to be inversely proportional to the cube of the distance which, besides, was to be expected in accordance with the usual law for van der Waals' forces between a pair of atoms. The functions $\epsilon(i\xi) - 1$ decrease monotonically with increasing ξ , tending toward zero. Therefore values of ξ , starting with a certain $\xi \sim \xi_0$, cease to give any essential contribution to the integral; the condition that l be small means that we must have $l \ll c/\xi_0$.

To estimate the accuracy of this limiting law, it is useful to have the next term in the expansion of the function $F(l)$. A calculation using the general formula (4.14) gives (for identical bodies separated by vacuum) the expression

$$-\frac{\hbar}{8\pi^2 c^2 l} \int_0^\infty \frac{\xi^2 [\epsilon(i\xi) - 1]^2}{\epsilon(i\xi) - 1} d\xi, \quad (4.16)$$

which must be added to (4.15). However, it is not possible to make any definite estimate of the range of validity of the limiting law without knowing the specific form of the function $\epsilon(i\xi)$.

One can, with an accuracy which is practically completely satisfactory, represent formula (4.14) in a still simpler form by neglecting unity compared with the term e^x in the square brackets. The accuracy of this simplification is associated with the fact that an integral of the form

$$\frac{a}{n!} \int_0^\infty \frac{x^n dx}{ae^x - 1} \quad (4.17)$$

changes insignificantly when a varies from ∞ to 1: it varies from 1 to 1.2 for $n = 2$, to 1.08 for $n = 3$, to 1.04 for $n = 4$, etc. Then the integration with respect to x can be carried out in an elementary fashion, and, in place of (4.15) we obtain

$$F = \frac{\hbar\bar{\omega}}{8\pi^2 l^3}, \quad \bar{\omega} = \int_0^\infty \frac{[\epsilon_1(i\xi) - \epsilon_3(i\xi)][\epsilon_2(i\xi) - \epsilon_3(i\xi)]}{[\epsilon_1(i\xi) + \epsilon_3(i\xi)][\epsilon_2(i\xi) + \epsilon_3(i\xi)]} d\xi. \quad (4.18)$$

The quantity $|\bar{\omega}|$ plays the part of a characteristic frequency for the absorption spectra of all three media.

We now proceed to the opposite limiting case of "large" distances: $l \gg \lambda_0$. Here, however, we shall assume that the distance is still not so large that we violate the inequality $lkT/\hbar c \ll 1$.

In the general formula (4.14) we introduce a new integration variable, $x = 2pl\xi/c$, but as the second variable we keep not ξ (as before), but rather p :

$$F = \frac{\hbar c}{32\pi^2 l^4} \int_0^\infty \int_0^\infty \frac{x^2}{p^2} \epsilon_3^{3/2} \left\{ \left[\frac{(s_1 + p)(s_2 + p)}{(s_1 - p)(s_2 - p)} e^x \sqrt{\epsilon_3} - 1 \right]^{-1} \right. \\ \left. + \left[\frac{(s_1 + p\epsilon_1/\epsilon_3)(s_2 + p\epsilon_2/\epsilon_3)}{(s_1 - p\epsilon_1/\epsilon_3)(s_2 - p\epsilon_2/\epsilon_3)} e^x \sqrt{\epsilon_3} - 1 \right]^{-1} \right\} dp dx, \\ \epsilon = \epsilon(ixc/2pl), \quad s = \sqrt{\epsilon(ixc/2pl) - 1 + p^2}.$$

Because of the presence of the term $\exp(x\sqrt{\epsilon_3})$ in the denominators, the important region in the integration with respect to x is that for values of $x \sim 1/\sqrt{\epsilon_3} \leq 1$, and since $p \geq 1$ the argument of the function for large values of l is close to zero over the whole important region of values of the variables. In accordance with this, we can replace $\epsilon_1, \epsilon_2, \epsilon_3$ simply by their values for $\xi = 0$, i.e., by the static dielectric constants. After doing this and also making the substitution $x \rightarrow x/\sqrt{\epsilon_{30}}$, we obtain the following final result:

$$F = \frac{\hbar c}{32\pi^2 l^4 \sqrt{\epsilon_{30}}} \int_0^\infty \int_0^\infty \frac{x^2}{p^2} \left\{ \left[\frac{(s_{10} + p)(s_{20} + p)}{(s_{10} - p)(s_{20} - p)} e^x - 1 \right]^{-1} \right. \\ \left. + \left[\frac{(s_{10} + p\epsilon_{10}/\epsilon_{30})(s_{20} + p\epsilon_{20}/\epsilon_{30})}{(s_{10} - p\epsilon_{10}/\epsilon_{30})(s_{20} - p\epsilon_{20}/\epsilon_{30})} e^x - 1 \right]^{-1} \right\} dp dx, \\ s_{10} = \sqrt{(\epsilon_{10}/\epsilon_{30}) - 1 + p^2}, \quad s_{20} = \sqrt{(\epsilon_{20}/\epsilon_{30}) - 1 + p^2}, \quad (4.19)$$

where $\epsilon_{10}, \epsilon_{20}, \epsilon_{30}$ are the static values of the dielectric constants.

In connection with the property of integrals of the type of (4.17) which was mentioned above, formula (4.19) can be represented with very high accuracy in the simpler form

$$F = \frac{3\hbar c}{16\pi^2 l^4 \sqrt{\epsilon_{30}}} \int_0^\infty \left\{ \frac{(s_{10} - p)(s_{20} - p)}{(s_{10} + p)(s_{20} + p)} \right. \\ \left. + \frac{(s_{10} - p\epsilon_{10}/\epsilon_{30})(s_{20} - p\epsilon_{20}/\epsilon_{30})}{(s_{10} + p\epsilon_{10}/\epsilon_{30})(s_{20} + p\epsilon_{20}/\epsilon_{30})} \right\} \frac{dp}{p^2}.$$

Here there remains only a single quadrature which can, in principle, be reduced to elementary functions; the result, however, is so complicated that for specific calculations it appears to be more reasonable to proceed to a numerical integration.

We have already pointed out above that if the two bodies are different and the space between them is filled with liquid, then the interaction may be either attractive or repulsive. Thus it is clear from (4.18) that, if in the important region of frequencies the dif-

ferences $\epsilon_{10} - \epsilon_{30}$ and $\epsilon_{20} - \epsilon_{30}$ have opposite signs, then F will be less than zero, i.e., the bodies repel each other at "small" distances. At "large" distances the nature of the force will be determined by the relative value of the static dielectric constants; for the same signs of the differences $\epsilon_{10} - \epsilon_{30}$ and $\epsilon_{20} - \epsilon_{30}$, we have $F > 0$, while for opposite signs we have $F < 0$. Moreover, since the relative values of ϵ_{10} , ϵ_{20} and ϵ_{30} are not in general related to the behavior of the functions $\epsilon_1(i\xi)$, $\epsilon_2(i\xi)$ and $\epsilon_3(i\xi)$ in the region of frequencies which is important for the bodies, it is possible in principle to have a case where F changes sign for a certain value of l .

