CALCULATION OF INTERMOLECULAR INTERACTION FORCES BETWEEN BODIES SEPARATED BY A FILM OF A STRONG ELECTROLYTE SOLUTION

V. N. GORELKIN and V. P. SMILGA

A theory of intermolecular interactions [1-5] is generalized to the case when the medium separating the interacting bodies has spatial dispersion. An expression is obtained for the force of interaction. A calculation of this force is made for the special case when the gap between the interacting bodies is filled with a solution of a strong electrolyte. The results of this calculation show that when the thickness of the film is greater than the Debye length, the component of the intermolecular force due to the interaction at zero frequency is strongly screened. Estimates for real systems show that this effect may result in a considerable weakening of the intermolecular interactions over distances of the order of 10^{-5}—10^{-4} cm.

1. A general theory of intermolecular interactions (van der Waals forces) between condensed bodies separated by a narrow gap was developed by Lifshitz,[1] and by Dzyaloshinskiĭ, Lifshitz, and Pitaevskiĭ,[2,3] (see also[4-6]). However, these treatments were limited to the case when the gap is filled with a dielectric whose permittivity does not exhibit spatial dispersion. Nevertheless, in a wide range of problems encountered in the physical chemistry of solutions, the physics of colloids, and in the problems of stability of thin films it would be of interest to calculate the intermolecular interactions between bodies separated by a film of an electrolyte solution. Consequently, it would be desirable to generalize the theory of intermolecular interactions to the case in which the substance in the gap between the two interacting bodies exhibits spatial dispersion of the permittivity.

2. Let us consider the solution of an electrolyte filling a gap of thickness l between two dielectrics of permittivity $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$. The permittivity of the pure solvent will be denoted by $\epsilon_3(\omega)$. We shall assume the usual (and most interesting from the experimental point of view) configuration when the electrolyte film is in contact with a large volume of the solution (which acts as the thermal reservoir) and the chemical potentials of the components of the solution in the film μ_a are governed by the corresponding chemical potentials in the thermal reservoir. Obviously, in this case it is most convenient to use the thermodynamic potential Ω.

We shall calculate the intermolecular interaction force on the basis of an expression for the variation of Ω, which is obtained in[2,3,5] for the case when the permittivity of the film exhibits no spatial dispersion. Trivial generalization to our case gives

$$\delta\Omega = \delta\Omega_0 - \frac{T}{8\pi} \sum_{\omega_n=-\infty}^{\infty} \frac{\omega_n^2}{c^2} \iint \delta\varepsilon_{ik}(\mathbf{r}, \mathbf{r}'; i|\omega_n|, l) \mathscr{D}_{ik}(\mathbf{r}, \mathbf{r}', \omega_n) \, d\mathbf{r} \, d\mathbf{r}'. \quad (1)$$

Here, Ω_0 is that part of the thermodynamic potential of the system which is not associated with the long-wavelength electromagnetic field; $\mathscr{D}_{ik}(\mathbf{r}, \mathbf{r}', \omega_n)$ represents the temperature Green's functions; $\omega_n = 2\pi Tn/\hbar$; $\epsilon_{ik}(\mathbf{r}, \mathbf{r}', i|\omega_n|)$ is the permittivity tensor.

As is known,[5] Eq. (1) is derived on the assumption that the momentum transfer in the scattering is small.

In our case, the usual condition which postulates that the second term in Eq. (1) describes the long-wavelength part of the field of transverse photons is supplemented by the requirement that the Debye parameter for the classical plasma in the electrolyte is small and, consequently, the whole treatment will be valid only for the Debye plasma.

