Dielectric constant of an inhomogeneous liquid

V. P. Russev and G. I. Salistra

Odessa State University

(Submitted 25 June 1987)
Zh. Eksp. Teor. Fiz. **94**, 195–208 (March 1988)

We obtain the contribution made by the inhomogeneous part of a long-wave fluctuating electromagnetic field to the static dielectric constant (DC) of a liquid bounded by solids. The DC component in question is inhomogeneous, anisotropic, and depends on the size and shape of the inhomogeneity. It is shown for plane films that the difference between their average DC depends on their thicknesses, and that birefringence is possible in sufficiently thick films. Numerical estimates point to the feasibility of observing these effects.

§1. INTRODUCTION

A liquid bounded by a solid (liquid film on the surface of a solid, a liquid in a gap between solids, a liquid with suspended large particles, and others) is inhomogeneous and anisotropic near the surfaces. For macroscopically small inhomogeneity dimensions (e.g., film thickness, gap width, suspended-particle radius, etc.) the thermodynamic properties of the liquid can depend on the shape and dimensions of the inhomogeneity. Among the known sources of such a dependence are Van der Waals forces. We calculate in the present paper, on the basis of the Dzyaloshinskiĭ-Pitaevskiĭ theory,[1] the contribution $\Delta\varepsilon^V$ of these forces to the static dielectric constant (DC) of a bounded liquid and discuss its various manifestations.

The cause of $\Delta\varepsilon^V$ can be easily determined by considering its relation to the inhomogeneous part of the long-wave electromagnetic field present in the system. For a liquid invariant to the inversion transformation, $\Delta\varepsilon^V$ is proportional to the mean square of the indicated field, which depends on the shape and dimensions of the inhomogeneity. The coefficient in this relation is the cubic susceptibility $\chi^{(3)}$ of the homogeneous liquid. The value of $\Delta\varepsilon^V$ is thus determined by the mean square of the fluctuating field of the inhomogeneous part of the photon temperature Green's function in the medium and by the nonlinear properties of the homogeneous liquid.[2]

To take into account the nonlinear properties of a liquid in the general theory of Van der Waals forces, it is necessary to retain, besides the diagrams that contain shaded loops, also diagrams with irreducible polygons. The latter describe scattering of light by light and by other long-wave, primarily hydrydynamic, modes. The interaction of long-wave photons with such modes is a fluctuational analog of polarized and depolarized molecular scattering of light. It will be shown below to result in a much larger contribution to $\Delta\varepsilon^V$ than that of the self-action of long-wave photons. In nonlinear problems it suffices to consider processes of this type only for rigid systems, in which the square of the applied field does not alter their density or optical properties. Real liquids are "softer," and this leads to a noticeably value of $\Delta\varepsilon^V$ and to a possibility of observing effects associated with it.

In §2 we obtain in general form the contribution of the long-range forces to the DC of an arbitrary inhomogeneous liquid. The expressions derived describe the inhomogeneity and the anisotropy of the DC at distances considerably larger than atomic from the boundaries of the inhomogeneities. In §3 we calcate effects determined by the dielectric properties of the film for simple and anisotropic liquids that fill a gap between solids, and for plane films of these liquids on surfaces of solids.

§2. CALCULATION OF THE CONTRIBUTION OF THE VAN DER WAALS FORCES TO THE DC OF AN INHOMOGENEOUS LIQUID

We place an inhomogeneous liquid (with Hamiltonian H) in a weakly inhomogeneous constant electric field of strength $\vec{\mathscr{E}}(\mathbf{r})$. We calculate the polarization $P_i(\mathbf{r},\vec{\mathscr{E}}) = \langle d_i(\mathbf{r})\rangle_{H(\vec{\mathscr{E}})}$ of the system, where $d_i(\mathbf{r})$ is the dipole-moment density operator, and the averaging is over a Gibbs distribution with the Hamiltonian of the system in the external field $H(\vec{\mathscr{E}})$. It is convenient to represent the polarization in the form

$$P_i(\mathbf{r},\vec{\mathscr{E}}) = T\int_0^{1/T} d\tau\,\langle d_i(\mathbf{r},\tau)\rangle_{H(\vec{\mathscr{E}})}, \tag{1}$$

where T is the temperature and

$$d_i(\mathbf{r},\tau) = \exp\{\tau H(\vec{\mathscr{E}})\}d_i(\mathbf{r})\exp\{-\tau H(\vec{\mathscr{E}})\}.$$

