The Theory of Molecular Attractive Forces between Solids

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A macroscopic theory is developed for the interaction of bodies whose surfaces are brought within a small distance of one another. The interaction is considered to come about through the medium of the fluctuating electromagnetic field. The limiting cases of separations small and large compared with the wavelengths of the absorption bands of the solid are studied. Upon going to the limiting case of rarefied media, the van der Waals forces of interaction between individual atoms are obtained. The effect of temperature on the interaction of the bodies is considered.

IT is well-known that the forces of interaction between neutral atoms, located at a distance R from one another which is large compared to their internal dimensions, leads to an attraction inversely proportional to R^7. These so-called van der Waals forces are obtained in the second approximation of perturbation theory, applied to the electrostatic interaction of two dipoles. Such a treatment is however valid only so long as the separation R is small compared to the wavelengths λ corresponding to transitions between the ground and excited states of the atom. For $R \gtrsim \lambda$, retardation effects become important. The interaction of atoms when these effects are taken into account was studied by Casimir and Polder [1]. Here the perturbation operator is the sum of the electrostatic interaction of the atoms and their interactions with the radiation field. The latter can, in the usual fashion, be regarded as the result of emission and absorption of virtual quanta. With respect to this interaction, the perturbation theory must be applied up to fourth order terms, and the calculations become rather unwieldy. In the limitting case of $R \gg \lambda$, the attractive force turns out to be proportional to R^{-8} rather than to R^{-7}.

The presence of attractive forces between neutral atoms naturally results in the presence of similar forces between two macroscopic bodies whose surfaces are brought to within a small distance of one another. However, the calculation of these forces, starting from the known interaction of the individual atoms, would be possible only for sufficiently rarefied bodies, i. e., for gases – a case which of course cannot be realized practically. We can however approach this problem in purely macroscopic fashion (since the distance between the bodies is assumed to be large compared to interatomic distances). From this point of view, the interaction of the objects is regarded as occurring through the medium of the fluctuating electromagnetic field which is always present in the interior of any absorbing medium, and also extends beyond its boundaries, – partially in the form of travelling waves radiated by the body, partially in the form of standing waves which are damped exponentially as we move away from the surface of the body. It must be emphasized that this field does not vanish even at absolute zero, at which point it is associated with the zero point vibrations of the radiation field.

The method for calculating interaction forces which is based on these considerations has full generality, and is applicable to any body at any temperature. It also automatically takes into account retardation effects, which become important for sufficiently large separations between the bodies. In the limiting case of rarefied media, the method must of course lead to the same results as are obtained by considering the interactions of individual atoms.

1. CALCULATION OF THE FLUCTUATING ELECTROMAGNETIC FIELD

We picture the interacting bodies as two media filling half spaces with plane-parallel boundaries separated from one another by a distance l (Fig. 1).

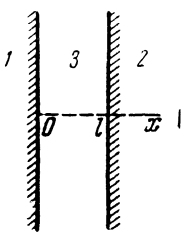

FIG. 1

To calculate the fluctuating field in the interior of the two media, we shall use the general theory which is due to Rytov and is described in detail in his book[2].

This method is based on the introduction into the Maxwell equations of a "random" field (just as, for example, one introduces a "random" force in the theory of Brownian motion).

[1] H. B. G. Casimir and D. Polder, Phys. Rev. **73**, 360 (1948)

[2] S. M. Rytov, *Theory of Electrical Fluctuations and Thermal Radiation*, Publishing House, Academy of Sciences, USSR, 1953

In a dielectric, nonmagnetic medium, these equations are, for a monochromatic field (time factor $e^{-i\omega t}$)*

$$\operatorname{curl} \mathbf{E} = i\frac{\omega}{c}\mathbf{H}, \qquad (1.1)$$

$$\operatorname{curl} \mathbf{H} = -i\frac{\omega}{c}\varepsilon \mathbf{E} - i\frac{\omega}{c}\mathbf{K},$$

where $\epsilon = \epsilon(\omega)$ is the complex dielectric constant, and $\mathbf{K}$ is the random field. The fundamental characteristic of the latter is the correlation function, determining the average value of the product of components of $\mathbf{K}$ at two different points in space. By the very nature of the introduction of a random field in a macroscopic fluctuation theory, in which atomic distances are considered to be negligibly small, this correlation has the character of a δ-function. According to Rytov, it is given by the formula

$$K_i(x, y, z)\, K_k(x', y', z') \qquad (1.2)$$

$$= A\varepsilon''(\omega)\,\delta_{ik}\delta(x - x')\,\delta(y - y')\,\delta(z - z'),$$

$$A = 4\hbar\left(\frac{1}{2} + \frac{1}{e^{\hbar\omega/T} - 1}\right) = 2\hbar \coth\frac{\hbar\omega}{2T},$$

where T is the temperature and ϵ'' is the imaginary part of $\epsilon = \epsilon' + i\epsilon''$ (for the quasistationary range of frequencies, an analogous formula was obtained by Leontovich and Rytov[4]).

We represent the function $\mathbf{K}(x, y, z)$ in the form of a Fourier integral, which we write for the half space $x < 0$ in the form:

$$\mathbf{K}(x, y, z) = \int_{-\infty}^{+\infty} \mathbf{g}(\mathbf{k})\, e^{i\mathbf{q}\cdot\mathbf{r}} \cos k_x x\, d\mathbf{k}. \qquad (1.3)$$

Here and in the sequel we denote by $\mathbf{q}$ a two-dimensional vector with components k_y, k_z (so that $k^2 = k_x^2 + q^2$), and by $\mathbf{r}$, the radius vector in the y-z plane. For the Fourier components $\mathbf{g}(\mathbf{k})$, the correlation function corresponding to the spatial correlation (1.2) is (cf. reference 2, No. 4):

$$\overline{g_i(\mathbf{k})\, g_k(\mathbf{k}')} = \frac{A\varepsilon''}{4\pi^3}\delta_{ik}\delta(\mathbf{k} - \mathbf{k}'). \qquad (1.4)$$

We now proceed to the solution of Eq. (1.1) with the appropriate boundary conditions on the surfaces of the two bodies. In medium 1 ($x < 0$), we look for fields $\mathbf{E}$ and $\mathbf{H}$ of the form:

$$\mathbf{E}_1 = \int_{-\infty}^{+\infty} \{\mathbf{a}_1(\mathbf{k}) \cos k_x x + i\mathbf{b}_1(\mathbf{k}) \sin k_x x\}\, e^{i\mathbf{q}\cdot\mathbf{r}}\, d\mathbf{k}$$

$$+ \int_{-\infty}^{+\infty} \mathbf{u}_1(\mathbf{q})\, e^{i\mathbf{q}\cdot\mathbf{r} - is_1 x}\, d\mathbf{q},$$

$$\mathbf{H}_1 = \frac{c}{\omega}\int_{-\infty}^{+\infty} \{([\mathbf{q}\mathbf{a}_1] + k_x[\mathbf{n}\mathbf{b}_1]) \cos k_x x \qquad (1.5)$$

$$+ i([\mathbf{q}\mathbf{b}_1] + k_x[\mathbf{n}\mathbf{a}_1]) \sin k_x x\}\, e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{k}$$

$$+ \frac{c}{\omega}\int_{-\infty}^{+\infty} \{[\mathbf{q}\mathbf{u}_1] - s_1[\mathbf{n}\mathbf{u}_1]\}\, e^{i\mathbf{q}\cdot\mathbf{r} - is_1 x}\, d\mathbf{q},$$

where $\mathbf{n}$ is a unit vector in the direction of the x axis, and

$$s_1 = \sqrt{\frac{\omega^2}{c^2}\varepsilon_1 - q^2}, \qquad (1.6)$$

where the sign of the root is to be chosen so that the imaginary part of s will be positive**. We have here made use of the first of Eqs. (1.1).

