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VAN DER WAALS FORCES IN LIQUID FILMS

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A previously developed theory[1] of the molecular forces of interaction between solid bodies, the surfaces of which are brought to very small distances of one another, is extended to the case where the space between the bodies is filled with a liquid medium. It is shown, in particular, that two identical bodies always attract one another whatever the "layer" between them.

We have obtained general formulas for the thermodynamic quantities (chemical potential) of the liquid film from the knowledge of the spectral properties [the dielectric constant $\epsilon(\omega)$] of the liquid and the solid substratum. We have found limiting laws for the dependence of the chemical potential on the film thickness. The problem of the stability of films is considered and different possible cases of instability in well determined ranges of film thickness are noted. The possibility of the existence of very small, but non-zero, contact angles is noted. Liquid helium films are discussed.

1. INTRODUCTION

We have developed earlier[1] a theory of the attractive molecular forces between solid bodies separated by a narrow gap. This theory was macroscopic in character, and in it the interaction between the bodies was considered to be caused through the intermediary of the fluctuating electromagnetic field. The attractive force itself was then evaluated as the appropriate component of the Maxwell stress tensor of the electromagnetic field at the surface of the body.

In reference 1 it was assumed that the space between the bodies was a vacuum, so that the evaluation of the Maxwell stresses was carried out using the usual formulas for the field in vacuo. A generalization of the theory to the case where the gap between the bodies is also filled with some medium was difficult because there were no formulas for the stress tensor in a variable field in absorbing media.

This difficulty is now no longer present, thanks to the fact that recently[2] there have been obtained general formulas for that part of the thermodynamic quantities (including the stress tensor) of an arbitrary absorbing medium which is due to the fluctuating electromagnetic field with wavelengths $\lambda \gg a$ (a being the interatomic distance). This field corresponds exactly to forces that have the same nature as the van der Waals forces between individual molecules large distances apart.

A general formula for the tensor of the stresses arising from the fluctuations of the electromagnetic field in an absorbing medium is given in Sec. 2. We shall see, however, that it is unnecessary in practice to use it again for explicit calculations, since it turns out to be possible to obtain the required formula for the interaction force between bodies separated by a "layer" through a simple transformation of the formula for bodies separated by a vacuum.

Different cases which may occur when two bodies interact are analyzed in Sec. 3. The indices 1 and 2 distinguish in all equations quantities referring to these two bodies, and the index 3 identifies quantities referring to the medium filling the gap (of width l) between the bodies. Although in all this we have assumed the gap to be plane-parallel, we must nevertheless bear in mind that in reality, for a correct statement of the problem of the interaction force between bodies, we must consider that at least one of them has finite dimensions and is surrounded on all sides by the medium 3, and we must determine the total force acting upon it. In view of the very steep decrease of molecular forces with distance, this resultant force can, in actual fact, be completely attributed to the forces acting across the narrow gap between the two bodies.

If one of the media 1 or 2 is replaced by a vacuum we then have the case of a thin film on the surface of a solid body. The thermodynamic quantities (the chemical potential) of a film are evaluated in Sec. 4, which also includes an investigation of the stability of films of different thicknesses. Liquid helium films are considered separately in Sec. 6.

In the case of a vacuum gap between bodies, the forces of the interaction between them can completely be reduced to the forces described by the fluctuating electromagnetic fields. When, however, the gap is filled with a liquid medium, there are forces of yet another origin, which are connected with the energies of the acoustic sound vibrations in that medium. Moreover, fluctuating surface vibrations at the interface of different media can also lead to a definite contribution. The same holds also for the evaluation of the chemical potential of the film. In actual fact, however, these additional contributions are small (as will be shown in Sec. 5) compared with the contribution from the electromagnetic fluctuations, i.e., from the van der Waals forces.

2. THE STRESS TENSOR IN A LAYER OF AN ABSORBING MEDIUM

It was shown in reference 2 that the additional stresses arising in an absorbing medium in which there is a fluctuating electromagnetic field can be expressed in terms of temperature Green's functions $\mathfrak{D}_{ik}(\mathbf{r}, \mathbf{r}'; \xi_n)$ of the electromagnetic field, which depend on a discrete imaginary frequency. These functions were introduced by Gor'kov, Abrikosov, and Dzyaloshinskiĭ and by Fradkin[3] and are Fourier expansions of the well-known temperature Green's functions of Matsubara.[4]

The general formula for the stress tensor of a fluctuating electromagnetic field has the following form:*

$$\sigma_{ik} = -\frac{\hbar T}{2\pi} \sum_{n=0}^{\infty}{}' \left\{ -\frac{1}{2}\delta_{ik}\left(\varepsilon - \rho\frac{\partial\varepsilon}{\partial\rho}\right)\mathfrak{D}^{E}_{ll}(\mathbf{r}, \mathbf{r}; \xi_n) + \varepsilon\mathfrak{D}^{E}_{ik}(\mathbf{r}, \mathbf{r}; \xi_n) - \frac{1}{2}\delta_{ik}\mathfrak{D}^{H}_{ll}(\mathbf{r}, \mathbf{r}; \xi_n) + \mathfrak{D}^{H}_{ik}(\mathbf{r}, \mathbf{r}; \xi_n)\right\} - \delta_{ik}p_0. \tag{1}$$