The force acting on the boundaries of the film at $x = 0$ and $x = l$ (the force is taken per unit area) is given by the formula

$$F = -\frac{1}{S} \left(\frac{\partial\Omega}{\partial l} \right)_{T, \{\mu_a\}}. \quad (2)$$

The electromagnetic properties of the electrolyte solution are described by its permittivity tensor and we shall find it convenient to separate from the tensor ϵ_{ik} the term which is associated solely with the spatial dispersion:[1)]

$$\varepsilon_{ik}(\mathbf{r}, \mathbf{r}'; i|\omega_n|, l) = \varepsilon_{ik}{}^*(x, l, i|\omega_n|)\delta(\mathbf{r} - \mathbf{r}') + \varepsilon_{ik}{}^{**}(\mathbf{r}, \mathbf{r}', i|\omega_n|, l).$$

We may assume that the tensor $\epsilon_{ik}(\mathbf{r}, \mathbf{r}', i|\omega_n|, l)$ describes the medium everywhere and that outside the gap $\epsilon_{ik}^*(x, l; i|\omega_n|)$ "degenerates into a scalar" and becomes identical with $\epsilon_1(i|\omega_n|)$ or $\epsilon_2(i|\omega_n|)$, whereas $\epsilon_{ik}^*(\mathbf{r}, \mathbf{r}', i|\omega_n|)$ is identically equal to zero if just one of the coordinates extends into a external region. We note that outside the gap ϵ_{ik}^* is not identical with $\epsilon_3(i|\omega_n|)$.

3. We shall now calculate the Fourier components $\epsilon_{ik}(\mathbf{r}, \mathbf{r}', \omega, l)$ of the tensor operator of the permittivity for an electrolyte solution in the gap.

At field frequencies lower than the effective frequencies of collisions in the solution the motion of ions can be described in a natural manner by the diffusion approximation. Then, the total current is

$$\mathbf{j}(\mathbf{r}, t) = \sum_a \mathbf{j}_a(\mathbf{r}, t),$$

[1)]Obviously, this division of the permittivity tensor into two parts does not restrict the generality of the approach if the medium being considered does not have any exotic properties such as absence of spatial dispersion along some particular direction.

and the currents of ions of any given species satisfy the standard equation

$$j_n(\mathbf{r}, t) = \sigma_a \mathbf{E}(\mathbf{r}, t) - z_a e D_a \operatorname{grad} n_a(\mathbf{r}, t). \tag{4}$$

Here, σ_a, D_a, $z_a e$, and n_a are, respectively, the electrical conductivity, the diffusion coefficient, the charge, and the concentration of particles of type a. The diffusion coefficient satisfies the well-known Einstein relationship

$$D_a = 1 / \varkappa_a^2 \tau_a. \tag{5}$$

Here, $\tau_a = \varepsilon_3(\omega)/4\pi\sigma_a$ is the partial relaxation time of the field and $\varkappa_a$ is the reciprocal of the partial Debye length:

$$\varkappa_a^2 = 4\pi z_a^2 e^2 n_a / \varepsilon_3(\omega) T.$$

The corresponding quantities for the electrolyte solution are given by

$$\varkappa^2 = \sum_a \varkappa_a^2, \quad \sigma = \sum_a \sigma_a, \quad \frac{1}{\tau} = \sum_a \frac{1}{\tau_a}.$$

We shall now consider the case when the boundaries of the film are not charged. In this case the concentration of the electrolyte in the film varies slowly with the coordinate x,

$$\frac{l \operatorname{grad} n_a(x)}{n_a(l/2)} \ll 1,$$

and we may assume that the conductivity is constant across the gap. On the other hand, since we are interested in fluctuation fields, it follows that $\Delta n(t) \ll \overline{n(t)}$, and, therefore, conductivity may be assumed to be independent of time.

If Eq. (4) is Fourier-transformed with respect to t, y, and z, we can easily find the conduction current in the gap and then determine the permittivity tensor in the standard way. If we assume that the polarization of the solvent is practically independent of the behavior of the Debye plasma because the concentration of ions is low, we find that the Fourier components of the permittivity tensor are given by

$$\varepsilon_{xx}^{*}(x, \omega, l) = \varepsilon_3(\omega), \quad \varepsilon_{ij}^{*}(x, \omega, l) = 0, \quad i \neq j,$$

$$\varepsilon_{yy}^{*}(x, \omega, l) = \varepsilon_3(\omega)(1 + i / \omega\tau), \quad \varepsilon_{zz}^{*}(x, \omega, l) = \varepsilon_3(\omega)(1 + i / \omega\tau),$$

$$\ddot{\varepsilon}_{xx}(x, x', \omega, l) = -\frac{2\pi i}{\omega} \sum_a \sigma_a q_a \mathscr{G}(x, x', q_a, l),$$