Let us turn to formula (4.19) and consider some of its special cases. A particularly simple result is obtained when both of the bodies are metals. For metals we know that the function $\epsilon(i\xi) \rightarrow \infty$ for $\xi \rightarrow 0$; therefore for such materials we may assume $\epsilon_0 = \infty$. Setting $\epsilon_{10} = \epsilon_{20} = \infty$, we have

$$F = \frac{\hbar c}{16\pi^2 l^4 \sqrt{\epsilon_{30}}} \int_0^\infty \int_1^\infty \frac{x^3 dp dx}{p^2 (e^x - 1)} = \frac{\pi^2}{240} \frac{\hbar c}{\sqrt{\epsilon_{30}^4}}. \quad (4.21)$$

This force in general does not depend on the nature of the metals (a property which does not hold at small distances, where the value of the interaction depends on the behavior of the function $\epsilon(i\xi)$ for all values of ξ and not just for $\xi = 0$). For $\epsilon_{30} = 1$, formula (5.6) coincides with the formula obtained by Casimir²⁰ for this special case by a treatment of the normal modes of the field in the gap between two walls which are ideally reflecting at all frequencies.

If the two bodies are the same ($\epsilon_{10} = \epsilon_{20}$), formula (4.19) can be represented as

$$F = \frac{\pi^2 \hbar c}{240 l^4 \sqrt{\epsilon_{30}}} \left(\frac{\epsilon_{10} - \epsilon_{30}}{\epsilon_{10} + \epsilon_{30}} \right)^2 \Phi_{DD} \left(\frac{\epsilon_{10}}{\epsilon_{30}} \right), \quad (4.22)$$

where $\Phi_{DD}(x)$ is a function whose computed values are given in Fig. 10 (curve DD) over the range of values of the argument from 1 to ∞ ; in the appendix we shall show that $\Phi_{DD}(0) = 0.52$. For $x \rightarrow \infty$, Φ_{DD} tends to unity according to the law

$$\Phi_{DD}(x) \approx 1 - \frac{1.1}{\sqrt{x}} \ln \frac{x}{7.6};$$

for $x \rightarrow 1$ it tends to a finite limit 0.35; (corresponding to the limiting law (4.35); cf. below).

On the same figure we show the curve DM of the analogous function describing the force of attraction between a dielectric and a metal ($\epsilon_{20} = \infty$) according to the formula

$$F = \frac{\pi^2 \hbar c}{240 l^4 \sqrt{\epsilon_{30}}} \frac{\epsilon_{10} - \epsilon_{30}}{\epsilon_{10} + \epsilon_{30}} \Phi_{DM} \left(\frac{\epsilon_{10}}{\epsilon_{30}} \right). \quad (4.23)$$

For $\epsilon_{30} \rightarrow \infty$ expression (4.19) tends to zero. This means that when the gap between the bodies is filled with a liquid metal, the force of attraction decreases at large distances with a higher power of $1/l$. This peculiar case has a certain interest in principle, although it can hardly have any practical significance.

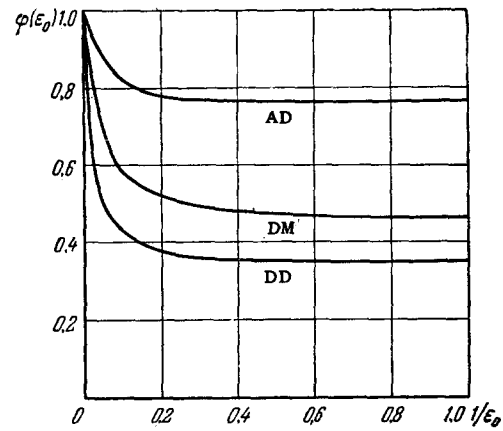


FIG. 10

To treat it one must turn to the initial formula (4.14) and include in it the specific law according to which the dielectric constant of the metal increases with decreasing frequency.

The behavior of $\epsilon(\omega)$ for a metal in the infrared region of the spectrum is described accurately enough by the formula

$$\epsilon(\omega) = -\frac{4\pi e^2 N}{m\omega^2}, \quad (4.24)$$

where N is the number density of free electrons. If we substitute $\epsilon(i\xi) = 4\pi Ne^2/m\xi^2$ in formula (4.14), the exponential factors in the denominators of the integrand become

$$\exp \left\{ \frac{2pl}{c} \sqrt{\frac{4\pi e^2}{mN}} \right\},$$

i.e., ξ drops out of them, and since p runs through values $p \geq 1$, we come to the conclusion that this region of frequencies gives a contribution to the force F which falls off exponentially with distance l .

The main contribution to the interaction in this case comes from the region of still smaller frequencies in which $\epsilon(\omega)$ is related to the usual electrical conductivity of the metal by the formula

$$\epsilon(\omega) = \frac{4\pi i\sigma}{\omega}. \quad (4.25)$$

Substituting $\epsilon_3(i\xi) = 4\pi\sigma_3/\xi$ in the integrand of formula (4.14) (in the exponents and in the factor $\epsilon_3^{3/2}$ it is sufficient in other places to set $\epsilon_3 = \infty$) and introducing in place of the integration variable ξ the variable $x = 4pl\sqrt{\pi\sigma_3\xi}/c^2$, we obtain

$$F = \frac{\hbar c^2}{27\pi^3 \sigma_3 l^6} \int_0^\infty \int_1^\infty \frac{x^4}{p^2} \left\{ \left[\left(\frac{\sqrt{p^2-1}+p}{\sqrt{p^2-1}-p} \right)^2 e^x - 1 \right]^{-1} + \frac{1}{e^x-1} \right\} dp dx.$$

The computation of the double integral [using the property pointed out above of integrals of the type of (4.17)] gives a value for it which is equal to 13.5 and, as a result, we get the following formula:

$$F = 0.0034 \frac{\hbar c^2}{\sigma_3 l^6}. \quad (4.26)$$

Thus, in the case of a liquid metal layer between the

bodies the molecular interaction force between them changes from the law l^{-3} at "small" distances to an l^{-5} law at "large" distances; the appearance of the latter is held back, it is true, by the presence in (4.26) of the small numerical coefficient.

Naturally the question arises of the actual value of λ_0 with which one must compare the distances l . An answer to this cannot be given in general form and depends on the specific form of the spectral distribution of the absorption of the bodies [i.e., on the properties of the function $\epsilon''(\omega)$]. Let us examine, for example, the region of applicability of formula (4.21) for the interaction of two metals (which we shall assume to be identical) which are separated by vacuum.

Formula (4.21) is obtained from (4.14) if we set $\epsilon_1 = \epsilon_2 = \infty$ ($\epsilon_3 = 1$) in the latter. But if we also want to obtain the next term in the expansion, we must use the form (4.24) of the function $\epsilon(\omega)$, which is valid in the important region of frequencies in the integral.