The first terms in these expressions represent a solution of the inhomogeneous Eqs. (1.1). Substituting them in the second equation of (1.1) and writing $\mathbf{K}$ in the form (1.3), we find the following relations, expressing $\mathbf{a}_1$ and $\mathbf{b}_1$ in terms of the Fourier components $\mathbf{g}_1$ of the random field:

$$\mathbf{a}_1 = \frac{1}{\varepsilon_1(k^2 - \omega^2\varepsilon_1/c^2)}\left[\frac{\omega^2}{c^2}\varepsilon_1\mathbf{g}_1\right.$$

$$\left. - \mathbf{q}(\mathbf{q}\cdot\mathbf{g}_{1r}) - k_x^2 g_{1x}\mathbf{n}\right], \qquad (1.7)$$

$$\mathbf{b}_1 = -\frac{k_x}{\varepsilon_1(k^2 - \omega^2\varepsilon_1/c^2)}[\mathbf{n}(\mathbf{q}\cdot\mathbf{g}_{1r}) + \mathbf{q}g_{1x}].$$

Two-dimensional vectors in the y-z plane are indicated by the subscript r from now on.

The second integrals in (1.6) represent the solution of the homogeneous equations (1.1) (i.e., the equations with $\mathbf{K}$ omitted), and describe the plane wave field reflected from the boundary of the medium. The condition for transversality of these waves is:

$$\mathbf{u}_{1r}\cdot\mathbf{q} - s_1 u_{1x} = 0. \qquad (1.8)$$

In the second medium (the half space $x > l$), the field $\mathbf{E}_2$, $\mathbf{H}_2$ is given by the same formulas (1.5), (1.7), (1.8), with the index 1 changed to 2,

* The question of the meaning of monochromatic components for quantities which are not expandable in the usual sense in a Fourier integral, (as is the case for the fluctuation field) is discussed in reference 2, No. 2, and reference 3, No. 117.

[3] L. D. Landau and E. Lifshitz, Statistical Physics, 3rd Edition, Gostekhizdat, 1951.

[4] M. A. Leontovich and S. M. Rytov, J. Exper. Theoret. Phys. USSR, **23**, 246 (1952)

** Since the imaginary part of the expression under the square root sign ($\omega^2\epsilon''/c^2$) is positive, when $\operatorname{Im} s > 0$ we also have $\operatorname{Re} s > 0$).

cos $k_x x$, sin $k_x x$ replaced by cos $k_x(x-l)$, sin $k_x(x-l)$ and change in the sign of s (the "reflected" waves now propagate along the positive x direction). Finally, in the space between the media (vacuum), we have $\epsilon = 1$, $\mathbf{K} = 0$, and the field is given by the general solution of the homogeneous equations, which we write in the form:

$$\mathbf{E}_3 = \int_{-\infty}^{+\infty} \{\mathbf{v}(\mathbf{q})\, e^{ipx} + \mathbf{w}(\mathbf{q})\, e^{-ipx}\}\, e^{i\mathbf{q}\cdot\mathbf{r}} d\,\mathbf{q}, \quad (1.9)$$

$$\mathbf{H}_3 = \frac{c}{\omega} \int_{-\infty}^{+\infty} \{[\mathbf{qv}] + p\,[\mathbf{nv}])\, e^{ipx}$$

$$+ ([\mathbf{qw}] - p\,[\mathbf{nw}])\, e^{-ipx}\}\, e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{q},$$

where

$$p = \sqrt{\frac{\omega^2}{c^2} - q^2}, \quad (1.10)$$

and $\mathbf{v}$ and $\mathbf{w}$ satisfy the transversality conditions

$$\mathbf{v}_r \cdot \mathbf{q} + p v_x = 0, \quad \mathbf{w}_r \cdot \mathbf{q} - p w_x = 0. \quad (1.11)$$

The boundary conditions on the surfaces of the media are the requirement of continuity of the tangential components of $\mathbf{E}$ and $\mathbf{H}$. On the plane $x = 0$, this gives the following equations:

$$\int_{-\infty}^{+\infty} \mathbf{a}_{1r}\, dk_x + \mathbf{u}_{1r} = \mathbf{v}_r + \mathbf{w}_r, \quad (1.12)$$

$$\int_{-\infty}^{+\infty} (\mathbf{q}\, a_{1x} - k_x \mathbf{b}_{1r})\, dk_x + \mathbf{q}\, u_{1x} + s_1 \mathbf{u}_{1r}$$

$$= \mathbf{q}(v_x + w_x) - p(\mathbf{v}_r - \mathbf{w}_r).$$

The conditions at the plane $x = l$ differ in having s_1, $\mathbf{a}_1$, $\mathbf{b}_1$, $\mathbf{v}$, $\mathbf{w}$ replaced by s_2, $\mathbf{a}_2$, $\mathbf{b}_2$, $\mathbf{v}\, e^{ipl}$, $\mathbf{w} e^{-ipl}$, respectively.

The collection of boundary conditions and continuity equations determines all the field amplitudes. In what follows, we shall need only the field between the two media. For a given value of $\mathbf{q}$, we resolve $\mathbf{v}_r$ and $\mathbf{w}_r$ along the mutually perpendicular vectors $\mathbf{q}$ and $\mathbf{nq}$, which we choose as y and z axes, respectively. The calculation leads to the following formulas for the components of $\mathbf{v}$ and $\mathbf{w}$, expressed in terms of the amplitudes $\mathbf{g}$ of the random field:

$$v_y = \int_{-\infty}^{+\infty} \frac{p}{\Delta} \left\{ s_1 e^{-ipl} (\varepsilon_2 p + s_2) \frac{q g_{1x} - s_1 g_{1y}}{k_x^2 - s_1^2} \right. \quad (1.13)$$

$$\left. + s_2 (\varepsilon_1 p - s_1) \frac{q g_{2x} + s_2 g_{2y}}{k_x^2 - s_2^2} \right\} dk_x,$$

$$w_y = \int_{-\infty}^{+\infty} \frac{p}{\Delta} \left\{ -s_1 e^{ipl} (\varepsilon_2 p - s_2) \frac{q g_{1x} - s_1 g_{1y}}{k_x^2 - s_1^2} \right.$$

$$\left. - s_2 (\varepsilon_1 p + s_1) \frac{q g_{2x} + s_2 g_{2y}}{k_x^2 - s_2^2} \right\} dk_x,$$