Here $\epsilon = \epsilon(\mathbf{r}, i\xi_n)$ is the dielectric constant of the substance as a function of the imaginary frequency $\omega = i\xi$; the summation is taken over the values $\xi_n = 2\pi nT/\hbar$ (where the term with $n = 0$ is taken with a factor $\frac{1}{2}$); T is the temperature; ρ is the density of the substance; $p_0 = p_0(\rho, T)$ is that density which would be present in the medium if there were no field for the given values of ρ and T. The functions $\mathfrak{D}^{E}_{ik}$ and $\mathfrak{D}^{H}_{ik}$ play the role of the average values of the derivatives of the corresponding stress components of the fluctuating field, and are connected with the temperature Green's functions $\mathfrak{D}_{ik}$ which play a similar role for the vector potential of the field through the relations

$$\mathfrak{D}^{E}_{ik}(\mathbf{r}, \mathbf{r}'; \xi_n) = -\xi_n^2\mathfrak{D}_{ik}(\mathbf{r}, \mathbf{r}'; \xi_n),$$
$$\mathfrak{D}^{H}_{ik}(\mathbf{r}, \mathbf{r}'; \xi_n) = \operatorname{curl}_{il}\operatorname{curl}'_{km}\mathfrak{D}_{lm}(\mathbf{r}, \mathbf{r}'; \xi_n) \tag{2}$$

The latter Green's function satisfies the equation

$$\varepsilon\xi_n^2\mathfrak{D}_{ik}(\mathbf{r}, \mathbf{r}'; \xi_n) + \operatorname{curl}_{il}\operatorname{curl}_{lm}\mathfrak{D}_{mk}(\mathbf{r}, \mathbf{r}'; \xi_n) = -4\pi\delta(\mathbf{r} - \mathbf{r}')\delta_{ik}. \tag{3}$$

At the interface between two media, the components of $\mathfrak{D}_{ik}$ must satisfy boundary conditions corresponding to the continuity of the tangential components of the electrical and magnetic fields (it is unnecessary to write these out explicitly here).

Let body 2 be separated from body 1 by a gap of width l and be surrounded on all sides by the medium 3. The total force acting upon body 2 can be evaluated as being the total momentum flux flowing from the medium 3 into the body, i.e., in the form of an integral $\oint \sigma_{ik}df_k$ of the stress tensor in the above mentioned medium taken over the surface of the body. From the condition that the chemical potential should be constant in a medium in equilibrium we have, however, (see reference 5, §15)*

$$p_0 + \frac{\hbar T}{2\pi}\sum_{n=0}^{\infty}{}' \frac{1}{2}\rho\frac{\partial\varepsilon_3}{\partial\rho}\mathfrak{D}^{E}_{ll} = \text{const.} \tag{4}$$

Because of this condition, part of the stress tensor turns out to be a uniform pressure which is constant in the medium and which does not contribute anything to the total force acting upon the body. To determine this force it is, thus, in fact sufficient to write the stress tensor in the medium 3 in the form (compare a similar derivation in reference 5, §16)

$$\sigma'_{ik} = -\frac{\hbar T}{2\pi}\sum_{n=0}^{\infty}{}' \left\{\varepsilon_3\left[\mathfrak{D}^{E}_{ik} - \frac{1}{2}\delta_{ik}\mathfrak{D}^{E}_{ll}\right] + \left[\mathfrak{D}^{H}_{ik} - \frac{1}{2}\delta_{ik}\mathfrak{D}^{H}_{ll}\right]\right\}. \tag{5}$$

This expression differs from the one which would be valid for a field in a vacuum only by the factor ϵ_3 in the first term. This fact enables us to re-

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*It must be understood that we have removed from this expression the divergent part that is connected with the equilibrium heat radiation in a homogenous medium.

*This condition assumes, in this form, that one may neglect the change in density of the medium itself under the influence of the field; taking this into account would lead to quantities of higher order in the field.

duce the problem to the case considered in reference 1, where the bodies were separated by a vacuum, through a simple transformation.

To do this we perform a coordinate transformation $\mathbf{r} = \tilde{\mathbf{r}}/\sqrt{\epsilon_3}$, at the same time introducing new $\mathfrak{D}$ functions by $\mathfrak{D}_{ik} = \tilde{\mathfrak{D}}_{ik}\sqrt{\epsilon_3}$; then, because of the definitions (2), we have

$$\mathfrak{D}^E_{ik} = \tilde{\mathfrak{D}}^E_{ik}\,\varepsilon_3^{1/2}, \qquad \mathfrak{D}^H_{ik} = \tilde{\mathfrak{D}}^H_{ik}\,\varepsilon_3^{3/2},$$

so that

$$\sigma'_{ik} = -\frac{\hbar T}{2\pi}\sum_{n=0}^{\infty}{}' \varepsilon_3^{3/2}\left[\tilde{\mathfrak{D}}^E_{ik} - \frac{1}{2}\delta_{ik}\tilde{\mathfrak{D}}^E_{ll} + \tilde{\mathfrak{D}}^H_{ik} - \frac{1}{2}\delta_{ik}\tilde{\mathfrak{D}}^H_{ll}\right]. \tag{6}$$

One sees easily that for the new functions $\tilde{\mathfrak{D}}_{ik}$ in the new coordinates we obtain equations of the same form as Eq. (3) in the regions 1, 2, and 3, where ϵ_1/ϵ_3, ϵ_2/ϵ_3, and 1 play, respectively, the role of ϵ in these equations. The interaction force between two bodies with dielectric constants ϵ_1 and ϵ_2 separated by a gap of width l filled with a medium ϵ_3 can thus be obtained from the expression for the interaction force of two bodies separated by a vacuum region by multiplying each term of the sum over n by $\epsilon_3^{3/2}$ and by replacing in all terms ϵ_1 and ϵ_2 by ϵ_1/ϵ_3 and ϵ_2/ϵ_3, respectively, and l by $l\sqrt{\epsilon_3}$.