[The region of still lower frequencies, in which $\epsilon(\omega)$ is given by formula (4.25), gives a very small contribution to this integral.] After substituting $\epsilon(i\xi)$ in (4.14), we must replace ξ by $x c/2pl$; expanding the integrand in powers of $1/l$, we get:

$$F = \frac{\hbar c}{32\pi^2 l^4} \left\{ \frac{2\pi^4}{15} - \frac{c}{el} \sqrt{\frac{m}{\pi N}} \int_0^\infty \frac{x^4 e^x dx}{(e^x - 1)^2} \int_1^\infty \frac{p^2 + 1}{p^4} dp \right\},$$

from which we have finally

$$F = \frac{\hbar c}{l^4} \frac{c^2}{240} \left\{ 1 - 7.2 \frac{c}{el} \sqrt{\frac{m}{N}} \right\}. \quad (4.27)$$

Setting $N = 5.9 \times 10^{22} \text{ cm}^{-3}$ (the case of silver), we find that the second term is small compared to the first if $l \gg 0.6 \times 10^{-4} \text{ cm}$. We note that the value for the next term in the expansion which we have found here could not be obtained by the method which Casimir used for getting the first term.

It is not the purpose of this paper to give a summary of the experimental data concerning van der Waals' forces. Here we mention only the fact that the first trustworthy measurement of molecular attractive forces between solids (quartz*) was made by B. V.

*The case of quartz presents certain peculiarities because of the specific properties of its absorption spectrum. Quartz has a strong absorption in the ultraviolet (beginning approximately at 0.15μ) and in the infrared (beginning at several μ) regions, between which it is transparent. For separations l which lie in the region of transparency, a reasonable estimate of the force F can be made by assuming that l is small compared with λ on the right, and large compared with λ on the left boundary of this region. The contribution of the ultraviolet absorption region to the force can be estimated according to formula (4.22), by setting $\epsilon_{10} = \epsilon_{20} = \epsilon_0$ ($\epsilon_{30} = 1$) equal to the square of the index of refraction in the optical region of transparency. The contribution of the infrared region is given by formula (4.18); in order of magnitude it is $l\omega_0/c$ times smaller (where ω_0 are the infrared absorption frequencies). Thus, to estimate the attractive forces one can use formula (4.22) with the optical (in place of the static) value of the dielectric constant for ϵ_0 . Such an estimate is too low for large separations and too high for small separations.

Deryagin and I. I. Abrikosova¹³ and I. I. Abrikosova,¹⁴ and turned out to be in good agreement with the theory. A detailed presentation and discussion of these data is given in the summary paper of Deryagin, Abrikosova, and Lifshitz.¹⁵ Similar measurements have also been made by Kitchener and Prosser¹⁶ and by DeJongh.¹⁷

c) The effect of temperature. All the formulas presented in Sec. 4b were obtained on the assumption that the inequality $kT/\hbar c \ll 1$ is satisfied; accordingly, in going from (4.13) to (4.14) we limited ourselves to just the first (zeroth) term in the expansion in powers of the temperature. To estimate the error made in this procedure we must find the next term in the expansion. Let us do this for two identical metals separated by vacuum.

The replacement of the sum by an integral which was done in deriving (4.14) corresponds to using the first term in the Euler summation formula

$$\sum_{n=0}^{\infty} f(n) = \int_0^{\infty} f(n) dn + \frac{1}{12} f'(0) - \frac{1}{30 \cdot 4!} f'''(0) + \dots$$

In the present case, the function $f(n)$ is the integral which appears under the summation sign in (4.13). In making the calculation we shall assume that l is small compared with $\hbar c/kT$, but still large compared with the quantity $(c/e) \sqrt{m/N}$ which is characteristic for the metal [cf. Eq. (4.27)]. Then $f'(0) = 0$, $f'''(0) = 2$ and thus,

$$F = \frac{\pi^2}{240} \frac{\hbar c}{l^4} \left[1 - \frac{48}{9} \left(\frac{lkT}{\hbar c} \right)^4 \right]. \quad (4.28)$$

So at room temperature the correction term is small even if $l \approx 5 \times 10^{-4}$; comparison with the criterion obtained from (4.27) shows that there is a region in which formula (4.21) is applicable.

For $lkT/\hbar c \gg 1$ we need to keep only the first term in the sum (4.13). However, we cannot immediately set $n = 0$ in it because of the indeterminacy which results (the factor ξ_n^3 goes to zero, but the integral over p diverges). This difficulty can be avoided by first introducing in place of p a new integration variable $x = 2p\xi_n l \sqrt{\epsilon_{30}}/c$ (as a result of which the factor ξ_n^3 disappears). Then setting $\xi_n = 0$ we get

$$F = \frac{kT}{16\pi l^3} \int_0^\infty x^2 \left[\frac{(\epsilon_{10} + \epsilon_{30})(\epsilon_{20} + \epsilon_{30})}{(\epsilon_{10} - \epsilon_{30})(\epsilon_{20} - \epsilon_{30})} e^x - 1 \right]^{-1} dx$$

$$\approx \frac{kT}{8\pi l^3} \frac{(\epsilon_{10} - \epsilon_{30})(\epsilon_{20} - \epsilon_{30})}{(\epsilon_{10} + \epsilon_{30})(\epsilon_{20} + \epsilon_{30})}. \quad (4.29)$$

Thus at sufficiently large distances the fall-off in the interaction forces is retarded, and again goes according to an l^{-3} law, with a coefficient depending on the temperature and the static values of the dielectric constants.

All the succeeding terms in the sum (4.13) fall off exponentially for large l . Thus, for two metals separated by vacuum, when the first correction term is included, we obtain the formula

$$F = \frac{kT}{8\pi l^3} \left[1 + 2 \left(\frac{4\pi kTl}{\hbar c} \right)^2 \exp \left(-\frac{4\pi kTl}{\hbar c} \right) \right]. \quad (4.30)$$

d) **Interaction of individual atoms.** We shall now show how one can go over from the macroscopic formula (4.14) to the interaction of individual atoms in vacuum. For this purpose we formally assume that both of the bodies are sufficiently rarefied. From the point of view of macroscopic electrodynamics this means that their dielectric constants are close to unity, i.e., the differences $\epsilon_1 - 1$ and $\epsilon_2 - 1$ are small.

Let us start with the case of "small" distances. From formula (4.15) with $\epsilon_3 = 1$ we have to the required accuracy:

$$\begin{aligned} F &= \frac{\hbar}{64\pi^2 l^3} \int_0^\infty x^2 e^{-x} (\epsilon_1 - 1)(\epsilon_2 - 1) dx d\xi \\ &= \frac{\hbar}{32\pi^2 l^3} \int_0^\infty [e_1(i\xi) - 1][e_2(i\xi) - 1] d\xi. \end{aligned} \quad (4.31)$$

Expressing $\epsilon(i\xi)$ in terms of $\epsilon''(\omega)$ on the real ω axis, in accordance with (3.11), we get

$$\begin{aligned} &\int_0^\infty [e_1(i\xi) - 1][e_2(i\xi) - 1] d\xi \\ &= \frac{4}{\pi^2} \int_0^\infty \int_0^\infty \int_0^\infty \frac{\omega_1 \omega_2 \epsilon_1''(\omega_1) \epsilon_2''(\omega_2)}{(\omega_1^2 + \xi^2)(\omega_2^2 + \xi^2)} d\xi d\omega_1 d\omega_2 \\ &= \frac{2}{\pi} \int_0^\infty \int_0^\infty \frac{\epsilon_1''(\omega_1) \epsilon_2''(\omega_2)}{\omega_1 + \omega_2} d\omega_1 d\omega_2, \end{aligned}$$

from which we find for the force F:

$$F = \frac{\hbar}{16\pi^2 l^3} \int_0^\infty \int_0^\infty \frac{\epsilon_1''(\omega_1) \epsilon_2''(\omega_2)}{\omega_1 + \omega_2} d\omega_1 d\omega_2. \quad (4.32)$$