$$\ddot{\varepsilon}_{yy}(x, x', \omega, l) = -\frac{2\pi k_\perp^2 i}{\omega} \sum_a \frac{\sigma_a}{q_a^3} \left[\frac{\partial^2 \mathscr{G}(x\, x', q_a, l)}{\partial x\, \partial x'} + 2 q_a \delta(x - x') \right],$$

$$\tag{6}$$

$$\ddot{\varepsilon}_{xy}(x, x', \omega, l) = -\frac{2\pi k_\perp}{\omega} \sum_a \frac{\sigma_a}{q_a} \frac{\partial \mathscr{G}(x, x', q_a, l)}{\partial x'}$$

$$\ddot{\varepsilon}_{yx}(x, x', \omega, l) = \frac{2\pi k_\perp}{\omega} \sum_a \frac{\sigma_a}{q_a} \frac{\partial \mathscr{G}(x, x'\, q_a, l)}{\partial x},$$

$$\ddot{\varepsilon}_{zz}(x, x', \omega, l) = 0.$$

Here,

$$q_a = [k_\perp^2 - i\omega\tau_n\varkappa_a^2]^{1/2}, \quad \mathbf{k}_\perp = \mathbf{k}k_z + \mathbf{j}k_y,$$

$$\mathscr{G}(x, x', q_a, l) = \frac{\operatorname{ch}[l - (x + x')]q_a - \operatorname{ch}[l - |x - x'|]q_a}{\operatorname{sh} l q_a}.$$

The y axis is directed along the vector $\mathbf{k}_\perp$.

4. We can now calculate the intermolecular interaction force. Using Eq. (3), we can rewrite Eq. (2) in the form

$$F = -\frac{1}{S}\left(\frac{\partial \Omega_0}{\partial l}\right)_{T,\{\mu_a\}} + \frac{T}{8\pi S} \sum_{n=-\infty}^{\infty} \frac{\omega_n^2}{c^2} \Big[\int_S \int_{l-\delta}^{l+\delta} \frac{\partial \varepsilon_{ii}^{*}(x, l, i\omega_n)}{\partial l} \mathscr{D}_{ii}(\mathbf{r}, \mathbf{r}', \omega_n) d\mathbf{r}$$

$$+ \int_S \int_0^{l-\delta} \int_S \int_0^{l-\delta} \frac{\partial \varepsilon_{ik}^{..}(\mathbf{r}, \mathbf{r}', i\omega_n, l)}{\partial l} \mathscr{D}_{ik}(\mathbf{r}, \mathbf{r}', \omega_n) d\mathbf{r}\, d\mathbf{r}'$$

$$+ \int_S \int_{l-\delta}^{l+\delta} \int_S \int_{l-\delta}^{l+\delta} \frac{\partial \varepsilon_{ik}^{..}(\mathbf{r}, \mathbf{r}', i\omega_n, l)}{\partial l} \mathscr{D}_{ik}(\mathbf{r}, \mathbf{r}', \omega_n) d\mathbf{r}\, d\mathbf{r}'$$

$$+ 2 \int_S \int_{l-\delta}^{l+\delta} \int_S \int_0^{l-\delta} \frac{\partial \varepsilon_{ik}^{*}(\mathbf{r}, \mathbf{r}', i\omega_n, l)}{\partial l} \mathscr{D}_{ik}(\mathbf{r}, \mathbf{r}', \omega_n) d\mathbf{r}\, d\mathbf{r}' \Big]. \tag{7}$$

The above formula takes into account the fact that the properties of the functions

$$\varepsilon_{ik}^{*}(\mathbf{r}, \mathbf{r}', i\omega_n, l), \quad \varepsilon_{ik}^{..}(\mathbf{r}, \mathbf{r}', i\omega_n, l), \quad \mathscr{D}_{ik}(\mathbf{r}, \mathbf{r}', \omega_n, l)$$

change drastically in a boundary layer of thickness δ, which is of the order of the atomic distance. Obviously, in the boundary layer the properties of all the functions of interest to us are governed by the dependence on the argument $(l - x)$, which is the distance from the boundary. Bearing this point in mind, the differentiation with respect to l in the surface layer can be replaced with the differentiation with respect to x. Dropping the terms containing small quantities of the order of δ/l and using the expressions in Eq. (6), we can rewrite formula (7) in the form