$$v_z = \int_{-\infty}^{+\infty} \frac{\omega^2}{c^2 \Delta'} \left\{ -s_1 e^{-ipl} (s_2 + p) \frac{g_{1z}}{k_x^2 - s_1^2} \right.$$

$$\left. + s_2 (s_1 - p) \frac{g_{2z}}{k_x^2 - s_2^2} \right\} dk_x,$$

$$w_z = \int_{-\infty}^{+\infty} \frac{\omega^2}{c^2 \Delta'} \left\{ s_1 e^{-ipl} (s_2 - p) \frac{g_{1z}}{k_x^2 - s_1^2} \right.$$

$$\left. - s_2 (s_1 + p) \frac{g_{2z}}{k_x^2 - s_2^2} \right\} dk_x,$$

$$v_x = -\frac{q v_y}{p}, \qquad w_x = \frac{q w_y}{p},$$

where we have introduced the notation:

$$\Delta = e^{ipl} (s_1 - \varepsilon_1 p)(s_2 - \varepsilon_2 p)$$

$$- e^{-ipl} (s_1 + \varepsilon_1 p)(s_2 + \varepsilon_2 p),$$

$$\Delta' = e^{ipl} (s_1 - p)(s_2 - p)$$

$$- e^{-ipl} (s_1 + p)(s_2 + p).$$

The quantity q runs through values from zero to infinity, while p runs through real values from ω/c to zero, and pure imaginary values from zero to $i\infty$. The first correspond to undamped plane waves in the space between the two media, while the second refer to exponentially damped (so-called "inhomogeneous") plane waves.

2. CALCULATION OF THE FORCE OF ATTRACTION

We shall calculate the force F of mutual attraction, acting on unit surface of each of the bodies, as the xx-component of the Maxwell stress tensor. The tensor calculated from the expressions obtained above for monochromatic field components must still be integrated over all frequencies. For the definition of the time factor which has been used, in particular in formula (1.2), the integration over $d\omega$ must be extended between the limits $-\infty$ and $+\infty$. We shall integrate only over positive values of ω and so shall define the stress tensor as twice its

usual expression. Thus

$$F=\int_0^\infty F_\omega\,d\omega=\frac{1}{4\pi}\int_0^\infty\{\overline{\mathbf{E}_{3r}^2}+\overline{\mathbf{H}_{3r}^2} \tag{2.1}$$
$$-\overline{E_{3x}^2}-\overline{H_{3x}^2}\}_{v=0}\,d\omega.$$

The dash over a symbol signifies a statistical averaging, to which the Fourier components $\mathbf{g}$ of the random field must be subjected. The averaging of components $\mathbf{g}$ referring to the same medium is carried out with the aid of Eq. (1.4) (with appropriate value of ϵ''). Quantities $\mathbf{g}_1$ and $\mathbf{g}_2$, referring to different media, are statistically independent, so the average of their products gives zero.

Writing the squares of the integrals (1.9) in the usual way as double integrals, and carrying out one integration over the δ - functions, we obtain after some transformations

$$F_\omega=\frac{1}{4\pi}\int_{-\infty}^{+\infty}\int_0^\infty\Big\{|v_y+w_y|^2+\frac{p^*}{p}|v_y-w_y|^2 \tag{2.2}$$
$$+\frac{c^2p^2}{\omega^2}|v_z+w_z|^2$$
$$+\frac{c^2|p|^2}{\omega^2}|v_z-w_z|^2\Big\}2\pi q\,dq\,dk_x,$$

where one must substitute in place of $\mathbf{v}$, $\mathbf{w}$, the expressions in the integrands of Eq. (1.13), and the average product $\overline{g_ig_k}$ is to be taken simply as $(A\epsilon''/4\pi^3)\,\delta_{ik}$. The integration over dk_x is carried out with the help of the formula

$$\int_{-\infty}^{+\infty}\frac{dk_x}{|k_x^2-s^2|^2}=\frac{i\pi}{|s|^2(s-s^*)}.$$

We replace the integration over dq by integration over dp, setting $q\,dq=p\,dp$.

After a sequence of transformations, we can represent F_ω in the following form:

$$F_\omega=\frac{\hbar}{4\pi^2}\operatorname{cth}\frac{\hbar\omega}{2T}$$
$$\times\int p^2\,dp\Big\{\Big[\frac{(s_1+p)(s_2+p)}{(s_1-p)(s_2-p)}e^{-2ipl}-1\Big]^{-1} \tag{2.3}$$
$$+\frac{1}{2}\Big[\frac{(s_1+\varepsilon_1p)(s_2+\varepsilon_2p)}{(s_1-\varepsilon_1p)(s_2-\varepsilon_2p)}e^{-2ipl}-1\Big]^{-1}$$
$$+\frac{1}{2}\Big\}+\text{c.c.}$$

where c.c. denotes the complex conjugate expression, and the integration with respect to p is to be carried out in the plane of the complex variable p, over the segment $(\omega/c,\ 0)$ of the real axis and over the whole upper half of the imaginary axis.

It is an essential point that it turns out to be possible to represent F_ω as the real part of an integral of an analytic function of p, despite the fact that the expression (2.2) was obtained by taking square moduli of the field components. This can be done, if we note that on our integration path p is either pure real or pure imaginary. The integrand in Eq. (2.3) coincides with the integrand in Eq. (2.2), (after carrying out the k_x integration in the latter, and replacing $q\,dq$ by $p\,dp$), for just such values of p. But, having verified this, we can from now on regard this expression as an analytic function over the whole plane of the complex variable p, which enables us to make various transformations of the path of integration.

The expression (2.3) is itself finite, but contains terms which diverge upon integration over ω. These are the terms with ω^3, which appear as a result of the p integration of the terms with ½ in the curly brackets. However, this divergent term does not depend on the separation l of the bodies, and therefore has no connection with the problem of interest to us of the force of mutual attraction, and should be dropped. It represents the back reaction of the field produced by the body on the body itself, and is in fact compensated by similar forces on the other sides of the body.

For the following investigation of the integral (2.3), we change the notation, replacing p by $\omega p/c$ and s by $\omega s/c$. Also omitting the terms with ½, we have, finally,

$$F=\frac{\hbar}{2\pi^2c^3} \tag{2.4}$$
$$\times\operatorname{Re}\int_0^\infty\int p^2\omega^3\operatorname{cth}\frac{\hbar\omega}{2T}\Big\{\Big[\frac{(s_1+p)(s_2+p)}{(s_1-p)(s_2-p)}e^{-2ip\omega l/c}-1\Big]^{-1}$$
$$+\Big[\frac{(s_1+\varepsilon_1p)(s_2+\varepsilon_2p)}{(s_1-\varepsilon_1p)(s_2-\varepsilon_2p)}e^{-2ip\omega l/c}-1\Big]^{-1}\Big\}dp\,d\omega,$$
$$s_1=\sqrt{\varepsilon_1(\omega)-1+p^2},$$
$$s_2=\sqrt{\varepsilon_2(\omega)-1+p^2}.$$

The paths of integration for p and ω are shown in Fig. 2a by the thick lines.

If we may consider the temperature of the bodies to be equal to zero (the necessary conditions for this will be explained later) then $\coth\frac{\hbar\omega}{2T}$ in Eq. (2.4) is replaced by unity. We shall first consider formula (2.4) for just this case.