This force corresponds to an interaction of atoms with an energy*

$$U = -\frac{3\hbar}{8\pi^4 R^6 N_1 N_2} \int_0^\infty \int_0^\infty \frac{\epsilon_1''(\omega_1) \epsilon_2''(\omega_2)}{\omega_1 + \omega_2} d\omega_1 d\omega_2, \quad (4.33)$$

where R is the separation of the atoms, N_1 and N_2 are the numbers of atoms per unit volume in the first and second bodies respectively. The imaginary part of the dielectric constant is related to the spectral density of the "oscillator strength" $f(\omega)$ by the relation

$$\omega \epsilon''(\omega) = \frac{2\pi e^2}{m} N f(\omega)$$

(cf., for example, reference 11, Sec. 62). Substituting this in (4.33), we find

$$U(R) = -\frac{3\hbar e^4}{2m^2 R^6} \int_0^\infty \int_0^\infty \frac{f_1(\omega_1) f_2(\omega_2)}{\omega_1 \omega_2 (\omega_1 + \omega_2)} d\omega_1 d\omega_2. \quad (4.34)$$

*If the interaction energy of molecules 1 and 2 is $U = -aR^{-6}$, the total energy of pair interactions of all the molecules in the two half-spaces separated by a gap l is equal to

$$\bar{U} = \frac{\alpha \pi N_1 N_2}{2l^2}. \text{ The force } F \text{ is}$$

$$F = -\frac{d\bar{U}}{dl} = -\frac{a\pi N_1 N_2}{6l^3}.$$

This also includes the correspondence of formulas (4.33) and (4.32).

This expression coincides precisely with the well-known London¹ formula which was obtained by using ordinary perturbation theory, applied to the dipole interaction of two atoms. Suppose, for example, we are considering the interaction of two hydrogen atoms. Using the familiar expression

$$f_{0n} = \frac{2m}{\hbar^2} (E_n - E_0) |\chi_{0n}|^2$$

for the oscillator strength of the transition between states E_n and E_0 (χ_{0n} is the corresponding matrix element of the coordinate of an electron in the atom), and changing in (4.34) from integration over the frequencies to summation over the energy levels of the atom, we obtain the London formula for hydrogen atoms

$$U(R) = -\frac{6e^4}{R^6} \sum_{n, m} \frac{|\chi_{0n}|^2 |\chi_{0m}|^2}{E_n - E_0 + E_m - E_0}.$$

Thus we see that this "microscopic" formula is derivable from a purely macroscopic theory.

At "large" distances the formula for the force of attraction of two rarefied bodies has the form

$$F = \frac{\hbar c}{32\pi^2 l^4} (\epsilon_{10} - 1)(\epsilon_{20} - 1) \int_0^\infty x^3 e^{-x} dx \int_1^\infty \frac{1 - 2p^2 + 2p^4}{8p^2} dp,$$

or

$$F = \frac{\hbar c}{l^4} \frac{23}{640\pi^2} (\epsilon_{10} - 1)(\epsilon_{20} - 1). \quad (4.35)$$

This force corresponds to an interaction of the two atoms with an energy

$$U = -\frac{23\hbar c}{4\pi R^7} \alpha_1 \alpha_2, \quad (4.36)$$

where α_1 and α_2 are the static polarizabilities of the two atoms ($\epsilon_0 = 1 + 4\pi N\alpha$). Formula (4.34) coincides with the result of the quantum-mechanical calculation of Casimir and Polder² for the attraction of two atoms at sufficiently large distances, when retardation effects become important.

In an analogous fashion, by considering only one of the bodies (suppose it to be body 2) as a rarefied medium, one can find the interaction of an individual molecule with a condensed body. Thus, in the case of "large" distance l of the molecule from the surface of the body, we obtain for the interaction energy the following formula:

$$U(l) = \frac{3\hbar c \alpha_2}{8\pi l^4} \frac{\epsilon_{10} - 1}{\epsilon_{10} + 1} \Psi_{AD}(\epsilon_{10}), \quad (4.37)$$

where

$$\begin{aligned} \Psi_{AD}(\epsilon) &= \frac{\epsilon + 1}{\epsilon - 1} \left\{ \frac{1}{3} + \epsilon + \frac{4 - \sqrt{\epsilon(\epsilon + 1)}}{2(\epsilon - 1)} \right. \\ &\quad - \frac{\text{Arsh} \sqrt{\epsilon - 1}}{2(\epsilon - 1)^{3/2}} [1 + \epsilon + 2\epsilon(\epsilon - 1)^2] \\ &\quad \left. + \frac{\epsilon^2}{\sqrt{\epsilon + 1}} \left(\text{Arsh} \sqrt{\epsilon} - \text{Arsh} \frac{1}{\sqrt{\epsilon}} \right) \right\}. \end{aligned} \quad (4.38)*$$

*Arsh = \sinh^{-1} .

The function φ_{AD} is shown graphically in Fig. 10. For $\epsilon_{10} \rightarrow \infty$ this function tends toward 1; the expression

$$U = \frac{3\alpha_2 \hbar c}{8\pi l^4} \quad (4.39)$$

coincides with the result of Casimir and Polder² for the energy of interaction between an atom and a metallic wall. For $\epsilon_{10} = 1$ the function

$$\varphi_{AD} = 2^3/30 = 0.77.$$

Now let us consider the interaction of two atoms which are in a liquid (Pitaevskii¹⁸). For this purpose we imagine that the two bodies are made up of weak solutions of atoms of different types, with concentrations (numbers of particles per cc) N_1 and N_2 , respectively, in the same solvent. Furthermore we shall assume that the gap is filled with pure solvent. The dielectric constants of the solutions, ϵ_1 and ϵ_2 , for low concentrations of dissolved atoms differ very little from the dielectric constant of the pure solvent which we denote by $\epsilon_3 = \epsilon$. To first order in the concentrations,

$$\epsilon_1 = \epsilon + N_1 \left(\frac{\partial \epsilon_1}{\partial N_1} \right)_{N_1=0}, \quad \epsilon_2 = \epsilon + N_2 \left(\frac{\partial \epsilon_2}{\partial N_2} \right)_{N_2=0}.$$

Keeping only terms of the same order in the formula (4.15) for the force at "small" distances, we obtain [in the same way as for the transition to formula (4.31)]:

$$F(l) = \frac{\hbar}{32\pi^2 l^3} N_1 N_2 \int_0^\infty \left(\frac{\partial \epsilon_1(i\xi)}{\partial N_1} \right)_{N_1=0} \left(\frac{\partial \epsilon_2(i\xi)}{\partial N_2} \right)_{N_2=0} \frac{d\xi}{\epsilon^2(i\xi)}.$$

To this force there corresponds an energy of interaction between the dissolved atoms equal to

$$U(R) = -\frac{3\hbar}{16\pi^3 R^6} \int_0^\infty \left(\frac{\partial \epsilon_1(i\xi)}{\partial N_1} \right)_{N_1=0} \left(\frac{\partial \epsilon_2(i\xi)}{\partial N_2} \right)_{N_2=0} \frac{d\xi}{\epsilon^2(i\xi)}. \quad (4.40)$$

In similar fashion we find for the energy at "large" distances

$$U(R) = -\frac{23\hbar c}{64\pi^3 \epsilon_0^{3/2} R^7} \left(\frac{\partial \epsilon_{10}}{\partial N_1} \right)_{N_1=0} \left(\frac{\partial \epsilon_{20}}{\partial N_2} \right)_{N_2=0}. \quad (4.41)$$

We see that when the molecules of the dissolved material interact strongly with the solvent, the interaction forces between them are no longer determined by their polarizabilities.