$$F = -\frac{1}{S}\left(\frac{\partial \Omega_0}{\partial l}\right)_{T,\{\mu_a\}} - \frac{T}{8\pi S} \sum_{n=-\infty}^{\infty} \frac{\omega_n^2}{c^2} \Big[\int_S \int_{l-\delta}^{l+\delta} \frac{\partial \varepsilon_{ii}^{*}(x, l, i\omega_n)}{\partial x} \mathscr{D}_{ii}(\mathbf{r}, \mathbf{r}', \omega_n) d\mathbf{r}$$

$$- \int_S \int_0^{l-\delta} \int_S \int_0^{l-\delta} \frac{\partial \varepsilon_{ik}^{..}(\mathbf{r}, \mathbf{r}', l, i\omega_n)}{\partial l} \mathscr{D}_{ik}(\mathbf{r}, \mathbf{r}', \omega_n) d\mathbf{r}\, d\mathbf{r}'$$

$$+ 2 \int_S \int_{l-\delta}^{l+\delta} \int_S \int_0^{l-\delta} \frac{\partial \varepsilon_{ik}^{..}(\mathbf{r}, \mathbf{r}', l, i\omega_n)}{\partial x} \mathscr{D}_{ik}(\mathbf{r}, \mathbf{r}', \omega_n) d\mathbf{r}\, d\mathbf{r}' \Big]. \tag{8}$$

We now have to determine the nature of the behavior of the Green's tensor as a function of x in a transition layer of thickness 2δ. This problem reduces to a rigorous allowance for the boundary conditions in the Maxwell equations. Applying the standard procedures we find that in the transition region $\mathscr{D}_{yy}(\mathbf{r}, \mathbf{r}', \omega_n)$ and $\mathscr{D}_{zz}(\mathbf{r}, \mathbf{r}', \omega_n)$ are constant whereas $\mathscr{D}_{xx}(\mathbf{r}, \mathbf{r}', \omega_n)$ and $\mathscr{D}_{xy}(\mathbf{r}, \mathbf{r}', \omega_n)$ satisfy the equations

$$\mathscr{D}_{xx}(x, x', \omega_n) = \frac{\varepsilon_{xx}^2(l-\delta)\mathscr{D}_{xx}(l-\delta, l-\delta+0, \omega_n)}{\varepsilon_{xx}^{*}(x)\varepsilon_{xx}^{*}(x')},$$

$$\mathscr{D}_{xy}(x, x', \omega_n) = \frac{\varepsilon_{xx}^2(l-\delta)\mathscr{D}_{xy}(l-\delta, l-\delta+0, \omega_n)}{\varepsilon_{xx}^{*}(x)}.$$

$$\tag{9}$$

Here, $l - \delta < x < x' < l + \delta$.

Using Eqs. (9) and (6) and going over to the Fourier component in Eq. (8), we obtain

$$F = -\frac{1}{S}\left(\frac{\partial \Omega_0}{\partial l}\right)_{T,\{\mu_a\}} - \frac{T}{16\pi^2} \sum_{n=-\infty}^{\infty} \frac{\omega_n^2}{c^2} \cdot$$

$$\times \int_0^\infty k_\perp dk_\perp \Big[(\varepsilon_2 - \varepsilon_l)(\mathscr{D}_{yy}(l-0, l-0, \omega_n, k_\perp) + \mathscr{D}_{zz}(l-0, l-0, \omega_n, k_\perp))$$

$$- \left(\frac{\varepsilon_3^2}{\varepsilon_2} - \varepsilon_3\right)\mathscr{D}_{xx}(l-0, l-0, \omega_n, k_\perp) - \int_0^l \int_0^l \frac{\partial \varepsilon_{ij}^{..}(x, x', i\omega_n, k_\perp)}{\partial l} \cdot$$

$$\times \mathscr{D}_{ij}(x, x', \omega_n, k_\perp) dx\, dx' - 2 \int_0^l [\varepsilon_{yx}^{..}(l-0, x', i\omega_n, k_\perp)\mathscr{D}_{xy}(x', l-0, \omega_n, k_\perp)$$

$$+ \varepsilon_{yy}^{..}(l-0, x', i\omega_n, k_\perp)\mathscr{D}_{yy}(x', l-0, \omega_n, k_\perp)] dx' \Big]. \tag{10}$$