3. THE MOLECULAR INTERACTION FORCES BETWEEN SOLID BODIES

One can usually neglect the influence of the temperature on the attractive force (compare reference 1) for those distances l which will be considered in connection with the problem under consideration. We then get a general formula for the attractive force F (per one cm^2 surface area of the body) by means of the above mentioned transformation from Eq. (2.9) of reference 1. This formula has the form

$$F = \frac{\hbar}{2\pi^2 c^3}\int_0^\infty\int_1^\infty p^2\xi^3\varepsilon_3^{3/2}\left\{\left[\frac{(s_1+p)(s_2+p)}{(s_1-p)(s_2-p)}\exp\left(\frac{2p\xi}{c}l\sqrt{\varepsilon_3}\right)-1\right]^{-1}\right.$$
$$\left.+\left[\frac{(s_1+p\varepsilon_1/\varepsilon_3)(s_2+p\varepsilon_2/\varepsilon_3)}{(s_1-p\varepsilon_1/\varepsilon_3)(s_2-p\varepsilon_2/\varepsilon_3)}\exp\left(\frac{2p\xi}{c}l\sqrt{\varepsilon_3}\right)-1\right]^{-1}\right\}dp\,d\xi, \tag{7}$$

where

$$s_1 = \sqrt{\varepsilon_1/\varepsilon_3 - 1 + p^2}, \qquad s_2 = \sqrt{\varepsilon_2/\varepsilon_3 - 1 + p^2},$$

and ϵ_1, ϵ_2, ϵ_3 are functions of imaginary frequency $\omega = i\xi$.

It will be remembered in this connection that $\epsilon(i\xi)$ is a real function, monotonically decreasing from the electrostatic value ϵ_0 (when $\xi = 0$) to 1 (when $\xi = \infty$). If the function $\epsilon''(\omega)$ (the imaginary part of the dielectric constant for real frequencies ω) is known from experiment, the function $\epsilon(i\xi)$ can be calculated from the formula (see reference 5, Sec. 62)

$$\varepsilon(i\xi) - 1 = \frac{2}{\pi}\int_0^\infty \frac{\omega\varepsilon''(\omega)}{\omega^2+\xi^2}\,d\omega \tag{8}$$

The transition to the limiting cases of "small" and "large" distances takes place in the same way as in reference 1. We thus get at small distances

$$F = \frac{\hbar}{16\pi^2 l^3}\int_0^\infty\int_0^\infty x^2\left[\frac{(\varepsilon_1+\varepsilon_3)(\varepsilon_2+\varepsilon_3)}{(\varepsilon_1-\varepsilon_3)(\varepsilon_2-\varepsilon_3)}e^x - 1\right]^{-1}dx\,d\xi. \tag{9}$$

At large distances, on the other hand,

$$F = \frac{\hbar c}{32\pi^2 l^4\sqrt{\varepsilon_{30}}}\int_0^\infty\int_1^\infty \frac{x^3}{p^2}\left\{\left[\frac{(s_{10}+p)(s_{20}+p)}{(s_{10}-p)(s_{20}-p)}e^x - 1\right]^{-1}\right.$$
$$\left.+\left[\frac{(s_{10}+p\varepsilon_{10}/\varepsilon_{30})(s_{20}+p\varepsilon_{20}/\varepsilon_{30})}{(s_{10}-p\varepsilon_{10}/\varepsilon_{30})(s_{20}-p\varepsilon_{20}/\varepsilon_{30})}e^x - 1\right]^{-1}\right\}dp\,dx,$$

$$s_{10} = \sqrt{\varepsilon_{10}/\varepsilon_{30} - 1 + p^2}, \qquad s_{20} = \sqrt{\varepsilon_{20}/\varepsilon_{30} - 1 + p^2}, \tag{10}$$

where ϵ_{10}, ϵ_{20}, ϵ_{30} are the electrostatic values of the dielectric constants. If both bodies are the same ($\epsilon_{10} = \epsilon_{20}$), one can put Eq. (10) in the form

$$F = \frac{\hbar c}{l^4}\frac{\pi^2}{240\sqrt{\varepsilon_{30}}}\left(\frac{\varepsilon_{10}-\varepsilon_{30}}{\varepsilon_{10}+\varepsilon_{30}}\right)^2\varphi\left(\frac{\varepsilon_{10}}{\varepsilon_{30}}\right), \tag{11}$$

where $\varphi(x)$ is the function the numerical values of which are given in Fig. 4 of reference 1 for arguments ranging from 1 to ∞; in addition we mention that $\varphi(0) = 0.52$.

With an accuracy which is completely sufficient for practical purposes, we can write Eqs. (9) and (10) in a simpler form by neglecting within the square brackets the quantity 1 compared to the terms with e^x. After this, the integration over dx is elementary, and there remains only a single integral* over $d\xi$ or dp. We get thus instead of Eq. (9)

$$F = \frac{\hbar\bar{\omega}}{8\pi^2 l^3}, \quad \text{where } \bar{\omega} = \int_0^\infty \frac{(\varepsilon_1-\varepsilon_3)(\varepsilon_2-\varepsilon_3)}{(\varepsilon_1+\varepsilon_3)(\varepsilon_2+\varepsilon_3)}\,d\xi. \tag{12}$$

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

When $\epsilon_{30} \to \infty$, expression (10) tends to zero. This means that when the gap between the bodies is filled by a liquid metal, the interaction force varies (at "large" distances) as a higher power

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*The accuracy of such a simplification is connected with the fact that an integral of the form

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

does not change appreciably when a changes from ∞ to 1; it changes from 1 to 1.2 if n = 2, to 1.08 if n = 3, to 1.04 if n = 4, and so on.

of $1/l$. To consider this case it is necessary to turn to the original Eq. (7) and to take into account the actual law according to which the dielectric constant of a metal increases when the frequency is decreased.