Another interesting example is the interaction of small spherical particles in a liquid. Let us assume that the two bodies constitute such an emulsion, formed by spherical particles of volume V , with dielectric constant ϵ' , in a liquid with dielectric constant ϵ . As before, the gap is filled with pure solvent. Under the condition $NV \ll 1$, (where N is the number of particles per unit volume), the dielectric constant of the emulsion has the form

$$\epsilon_1 = \epsilon_2 = \epsilon + 3NV \frac{(\epsilon' - \epsilon)\epsilon}{\epsilon' + 2\epsilon}$$

(cf., for example, reference 11, Sec. 9). Making use of

the smallness of the differences $\epsilon_1 - \epsilon$ and $\epsilon_2 - \epsilon$ in the same way as above, we find for the interaction energy of the particles in the emulsion

$$U(R) = -\frac{27\hbar V^2}{16\pi^3 R^6} \int_0^\infty \left[\frac{\epsilon'(i\xi) - \epsilon(i\xi)}{\epsilon'(i\xi) + 2\epsilon(i\xi)} \right]^2 d\xi, \quad R \ll \lambda_0, \quad (4.42)$$

$$U(R) = -\frac{207V^2}{64\pi^3 R^7} \frac{\hbar c}{\sqrt{\epsilon(0)}} \left[\frac{\epsilon'_0 - \epsilon_0}{\epsilon'_0 + 2\epsilon_0} \right]^2, \quad R \gg \lambda_0, \quad (4.43)$$

respectively at "small" and "large" distances. The dimensions of the particles themselves must be small only compared with the distance between them (but not necessarily compared with λ_0).

5. THIN FILMS ON THE SURFACE OF A SOLID

a) Chemical potential of a film. The general theory of van der Waals' forces developed here can also be applied for calculating thermodynamic quantities for a thin liquid film located on the surface of a solid; the thickness l of the film is, of course, assumed to be large compared with interatomic distances.

Above we have derived formula (3.25) for the chemical potential of a liquid, per unit mass, in terms of the Green's function of the fluctuating electromagnetic field existing in the film. However, this formula is inconvenient for two reasons: first, it contains the quantity $\partial\epsilon/\partial\rho$ for the whole frequency range, and this quantity has not at all been studied experimentally; secondly, it gives the chemical potential ζ as a function of density ρ , whereas we need to know ζ as a function of pressure p .

Let us consider a film 3, located on the surface of the solid body 1 and in equilibrium with its vapor 2 (Fig. 11). With respect to its electromagnetic properties we shall treat the vapor as a vacuum, i.e., we shall set its dielectric constant ϵ_2 equal to unity throughout.

According to the condition for mechanical equilibrium, the normal component σ_{xx} of the stress tensor must be continuous at the surface of the film. From this we find the equation

$$p = p_0(Q, T) - \bar{\sigma}_{xx},$$

where p is the vapor pressure, $p_0(\rho, T)$ is the pressure of the liquid mass at given density and temperature, and $\bar{\sigma}_{xx}$ denotes all the terms in expression (3.24) for the stress tensor in the film, except for the first term. Solving this equation for ρ , we find the density expressed in the form*

$$\rho = \rho_0(p + \bar{\sigma}_{xx}, T).$$

Now substituting this expression in formula (3.25) for the chemical potential, we find

$$\zeta = \zeta_0(p + \bar{\sigma}_{xx}, T) + \frac{T}{4\pi} \sum_{n=0}^{\infty} \frac{\partial \epsilon}{\partial Q} \mathfrak{D}_{ii}^E(\mathbf{r}, \mathbf{r}'; \xi_n),$$

* $\bar{\sigma}_{xx}$ is also a function of ρ , but since σ_{xx} is a small correction to the pressure, we may set $\rho = \rho_0(p, T)$ in it.

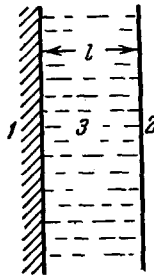


FIG. 11

where now $\zeta_0(p, T)$ is the chemical potential of the bulk liquid. Expanding ζ_0 in powers of the small quantity $\bar{\sigma}_{xx}$ and using the thermodynamic relation $(\partial\zeta/\partial p)_T = 1/\rho$, we bring this expression to the form

$$\zeta(p, T) = \zeta_0(p, T) + \frac{1}{\rho} \bar{\sigma}_{xx} + \frac{T}{4\pi} \sum_{n=0}^{\infty} \frac{\partial \epsilon}{\partial Q} \mathfrak{D}_{ii}^E.$$

Finally, substituting the expression for $\bar{\sigma}_{xx}$ from (3.24), we find that the term with $\partial\epsilon/\partial\rho$ drops out, and we are left with

$$\zeta(p, T) = \zeta_0(p, T) + \frac{1}{\rho} \sigma'_{xx},$$

where σ'_{xx} is the component of the "truncated" stress tensor (4.2). This quantity is constant throughout the thickness of the film (as a result of the constancy of the momentum flux) and the force $F(l)$ is determined by it in accordance with (4.3).

We introduce the notation μ for the "van der Waals' part" of the chemical potential of the film, per unit volume of liquid:

$$\zeta = \zeta_0 + \frac{\mu}{\rho}. \quad (5.1)$$

According to the previous statements,

$$\mu = \sigma'_{xx} = F(l).$$

When l tends to ∞ , i.e., for the bulk liquid, μ tends to zero.

Thus, for the determination of the quantity μ in which we are interested, there is no need to repeat any of the computations. It is determined by the formulas obtained above for $F(l)$ [the general formula (4.13) and the limiting formulas considered in Sec. 4b], in which we need only set $\epsilon_2 = 1$.

The function $\mu(T, l)$ determines all the thermodynamic properties of the film. Thus if the film is in equilibrium with vapor at pressure p , the condition for equality of the chemical potentials of liquid and vapor leads to the well-known equation

$$\mu(l) = \frac{kT_0}{m} \ln \frac{p}{p_{\text{sat}}}, \quad (5.2)$$

where m is the mass of a molecule, and p_{sat} is the saturation vapor pressure above the surface of the bulk liquid at given temperature T . The equilibrium thick-

ness of the film is determined by this equation.*

If we are dealing with a liquid film forming on a vertical wall in a gravity field, then $p = p_{\text{sat}} \exp(-mgz/kT)$ (where z is the height above the level of the liquid in the vessel), and we find from (5.2) the equation

$$\mu(l) + \rho g z = 0, \quad (5.3)$$

which determines the profile of the liquid, i.e., the dependence of its thickness on height.