We change in (1) to the interaction representation in an external field, and expand in powers of the field. Assuming the inhomogeneous liquid to be symmetric enough, we retain in the expansion only the odd powers of the field:

$$\begin{aligned} P_i(\mathbf{r},\vec{\mathscr{E}}) &= T\int_0^{1/T} d\tau\,d\tau_1 \int d\mathbf{r}_1\,\langle T_\tau \tilde{d}_i(\mathbf{r},\tau)\,\tilde{d}_k(\mathbf{r}_1,\tau_1)\rangle_H\,\mathscr{E}_k(\mathbf{r}_1) \\ &+ \frac{T}{6}\int_0^{1/T} d\tau\,d\tau_1\,d\tau_2\,d\tau_3 \int d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3 \\ &\quad\times\langle\{T_\tau \tilde{d}_i(\mathbf{r},\tau)\,\tilde{d}_k(\mathbf{r}_1,\tau_1)\,\tilde{d}_l(\mathbf{r}_2,\tau_2)\,\tilde{d}_m(\mathbf{r}_3,\tau_3)\}\rangle \\ &\quad\times\mathscr{E}_k(\mathbf{r}_1)\,\mathscr{E}_l(\mathbf{r}_2)\,\mathscr{E}_m(\mathbf{r}_3) + \ldots, \end{aligned} \tag{2}$$

where $\tilde{d}_i(\mathbf{r},\tau) = e^{\tau H}d_i(\mathbf{r})e^{-\tau H}$ and $\langle\{\ldots\}\rangle_H$ is the irreducible part of the mean value of the four operators above.

To transform (2) into a series in the field in the system, we represent the field in the form

$$\begin{aligned} \mathscr{E}_i^M(\mathbf{r}) &= \langle\mathscr{E}_i(\mathbf{r}) + E_i(\mathbf{r})\rangle_{H(\vec{\mathscr{E}})} \\ &= \mathscr{E}_i(\mathbf{r}) + T\int_0^{1/T} d\tau\,\langle E_i(\mathbf{r},\tau)\rangle_{H(\vec{\mathscr{E}})}, \end{aligned} \tag{3}$$

0038-5646/88/030542-08$04.00

where $E_i(\mathbf{r})$ is the electric-field-strength operator. The expansion in terms of the external field takes then the form

$$\mathscr{E}_i^M(\mathbf{r})=\mathscr{E}_i(\mathbf{r})+T\int_0^{1/T} d\tau\, d\tau_1 \int d\mathbf{r}_1 \langle T_\tau \tilde{E}_i(\mathbf{r},\tau)\tilde{d}_k(\mathbf{r}_1,\tau_1)\rangle_H \mathscr{E}_k(\mathbf{r}_1)$$

$$+\frac{T}{6}\int_0^{1/T} d\tau\, d\tau_1\, d\tau_2\, d\tau_3 \int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3 \langle \{T_\tau \tilde{E}_i(\mathbf{r},\tau)\tilde{d}_k(\mathbf{r}_1,\tau_1)$$

$$\times \tilde{d}_l(\mathbf{r}_2,\tau_2)\tilde{d}_m(\mathbf{r}_3,\tau_3)\}\rangle_H \mathscr{E}_k(\mathbf{r}_1)\mathscr{E}_l(\mathbf{r}_2)\mathscr{E}_m(\mathbf{r}_3)+\dots. \tag{4}$$

We separate in H the interaction of the atoms with the long-wave photons:

$$H=H_0-\int d\mathbf{r}\, d_i(\mathbf{r})E_i(\mathbf{r}), \tag{5}$$

and transform in (2) and (4) to the interaction representation in terms of this part of the Hamiltonian. We introduce the notation

$$P_{ik}^{(1)}=\langle T_\tau d_i(\tau,\mathbf{r})\, d_k(\tau_1,\mathbf{r}_1)\rangle_{H_0},$$

$$P_{iklm}^{(3)}=\langle\{T_\tau d_i(\tau,\mathbf{r})\, d_k(\tau_1,\mathbf{r}_1)\, d_l(\tau_2,\mathbf{r}_2)\, d_m(\tau_3,\mathbf{r}_3)\}\rangle_{H_0},$$

$$D_{ik}^{(0)}=\langle T_\tau E_i(\tau,\mathbf{r})E_k(\tau_1,\mathbf{r}_1)\rangle_{H_0}. \tag{6}$$

Here

$$d_i(\tau,\ \mathbf{r})=\exp(\tau H_0)d_i(\mathbf{r})\exp(-\tau H_0). \tag{7}$$

We represent the functions $P^{(1)}$ and $P^{(3)}$ by a shaded loop and rectangle, respectively, and the function $D^{(0)}$ by a thin dashed line. If only the shaded loops and rectangles are used, the polarization and the field in the system are expressed in terms of the three indicated topological elements and the external fields. Eliminating the external field, we find for the polarization an expansion in terms of the field in the system; this expansion can be represented by the series shown schematically in Fig. 1. A solid line with a forked end denotes the field in the system. The operation $T\int d\tau$ is carried out in the free point of the polygon and the integration $\int d\tau \int d\mathbf{r}$ is carried out over the internal points. Partial summation permits a transition to complete Green's functions, represented by the thick dashed lines. The result is shown in Fig. 2.