The variation of $\epsilon(\omega)$ of a metal in the infrared region of the spectrum is given by

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

where N is the number density of the free electrons. When we substitute $\epsilon_3(i\xi) = 4\pi e^2 N/m\xi^2$ into Eq. (7), the exponential factors in the denominators of the integrand take on the form

$$\exp\{(2pl/c)\sqrt{4\pi e^2/Nm}\},$$

i.e., ξ disappears from them, and since $p \geq 1$, we are led to the conclusion that the contribution to the force F from the region of frequencies under consideration decreases exponentially with the distance l.

But the main contribution to the interaction force is given in this case by the region of even smaller frequencies where $\epsilon(\omega)$ is connected with the usual electrical conductivity of the metal σ by the well-known formula

$$\varepsilon(\omega) = 4\pi i\sigma / \omega.$$

Substituting $\epsilon_3(i\xi) = 4\pi\sigma_3/\xi$ into the integrand in Eq. (7) (in the exponents and in the factor $\epsilon_3^{3/2}$; in other places it is sufficient to put $\epsilon_3 = \infty$), and introducing the variable $x = 4pl\sqrt{\pi\sigma_3\xi/c^2}$ instead of the integration variable ξ, we get

$$F = \frac{\hbar c^2}{2^7\pi^3\sigma_3 l^5}\int_0^\infty\int_1^\infty \frac{x^4}{p^2}\left\{\left[\left(\frac{\sqrt{p^2-1}+p}{\sqrt{p^2-1}-p}\right)^2 e^x - 1\right]^{-1} + \frac{1}{e^x-1}\right\} dp\, dx.$$

The value of the double integral (evaluated by the method mentioned in footnote* of page 163) is 13.5 and, as a result, we obtain

$$F = 0.0034 \cdot \hbar c^2 / \sigma_3 l^5. \tag{13}$$

The force of molecular attraction thus goes, in the case of a metallic "layer" between bodies, from an l^{-3} law at "small" distances to an l^{-5} law at "large" distances; the beginning of the latter is delayed, though, by the occurrence in Eq. (13) of a small numerical coefficient.

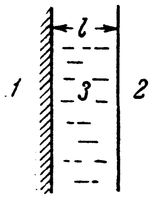
Returning to the general Eq. (7), we note that if both bodies are the same ($\epsilon_1 = \epsilon_2$) the integrand in Eq. (7) is always positive* and decreases monotonically with increasing l for all values of p and ξ. It follows hence that both $F > 0$ and $dF/dl < 0$, i.e., identical bodies attract one another whatever the layer is between them, and the force F decreases monotonically with increasing distance.*

If, however, the bodies are different, the force acting between them can be either attractive or repulsive. It is clear from Eq. (12) that if the differences $\epsilon_1 - \epsilon_3$ and $\epsilon_2 - \epsilon_3$ have different signs in the essential frequency region, we have $F < 0$, that is, at "small" distances the bodies repel one another. At "large" distances, however, the character of the force is determined by the relative magnitude of the electrostatic values of the dielectric constants: if the signs of the differences $\epsilon_{10} - \epsilon_{30}$ and $\epsilon_{20} - \epsilon_{30}$ are the same we have $F > 0$, and if they are different $F < 0$. Moreover, since the relative magnitudes of ϵ_{10}, ϵ_{20}, and ϵ_{30} are, generally speaking, not connected with the behavior of the functions $\epsilon_1(i\xi)$, $\epsilon_2(i\xi)$, and $\epsilon_3(i\xi)$ in those frequency regions which are essential for the given bodies, it is possible, in principle, that there are cases where the function $F(l)$ changes sign for some l. (This is discussed in more detail in Sec. 4.)

4. A THIN FILM ON THE SURFACE OF A SOLID BODY

We can also apply Eq. (7) to evaluate the thermodynamic quantities of a thin liquid film on the surface of a solid body (Fig. 1). We assume here that the thickness l of the film (as the gap width in the previous case) is large compared with interatomic distances.

FIG. 1



We consider a film on a solid wall situated vertically in the gravitational field. The condition that the chemical potential be constant in the film (medium 3) (which is in equilibrium) is expressed by Eq. (4), where we must add in the left-hand side a term ρgz (where z is the height). One other condition must express the fact that at any free surface of the film a constant pressure, the black-body radiation pressure acts from the direction of the vacuum. The σ_{xx} component (x is the normal to the surface of the film) of the stress tensor, Eq. (1), evaluated in the film, must therefore

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*This is easily checked if we note that for $s = \sqrt{\varepsilon - 1 + p^2}$ (where $p \geq 1$) the inequality $\varepsilon p > s > p$ holds if $\varepsilon > 1$, and $\varepsilon p < s < p$ if $\varepsilon < 1$.

*This statement was already made by Hamaker,[6] based upon an assumption about the additivity of molecular forces (which in actual fact does not take place).

also be constant (independent of z). Combining these two conditions we get

$$\sigma'_{xx} + \rho g z = \text{const},$$

where σ'_{xx} is the component of the "truncated" stress tensor, Eq. (5). However, σ'_{xx} in medium 3 is none other than the quantity $F(l)$ evaluated above, so that we have

$$F(l) + \rho g z = \text{const}. \tag{14}$$

Equation (14) is nothing but the condition that the chemical potential be constant in the system, so that $F(l)$ is that part of its chemical potential μ which depends on the film thickness. (We define μ here as the thermodynamic potential referred to the mass ρ; we consider the liquid density to be constant.) Thus $\mu = \mu_0 + F(l)$, where μ_0 is the chemical potential of the "bulk" liquid (compare reference 7, Sec. 141). If we measure the chemical potential from the value μ_0, we can simply write $\mu(l)$ instead of $F(l)$.* Measuring also the height z from the surface of the liquid in the vessel, the constant of Eq. (14) vanishes, so that