For "small" thicknesses of the film (in the sense described in Sec. 4), we have the limiting law [cf. (4.18)]

$$\mu = -\frac{\hbar\omega}{8\pi^2 l^3}, \quad \bar{\omega} = \int_0^{\infty} \frac{(\epsilon_3 - 1)(\epsilon_3 - \epsilon_1)}{(\epsilon_3 + 1)(\epsilon_3 + \epsilon_1)} d\xi. \quad (5.4)$$

For "large" thicknesses $\mu(l)$ is proportional to l^{-4} , with a coefficient which is determined [in accordance with (4.20)] by the static dielectric constants of the film (ϵ_{30}) and the solid (ϵ_{10}); here the sign of μ coincides with the sign of the difference $\epsilon_{30} - \epsilon_{10}$.† The function $\mu(l)$ can have a varying sign and be non-monotonic [cf. the analogous remark concerning the force $F(l)$ on page 168]. The breakdown of monotonic behavior of $\mu(l)$ in some region of values of l is related in general with a change in sign of the difference $\epsilon_3(i\xi) - \epsilon_1(i\xi)$ in the wave length region $\lambda \sim l$.

In addition to the potential μ it is convenient to use for describing the properties of the film the "effective surface tension" α on the boundary between the solid and the vapor 2, taking into account the presence of the liquid layer between them. This can be done formally by using the well-known formula of adsorption theory

$$\gamma = -\left(\frac{\partial\alpha}{\partial\xi'}\right)_T,$$

where γ is the surface concentration of adsorbed material (number of particles per square cm), ξ' is its chemical potential per particle (cf., for example, reference 19, Sec. 144). With our definition of μ (here and throughout the following we assume that the liquid is incompressible) this relation is expressed as

$$l = -\left(\frac{\partial\alpha}{\partial\mu}\right)_T,$$

and is applicable both to macroscopically thick ("wetting") films, as well as to adsorbed films of "molecular thickness"; in the latter case, of course,

*In deriving (5.2) we use the formula

$$\zeta_{\text{vap}} = \zeta(p_{\text{sat}}, T) + \frac{kT}{m} \ln \frac{p}{p_{\text{sat}}}$$

for the chemical potential of the vapor, while the liquid is assumed to be incompressible, i.e., we neglect the dependence of the chemical potential of the bulk liquid on pressure.

†So long as no important dispersion in the dielectric constant sets in (as it does, for example, in water) for very large wave lengths.

l has only a conventional meaning of a quantity which is proportional to the surface concentration γ ($l = m\gamma/\rho$, m is the mass of the molecule). Integrating (5.4) and assuming that as $l \rightarrow \infty$ the function $\alpha(l)$ must go over into the sum $\alpha_{13} + \alpha_{32}$ of the surface tensions at the boundaries of the bulk phases 1, 3 and 3, 2, we get

$$\alpha(l) = \int_l^{\infty} l \frac{d\mu}{dl} dl + \alpha_{13} + \alpha_{32}. \quad (5.5)$$

We also note that the necessary condition for thermodynamic stability of the film is the inequality

$$\left(\frac{\partial\mu}{\partial l}\right)_T > 0. \quad (5.6)$$

If Eq. (5.2) is satisfied for several values of l , then the stable state of the film corresponds to that one for which α is a minimum; the larger values then correspond to metastable states.

Let us look at a few typical cases which may occur, depending on the nature of the function $\mu(l)$:

a) If $\mu(l)$ is a monotonically decreasing, everywhere positive function (Fig. 12a), the liquid does not wet the solid surface, and no film is formed at all. We emphasize that we are talking of macroscopically thick films, to which the whole theory developed here applies.

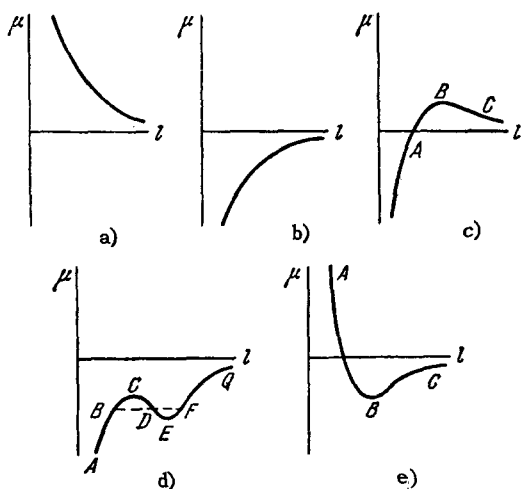


FIG. 12

As for adsorption in the narrow sense of the word, we know it always occurs to a greater or lesser extent. To this there corresponds the fact that, no matter what the behavior of the function $\mu(l)$, in the region of molecular dimensions (not shown in Fig. 12) it finally tends (for $l \rightarrow 0$) to $-\infty$ according to the law $\mu \sim \ln l$, corresponding to "a weak solution" of the adsorbed material on the surface.

b) If $\mu(l)$ is a monotonically increasing, everywhere negative, function (Fig. 12b), then this usually corresponds to a liquid which completely wets the surface of the solid and (depending on the vapor pressure over it) forms a stable film of arbitrary thickness. In

particular, on a vertical wall there is formed a film with a thickness which tends toward zero for $z \rightarrow \infty$; the decrease first occurs according to the law $l \sim z^{-1/4}$ and then as $z^{-1/3}$.

However, in this case also the liquid may not wet if the behavior of $\mu(l)$ in the microscopic region is such that it leads to smaller values of the surface tension α ; then the molecular absorption film, and not the wetting film, will be stable.*

c) $\mu(l)$ goes through zero and has a maximum as shown in Fig. 12c. With the same comments as in case b), we here have a case of wetting, but with formation of a film which is stable only for thicknesses less than some definite limit. In equilibrium with the saturated vapor there is a film of finite thickness corresponding to point a. This state is separated from the other stable state — the equilibrium of the solid wall with the bulk liquid — by the metastable region AB and the region of complete instability BC.

The curve $\mu(l)$ of this type must lead to interesting peculiarities in the formation of the angle of contact θ of a liquid drop on a solid surface. In this case the drop is in equilibrium with a film of finite thickness l_{\max} (Fig. 13), and according to the usual elementary formula we have:

$$\cos \theta = \frac{\alpha(l_{\max}) - \alpha_{13}}{\alpha_{23}}, \quad (5.7)$$

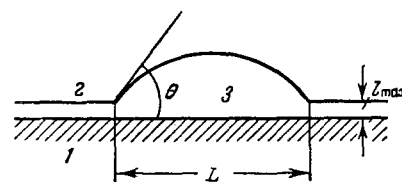


FIG. 13

where $\alpha(l_{\max})$ with $\alpha(l)$ from (5.5) plays the role of the surface tension between phases 1 and 2. Since the term in (5.5) is a small quantity, we obtain from (5.7)

$$\theta^2 \cong -\frac{2}{\alpha_{23}} \int_{l_{\max}}^{\infty} l \frac{d\mu}{dl} dl = \frac{2}{\alpha_{23}} \int_{l_{\max}}^{\infty} \mu dl. \quad (5.8)$$

Interpolating between the laws $\mu \sim l^{-3}$ and $\mu \sim l^{-4}$, we then obtain the estimate

$$\theta \sim \frac{1}{10l_{\max}} \sqrt{\frac{\hbar\bar{\omega}}{\alpha_{23}}} \quad (5.9)$$

with $\bar{\omega}$ from (5.4). Thus for $\hbar\bar{\omega} \sim 10$ ev, $\alpha_{23} \sim 20$ erg/cm², $l_{\max} \sim 5 \times 10^{-5}$ cm, we then obtain $\theta \sim 0.1^\circ$.