Formula (2.4) is inconvenient because it is in complex form, and because the integrand contains the expression $e^{-2i\omega pl/c}$, which oscillates along

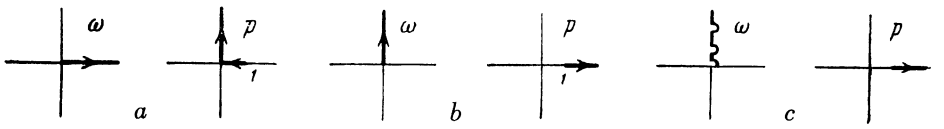

FIG. 2

the real part of the path of integration over p. The last fact makes the integration particularly difficult for large values of l, when the oscillation becomes very rapid. We can eliminate these difficulties by suitable changes of the paths of integration in the planes of the complex variables ω and p. Namely, we shall transform these paths so that the p integration is taken only over real, and the ω integration only over imaginary values; then the exponent in $e^{2i\omega pl/c}$ will be real everywhere.

For the brevity, we shall denote the upper right quadrants of the ω and p planes (together with the semi-axes which bound them) as Q_ω and Q_p . We break up the path of integration over p in Eq. (2.4) into two parts, and first consider the one in which p runs through real values from unity to zero. Since we want to change the path of the ω integration from the positive real to the positive imaginary axis, we must investigate the question of the existence of singular points of the integrand as a function of ω in the region Q_ω.

According to the well-known general properties of the function $\epsilon(\omega)$, its imaginary part $\epsilon'' > 0$ everywhere in Q_ω except on the imaginary axis, where $\epsilon'' = 0$. On the latter, $\epsilon(\omega)$ is real and positive, decreasing monotonically from some value $\epsilon(0) > 1$ for $\omega = 0$ to unity for $\omega = i\infty$. Therefore the square root $s = \sqrt{\epsilon - 1 + p^2} = s' + is''$ (with real p) does not vanish anywhere within Q_ω, i.e., there are no branch points. From this it follows in turn that the inequalities $s' > 0$, $s'' > 0$, which are valid on the real semi-axis, are also valid everywhere within Q_ω.

The integrand might have poles at the roots of the denimonator in Eq. (2.4), i.e., the roots of the equations

$$\frac{(s_1 + p)(s_2 + p)}{(s_1 - p)(s_2 - p)} = e^{2ip\omega l/c}, \qquad (2.5)$$

$$\frac{(s_1 + \varepsilon_1 p)(s_2 + \varepsilon_2 p)}{(s_1 - \varepsilon_1 p)(s_2 - \varepsilon_2 p)} = e^{2ip\omega l/c}.$$

But since s', s'', and ϵ'' are positive (in the region Q_ω) it is easy to see that for real p the moduli

$$\left|\frac{s+p}{s-p}\right| > 1, \quad \left|\frac{s+\varepsilon p}{s-\varepsilon p}\right| > 1,$$

and since $|e^{2ip\omega l/c}| \leq 1$, it is clear that Eqs. (2.5) can have no roots. Thus the integrand has no singularities in Q_ω. It also drops sufficiently rapidly at infinity, so the path of integration over ω can be shifted to the imaginary axis.

Next we turn to that part of the integral in which p runs through pure imaginary values from zero to $i\infty$. Here we must change both paths of integration, over p and over ω. However, we cannot make these changes in a simple succession, since, for example, it is impossible to show that in the general case there are no poles of the integrand in Q_ω for arbitrary imaginary values of p. But in integrating a function of several (in our case, two) complex variables, we have very great freedom in shifting the contours. Thus we can change from integration over certain contours C_ω and C_p to other paths C'_ω and C'_p, if we can in any way simultaneously shift the paths without having them pass through any singular points of the integrand. In the present case, such a procedure would be the simultaneous shift of the paths in the quadrants Q_ω and Q_p, during which the product $i\omega p$ remains real (and, clearly, negative):

$$\mathrm{Im}\,\{i\omega p\} = 0; \quad \mathrm{Re}\,\{i\omega p\} < 0. \qquad (2.6)$$

In particular, the initial paths (real semi-axis for ω, imaginary semi-axis for p) and the final paths (imaginary semi-axis for ω, real semi-axis for p) satisfy this condition.

Such a transformation is , in fact, possible, for example, by introducing in place of the variable ω in the original integral the real positive variable $x = -i\omega p$, then shifting the integration over p from the imaginary to the real axis (for fixed values of x), and finally introducing ω once more as the imaginary quantity $\omega = ix/p$. Here, too, the integrand can have no branch points, since s could go to zero only for simultaneous pure imaginary values of ω and p, which event is excluded by condition (2.6). Therefore, we need only show that there are no roots of Eqs. (2.5) for values of p in the region Q_p for arbitrary real values of x. This presents no difficulties for the first of the equations, since the modulus $\left|\frac{s+p}{s-p}\right| \geq 1$ generally for all ω and p in Q_ω and Q_p , which is easily

demonstrated by noting that $s' > 0$, $s'' > 0$.

The investigation is far more complicated for the second of Eqs. (2.5). We shall here outline the method of proof, assuming for simplicity that the two media are identical. From the equality:

$$\left(\frac{s+\varepsilon p}{s-\varepsilon p}\right)^2 = e^{-2xl}, \qquad (2.7)$$

$$s = \sqrt{\varepsilon(ix/p) - 1 + p^2},$$

we conclude that $(s+\epsilon p)/(s-\epsilon p)$ must be a real number less than unity in absolute value. From this it follows in turn that there must be a relation between the values of the complex quantities s, p, ϵ of the form

$$s = -a\varepsilon p, \quad a > 0, \qquad (2.8)$$

where a is some positive real number; one verifies easily that such a relation is possible only for $\epsilon' > 0$. This in turn excludes the possibility of having roots for values of x and p for which the argument of the function $\epsilon(ix/p)$ is very small or very large, since we know that $\epsilon' > 0$ in both these cases. There can also be no roots for very large values of p, since then $s \approx p$, and it would follow from (2.8) that $s = -1/a$, i.e., the value of s would be real and negative, which is impossible.

We shall first show that Eq. (2.7) has no roots for infinitesimal values of the parameter l. As we have pointed out, very large values of x are excluded for arbitrary l. For finite x, the right side of Eq. (2.7) approaches unity as $l \to 0$. The left side of the equation can tend to unity only if $p \to 0$, (since s does not go to zero anywhere). But then we would also have to have $x \to 0$ (in order that the ratio x/p remain finite), and the right side of Eq. (2.7) will approach unity for $l \to 0$ faster than the left side, so that for sufficiently small l, there can be no roots in any case.

We show further that for arbitrary values of l there are no roots on the boundaries of the region Q_p[‡]. In fact, infinitely large values of p are excluded as shown above, while the axis of abscissas (real p) is out, since the function $\epsilon(ix/p)$ of imaginary argument is real and positive. The ordinate axis (imaginary p) is excluded, since for such p the relation (2.8), when squared, would give a quadratic equation for ϵ:

$$\epsilon^2 a^2 |p| + \epsilon - (1 + |p|^2) = 0$$

from which it would follow that ϵ were real, which is impossible (for real argument ix/p).