$$\mu(l) + \rho g z = 0. \tag{15}$$

The function $\mu(l)$ determines all the thermodynamic properties of the film; it is defined by Eqs. (7) to (10), in which we must put $\epsilon_2 = 1$ (the medium 2 is vacuum).† We must also introduce an "effective" coefficient of surface tension α at the boundary of the phases 1 and 2, taking into account the existence of a liquid film between them. This can be done by formally using the well-known formula from adsorption theory $\gamma = -(\partial\alpha/\partial\mu')_T$ where γ is the surface concentration of the adsorbed substance (number of particles per cm^2) and μ' its chemical potential (defined as the thermodynamical potential referred to one particle; see, e.g., reference 7, Sec. 139). When we use the definition of μ given here this relation can be written

$$l = -(\partial\alpha/\partial\mu)_T, \tag{16}$$

which is applicable both to macroscopically thick ("wetting") films and to adsorption films of "molecular thickness," in the latter case, finally, l has only a formal meaning as a quantity proportional to the surface concentration ($l = \gamma m/\rho$, m being the mass of a molecule). Integrating Eq. (16) and taking into account that as $l \to \infty$ the function $\alpha(l)$ must go over into $\alpha_{13} + \alpha_{32}$ (the sum of the surface tensions at the boundaries of the "bulk" phases 1, 2, and 3, we get

$$\alpha(l) = \int_l^\infty l \frac{d\mu}{dl}\, dl + \alpha_{13} + \alpha_{32}. \tag{17}$$

As $l \to 0$, $\alpha(l)$ must tend to the surface tension at the boundary of the "pure" phases 1 and 2, so that

$$\int_0^\infty l \frac{d\mu}{dl}\, dl = \alpha_{12} - \alpha_{13} - \alpha_{32}. \tag{18}$$

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

$$(\partial\mu/\partial l)_T > 0 \tag{19}$$

be satisfied, or $(\partial\alpha/\partial l)_T < 0$ (compare reference 7, Sec. 139). If that condition is satisfied a film will be in equilibrium with the vapor if its thickness is such that $\mu(l) = \mu_{\text{vap}}$ (for a saturated vapor $\mu_{\text{vap}} = 0$, for an unsaturated vapor $\mu_{\text{vap}} < 0$). If there are more than one such values of l the film with the smallest value of α will correspond to the stable state; a larger value of α will then correspond to a metastable state.

We shall consider some typical cases that may occur, depending on the character of the function $\mu(l)$. It is necessary to bear particularly in mind that the function $\mu(l)$ may change sign and may not be monotonic; this is already clear from the fact that the signs in the limiting expressions for $\mu(l)$, for large and for small l, are practically independent of one another (compare the end of Sec. 3).

a) If $\mu(l)$ is a monotonically decreasing, everywhere positive function (Fig. 2a), the liquid will not, in general, wet the solid surface; hence

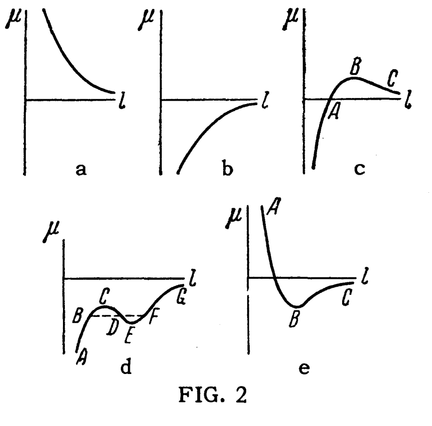

FIG. 2

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*For a convenient comparison we note that the quantity μ defined in this way is the same (with the opposite sign) as the "separating pressure" P used in the papers by Deryagin and his collaborators (see, e.g., reference 8).

†Region 2 is actually filled with the vapor of substance 3 which is in thermodynamic equilibrium with the liquid in the vessel and in the film; in view of the rareness of this medium, we can fully consider it to be a vacuum in the electrodynamic sense.

no film is formed at all. We emphasize that we are dealing here just with macroscopically thick films, to which the whole of the theory developed here refers. As regards adsorption in the narrow sense of the word, this always takes place to some extent as is well-known. This corresponds to the fact that whatever the behavior of the function $\mu(l)$, in the region of molecular distances (not depicted in Fig. 2) it ultimately tends to $-\infty$ according to the law $\mu \sim \ln l$, which corresponds to a "weak solution" of the adsorbed substance on the surface.

b) If $\mu(l)$ is a monotonically increasing everywhere negative function (Fig. 2b), this will normally correspond to a liquid which fully wets the solid surface and (depending on the vapor pressure above it) forms a stable film of arbitrary thickness. In particular, there will be formed on a vertical wall a film with a thickness which tends to zero as $z \rightarrow \infty$; the decrease goes at first as $l \sim z^{-1/4}$ and later as $z^{-1/3}$.

However, also in that case, the liquid may turn out to be nonwetting if the behavior of $\mu(l)$ in the microscopic region is such that it leads there to a smaller value of the surface tension α; a molecular adsorption film, and not a wetting film will then be the stable one.*

c) $\mu(l)$ goes through zero and possesses a maximum as shown in Fig. 2c. With the same reservation as in the case b), we shall have here a case of wetting, but with formation of a film that is stable only for thicknesses less than a well-defined limit. A film of finite thickness corresponding to the point A is in equilibrium with the saturated vapor. This state is separated from another stable state — the equilibrium of the solid wall with the "bulk" liquid — by a metastable region AB and a region of total instability BC.