Thus in this case the angle of contact should have a finite, but very small value (different from the value $\theta = 0$ when there is complete wetting, and $\theta \sim 1$ for the usual cases when there is no wetting). Of course, such an assertion has a truly observable meaning only

*Such a behavior can be regarded as a big "bump" on the curve $\mu(l)$ in the molecular region of "thicknesses."

on the condition that the thickness of the drop be large compared with the thickness of the film, i.e., we must have $L\theta \gg l_{\max}$, where L is the diameter of the drop (Fig. 13).

d) The curve shown in Fig. 12d corresponds to a film which is unstable over a definite range of thicknesses. The straight line BF, which cuts off equal areas BCD and DEF, joins points B and F with the same values of α (for the same values of μ), as is easily seen from (5.5). The branches AB and FQ correspond to a stable film; the interval CE is completely unstable, while the intervals BC and EF are metastable.

Both boundaries of the instability region (points B and F) in this case correspond to macroscopic thicknesses of the film. The instability in the interval from some macroscopic thickness to molecular dimensions should correspond to the curve shown in Fig. 12e (for $l \rightarrow \infty$ this curve, like the curve of Fig. 12a, tends toward $-\infty$). Actually, however, such a curve will most likely simply lead to the case where there is no wetting. In fact, the boundary of stability would correspond to such a point on the branch BC at which the horizontal line would cut off equal areas below the upper and above the lower parts of the curve. But the latter area, which is associated with van der Waals' forces, will be small compared to the first which is associated with the much greater forces at molecular distances. This means that the surface tension over the whole branch BC will be greater than that which corresponds to molecular absorption on the surface of the solid, and thus the film will be metastable.

b) Forces of nonelectromagnetic origin. As already mentioned at the beginning of Sec. 4b, in addition to the van der Waals' forces there is a definite contribution to the chemical potential of a film from sources of nonelectromagnetic origin; this contribution, however, is usually small. We here present the appropriate estimates without going into detail on particular calculations.

Acoustic fluctuations (in media which are acoustically nondispersive) at the absolute zero of temperature give a contribution to the chemical potential of

$$\mu_{ac} \sim \hbar u / l^4,$$

where u is the velocity of sound.* It should be comparable with the electromagnetic part $\mu_{e.m.} \sim \hbar c / l^4$ for $l \gg \lambda_0$ or $\mu_{e.m.} \sim \hbar c / l^3 \lambda_0$ for $l \ll \lambda_0$. It is clear that $\mu_{ac} \ll \mu_{e.m.}$ at all distances which are large compared to atomic dimensions, which is the only case when the entire theory presented here is applicable.

*This expression is analogous to the expression $\mu \sim \hbar c / l^4$ for the electromagnetic part (in a nondispersive medium). It can be obtained, for example, by computing the energy of the zero point acoustical vibrations in the gap (of width l) in the same way as was done by Casimir²⁰ for the electromagnetic zero point vibrations. We note that the result of Atkins,²¹ who obtained for μ_{ac} a different dependence on film thickness ($\sim l^{-2}$), is related to an incorrect procedure for cutting off the divergent integral.

At temperatures other than absolute zero, there occurs in general for μ_{ac} the opposite limiting case, where the influence of temperature is predominant. The appropriate criterion is the value of the ratio $\hbar kT / \hbar u$. The condition $\hbar kT / \hbar u \gg 1$ (like the condition $\hbar kT / \hbar c \gg 1$ for the electromagnetic case) is essentially a condition for classical behavior ($\hbar \omega \ll kT$ with $\omega \sim l/u$ or $\omega \sim l/c$). Therefore it is clear beforehand that the corresponding contribution to μ should not contain \hbar , and then, simply from dimensionality considerations, it is obvious that

$$\mu_{ac} \sim \frac{kT}{j^3}$$

[cf. formula (4.29)]. This quantity is comparable with $\mu_{e.m.}$ only at distances $l \sim \hbar c / kT$, which are so large that μ is already very small.

The same applies to the contribution of surface vibrations. The dependence of frequency on wave vector κ for capillary oscillations on the surface layer of a liquid of depth l is given by the well-known formula*

$$\omega^2 = \frac{\alpha \kappa^3}{\rho} \operatorname{th} \kappa l,$$

where α is the surface tension (cf., for example, Landau and Lifshitz,²² Sec. 61); in a deep liquid ($l \rightarrow \infty$), $\omega^2 = \alpha \kappa^3 / \rho$. Computing the energy of zero point vibrations (and subtracting the same energy for $l \rightarrow \infty$), we find that at absolute zero the corresponding contribution to the chemical potential is

$$\mu_{\text{surf}} \sim \frac{\hbar}{j^{3/2}} \sqrt{\frac{\alpha}{\rho}}.$$

Actually, however, there exists an opposite limiting case when $(\hbar/kT) \sqrt{\alpha/\rho} l^{-3/2} \ll 1$, i.e., when the condition for classical behavior is satisfied; the calculation according to general rules of statistics leads to the natural result that the contribution $\mu_{\text{surf}} \sim kT/l^3$ is of the same order as in the acoustic case.†

To understand the properties of helium films, various authors have also invoked mechanisms associated with inhomogeneity of the distribution of the liquid density throughout the film thickness. In its crudest form the corresponding calculation is carried out by treating the helium in the film as an ideal gas, the wave functions of whose particles have nodes at the wall and the surface of the film. Such a model leads to a markedly inhomogeneous distribution of density, with a maximum at the center and a contribution to the chemical potential μ which is proportional to l^{-2} . However, such a treatment is completely inapplicable (as already pointed out by Mott²³), since the interaction between atoms actually smooths out the wave func-

* $\operatorname{th} = \tanh$.

†Throughout we give only algebraic estimates, but it should be remembered that actually the expressions μ_{surf} and μ_{ac} still contain (as more detailed analysis shows) small numerical coefficients, just as do the expressions for the electromagnetic part $\mu_{e.m.}$. The occurrence of comparatively small numerical coefficients is a characteristic of the theory presented here.

tion of the ground state of the system, and the inhomogeneity in the density is pushed (at the bottom of the liquid) only to a distance of the order of interatomic distances. The contribution to the chemical potential associated with this inhomogeneity falls off exponentially with film thickness.