With increasing l, roots could steal into the region Q_p only across its boundaries. Therefore, the absence of roots for very small l, and the fact that there are no roots on the boundaries of Q_p for arbitrary l, shows that there are no roots anywhere in Q_p for arbitrary values of l[+].

Thus the required change of integration path can be carried out in both parts of the integral. Upon adding the two parts, the integrals over p from zero to unity cancel, and we obtain the following expression for the force of interaction for $T = 0$):

$$F = \frac{\hbar}{2\pi^2 c^3} \times \int_0^\infty \int_1^\infty p^2 \xi^3 \left\{ \left[\frac{(s_1+p)(s_2+p)}{(s_1-p)(s_2-p)} e^{2p\xi l/c} - 1 \right]^{-1} + \left[\frac{(s_1+p\varepsilon_1)(s_2+p\varepsilon_2)}{(s_1-p\varepsilon_1)(s_2-p\varepsilon_2)} e^{2p\xi l/c} - 1 \right]^{-1} \right\} dp\, d\xi \qquad (2.9)$$

(the path of integration is shown in Fig. 2b). Here we have introduced the notation $\omega = i\xi$ for imaginary values of ω, and ϵ_1 and ϵ_2 are to be taken as the real functions $\epsilon_1(i\xi)$ and $\epsilon_2(i\xi)$. We have dropped the "Re", since the expression given is manifestly real. Formula (2.9) makes it possible, in principle, to compute the force F for any separation l, if only the functions $\epsilon(i\xi)$ are known for both bodies. The latter can be expressed in terms of the value of the imaginary part of the function $\epsilon(\omega)$ for real ω by

$$\varepsilon(i\xi) - 1 = \frac{2}{\pi} \int_0^\infty \frac{\omega \varepsilon''(\omega)}{\omega^2 + \xi^2} d\omega. \qquad (2.10)$$

Thus we may say that the law of interaction of bodies is determined if we give the functions $\epsilon''(\omega)$; (we shall see, in Sec. 5, that this remains true for temperatures different from zero).

3. THE CASE OF SMALL SEPARATIONS

We first consider the limiting case of distances l which are small compared to the wavelengths that are important in the absorption spectra of the bodies (for a more exact formulation of this condition, see below). The temperatures which can occur for condensed bodies are always small compared to the values $\hbar\omega$ (e.g., in the visible region of the spectrum) which are important here. Therefore we may set $T \approx 0$, and use formula (2.9).

‡ Except for the irrelevant, trivial root $p = 0$ for $x = 0$, whose position does not depend on l.

+ The possibility of a root sneaking in at the point $\omega = 0$ is also excluded: for this to occur there would have to be a double root at $\omega = 0$ for some value of l, which does not occur.

Because of the presence of the exponentially increasing factor $e^{2p\xi l/c}$ in the denominators of the integrands, the main contributions to the integral over p come from values of p, for which $p\xi l/c \sim 1$. But then $p \gg 1$, so that, in finding the leading terms, we can set $s_1 \approx s_2 \approx p$. In this approximation, the first term in square brackets in Eq. (2.9) becomes zero. After introducing the integration variable $x = 2lp\xi/c$, the second term gives*

$$F = \frac{\hbar}{16\pi^2 l^3} \int_0^\infty \int_0^\infty \frac{x^2 dx\, d\xi}{\left(\frac{\varepsilon_1+1}{\varepsilon_1-1}\right)\left(\frac{\varepsilon_2+1}{\varepsilon_2-1}\right) e^x - 1} \qquad (3.1)$$

(in this approximation, the lower limit $2l\xi/c$ of the x integration is set equal to zero).

Formula (3.1) determines the force of attraction in the limiting case of small l. The force turns out to be inversely proportional to the cube of the separation, which, as was to be expected, is in accordance with the usual van der Waals force between two atoms(neglecting retardation). With increasing ξ, the functions $\epsilon(i\xi) - 1$ decrease monotonically to zero. Thus, starting with some $\xi \sim \xi_0$, larger values of ξ cease giving any significant contribution to the integral; the condition on the smallness of l is that $l \ll c/\xi_0$.

Let us show how the transition to the limit of interaction of individual atoms is carried out in Eq. (3.1). For this purpose, we assume that both media are sufficiently rarefied. Then the differences $\epsilon_1 - 1$ and $\epsilon_2 - 1$ are close to zero, and we have, from Eq. (3.1), to sufficient accuracy,

$$F = \frac{\hbar}{64\pi^2 l^3} \int_0^\infty \int_0^\infty x^2 e^{-x} (\varepsilon_1 - 1)(\varepsilon_2 - 1)\, dx\, d\xi$$

$$= \frac{\hbar}{32\pi^2 l^3} \int_0^\infty [\varepsilon_1(i\xi) - 1][\varepsilon_2(i\xi) - 1]\, d\xi.$$

Expressing $\epsilon(i\xi)$ in terms of the values of $\epsilon''(\omega)$ on the real axis of ω, in accordance with Eq. (2.10), we obtain

$$\int_0^\infty [\varepsilon_1(i\xi) - 1][\varepsilon_2(i\xi) - 1]\, d\xi$$

$$= \frac{4}{\pi^2} \int_0^\infty \int_0^\infty \int_0^\infty \frac{\omega_1 \omega_2 \varepsilon_1''(\omega_1)\, \varepsilon_2''(\omega_2)}{(\omega_1^2 + \xi^2)(\omega_2^2 + \xi^2)}\, d\xi\, d\omega_1\, d\omega_2$$

$$= \frac{2}{\pi} \int_0^\infty \int_0^\infty \frac{\varepsilon_1''(\omega_1)\, \varepsilon_2''(\omega_2)}{\omega_1 + \omega_2}\, d\omega_1\, d\omega_2,$$

and find for the force F

$$F = \frac{\hbar}{16\pi^3 l^3} \int_0^\infty \int_0^\infty \frac{\varepsilon_1''(\omega_1)\, \varepsilon_2''(\omega_2)}{\omega_1 + \omega_2}\, d\omega_1\, d\omega_2. \qquad (3.2)$$

This force corresponds to an interaction of the atoms with energy

$$U = -\frac{3\hbar}{8\pi^4 R^3 N^2} \times \int_0^\infty \int_0^\infty \frac{\varepsilon_1''(\omega_1)\, \varepsilon_2''(\omega_2)}{\omega_1 + \omega_2}\, d\omega_1\, d\omega_2, \qquad (3.3)$$

where N is the number of atoms per unit volume. [Equation (3.2) is obtained from Eq. (3.3) by integrating over both half-spaces and then differentiating with respect to the distance l between them]. Formula (3.3) agrees exactly with the well-known formula of London[5], obtained by applying ordinary perturbation theory to the dipole interaction of two atoms. In making the comparison, one must note that the imaginary part of $\epsilon(\omega)$ is related to the spectral density $f(\omega)$ of "oscillator strengths" by the relation

$$\omega\varepsilon''(\omega) = (2\pi^2 e^2/m)\, Nf;$$

while the oscillator strengths are themselves expressed as usual in terms of the squares of the matrix elements of the dipole moment of the atom.