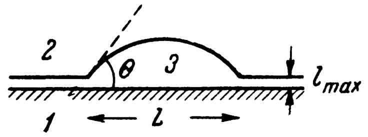
A $\mu(l)$ curve of such a type must lead to interesting features in the formation of a contact angle θ of drops of liquid on a solid surface. In this case a drop will be in equilibrium with a film of finite thickness $l_{\max}$ (Fig. 3), and from the usual elementary formula we have

$$\cos\theta = [\alpha(l_{max}) - \alpha_{13}] / \alpha_{23}, \tag{20}$$

where $\alpha(l_{\max})$ [with $\alpha(l)$ from Eq. (17)] plays the role of the coefficient of the surface tension between phases 1 and 2. Since the first term in Eq. (17) is a small quantity, we get from Eq. (20)

$$\theta^2 \approx -\frac{2}{\alpha_{23}} \int\limits_{l_{max}}^{\infty} l \frac{d\mu}{dl}\, dl = \frac{2}{\alpha_{23}} \int\limits_{l_{max}}^{\infty} \mu\, dl. \tag{21}$$

FIG. 3



Interpolating between the $\mu \sim l^{-3}$ and the $\mu \sim l^{-4}$ laws, we get as an estimate

$$\theta \sim (1/10\, l_{max}) \sqrt{\hbar |\overline{\omega}| / \alpha_{23}} \tag{22}$$

with $\overline{\omega}$ from Eq. (12). Thus if $\hbar\overline{\omega} \sim 10$ ev, $\alpha_{23} \sim 20$ erg cm^{-2}, and $l_{\max} \sim 5 \times 10^{-5}$ cm we get $\theta \sim 0.1°$.

In our case the contact angle must thus have a finite, but very small, value (in contradistinction to the value $\theta = 0$ for complete wetting and $\theta \sim 1$ for the usual cases of nonwetting). Such a statement has, of course, a really specific meaning only if the thickness of the drop is large compared to the thickness of the film, i.e., if $L\theta \gg l_{\max}$, where L is the size of the drop (Fig. 3).

d) A curve of the type depicted in Fig. 2d corresponds to a film which is not stable in a well-defined range of thicknesses. The straight line BF which cuts off the equal areas BCD and DEF connects the points B and F with the same values of α [for identical μ; this can easily be seen from Eq. (17)]. Stable films correspond to the branches AB and FG; the range CE is completely unstable, and the ranges BC and EF are metastable.

Both limits of the region of instability (the points B and F) correspond in this case to macroscopic film thicknesses. Instability in a range from some macroscopic thickness to a molecular one would correspond to a curve of the type depicted in Fig. 2e. (This curve tends to $-\infty$ as $l \rightarrow 0$, as did the curve of Fig. 2b.) In reality, however, such a curve will most likely lead simply to a case of nonwetting. Indeed, the limit of stability would correspond to such a point on the branch BC that the horizontal intersect would cut off equal areas under the upper and above the lower parts of the curve. The latter area, however, is connected with van der Waals forces and would be small compared with the former one, which is connected with the appreciably larger forces at molecular distances. This means that the surface tension on the whole of the branch BC will be larger than the one corresponding to molecular adsorption at the surface of the substratum, and a film will thus be metastable.

The phenomenon of film instability in well-defined ranges of thickness has been observed by several authors, in particularly clear form by Frumkin, Deryagin and their co-workers.[9,10]

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*Such behavior may occur as a high "bump" on the $\mu(l)$ curve in the molecular region of "thicknesses."

Frumkin[9] had already long ago considered different kinds of $\alpha(l)$ curves (without explicitly distinguishing between absorptive and wetting films) in order to interpret these phenomena phenomenologically. We should like to emphasize here the connection of these curves with the properties of the van der Waals forces, and through them with the spectral properties of the liquid and of the solid substratum.

We note, in particular, that the sign of the function $\mu(l)$ for sufficiently large film thicknesses is determined by the ratio of the electrostatic values ϵ_{10} and ϵ_{30}:* in this region $\mu > 0$ if $\epsilon_{30} > \epsilon_{10}$, and $\mu < 0$ if $\epsilon_{30} < \epsilon_{10}$. The sign of $\mu(l)$, however, in the opposite limiting case of sufficiently small l is the same as the sign of

$$\bar{\omega} = \int_0^\infty \frac{(\varepsilon_3 - 1)(\varepsilon_3 - \varepsilon_1)}{(\varepsilon_3 + 1)(\varepsilon_3 + \varepsilon_1)} d\xi.$$

A violation of the monotonic behavior of $\mu(l)$ in some range of l -values is, generally speaking, connected with the change in sign of the difference $\epsilon_3 - \epsilon_1$ in the wavelength region $\lambda \sim l$.

5. FORCES OF NONELECTROMAGNETIC ORIGIN

We shall estimate the contribution of forces of nonelectromagnetic origin to the chemical potential of a film.

Acoustical fluctuations (in an acoustically nondispersive medium) contribute $\mu_{ac} \sim \hbar u/l^4$ (where u is the sound velocity) to the chemical potential at the absolute zero.† This must be compared 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 $l \ll \lambda\!\!\!^{-}_0$ ($\lambda\!\!\!^{-}_0$ is a characteristic wavelength in the spectrum of the absorbing body). It is clear that $\mu_{ac} \ll \mu_{e.m.}$ for all distances large compared to atomic dimensions, and this precisely is the only region where the whole theory given here is applicable.

At nonzero temperatures the opposite limiting case, where the influence of the temperature is the dominant factor, holds, generally speaking, for μ_{ac}. The appropriate criterion is the ratio $l\kappa T/\hbar u$ (where κ is Boltzmann's constant); if this ratio is large $\mu_{ac} \sim \kappa T/l^3$ [similar to Eq. (5.5) in reference 1]. * This quantity is compared with $\mu_{e.m.}$ only at distances $l \sim \hbar c/\kappa T$, which are so large that μ becomes very small in any case.