A similar procedure can be used with account taken of all the powers of the external field and of all the irreducible polygons. It is unnecessary, however, since the nonlinearity is weak and only the contribution of the inhomogeneity to the linear susceptibility is calculated. We therefore confine ourselves hereafter to a linear approximation in the temperature Green's function and to a cubic approximation in the external field, retaining in the expansion only one rectangle. In this approximation,

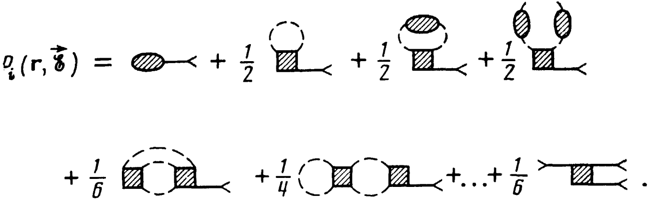

FIG. 1

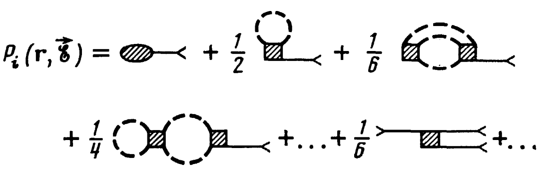

FIG. 2

$$P_i(\mathbf{r},\vec{\mathscr{E}})=T\int d\tau\, d\tau_1\int d\mathbf{r}_1\, P_{ik}^{(1)}(\tau,\tau_1;\mathbf{r},\mathbf{r}_1)\mathscr{E}_k^M(\mathbf{r}_1)$$

$$+\frac{T}{2}\int d\tau\, d\tau_1\, d\tau_2\, d\tau_3\int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3 P_{ikm}(\tau,\tau_1,\tau_2,\tau_3;\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$$

$$\times\Big\{D_{kl}(\tau_1,\tau_2;\mathbf{r}_1,\mathbf{r}_2)\mathscr{E}_m^M(\mathbf{r}_3)+\frac{1}{3}\mathscr{E}_k^M(\mathbf{r}_1)\mathscr{E}_l^M(\mathbf{r}_2)\mathscr{E}_m^M(\mathbf{r}_3)\Big\}. \tag{8}$$

We assume that the thick dashed line in the second term represents the inhomogeneous part of the Green's function. The diagram with the homogeneous part has been transferred to the first term and renormalizes the shaded loop.

The following can be concluded from (8). If the quantities defined in (6) contain no contribution of the inhomogeneity and of the external field, the loop and the rectangle are the true linear and cubic susceptibilities of a homogeneous liquid in the absence of an external field, while the second term of (8) is the sought-for contribution of the inhomogeneity to the DC of the liquid. This, is not so, however, since only the interaction of the atoms with the long-wave photons was separated in (5). The averages over H_0 in (6) contain both the interaction of the latter with other modes that are not of electromagnetic origin and the external field, so that the second term in (8) does not constitute the total $\Delta\varepsilon^V$. This circumstance, naturally, is important only if the nonlinear properties of the medium are taken into account.

To calculate the total contribution of the inhomogeneity to the DC of the liquid, it is necessary to carry out in (6) additional separation of the inhomogeneity and of the external field. This can be done by various methods. For a confined geometry and an inhomogeneous electric field it can be assumed that the system is in local equilibrium and its state at each point is described by a set of thermodynamic variables, viz., scalars (density, temperature, etc.) and tensors (strain, anisotropy, etc.), which depend on the fluctuating and the external fields, and the averaging is over a distribution function that depends on the indicated set of variables. The choice of this set is determined by the phenomenological model of the system. We confine ourselves for the sake of argument to the density and the anisotropy.

We calculate the distribution of these variables in the considered inhomogeneous dielectric in an external field, accurate to terms linear in the inhomogeneous part of the Green's function and quadratic in the field in the system. The operators of the density and of the anisotropy tensor at the point $\mathbf{r}$ will be designated $\rho(\mathbf{r})$ and $\xi_{ik}(\mathbf{r})$. We introduce the functions

$$P_{ik}^{(2)\rho}=\langle T_\tau \Delta\rho(\tau,\mathbf{r})\, d_i(\tau_1,\mathbf{r}_1)\, d_k(\tau_2,\mathbf{r}_2)\rangle_{H_0}, \tag{9}$$

$$P^{(2)t}_{iklm}=\langle T_\tau \xi_{lm}(\tau,\mathbf{r})\, d_i(\tau_1,\mathbf{r}_1)\, d_k(\tau_2,\mathbf{r}_2)\rangle_{H_0}. \qquad (10)$$

We represent them by triangles with indices s and t. In the calculation of the mean values $\langle\rho(\mathbf{r})\rangle_{H(\vec{\mathscr{E}})}$ and $\langle\xi_{ik}(\mathbf{r})\rangle_{H(\vec{\mathscr{E}})}$ we carry out the same operations as in the previous calculation of the polarization. As a result we get

$$\begin{aligned}\langle\rho(\mathbf{r})\rangle_{H(\vec{\mathscr{E}})} &= \rho_0+\frac{T}{2}\int d\tau\, d\tau_1\, d\tau_2 \int d\mathbf{r}_1\, d\mathbf{r}_2 P^{(2)s}_{ik}(\tau,\tau_1,\tau_2;\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)\\ &\times\{D_{ik}(\tau_1,\tau_2;\mathbf{r}_1,\mathbf{r}_2)+\mathscr{E}_i{}^M(\mathbf{r}_1)\mathscr{E}_k{}^M(\mathbf{r}_2)\},\end{aligned} \qquad (11)$$

$$\begin{aligned}\langle\xi_{lm}(\mathbf{r})\rangle_{H(\vec{\mathscr{E}})} &= \frac{T}{2}\int d\tau\, d\tau_1\, d\tau_2 \int d\mathbf{r}_1\, d\mathbf{r}_2 P^{(2)t}_{iklm}(\tau,\tau_1,\tau_2;\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)\\ &\times\{D_{ik}(\tau_1,\tau_2;\mathbf{r}_1,\mathbf{r}_2)+\mathscr{E}_i{}^M(\mathbf{r}_1)\mathscr{E}_k(\mathbf{r}_2)\}.\end{aligned} \qquad (12)$$