Here,

$$\varepsilon_l = \varepsilon_3(\omega_n)\left(1 + \sum_a \frac{\varkappa_a^2}{k_\perp^2 + \omega_n^2 \tau_a \varkappa_a^2}\right), \qquad \varepsilon_t = \varepsilon_3(\omega_n)\left(1 + \frac{1}{\omega_n \tau_a}\right)$$

are the longitudinal and transverse components of the permittivity in the bulk of the solution. Since our expressions now contain only smoothly varying functions, we have extended integration to the interval (0, l).

We note that Eq. (10) is derived without any recourse to the diffusion approximation. In fact, the only requirements used are the diagonality of the tensor ε_{ik}^* within the gap and the zero value of the current j_x at the boundary.

For the sake of simplicity the rest of the treatment will be restricted to electrolytes for which either one of the diffusion coefficients is much larger than all the others or the diffusion coefficients of all the ions are approximately equal. Then, using the formulas in Eq. (6) and integrating Eq. (10) by parts, we find that basically simple procedures lead to

$$F = -\frac{1}{S}\left(\frac{\partial \Omega_0}{\partial l}\right)_{T,\{\mu_a\}} - \frac{T}{16\pi^2}\sum_{n=-\infty}^{\infty}\frac{\omega_n^2}{c^2}\int k_\perp dk_\perp \Big\{(\varepsilon_2 - \varepsilon_l)$$

$$\times \mathscr{D}_{yy}(l-0, l-0) + (\varepsilon_2 - \varepsilon_l)\mathscr{D}_{zz}(l-0, l-0)$$

$$-\frac{\varepsilon_3}{\varepsilon_2}(\varepsilon_3 - \varepsilon_2)\mathscr{D}_{xx}(l-0, l-0) - \int_0^l\int_0^l \frac{\partial \varepsilon_{xx}''(x, x')}{\partial l} \tag{11}$$

$$\times\left[\mathscr{D}_{xx}(x, x') + \frac{2ik_\perp}{q^2}\frac{\partial\mathscr{D}_{yx}(xx')}{\partial x'} + \frac{k_\perp^2}{q^4}\frac{\partial^2\mathscr{D}_{yy}(xx')}{\partial x \partial x'}\right] dx\, dx'\Big\}.$$

If the spatial dispersion is absent, the double integral vanishes and Eq. (11) reduces to the well-known result[3] which is given above in a somewhat modified form.

If we now solve the electrodynamic problem, find the Green's tensor, and substitute the results into Eq. (11), we obtain a general expression for the interaction force. The Green's functions can be determined relatively easily both in our problem and in the opposite limiting case of a collisionless plasma in the gap but the final formulas are quite cumbersome and we shall not give them here.

It follows from physical considerations that at high frequencies the effect of the spatial dispersion should disappear. The characteristic parameter is obviously the product $\tau\omega$. Since the relaxation time τ of the Debye solutions of electrolytes is of the order of $10^{-6}-10^{-8}$ sec and at room temperatures $\omega_1 = 2\pi T/\hbar \approx 2.5 \times 10^{14}$ sec^{-1}, we find that even at the first frequency $\tau\omega_1 \sim 10^6 \gg 1$ and the effects associated with the spatial dispersion disappear.

The spatial dispersion can also have a specific effect associated with the influence of the boundaries and this effect may be manifested if a particle in the bulk of the gap "feels" the interaction at the boundaries. An analysis of this effect shows that it is important only if the condition $Te^2/\hbar D^2 \ll 1$ is satisfied, which is not true of electrolyte solutions. Therefore, all the terms, beginning from the first frequency, should be of the same form as in the absence of spatial dispersion.