The same is true of the contribution of the surface oscillations. The dependence of the frequency on the wave vector for capillary oscillations on the surface of a liquid layer of thickness l is given by the well-known formula

$$\omega^2 = (\alpha k^3/\rho) \tanh kl,$$

where α is the surface tension (see, e.g., reference 13, Sec. 61). On a deep liquid ($l \to \infty$) we have $\omega^2 = \alpha k^3/\rho$. Evaluating the energy of the zero-point oscillations (subtracting the same energy for $l \to \infty$) we find that at the absolute zero the corresponding contribution to the chemical potential is

$$\mu_{surf} \sim \hbar \sqrt{\alpha/\rho}\, l^{-7/2}.$$

In actual fact, however, the opposite limiting case, is realized, when $(\hbar/\kappa T)\sqrt{\alpha/\rho}\; l^{-3/2} \ll 1$, i.e., the condition for classical physics is satisfied. Calculation by the general rules of statistics leads then, of course, to a contribution of the same order of magnitude, $\mu_{surf} \sim \kappa T/l^3$, as in the acoustical case.†

To explain the properties of helium films several authors also introduced mechanisms connected with the inhomogeneity of the density distribution of the liquid along the thickness of the film. In its roughest form, the corresponding calculation is performed by considering the helium in the film to be a perfect gas, with particles whose wave functions possess nodes at the wall and at the film surface. Such a model leads to a strongly inhomogeneous density distribution with a maximum at the center and to a contribution to the chemical potential μ proportional to l^{-2}. Such a consideration is, however, totally unacceptable (as was already stated by Mott[14]), since

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*Provided that no important dispersion of the dielectric constant occurs at very long wavelengths (as, for instance, in water).

†This expression is analagous to the expression $\mu \sim \hbar c/l^4$ for the electromagnetic part (in a nondispersive medium). One can obtain it, for instance, by evaluating the energy of the acoustical zero-point vibrations in the gap (of width l) in a way similar to the one used by Casimir[11] for the electromagnetic zero-point vibrations. We note that the result of Atkins[12] who obtained for μ_{ac} a different dependence on the film thickness ($\sim l^{-2}$) is due to an incorrect way of cutting off the divergent integral.

*The condition $l\kappa T/\hbar u \gg 1$, like the condition $l\kappa T/\hbar c \gg 1$ in the electromagnetic case, is essentially the condition for classical physics to hold ($\hbar\omega \ll \kappa T$ with $\omega \sim l/u$ or $\omega \sim l/c$). It is thus clear a priori that the corresponding contribution to μ cannot contain $\hbar$ and the expression $\kappa T/l^3$ follows therefore from dimensional considerations.

†We always give estimates without numerical factors, but one must bear in mind that in reality the expressions for μ_{surf} and μ_{ac} still contain (as is shown by a more detailed analysis) small numerical coefficients, as do the expressions for the electromagnetic part $\mu_{e.m.}$. The occurrence of relatively small numerical coefficients is generally a feature of the theory given here.

the interaction between the atoms will, in actual fact, smooth out the wave function of the ground state of the system, and the inhomogeneity in the density will extend (into the liquid) only over distances of the order of interatomic ones. The contribution to the chemical potential connected with this inhomogeneity decreases with the film thickness according to an exponential law.

The contribution connected with the specific properties (superfluidity) of helium below the λ point decreases according to the same law. Only in the immediate vicinity of the λ point, where the density of the superfluid component is very small, will the inhomogeneity in the distribution of the latter lead to an appreciable effect (see reference 15). At a distance of about 0.01° from the λ point, however, the decrement of the exponential decrease becomes comparable with interatomic distances. On the other hand, the result of Franchetti,[16] who obtained a contribution to the chemical potential proportional to l^{-2}, is due to the fact that the model he used of noninteracting elementary excitations in helium was inadequate.

6. THE LIQUID HELIUM FILM

We shall consider separately liquid helium films to which a great deal of literature has been devoted.

The general Eq. (7) can be appreciably simplified for helium films if one uses the fact that the dielectric constant of liquid helium is very nearly equal to unity, i.e., that the difference $\epsilon_3(i\xi) - 1$ is small. Performing the appropriate expansion in the integrand of (7) we get

$$\mu(l) = -\frac{\hbar}{8\pi^2 c^3}\int_0^\infty\int_1^\infty \left\{\frac{s_1 - p}{s_1 + p} + (2p^2 - 1)\frac{p\varepsilon_1 - s_1}{p\varepsilon_1 + s_1}\right\}$$

$$\times (\varepsilon_3 - 1)\xi^3 e^{-2p\xi l/c}dp\, d\xi,$$

$$s_1 = \sqrt{\varepsilon_1(i\xi) - 1 + p^2}. \tag{23}$$

The calculation, however, even with this simplified formula, is made difficult by the necessity to know the form of the function $\epsilon(i\xi)$ for liquid helium and for the solid wall in a wide range of frequencies, particularly in the extreme ultraviolet region. In the integral (23) the region of wavelengths $\lambdabar \sim l$ is the important one, and actual thicknesses of the helium film are of the order of 10^{-6} cm.

A reasonable approximation is a further simplification of Eq. (23), based on the fact that the main absorption region of helium lies in the extreme ultraviolet, whereas the main absorption of the solid wall (metals, quartz) is at appreciably lower frequencies. In other words, we assume that the function $\epsilon_3(i\xi)$ is practically the same as the electrostatic value ϵ_{30} in the whole range of ξ in which the difference $\epsilon_1(i\xi) - 1$ [and with it the whole integrand in Eq. (23)] is not yet too small. One can then remove $\epsilon_3 - 1$ from under the integral sign and proceed with the remaining integral as in the limiting case of small thicknesses l (l is small compared with the wavelengths $\lambdabar_0$ in the main absorption regions of the solid body). Thus, introducing the integration variable $x = 2p\xi l/c$ instead of p and taking into account that the values of $x \sim 1$ correspond to large values of p, we replace the curly brackets in Eq. (23) by $2p^2(\epsilon_1 - 1)/(\epsilon_1 + 1)$, and obtain as a result

$$\mu(l) = -\hbar\bar{\omega}(\varepsilon_{30} - 1)/16\pi^2 l^3, \tag{24}$$

where we have introduced the quantity

$$\bar{\omega} = \int_0^\infty \frac{\varepsilon_1(i\xi) - 1}{\varepsilon_1(i\xi) + 1}\, d\xi, \tag{25}$$

which is some average frequency that is characteristic of the given solid body.