The terms containing the Green's function of the homogeneous liquid are referred to the equilibrium values. In (11) we have

$$\Delta\rho(\tau,\mathbf{r})=\rho(\tau,\mathbf{r})-\rho_0$$

and ρ_0 is the density of the homogeneous liquid.

The principal topological elements are now the two triangle types introduced in (9) and (10). In the considered cubic approximation for $\Delta\varepsilon^V$ these triangles do not contain the inhomogeneity and the field, and constitute the susceptibilities of a homogeneous dielectric in the absence of a field. It can be shown[3] that the triangles are the vertices of the temperature Green's function of the photons. For the conserved quantities (density and energy and momentum densities) they reduce to derivatives of the dielectric constant. To calculate them for nonconserved quantities (anisotropy and strain tensors, etc.) we must invoke the phenomenological model of the medium.

The next problem is how to transform from the linear susceptibility of an inhomogeneous medium, defined by (6), to the susceptibility of a homogeneous unbounded liquid. The need for such a procedure is encountered frequently, inasmuch as in nonlinear problems dynamic perturbations always generate inhomogeneities or thermal perturbations.[4] Various methods were developed for operating with local-equilibrium states. We shall use of them,[5,6] in which the nonequilibrium distribution function is replaced by an equilibrium one by changing over to an effective Hamiltonian. The latter contains auxiliary weakly inhomogeneous fields whose potentials meet the condition that the density anisotropy deviations from the equilibrium values, generated by these fields, coincide in the linear approximation with those given in Eqs. (11) and (12).

We express the effective Hamiltonian H_0' in the form

$$H_0'=H_0-\int d\mathbf{r}\,\rho(\mathbf{r})\,\delta\varphi(\mathbf{r})-\int d\mathbf{r}\,\xi_{ik}(\mathbf{r})\,\delta u_{ik}(\mathbf{r}), \qquad (13)$$

where $\delta\varphi(\mathbf{r})$ and $\delta u_{ik}(\mathbf{r})$ are the potentials of the auxiliary field that satisfy the condition indicated above. In an equilibrium state with Hamiltonian H_0' the density and the anisotropy can be represented in the form

$$\begin{aligned}\langle\rho(\mathbf{r})\rangle_{H_0'} &= \rho_0+\beta_T\,\delta\varphi(\mathbf{r}),\\ \langle\xi_{ik}(\mathbf{r})\rangle_{H_0} &= \beta_{iklm}\,\delta u_{lm}(\mathbf{r}),\end{aligned} \qquad (14)$$

where β_T and β_{iklm} are the static density-density and anisotropy-anisotropy response functions with spatial dispersion neglected. Equating the corresponding expressions in (11), (12), and (14) we obtain the potentials of the auxiliary fields:

$$\begin{aligned}\delta\varphi(\mathbf{r}) &= \frac{T}{2}\beta_T{}^{-1}\int d\tau\, d\tau_1\, d\tau_2\int d\mathbf{r}_1\, d\mathbf{r}_2 P^{(2)s}_{ik}(\tau,\tau_1,\tau_2;\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)\\ &\times\{D_{ik}(\tau_1,\tau_2;\mathbf{r}_1,\mathbf{r}_2)+\mathscr{E}_i{}^M(\mathbf{r}_1)\mathscr{E}_k{}^M(\mathbf{r}_2)\},\end{aligned} \qquad (15)$$

$$\begin{aligned}\delta u_{ik}(\mathbf{r}) &= \frac{T}{2}\beta^{-1}_{iklm}P^{(2)t}_{iklm}(\tau,\tau_1,\tau_2;\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)\\ &\times\{D_{ik}(\tau_1,\tau_2;\mathbf{r}_1,\mathbf{r}_2)+\mathscr{E}_i{}^M(\mathbf{r}_1)\mathscr{E}_k{}^M(\mathbf{r}_2)\};\end{aligned} \qquad (16)$$

Eqs. (13) together with (15) and (16) define uniquely the effective Hamiltonian.