Formula (3.1) can be represented sufficiently accurately for all practical purposes in a simple form. Let us assume, for brevity, that both bodies are identical. The integral with respect to x, in Eq. (3.1), depends, aside from the parameter, on the quantity $[(\epsilon + 1)/(\epsilon - 1)]^2$, which takes on values never less than unity (unity is reached for $\epsilon \to \infty$). Figure 3 shows a graph of the integral

$$I = \frac{a}{2} \int_0^\infty \frac{x^2\, dx}{ae^x - 1}$$

as a function of the parameter a. This integral tends to unity for $a \to \infty$, but we see that even for $a = 1$ it differs from unity by at most 20% and that this difference drops rapidly with increasing a. So we can

* This same result could have been gotten directly from Eq. (2.4), with the paths of integration shown in Fig. 2a, by noting that the main contribution to the integral comes from imaginary values of p. As already noted, imaginary values of p correspond to exponentially damped ("inhomogeneous") plane waves. It is entirely natural that just this part of the fluctuation field (and not the undamped, true plane waves) gives the main contribution to the interaction force for separations at which retardation effects are still unimportant.

[5] R. Eisenschitz and F. London, Z. Physik 60, 491 (1930)

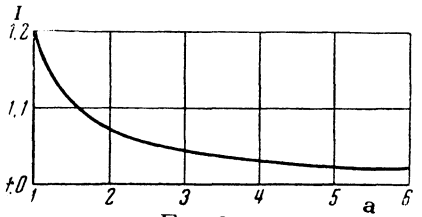

FIG. 3

practically write Eq. (3.1) in the form

$$F = \frac{\hbar}{8\pi^2 l^3}\int_0^\infty \left(\frac{\varepsilon(i\xi)+1}{\varepsilon(i\xi)-1}\right)^2 d\xi \qquad (3.4)$$

(with a similar formula if the bodies are different).

To evaluate the accuracy of the limiting law of interaction which we have obtained, it is useful to have the next term in the expansion of the function $F(l)$. A calculation using the same general formula (2.9) gives (for identical bodies) the expression

$$-\frac{\hbar}{8\pi^2 c^2 l}\int_0^\infty \frac{\xi^2[\varepsilon(i\xi)-1]^2}{\varepsilon(i\xi)+1}d\xi, \qquad (3.5)$$

which should be added to Eq. (3.4). However, it is impossible to give a concrete evaluation of the range of applicability of the limiting law without specific knowledge of the function $\epsilon(i\xi)$.

4. THE CASE OF LARGE SEPARATIONS

We now go over to the opposite limiting case of distances which are large compared to the fundamental wavelengths in the absorption spectrum of the bodies. Once again we shall first take the temperature to be equal to zero; for the meaning of this approximation in the present case, see below.

Again we introduce a new integration variable $x = 2pl\xi/c$ in the general formula, but we now keep as our second variable not ξ (as in Sec. 3), but rather p:

$$F = \frac{\hbar c}{32\pi^2 l^4}\int_0^\infty\int_1^\infty \frac{x^3}{p^2}\left\{\left[\frac{(s_1+p)(s_2+p)}{(s_1-p)(s_2-p)}e^x - 1\right]^{-1} + \left[\frac{(s_1+\varepsilon_1 p)(s_2+\varepsilon_2 p)}{(s_1-\varepsilon_1 p)(s_2-\varepsilon_2 p)}e^x - 1\right]^{-1}\right\} dp\,dx, \qquad (4.1)$$

$$\varepsilon = \varepsilon\left(i\frac{xc}{2pl}\right), \quad s = \sqrt{\varepsilon\left(i\frac{xc}{2pl}\right) - 1 + p^2}.$$

Because of the presence of e^x in the denominators, the main contribution to the x integral comes from $x \sim 1$, so since $p \geq 1$, the argument of the function ϵ, for large l, is close to zero over the whole important range of values of the variables. In accordance with this, we may simply replace ϵ_1 and ϵ_2 by their values for $\omega = 0$, i.e., by the static dielectric constants, which we denote by ϵ_{10}, ϵ_{20}. We know that for metals the function $\epsilon(\omega)$ tends toward infinity as $\omega \to 0$; in this case we must set $\epsilon_0 = \infty$. In this way we finally obtain the following result:

$$F = \frac{\hbar c}{32\pi^2 l^4}\int_0^\infty\int_1^\infty \frac{x^3}{p^2}\left\{\left[\frac{(s_{10}+p)(s_{20}+p)}{(s_{10}-p)(s_{20}-p)}e^x - 1\right]^{-1} + \left[\frac{(s_{10}+\varepsilon_{10}p)(s_{20}+\varepsilon_{20}p)}{(s_{10}-\varepsilon_{10}p)(s_{20}-\varepsilon_{20}p)}e^x - 1\right]^{-1}\right\} dp\,dx, \qquad (4.2)$$

$$s_{10} = \sqrt{\varepsilon_{10}-1+p^2}, \quad s_{20} = \sqrt{\varepsilon_{20}-1+p^2}.$$

Here the force of attraction is inversely proportional to l^4. It should be noted that in this limiting case it depends only on the static dielectric constants of the two media.

The integration with respect to p in Eq. (4.2) can be carried out in terms of elementary functions, after which there remains a single integral over x, depending on the two constant parameters ϵ_{10} and ϵ_{20}. We shall not give the corresponding, very complicated, general expressions, the more so since for purposes of numerical integration it is clearly more convenient to start directly from the double integral of Eq. (4.2).

Let us consider some special cases. In particular, a simple result is obtained for two metals. Setting $\epsilon_{10} = \epsilon_{20} = \infty$, we get

$$F = \frac{\hbar c}{16\pi^2 l^4}\int_0^\infty\int_1^\infty \frac{x^3 dp dx}{p^2(e^x-1)} = \frac{\hbar c}{l^4}\frac{\pi^2}{240}. \qquad (4.3)$$

This force does not depend in any way on the nature of the metals [which was not the case for small separations (Sec. 3), where the magnitude of the interaction depended on the function $\epsilon(i\xi)$ for all values of ξ, and not just at $\xi = 0$]. Formula (4.3) coincides with the formula, obtained by Casimir[6], for this special case, by considering the normal modes of the field in the gap between two walls which are ideally reflecting at all frequencies.

For two identical dielectrics ($\epsilon_{10} = \epsilon_{20} = \epsilon_0$) we give the result obtained from Eq. (4.2) by numerical integration:

$$F = \frac{\hbar c}{l^4}\frac{\pi^2}{240}\left(\frac{\varepsilon_0-1}{\varepsilon_0+1}\right)^2 \varphi(\varepsilon_0), \qquad (4.4)$$

[6] H. B. G. Casimir, Proc. Nederl. Akad. Wetensch., 51, 793 (1948)

where $\varphi(\epsilon_0)$ is a function whose values are shown in the graph of Fig. 4 (the curve *DD*). For $\epsilon_0 \to \infty$, this function approaches unity according to the law

$$\varphi(\varepsilon_0) = 1 - \frac{1.11}{\sqrt{\varepsilon_0}} \ln \frac{\varepsilon_0}{7.6} \qquad (4.5)$$

(Note that this formula is accurate only for very large values of ϵ_0). For $\epsilon_0 \to 1$, the function $\varphi(\epsilon_0)$ approaches a finite limit, 0.35, corresponding to the limiting law (4.7) (see below). This limit is, however, practically reached for $\epsilon_0 \approx 4$, after which $\varphi(\epsilon_0)$ remains practically constant.