The contribution associated with the specific properties (superfluidity) of helium below the λ point also falls off according to this same law. Only in the immediate vicinity of the λ point, where the density of the superfluid component is very small, does the inhomogeneity of the distribution of the latter lead to a significant effect (cf. Ginzburg and Pitaevskii²⁴). But already at a distance of the order of 0.01° from the λ point the decrement of the exponential becomes comparable with interatomic distances. The result of Franchetti,²⁵ who found the contribution to the chemical potential to be proportional to l^{-2} , is associated with the inadequacy of the model of noninteracting elementary excitations in helium which he used.

c) Film of liquid helium. Let us consider in particular films of liquid helium, to which an extensive literature has been devoted.

For helium films the general formula (4.14) can be simplified considerably if we use the fact that the dielectric constant of liquid helium is very close to unity, i.e., the difference $\epsilon_3(i\xi) - 1$ is small. Carrying out the appropriate expansions in the integrand of (4.14) we obtain:

$$\mu(l) = -\frac{\hbar}{8\pi^2 c^3} \int_0^\infty \int_1^\infty \left\{ \frac{s_1 - p}{s_1 + p} + (2p^2 - 1) \frac{p\epsilon_1 - s_1}{p\epsilon_1 + s_1} \right\} \times (\epsilon_3 - 1) \xi^3 e^{-2p\xi l/c} dp d\xi. \quad (5.10)$$

However, the calculation even with this simplified formula is difficult because one must know the form of the functions $\epsilon(i\xi)$ for liquid helium and for the solid wall over a wide range of frequencies, and in particular in the far ultraviolet region: in the integral (5.10) the important region of wave lengths is $\lambda \sim l$, while the actual thickness of the helium layer is of the order of 10^{-6} cm.

It is reasonable to make a further simplification of formula (5.10) by making use of the fact that the main absorption region of helium is in the far ultraviolet, whereas the main absorption of the solid wall (metals or quartz) is at much lower frequencies. In other words, we shall assume that the function $\epsilon(i\xi)$ practically coincides with the static value ϵ_{30} over the whole range of variation of ξ in which the difference $\epsilon_1(i\xi) - 1$ [and with it the whole integrand in (5.10)] is still not too small. Then $\epsilon_3 - 1$ can be taken out from under the integral sign and we can proceed with the remaining integral in the same way as in the limiting case of small thicknesses l (l small compared with wave lengths λ_0 in the main absorption region for the solid). In other words, by introducing in place of p the integration variable $x = 2p\xi l/c$ and noting

that to values $x \sim 1$ there correspond large values of p , we replace the curly bracket in (5.10) by $2p^2(\epsilon_1 - 1)/(\epsilon_1 + 1)$ and obtain as a result:

$$\mu(l) = -\frac{\hbar \bar{\omega} (\epsilon_{30} - 1)}{16\pi^2 l^3}, \quad (5.11)$$

where we have introduced the quantity

$$\bar{\omega} = \int_0^\infty \frac{\epsilon_1(i\xi) - 1}{\epsilon_1(i\xi) + 1} d\xi, \quad (5.12)$$

which is some average frequency characteristic for the particular solid.

We note that the function $[\epsilon(\omega) - 1]/[\epsilon(\omega) + 1]$ has the same analytic properties in the upper half plane of the complex variable ω as the function $\epsilon(\omega) - 1$. This is enough to enable us to apply to it the same formula for transformation of an integral along the imaginary axis into an integral along the real axis which is valid for the function $\epsilon(\omega) - 1$ (cf. reference 11, Sec. 62). Namely, we can represent the integral in the form

$$\bar{\omega} = \int_0^\infty \text{Im} \frac{\epsilon_1(\omega) - 1}{\epsilon_1(\omega) + 1} d\omega = \int_0^\infty \frac{2\epsilon_1''(\omega) d\omega}{(\epsilon_1'(\omega) + 1)^2 + (\epsilon_1''(\omega))^2}, \quad (5.13)$$

where $\epsilon'(\omega)$ and $\epsilon''(\omega)$ are the real and imaginary parts of the dielectric constant for real values of the frequency, i.e., these are quantities directly measurable in experiment.

Thus, for the actually observed thicknesses of helium films we should expect the dependence $\mu \sim l^{-3}$ and the corresponding film shape $l \sim z^{-1/3}$. Calculation of the coefficient in this formula requires, however, a knowledge of the optical properties of the solid body (the wall) over a broad range of frequencies. We must emphasize that the computation of this coefficient on the basis of data concerning interaction of individual atoms of the solid with helium is not admissible.

We also give an expression for μ for "large" film thicknesses ($l \gg \lambda_0$). The corresponding transition in (5.10) is carried out by introducing the variable $x = 2p\xi l/c$ in place of ξ and replacing ϵ_1 by ϵ_{10} . The integration over both x and p is carried out analytically, and as a result we find

$$\mu(l) = -\frac{3\hbar c (\epsilon_{30} - 1)}{32\pi^2 l^4} \frac{\epsilon_{10} - 1}{\epsilon_{10} + 1} \varphi_{AD}(\epsilon_{10}) \quad (5.14)$$

with the function φ_{AD} of (4.38). For a metal $\varphi_{AD} = 1$ ($\epsilon_{10} = \infty$). For quartz, which has a broad region of transparency (from $\sim 0.15\mu$ to several microns), it is also meaningful to consider the case where the thickness l lies in this region of sizes. The corresponding law for $\mu(l)$ is then determined from the same formula (5.14), in which however we should understand by ϵ_{10} not the static, but the optical value ϵ_1 , i.e., the square of the index of refraction in the optical region of transparency (cf. the footnote on page 169).

Expressions (5.10), (5.11), and (5.14) do not contain the temperature, i.e., they refer, strictly speaking, to

absolute zero. However, temperature corrections should be relatively small, and there is no reason to expect any essential change in the profile of the film when the temperature is changed, in particular below and above the λ -point (except in the immediate vicinity of the λ -point).

The difficulties in an experimental determination of thickness and profile shape of a helium film under conditions sufficiently close to the ideal case of thermal equilibrium are very great, and apparently only very recently have these been overcome to the extent that the results obtained in the helium II region can be considered in any way trustworthy (see the summaries of Jackson and Grimes²⁶ and Atkins²⁷).

In accordance with our remarks in Sec. 5 there is no physical reason to expect the profile of the film to have the form $\rho gz = al^{-3} + bl^{-2}$.

Anderson, Liebenberg, and Dillinger²⁸ point out that their results on the thickness of a helium film on a steel surface (up to heights of 40 cm) are well described by the law $\rho gz = al^{-3}$ (the absolute values of the thicknesses are not given). This same law describes the results of the measurements of Hamm and Jackson²⁹ and Grimes and Jackson³⁰ (in the interval of heights from 0.4 to 7 cm) with a coefficient $a \approx 4.5 \times 10^{-15}$ erg. Comparing this value with the coefficient of l^{-3} in formula (5.11) (setting $\epsilon_{30} - 1 = 0.057$) we obtain $\hbar\bar{\omega} \approx 7.5$ ev. This value is reasonable for a metal (steel).

The coefficients in formulas (5.11) and (5.14) (for $\epsilon_{10} \rightarrow \infty$) are comparable for $l \sim 3c/2\bar{\omega}$, i.e., in the present case for $l \sim 5 \times 10^{-6}$ cm. This means that in the interval of film thicknesses (100–400 Å) observed in experiment we are near a region which represents the transition between the l^{-3} and l^{-4} laws.

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