We note that the function $[\epsilon(\omega) - 1]/[\epsilon(\omega) + 1]$ possesses in the upper half-plane of the complex variable ω the same analytical properties as the function $\epsilon(\omega) - 1$. This is sufficient to let us apply to it the same formula for the transformation of an integral over the imaginary axis to an integral along the real axis as was valid for the function $\epsilon(\omega) - 1$ (see reference 5, Sec. 62). We can thus write the integral in the form

$$\bar{\omega} = \int_0^\infty \operatorname{Im}\frac{\varepsilon_1(\omega) - 1}{\varepsilon_1(\omega) + 1}\, d\omega = \int_0^\infty \frac{2\varepsilon_1''(\omega)\, d\omega}{[\varepsilon_1'(\omega) + 1]^2 + [\varepsilon_1''(\omega)]^2}, \tag{26}$$

where $\epsilon'(\omega)$ and $\epsilon''(\omega)$ are the real and imaginary parts of the dielectric constant for real values of the frequency; i.e., they are quantities directly measured experimentally (one can transform the integral $\bar{\omega}$ in Eq. (12) in a similar way).

One must thus expect a $\mu(l) \sim 1/l^3$ dependence for the actually observed thicknesses of the helium film and hence a $l \sim z^{-1/3}$ form of the film profile. To evaluate the coefficient in this law we must, however, know the optical properties of the solid body (wall) in a wide range of frequencies. We should like to emphasize that an evaluation of this coefficient on the basis of data on the interaction of separate helium atoms with a solid body is in any case inadmissible.*

We shall also write down an expression for $\mu(l)$ for "large" film thicknesses ($l \gg \lambdabar_0$). The

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*We think, in particular, that the estimates given by Schiff[17] cannot be trusted at all.

corresponding transition in Eq. (23) occurs by introducing the variable $x = 2p\xi l/c$ instead of ξ and replacing ϵ_1 by ϵ_{10}. The integration both over dx and over dp is performed analytically, and as a result we get

$$\mu(l) = -3\hbar c(\varepsilon_{30} - 1) f(\varepsilon_{10}) / 32\pi^2 l^4,$$

$$f(\varepsilon) = \frac{1}{3} + \varepsilon + \frac{4 - \sqrt{\varepsilon}(\varepsilon + 1)}{2(\varepsilon - 1)} - \frac{\sinh^{-1}\sqrt{\varepsilon - 1}}{2(\varepsilon - 1)^{3/2}}[1 + \varepsilon + 2\varepsilon(\varepsilon - 1)^2] + \frac{\varepsilon^2}{\sqrt{\varepsilon + 1}}\left(\sinh^{-1}\sqrt{\varepsilon} - \sinh^{-1}\frac{1}{\sqrt{\varepsilon}}\right). \tag{27}$$

For a metal $\epsilon_{10} \to \infty$ and $f(\infty) = 1$. For quartz, which has a wide band of transparency (from $\sim 0.15\,\mu$ to several μ), it is reasonable to consider the case when the thickness l falls in that range of lengths. The corresponding dependence of μ on l is then determined by the same Eq. (27) in which, however, one must understand by ϵ_{10} not the electrostatic, but the optical value ϵ_1, i.e., the square of the refractive index in the optical range of transparency (compare the note added in proof in reference 1).

Expressions (23), (24), and (27) do not contain the temperature; i.e., they refer to the absolute zero. Temperature corrections, however, must be relatively small, and there is no reason to expect any important change in the form of the film profile when the temperature is changed, in particular, below and above the λ point (outside its immediate vicinity).

The difficulties of an experimental determination of the thickness and the form of helium film profile under conditions which are sufficiently close to ideal conditions of thermal equilibrium are very great, and only in very recent times have they been overcome to a sufficient extent to permit the results obtained (in the helium II region) to be considered at all trustworthy (see the surveys by Jackson and Grimes,[18] and Atkins[19]).

As was already mentioned, there are no physical grounds whatever to expect a film profile of the form $\rho gz = a/l^3 + b/l^2$.

Anderson, Liebenberg, and Dillinger[20] state in a recent communication that data obtained by them on the thickness of a helium film on a steel surface (up to a height of 40 cm) are satisfactorily described by a law of the form $\rho gz = a/l^3$ with a constant $a \approx 3.4 \times 10^{-15}$ erg. Comparing this value with the coefficient of l^{-3} in Eq. (24) (inserting $\epsilon_{30} - 1 = 0.057$) we get $\hbar\overline{\omega} \sim 6$ ev. The data of Jackson, Ham, and Grimes[21] lead to approximately the same value ($\hbar\overline{\omega} \sim 7.5$ ev). This value is reasonable for a metal (steel).

The coefficients in Eqs. (24) and (27) (with $\epsilon_{10} \to \infty$) become equal for $l = 3c/2\overline{\omega}$, i.e., in the given case for $l \sim 5 \times 10^{-6}$ cm. This means that in the range of film thicknesses (100 – 400 A) which were experimentally observed, we are near the region where the transition from the l^{-3} to the l^{-4} law takes place.

In conclusion we express our sincere thanks to Academician L. D. Landau for a discussion of the problems considered here. We are also grateful to Professor B. V. Deryagin for informing us of his studies of films.

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