A shaded loop is an equilibrium average over a system with Hamiltonian H_0'. We transform in it to the interaction representation with respect to the auxiliary fields. In the first approximation we obtain

$$\begin{aligned}P^{(1)}_{ik} &= \langle T_\tau d_i(\mathbf{r},\tau)\, d_k(\mathbf{r}_1,\tau_1)\rangle_{H_0}\\ &+\int_0^{1/T} d\tau_2\int d\mathbf{r}_2\langle T_\tau d_i(\mathbf{r},\tau)\, d_k(\mathbf{r}_1,\tau_1)\\ &\times\Delta\rho(\mathbf{r}_2,\tau_2)\rangle_{H_0}\delta\varphi(\mathbf{r}_2)\\ &+\int_0^{1/T} d\tau_2\int d\mathbf{r}_2\langle T_\tau d_i(\mathbf{r},\tau)\, d_k(\mathbf{r}_1,\tau_1)\,\xi_{lm}(\mathbf{r}_2,\tau_2)\rangle_{H_0}\delta u_{lm}(\mathbf{r}_2).\end{aligned} \qquad (17)$$

Substituting (15) and (16) in (17) we obtain the result shown in Fig. 3. A straight line stands here for $\beta_T{}^{-1}$ and a wavy one for β^{-1}_{iklm}. An unshaded loop corresponds to the linear susceptibility of a homogeneous liquid, and the remaining terms to contributions linear in the Green's function and quadratic in the mean field; these contributions are connected with the non-electromagnetic collective degrees of freedom of the system.

Returning to (8), we obtain in the adopted cubic approximation the polarization in the form shown in Fig. 4. In a homogeneous liquid, the terms containing D_{ik} vanish and

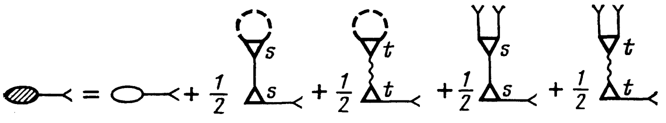

FIG. 3

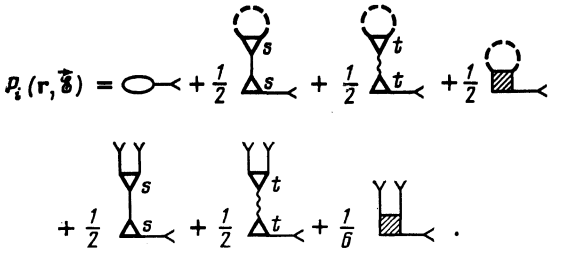

FIG. 4

$$^1/_2\{P_{ik}^{(2)s}\,\beta_T{}^{-1}P_{lm}^{(2)s}+P_{iklm}^{(2)t}\beta_{pqst}^{-1}P_{stlm}^{(2)t}+{}^1/_3P_{iklm}\}\tag{18}$$

is the total true cubic susceptibility of a homogeneous liquid in the assumed phenomenological model. The contribution of the Van der Waals forces to the dielectric constant of an inhomogeneous liquid turns out to be

$$\Delta\varepsilon^V=2\pi\Big\{P_{ik}^{(2)s}\,\beta_T{}^{-1}P_{lm}^{(2)s}\,D_{lm}+P_{iklm}^{(2)t}\beta_{pqst}^{-1}P_{stlm}^{(2)t}D_{lm}+\frac{1}{3}P_{iklm}^{(3)}D_{lm}\Big\}.\tag{19}$$

Let us examine the symmetries of the various contributions to (19). In the low-frequency region, the rectangle defined by (6) is symmetric in all the indices, and the cubic-susceptibility part $\gamma_{iklm}=P_{iklm}^{(3)}/6$ connected with it can be represented in the form

$$\gamma_{iklm}=\gamma_V\delta_{iklm}=\gamma_V(\delta_{ik}\delta_{lm}+\delta_{il}\delta_{km}+\delta_{im}\delta_{kl}).\tag{20}$$

For a field in a system directed along the x axis, the refractive indices $n_0=\varepsilon_\perp{}^{1/2}=\varepsilon_{yy}^{1/2}$ and $n_e=\varepsilon_\parallel{}^{1/2}=\varepsilon_{xx}^{1/2}$ of the ordinary and extraordinary rays from (20) are equal to

$$n_0=n+2\pi\gamma_V(\vec{\mathscr{E}}^M)^2,\ n_e=n+6\pi\gamma_V(\vec{\mathscr{E}}^M)^2.\tag{21}$$

This leads to the well-known[7] result

$$(n_e-n)/(n_0-n)=3.\tag{22}$$

Such a relation holds for weak birefringence in simple liquids and gases. It is not connected with collective processes in the fluid, and is caused by deformation of the electron shells of the atoms by the electric field. The Kerr constant for these cases is unusually small and reduces to γ_V, called the Voigt contribution.[7]

The symmetry of the triangles follows from (9), (10): $P_{ik}^{(2)s}\sim\delta_{ik}$, $P_{iklm}^{(2)t}\sim\Delta_{ik,lm}$, where

$$\Delta_{ik,lm}={}^3/_4(\delta_{il}\delta_{km}+\delta_{im}\delta_{kl})-{}^1/_2\delta_{ik}\delta_{lm},$$
$$P_{ik}^{(2)s}\,\beta_T{}^{-1}P_{lm}^{(2)s}\equiv\gamma_{\text{str}}\delta_{ik}\delta_{lm}\tag{23}$$

and constitutes the isotropic part of the cubic susceptibility. In this case $\delta\varepsilon_{ik}=\delta\varepsilon\delta_{ik}$ and the refractive indices of the ordinary and extraordinary rays are equal, i.e., this part of the susceptibility describes striction. We obtain next

$$P_{ikpq}^{(2)t}\gamma_{pqst}^{-1}P_{stlm}^{(2)t}\sim\Delta_{ik,pq}\Delta_{pq,st}\Delta_{st,lm}\sim\Delta_{ik,lm},\tag{24}$$

i.e.,

$$P_{ikpq}^{(2)t}\beta_{pqst}^{-1}P_{stlm}^{(2)t}\equiv\gamma_{ik,lm}^{or}=\frac{4}{3}\gamma_{\text{op}}\Delta_{ik,lm}.\tag{25}$$