However, the zero-frequency term differs considerably from the corresponding expression obtained without allowance for spatial dispersion. If we substitute the zero-frequency Green's function into Eq. (11) (obviously,

this yields the result of the electrostatic problem, as shown in[7]), the double integral vanishes, which is quite expected because when $\omega = 0$ the force is governed only by the electrostatic component of the stress tensor, which is included in the single integral. This integral also simplifies considerably in the static case so that finally Eq. (11) becomes

$$F = P_\infty - \frac{T}{16\pi l^3}\int_{2\varkappa l}^{\infty} x^2\left[\frac{(\varepsilon_{30} + \varepsilon_{10}R)(\varepsilon_{30} + \varepsilon_{20}R)}{(\varepsilon_{30} - \varepsilon_{10}R)(\varepsilon_{30} - \varepsilon_{20}R)}e^x - 1\right]^{-1}dx$$

$$+\frac{T}{\pi}\sum_{n=1}^{\infty}\int k_\perp dk_\perp W_3\left(\frac{1}{\Delta} + \frac{1}{\overline{\Delta}}\right), \qquad R = \left[1 - \left(\frac{2\varkappa l}{x}\right)^2\right]^{1/2}. \tag{12}$$

Here, ε_{10}, ε_{20}, and ε_{30} are the static values of the permittivity whereas Δ and $\overline{\Delta}$ are given by the formulas[2,3,5]

$$\Delta = 1 - e^{2W_3 l}\frac{(W_1 + W_3)(W_2 + W_3)}{(W_1 - W_3)(W_2 - W_3)}, \tag{13}$$

$$\overline{\Delta} = 1 - e^{2W_3 l}\frac{(\varepsilon_1 W_3 + \varepsilon_3 W_1)(\varepsilon_2 W_3 + \varepsilon_3 W_2)}{(\varepsilon_1 W_3 - \varepsilon_3 W_1)(\varepsilon_2 W_3 - \varepsilon_3 W_3)}, \tag{14}$$

where $W_i = [\varepsilon_i\omega_n^2 + k^2]^{1/2}$.

It is known[1] that in the absence of spatial dispersion the zero-frequency term is of the form

$$\Delta F_{\omega=0} = -\frac{T}{16\pi l^3}\int_0^{\infty} x^2\left[\frac{(\varepsilon_{30} + \varepsilon_{10})(\varepsilon_{30} + \varepsilon_{20})}{(\varepsilon_{30} - \varepsilon_{10})(\varepsilon_{30} - \varepsilon_{20})}e^x - 1\right]^{-1}dx. \tag{15}$$

We can see that the main difference from our case lies in the change in the lower limit of integration. In fact, the integral in Eq. (15) can be described approximately as an exponentially decreasing function of the lower limit.

It is worth noting that the restrictions which we have imposed on the diffusion coefficients of the electrolyte ions in the course of derivation of Eq. (11) are actually of no significance and Eq. (12) is valid in general. This can be seen if only from the fact that the diffusion coefficients do not enter the final expression. It is interesting to note that Eq. (12) is obtained also if the use is made of the collisionless plasma approximation with specular reflection from the walls.

The correction due to the spatial dispersion is particularly simple in the two limiting case $\varepsilon_{10} \sim \varepsilon_{20} \to \infty$ and $\varepsilon_{30} \gg \varepsilon_{10} \sim \varepsilon_{20}$. The first case describes the behavior of a solution film between two metals, whereas the second represents the behavior of a free film of an aqueous solution ($\varepsilon_{30} \approx 0$). In this case, we obtain

$$\Delta F_{\omega=0} = -\frac{T}{16\pi l^3}\int_{2\varkappa l}^{\infty}\frac{x^2 dx}{e^x - 1}. \tag{16}$$

5. Let us now estimate the film thickness at which the correction due to the spatial dispersion of the permittivity becomes important. As pointed out earlier, the influence of the spatial dispersion is manifested, firstly, by the considerable change in $\Delta F_{\omega=0}$ and, secondly, by the appearance of a specific influence of the boundary on the spatial dispersion. The latter is important only for very thin films ($l \sim 10^{-7}$ cm) of special solutions such as those of metals in ammonia for which the diffusion coefficients are $D \sim 10-25$ cm^2/sec.[8]