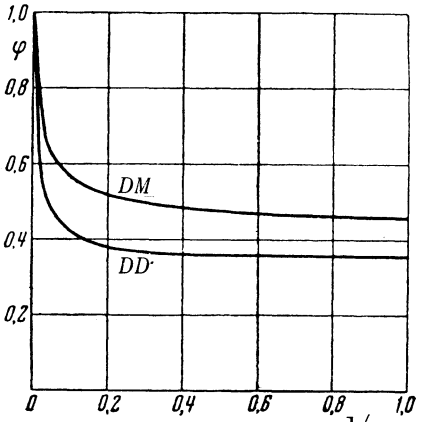

FIG. 4

In the same Fig. 4 we show the curve (*DM*) of the similar function which gives the force of attraction between a metal and a dielectric ($\epsilon_{10} = \infty$, $\epsilon_{20} = \epsilon_0$) according to the formula:

$$F = \frac{\hbar c}{l^4} \frac{\pi^2}{240} \frac{\varepsilon_0 - 1}{\varepsilon_0 + 1} \varphi(\varepsilon_0). \qquad (4.6)$$

Finally we carry out the transition to interaction of individual atoms in Eq. (4.2). To do this, we assume as in Sec. 3 that both media are sufficiently rarefied, i.e., that the differences $\epsilon_{10} - 1$ and $\epsilon_{20} - 1$ are small.

Keeping only the first non-vanishing terms in the expansion of the integrands of Eq. (4.2) in powers of these differences, we get

$$F = \frac{\hbar c}{32\pi^2 l^4} (\varepsilon_{10} - 1)(\varepsilon_{20} - 1) \times \int_0^\infty x^3 e^{-x}\, dx \int_1^\infty \frac{1 - 2p^2 + 2p^4}{8p^6}\, dp$$

or

$$F = \frac{\hbar c}{l^4} \frac{23}{640\pi^2} (\varepsilon_{10} - 1)(\varepsilon_{20} - 1). \qquad (4.7)$$

This force corresponds to interaction of the atoms with energy

$$U = -\frac{23\hbar c}{64\pi^5 R^7} \frac{(\varepsilon_{10} - 1)(\varepsilon_{20} - 1)}{N^2} = -\frac{23\hbar c}{4\pi R^7} \alpha_1 \alpha_2, \qquad (4.8)$$

where α_1, α_2 are the static polarizabilities of the two atoms. This formula coincides with the results of reference 1 for the van der Waals forces, including retardation effects; we have here obtained it from macroscopic considerations.

To estimate the accuracy and range of validity of the formulas obtained, we must again, as in Sec. 3, find the next term in the expansion of the function $F(l)$[+]. We shall do this for the case of two metals, which we assume to be identical.

Formula (4.3) is gotten from (4.1) if we set $\epsilon_1 = \epsilon_2 = \infty$ in the latter. But if we also want to get the next term in the expansion, we must use that form for the function $\epsilon(\omega)$ which is valid in the frequency region which is important in the integration. As we have seen, the important region is $\omega/c \sim 1/l$, i.e., $\lambda \sim l$. Accordingly, we set

$$\varepsilon(\omega) = -4\pi e^2 N / m\omega^2, \qquad (4.9)$$

where N is the number density of free electrons in the metal; this formula, which is sufficiently good for our purposes, gives the general behavior of $\epsilon(\omega)$ in the infrared region of the spectrum[‡]. When substituting in Eq. (4.1), we must replace ω by $icx/2pl$; then expanding the integrand in powers of $1/l$, we obtain

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

from which, finally,

$$F = \frac{\hbar c}{l^4} \frac{\pi^2}{240} \left\{ 1 - 7{,}2 \frac{c}{el} \sqrt{\frac{m}{N}} \right\}. \qquad (4.10)$$

[+] If we set $\epsilon(i\xi) = 1 + a/(\omega_0^2 + \xi^2)$ (so that $\epsilon_0 = 1 + a/\omega_0^2$), then calculation of F from formulas (3.4) and (4.4) shows that the two values match for $l \cong c/\omega_0$. This computation allows us to conclude that the characteristic length for comparison with l is not the wavelength in the absorption region, but rather $\lambda/2\pi$.

[‡] For still larger values of λ, the function $\epsilon(\omega)$ goes over into $\epsilon = 4\pi i\sigma/\omega$, where σ is the ordinary electrical conductivity of the metal. However, the corresponding frequency region gives a very small contribution to the integral.

So, tentatively setting $N = 5.9 \times 10^{22} cm^{-3}$ (for silver), we find that the second term is small compared to the first, if $l \gg 0.6\ \mu$.

We note that the second term in the expansion, which we have found here, could not be obtained by the method applied in reference 6 for getting the leading term.

5. THE EFFECT OF TEMPERATURE ON THE FORCE OF INTERACTION

While we can practically always consider the temperature of the bodies to be equal to zero for the limiting case of small separations (sec. 3), the effect of temperature may be substantial for large separations. Anticipating later results, we state that the condition for setting $T = 0$ is roughly speaking, $lT/\hbar c \ll 1$. For sufficiently low temperatures, this condition will of course always be compatible with the condition determining the lower bound of values of l for which the limiting law obtained in Sec. 4 is valid. But these two conditions may, as for example at room temperature, turn out to be incompatible; then the region in which the limiting laws obtained in Sec. 4 are applicable actually does not exist.

To obtain the formulas including the effect of temperature, we turn to the original expression (2.4) and see how, for $T \neq 0$, we must change the transformations which led to formula (2.9) in the case of $T = 0$. The function $\coth \hbar\omega / 2T$ has an infinite number of poles, located on the imaginary axis, and equal to

$$\omega_n = i\xi_n = i\frac{2\pi T}{\hbar} n, \tag{5.1}$$

where n is an integer. Therefore, upon shifting the path of integration to the imaginary axis, we must go around these poles on semicircles (as shown in Fig. 2c). These circuits give contributions to the real part of the integral, which are equal to $i\pi$ times the residue of the integrand at the pole. (The integration over the segments of the imaginary axis between the poles gives a pure imaginary number, which drops out when we take the real part of the expression).

The point with $n = 0$ ($\omega = 0$) requires special consideration. At first glance it might appear that this point is not a pole of the integrand in the integral over ω in (2.4), because of the presence of the factor ω^3. However, this factor vanishes upon integration over p [cf. also the expression (2.3) for F_ω]. The presence of a pole at the point $\omega = 0$ does not of course lead to divergence of (2.4), since for $\omega \to 0$ along the real axis the divergent contribution to the integral is pure imaginary, and drops out when we take the real part. [This can be seen more clearly from the expression (2.3) for F_ω, which remains finite for $\omega = 0$].