For the refractive indices of the ordinary and extraordinary rays we get

$$(n_e-n)/(n_0-n)=-2.\tag{26}$$

This relation is satisfied for anisotropic liquids with a Kerr constant $\gamma_{or}\gg\gamma_V$ (Ref. 7). Thus, the considered term describes birefringence.

Substituting (20), (24), and (25) in (19) we obtain an analytic expression for the Van der Waals contribution to the DC:

$$\Delta\varepsilon_{ik}^V(\mathbf{r})=4\pi\delta_{ik}T\sum_{n=0}^{\infty}{}'\gamma_{\text{str}}(0,i\xi_n,i\xi_n)\xi_n{}^2D_{ll}(\mathbf{r},\mathbf{r};\xi_n)$$
$$+\frac{16\pi}{3}\Delta_{ik,lm}T\sum_{n=0}^{\infty}{}'\gamma_{or}(0,i\xi_n,i\xi_n)\xi_n{}^2D_{lm}(\mathbf{r},\mathbf{r};\xi_n)$$
$$+4\pi\delta_{iklm}T\sum_{n=0}^{\infty}{}'\gamma_V(0,i\xi_n,i\xi_n)\xi_n{}^2D_{lm}(\mathbf{r},\mathbf{r};\xi_n).\tag{27}$$

Thus, the liquid in inhomogeneous and optically anisotropic, and $\Delta\varepsilon^V$ depends on the form and size of the inhomogeneity. Expression (27) is valid at distances from the interface that are greater than the monocmolecular-layer thickness.

The functions $P^{(2)s}, P^{(2)t}, P^{(3)}$, that define $\Delta\varepsilon^V$ were identified with different parts of the cubic susceptibilities, and it is possible to use in the calculations the experimental data known for them. On the other hand, macroscopic considerations s yielded for them the analytic expressions

$$P_{ik}^{(2)s}\beta_T^{-1}P_{lm}^{(2)s}=\int_0^{1/T}d\tau\,d\tau'\int d\mathbf{r}\,\langle T_\tau d_i(\mathbf{r}_1,\tau_1)\,d_k(\mathbf{r}_2,\tau_2)\times\Delta\rho(\mathbf{r},\tau)\rangle_{H_0}\beta_T^{-1}\langle T_\tau\Delta\rho(\mathbf{r},\tau')\times d_l(\mathbf{r}_3,\tau_3)\,d_m(\mathbf{r}_4,\tau_4)\rangle_{H_0},$$
$$P_{ikpq}^{(2)t}\beta_{pqst}^{-1}P_{stlm}^{(2)t}=\int_0^{1/T}d\tau\,d\tau'\int d\mathbf{r}\,\langle T_\tau\,d_i(\mathbf{r}_1,\tau_1)\,d_k(\mathbf{r}_2,\tau_2)\,\xi_{pq}(\mathbf{r},\tau)\rangle_{H_0}\beta_{pq,st}^{-1}\times\langle T_\tau\xi_{st}(\mathbf{r},\tau')\,d_l(\mathbf{r}_3,\tau_3)\,d_m(\mathbf{r}_4,\tau_4)\rangle_{H_0},\tag{28}$$

which can be used to calculate the cubic susceptibility. Thus the striction part can be immediately calculated:

$$\gamma_{\text{str}}(0,i\omega,i\omega)=\frac{1}{16\pi^2}\rho\Big(\frac{\partial\rho}{\partial p}\Big)_T\Big(\frac{\partial\varepsilon(i\omega)}{\partial\rho}\Big)_T\Big(\frac{\partial\varepsilon(0)}{\partial\rho}\Big)_T.\tag{29}$$

Calculation of γ_{or} from (28) calls for specification of a detailed microscopic model.

§3. APPLICATION TO PLANAR LIQUID FILMS

Let us apply the foregoing general results to particular cases of a liquid filling a planar gap of width l between two solids, and to a plane liquid film of thickness l on the surface of a solid. In this case, let x be perpendicular to the film, and let the DC $\varepsilon+\Delta\varepsilon_{ik}$ of the film depend on x and l. At distances from the boundaries much larger than a, the value of the asymptotic part of $\Delta\varepsilon_{ik}$, viz., $\Delta\varepsilon_{ik}^{V}(x,l)$, is determined by (27) and can be completely calculated. At shorter distances, $\Delta\varepsilon_{ik}$ is determined by the short-range forces. Let us discuss the possible manifestations of $\Delta\varepsilon_{ik}^{V}(x,l)$.