The zero-frequency correction is important if the condition $2\varkappa l \gg 1$ is satisfied. In practice, the integral is negligible even for $\varkappa l \sim 3-5$. Typical values of $\varkappa$ for aqueous solutions of electrolytes are 10^4 cm$^{-1} < \varkappa$

$< 10^7$ cm^{-1} and the value of $\kappa = 10^4$ cm^{-1} is due to the dissociation of the water molecules at room temperature. Thus, even in electrolyte solutions of moderate concentrations we can expect the term $\Delta F_{\omega = 0}$ to be completely negligible. Therefore, it is obvious that the change in the intermolecular interaction force in electrolyte solutions is significant only over distances for which $\Delta F_{\omega = 0}$ would have played a significant role in the absence of spatial dispersion.

Suitable estimates can be made quite easily using approximate expressions for the force of interaction derived in[1-5]. The results show that for water films the term $\Delta F_{\omega = 0}$ predominates over distances $l \sim 10^{-4}$ cm and can make a contribution of the order of 50% over distances $l \sim 10^{-5}$ cm. The results of direct measurements of the van der Waals forces between solids in air[9,10] are in agreement with this conclusion. In the absence of spatial dispersion the contribution of $\Delta F_{\omega = 0}$ is unimportant over shorter distances and its disappearance in case of solutions of fairly concentrated electrolytes has no influence on the van der Waals interaction force.

6. It is interesting to note that screening of the intermolecular interaction forces at zero frequency can be deduced also from quite different considerations. If we calculate the free energy of a plasma (electrolyte ions) in a thin gap with neutral boundaries, we find—in addition to the usual volume Debye correction—that there is a further correction which gives rise to a disjoining pressure on the walls. It follows from the theory of solutions that the free energy of an electrolyte is an additive term in the total free energy of the system.

The appearance of a disjoining pressure can be interpreted quite clearly in terms of the theory of electrolytic solutions. It is known that the image forces near a neutral boundary of a solution raise the concentration of ions compared with that in the bulk of the solution and this gives rise to an Onsager layer whose presence reduces the surface tension of the electrolyte solution. The disjoining pressure in films of thickness $l \sim \kappa$ is thus the result of overlap of Onsager layers.

This disjoining pressure has been determined in[7] for the two limiting cases $\epsilon_{10} \sim \epsilon_{20} \gg \epsilon_{30}$ and $\epsilon_{30} \gg \epsilon_{10} \sim \epsilon_{20}$. The free energy of an electrolyte was calculated using the method of Bogolyubov correlation functions which made it possible to develop the most consistent approach to the problem. The generalization of the result to arbitrary values of ϵ_{10}, ϵ_{20}, and ϵ_{30} could be made using the framework of the same method. However, the relationship between the results obtained and the intermolecular forces was not determined in[7]. Nevertheless, if we use the formula for the intermolecular forces deduced without allowance for the spatial dispersion[3] and subtract it from the disjoining pressure calculated in[7], we find that the net interaction force

is identical with that derived in the present paper [Eq. (12)] if we ignore small corrections which are due to the spatial dispersion at nonzero frequencies.

Thus, an allowance for the correlation of electrolyte ions in a gap due to the static Coulomb interaction, made within the framework of the self-consistent field method (the first approximation of the Bogolyubov correlation function method), yields simply the correction to the intermolecular interaction force at zero frequency.

The results obtained in the present investigation should be allowed for in dealing with molecular interactions between forces separated by a plasma film. Moreover, they are of some methodological interest because, on the one hand, they reveal a characteristic screening of intermolecular interaction forces by a plasma film and, on the other, they demonstrate the capabilities of the method developed in[1-5].

[1] E. M. Lifshitz, Zh. Eksp. Teor. Fiz. 29, 94 (1955) [Sov. Phys.-JETP 2, 73 (1956)].

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

[3] I. E. Dzyaloshinskiĭ, E. M. Lifshitz, and L. P. Pitaevskiĭ, Zh. Eksp. Teor. Fiz. 37, 229 (1959) [Sov. Phys.-JETP 10, 161 (1960)].

[4] L. D. Landau and E. M. Lifshitz, Elektrodinamika sploshnykh sred, Gostekhizdat, M., 1957 (Electrodynamics of Continuous Media, Pergamon Press, Oxford, 1960).