To take this point into account when transforming the path of integration, we shall suppose that the integration over ω in Eq. (2.4) is carried from some sufficiently small δ to ∞ (and not from zero to infinity); as we showed above, the real part of the integral is not changed when we do this. Upon shifting the contour to the imaginary axis, a circuit is added along a quarter-circle around the point $\omega = 0$ (Fig. 2c). This circuit gives a contribution to the integral equal to $i\pi/2$ times the corresponding residue.

To simplify writing of formulas, we shall assume the bodies to be identical; generalization to different bodies, on the basis of the general form of Eq. (2.4), is obvious.

We thus obtain the following formula:

$$F = \frac{T}{\pi c^3} \sum_{n=0}^{\infty}{}' \int_1^\infty p^2 \xi_n^3 \left\{ \left[\left(\frac{s_n + p}{s_n - p} \right)^2 e^{2p\xi_n l/c} - 1 \right]^{-1} + \left[\left(\frac{s_n + \varepsilon_n p}{s_n - \varepsilon_n p} \right)^2 e^{2p\xi_n l/c} - 1 \right]^{-1} \right\} dp,$$

$$s_n = \sqrt{\varepsilon_n - 1 + p^2}, \quad \varepsilon_n = \varepsilon(i\xi_n). \tag{5.2}$$

The prime on the summation sign means that the term with $n = 0$ should be taken with a factor ½. Replacing p by the integration variable $x = pn$, we rewrite (5.2) in the form:

$$F = \frac{8\pi^2 T^4}{\hbar^3 c^3} \sum_{n=0}^{\infty}{}' \int_n^\infty x^2 \left\{ \left[\left(\frac{ns_n + x}{ns_n - x} \right)^2 e^{4\pi l T x/\hbar c} - 1 \right]^{-1} + \left[\left(\frac{ns_n + \varepsilon_n x}{ns_n - \varepsilon_n x} \right)^2 e^{4\pi l T x/\hbar c} - 1 \right]^{-1} \right\} dx, \tag{5.3}$$

$$ns_n = \sqrt{n^2(\varepsilon_n - 1) + x^2}, \quad \varepsilon_n = \varepsilon\left(i\frac{2\pi T}{\hbar} n \right).$$

Formula (5.2) or (5.3) enables us, in principle, to calculate the force F for any value of l and any temperature. We see that, for $T \neq 0$ also, it is sufficient to know the values of the function $\epsilon(i\xi)$.

For $T \to 0$, the distances between poles also tend to zero, the summation over n can be replaced by an integration over ξ, and we return to formula (2.6) which does not contain T. By determining the first correction to this formula, we can establish a criterion for setting $T = 0$ in calculating the attractive force. We shall do this for metals, applying formula (4.9) for $\epsilon(\omega)$ as we did in Sec. 4.

According to the Euler sum formula we have, for

a function $f(n)$ which together with all its derivatives goes to zero for $n \to \infty$,

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

In our case the function $f(n)$ is the integral under the summation sign in (5.3). In the calculation we shall assume that l is small compared to $\hbar c/T$, but still large compared to the quantity $(c/e)\sqrt{m/N}$ which is characteristic for the metal. Then $f'(0) = 0$, $f'''(0) = 2$ and thus

$$F = \frac{\pi^2}{240}\frac{\hbar c}{l^4}\left[1 - \frac{48}{9}\left(\frac{lT}{\hbar c}\right)^4\right]. \tag{5.4}$$

Thus, at room temperature the correction is already small if $l < 5\mu$; comparison with the criterion obtained in Sec. 4 shows that in this case there is a region in which the formulas there obtained are applicable*.

In the opposite limiting case of large values of $lT/\hbar c$, we need keep only the first term in the sum in Eq. (5.3), i.e., $n = 0$:

$$F = \frac{4\pi^2 T^4}{\hbar^3 c^3} \times \int_0^\infty \frac{x^2 dx}{[(\varepsilon_0+1)/(\varepsilon_0-1)]^2 \exp\left\{\frac{4\pi lT}{\hbar c}x\right\} - 1}$$

or

$$F = \frac{T}{16\pi l^3}\int_0^\infty \frac{x^2 dx}{[(\varepsilon_0+1)/(\varepsilon_0-1)]^2 e^x - 1} \approx \frac{T}{8\pi l^3}\left(\frac{\varepsilon_0-1}{\varepsilon_0+1}\right)^2. \tag{5.5}$$

Thus for sufficiently large separations, the interaction force stops dropping so rapidly, and once again follows a $1/l^3$ law, with a coefficient which depends on the temperature and on the static value of the dielectric constant. This fact has apparently not been previously noted anywhere in the literature.

All the other terms in the sum (5.3) decrease exponentially for large $lT/\hbar c$. So, including the first correction term, we obtain for two metals

$$F = \frac{T}{8\pi l^3}\left[1 + 2\left(\frac{4\pi Tl}{\hbar c}\right)^2 \exp\{-4\pi Tl/\hbar c\}\right]. \tag{5.6}$$

Let us say a few words about the comparison of the results of the theory presented in this paper with experiment. Direct measurements of molecular attractive forces are very difficult, and apparently the only work in which the authors have succeeded in eliminating all spurious effects is that of Abrikosova and Deriagin[7]. These authors measured the attractive force between quartz plates for separations 0.1 - 0.4 μ. Exact comparison with theory would require sufficiently complete knowledge of the optical characteristics of the material over its absorption regions; without this we cannot construct the function $\epsilon(i\xi)$. However, the character of the absorption in quartz enables us to make an approximate theoretical estimate**. Considering the crudeness of this estimate, and possible errors in the measurement, we may state that the agreement between the theory and the experimental data is satisfactory.

In conclussion I express my sincere thanks to Academician L. D. Landau for discussion of the problems considered here. I also thank I. I. Abrikosova and B. V. Deriagin for discussion of the experimental data, and I. G. Krutikova who carried out the numerical calculations mentioned in the text.

* With the function $\epsilon = 4\pi i\sigma/\omega$ (cf footnote, p. 81) we would get a very much greater upper limit for l.

[7] I. I. Abrikosova and B. V. Deriagin, Dokl. Akad. Nauk SSSR, **90**, 1055 (1953); I. I. Abrikosova. Dissertation, Phys. Chem. Inst., Academy of Sciences USSR, 1954.

** *Note added in proof.*- Quartz has strong absorption in the ultraviolet (starting at about 0.15 μ) and in the infrared (starting at a few μ), between which regions it is transparent. The separations used in the experiments fall in the region of transparency; in making the estimate we may assume that l is small compared to $\lambda/2\pi$ (cf footnote, p.) for the right absorption edge, and large compared to the left absorption edge. The contribution of the ultraviolet absorption region to the force F can be evaluated from formula (4.4), setting ϵ_0 equal to the square of the refractive index in the region of optical transparency. The contribution of the infrared region is given by formula (3.4); in order of magnitude it is a factor $l\omega_0/c$ smaller (ω_0 is the infrared absorption frequency), and can be neglected in a rough estimate of F. Thus we obtain for the force a $1/l^4$ law, with a coefficient determined as above. This estimate is raised for larger separations and lowered for smaller separations.

Translated by M. Hamermesh
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