It follows from (27) that for the orientational contribution $\Delta\varepsilon_{xx}^{V}(x,l) \neq \Delta\varepsilon_{yy}^{V}(x,l)$ also in the Van der Waals part of a sufficiently sufficient film ($l \gg \lambda$, where λ is the wavelength of the incident light). The refractive indices of the ordinary and extraordinary rays are different, i.e., the indicated part of the film has the properties of a uniaxial crystal with optical axis directed along x, and under suitable conditions one can observe birefringence induced by the inhomogeneous long-wave fluctuation field.

Another possibility is afforded by capacitive measurements of the film-thickness differences, when the substrates are used as capacitor electrodes. The DC of the film differs from the DC of the liquid in the bulk by an amount

$$\Delta\varepsilon(l) = l^{-1}\int_0^l \Delta\varepsilon_{xx}(x,l)\,dx. \tag{30}$$

In this case, for a liquid in a planar gap, the difference between the reciprocal capacitances of gaps of widths l_1 and l_2 takes the form

$$C^{-1}(l_1) - C^{-1}(l_2) = \frac{l_1 - l_2}{\varepsilon S}\left[1 - \frac{f(l_1,l_2)}{\varepsilon(l_1 - l_2)}\right], \tag{31}$$

where

$$f(l_1,l_2) = l_1\Delta\varepsilon(l_1) - l_2\Delta\varepsilon(l_2), \tag{32}$$

where S is the electrode area. For a liquid film, similarly, the capacitance difference between capacitors (d is the distance between the electrodes) with films of respective thicknesses l_1 and l_2 is equal to

$$\frac{C(l_1) - C(l_2)}{C(d)} = \frac{\varepsilon - 1}{d\varepsilon}(l_1 - l_2)\left[1 + \frac{1}{\varepsilon(\varepsilon - 1)}\,\frac{f(l_1,l_2)}{l_1 - l_2}\right], \tag{33}$$

where $C(d)$ is the capacitance of the empty capacitor. In the cases considered, the contribution of the inhomogeneity is determined by the function (32). The short-range finite-radius forces, obviously, do not contribute to the function $f(l_1,l_2)$. On the other hand, the Green's function of the film and accordingly $\Delta\varepsilon_{xx}^{V}(x,l)$ can be represented for all l as a sum of terms that diverge at $x = 0$ and $x = l$ and are not singular at the liquid boundaries. What is left of the first terms in $f(l_1,l_2)$ is an integral with respect to x in the interval from l_2 to l_1 ($l_2 < l_1$). It is obviously independent of the cutoff parameter. The contribution of the nonsingular terms to the considered function is independent of the cutoff parameter, accurate to contributions of first order in the ratio of the short-range-force radius to the film thickness.

Thus, $f(l_1,l_2)$ and the capacitance contributions indicated in (31) and (33) are determined only by the long-range forces, and have a universal dependence on the film thickness.

The presently achieved high accuracy in the measurements of the capacitance and of the phase shift in birefringence makes it possible to observe the indicated effects and their use for precision measurements of the parameters that enter in the Van der Waals part of the DC.

3.1. Inhomogeneous part of the film's Green's function

In the cases considered, $D_{ik}(\mathbf{r},\mathbf{r}';\xi_n)$ is a sum of functions $D_{ik}^{(-)}(x - x';\xi_n)$ and $D_{ik}^{(+)}(x + x';\xi_n)$ that depend on $x - x'$ and $x + x'$. The first function is known,[1] and we obtain the second from the equations of that reference. As a result, the diagonal components of the function $D_{ik}(x,x,\mathbf{q};\xi_n)$ ($\mathbf{q}$ is the Fourier-transform of the vector $\mathbf{p}(0,y - y',z - z')$) which are needed for the calculation of $\Delta\varepsilon_{xx}^{V}(x,l)$, take, at equal values of the arguments, the form

$$D_{zz}(x,x,\mathbf{q};\xi_n) = \frac{2\pi}{p\Delta}(2 - Q),$$

$$D_{yy}(x,x,\mathbf{q};\xi_n) = \frac{2\pi p}{\varepsilon\xi_n^2\bar{\Delta}}(2 - \bar{Q}),$$

$$D_{xx}(x,x,\mathbf{q};\xi_n) = -\frac{2\pi q^2}{\varepsilon\xi_n^2 p\bar{\Delta}}(2 + \bar{Q}), \tag{34}$$

where

$$Q = W_1 e^{2px} + W_2 e^{2p(l-x)}, \quad \bar{Q} = \overline{W}_1 e^{2px} + \overline{W}_2 e^{2p(l-x)},$$
$$\Delta = 1 - e^{2pl}W_1W_2, \quad \bar{\Delta} = 1 - e^{2pl}\overline{W}_1\overline{W}_2,$$

$$W_{1,2} = \frac{p_{1,2} + p}{p_{1,2} - p}, \quad \overline{W}_{1,2} = \frac{\varepsilon_{1,2}p + \varepsilon p_{1,2}}{\varepsilon_{1,2}p - \varepsilon p_{1,2}},$$
$$p = (\varepsilon\xi_n^2 + q^2)^{1/2}, \quad p_{1,2} = (\varepsilon_{1,2}\xi_n^2 + q^2)^{1/2}. \tag{35}$$