[5] A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskiĭ, Metody kvantovoĭ teorii polya v statisticheskoĭ fizike, Fizmatgiz, M., 1962 (Methods of Quantum Field Theory in Statistical Physics, Prentice-Hall, Englewood Cliffs, N.J., 1963).

[6] M. L. Levin and S. M. Rytov, Teoriya ravnovesnykh teplovykh fluktuatsiĭ v elektrodinamike (Theory of Equilibrium Thermal Fluctuations in Electrodynamics), Nauka, M., 1967.

[7] V. P. Smilga and V. N. Gorelkin, Issledovaniya v oblasti poverkhnostnykh sil (Investigations of Surface Forces), Nauka, M., 1967, p. 175.

[8] D. K. Belashchenko, Yavleniya perenosa v zhidkikh metallakh i poluprovodnikakh (Transport Phenomena in Liquid Metals and Semiconductors), Atomizdat, M., 1970.

[9] B. V. Deryagin, I. I. Abrikosova, and E. M. Lifshitz, Usp. Fiz. Nauk 64, 493 (1958).

[10] R. H. S. Winterton, Contemp. Phys. 11, 559 (1970).

completely pure sound; its phase velocity differs from s_t by a quantity of the order of ζ).

The TMAR phenomenon can be used for intense excitation of spin waves in antiferromagnets by means of sound waves (for example, by producing elastic deformations in the crystal) or for the intense excitation of sound waves in antiferromagnets by means of an external magnetic field.

The transformation coefficient of a sound wave into a spin wave (defined as the ratio of the energy density of the magnetic field accompanying the spin wave to the energy density of the sound wave) is equal, in order of magnitude, to

$$T_{t \to m} \sim \frac{1}{\eta} \left(\frac{\omega^2}{\omega^2 - v_s^2 k^2} \right)^2 \zeta. \tag{5}$$

The transformation coefficient of a spin wave into a sound wave is equal, in order of magnitude, to

$$T_{m \to e} \sim \frac{1}{\eta} \left(\frac{\omega^2}{\omega^2 - \omega_{t,t}^2} \frac{\omega}{\Delta\omega} \right)^2 \zeta, \tag{6}$$

where $\Delta\omega$ is the width of the ordinary antiferromagnetic resonance. We see that these coefficients increase by a factor of $\zeta^{-1} \sim 10^4 - 10^6$ near the TMAR.

We emphasize that the resonance transformation of waves in the case of TMAR takes place for a width range of frequencies, while in the ordinary case of resonance transformation, the incident wave must be very monochromatic (the condition $(\omega - \omega_S)/\omega_S \sim \sqrt{\zeta}$

must be satisfied). The width of the resonance frequency range is limited only by the magnetic anisotropies of the crystal in the basis plane $\beta_\perp$, $\omega > gM_0(\eta\beta_\perp)^{1/2}$. The temperature of the crystal in this case can differ from its resonance value only by the amount $\Delta T \lesssim \sqrt{\zeta}\eta \, (\partial\eta/\partial T)^{-1}$ ($\sim 0.1-1$ deg).

Apparently the TMAR phenomenon takes place only in the case of weak damping of the waves $\gamma < \sqrt{\zeta}\omega$, where γ is the damping decrement.

[1] J. S. Kouvel and C. C. Hartelius, J. Appl. Phys. 33, 1343S (1962).

[2] V. G. Bar'yakhtar, M. A. Savchenko, and V. V. Tarasenko, Zh. Eksp. Teor. Fiz. 49, 944 (1965) [Soviet Phys.-JETP 22, 657 (1966)].

[3] A. I. Akhiezer, V. G. Bar'yakhtar, and S. V. Peletminskii, Spinovye volny (Spin Waves) (Nauka, 1967).

[4] L. D. Landau and E. M. Lifshitz, Teoriya yprugosti (Theory of Elasticity) (Nauka, 1965).

[5] V. G. Bar'yakhtar and V. V. Gann, Fiz. Tverd. Tela 9, 2052 (1967) [Soviet Phys.-Solid State 9, 1611 (1968)].

Translated by R. T. Beyer
156