ε is the DC of the liquid in the gap between identical solids, $\varepsilon_1 = \varepsilon_2$ is the DC of the solid, while for the liquid film ε_1 is the DC of the solid and $\varepsilon_2 = 1$. We assume that the absorption by the liquid is at frequencies higher than that by the substrate. For the two length parameters $1/\omega_0$ (ω_0 is the characteristic frequency in the spectrum of the liquid) and $1/T$ (T is the temperature), three limiting film thicknesses l are of importance: $l \ll 1/\omega_0$, $1/\omega_0 \ll l \ll 1/T$ and $l \gg 1/T$.

We consider a liquid in the gap at $l \ll 1/\omega_0$. At frequencies $\xi \ll \omega_0$ we have $\varepsilon_1(i\xi) \gg \varepsilon(i\xi)$. In this case $\varepsilon p_1 \ll \varepsilon_1 p$ for all q and $\overline{W}_1 \approx 1$. For $q \ll \varepsilon_1^{1/2}\xi$ we have $p_1 \approx \varepsilon_1^{1/2}\xi$ and $W_1 \approx 1$. For $q \gg \varepsilon_1^{1/2}\xi$ we have $p_1 = p_2 = p$ and $W_1 \approx 4q^2/\varepsilon_1\xi^2$. This allows us to use for all q the estimate

$$W_1 \approx 1 + 4p^2/\varepsilon_1\xi^2. \tag{36}$$

For the DC ε_1 of the substrate we assume the following expression:

$$\varepsilon_1(i\xi_n)\xi_n \approx \begin{cases} 0, & n = 0 \\ \omega_0^2, & n \neq 0 \end{cases} \tag{37}$$

For a film we have $W_1 \neq W_2$ and $\overline{W}_1 \neq \overline{W}_2$. The estimates obtained above are valid for W_1 and $\overline{W}_1$. For $q^2 \ll \xi^2$ we have $W_2 \approx -(\varepsilon^{1/2} + 1)/(\varepsilon^{1/2} - 1)$ and for $q_2 \gg \varepsilon\xi^2$ we have $W_2 \approx -4q^2/(\varepsilon - 1)\xi^2$. We use therefore for any q the estimate

$$W_2 \approx -\frac{\varepsilon^{1/2} + 1}{\varepsilon^{1/2} - 1} - \frac{4q^2}{(\varepsilon - 1)\xi^2}. \tag{38}$$

From (35) we get

$$\overline{W}_2 = (1 + \varepsilon^{1/2})/(1 - \varepsilon^{1/2}), \quad q^2 \ll \xi^2, \tag{39}$$
$$\overline{W}_2 = (1 + \varepsilon)/(1 - \varepsilon), \quad q^2 \gg \varepsilon\xi^2.$$

3.2. Films of simple liquids

In this case $\gamma_{or} \approx 0$, $\gamma_V \ll \gamma_{\text{str}}$, and we need retain in (27) only the first term

$$\Delta\varepsilon_{xx}^{V}(x,l)=4\pi T\sum_{n=0}^{\infty}{}' \gamma_{\rm str}(0,i\xi_n,i\xi_n)\xi_n^2 D_{ll}(x,x,\xi_n). \tag{40}$$

At $l\ll 1/\omega_0$ we change from summation over n to integration with respect to ξ and take it into account that the main contribution to the integral with respect to q is made by $q\sim 1/l\gg\omega_0\gtrsim\xi$ and that $W_{1,2}\to\infty$. As a result we obtain from (34), (35), and (40)

$$\Delta\varepsilon_{xx}^{V}(x,l)=-4\int_0^{\infty}d\xi\,\frac{\gamma_{\rm str}(0,i\xi,i\xi)}{\varepsilon(i\xi)}\int_0^{\infty}\frac{dq\,q^3}{p}\frac{\overline{Q}}{\overline{\Delta}}. \tag{41}$$

In simple liquids $\varepsilon(i\xi)$ and $\gamma_{\rm ctp}(0,i\xi,i\xi)$ differ little from their static values up to electron frequencies $\omega\sim 2\cdot 10^{16}$. At higher frequencies they vanish rapidly and the following estimate can be used:

$$\int_0^{\infty}d\xi\,\frac{\gamma_{\rm str}(0,i\xi,i\xi)}{\varepsilon(i\xi)}=\frac{\omega_0\gamma_{\rm str}}{\varepsilon}. \tag{42}$$

Substituting in (41) the functions $\overline{Q}$ and $\overline{\Delta}$ from (35), we get

$$\Delta\varepsilon_{xx}^{V}(x,l)=4\,\frac{\omega_0\gamma_{\rm str}}{\varepsilon}\int_0^{\infty}p^2\,dp\,\frac{e^{2p(l-x)}-Ce^{2px}}{e^{2pl}+C}, \tag{43}$$

where

$C=[(\varepsilon-1)/(\varepsilon+1)]\in(0,1)$.

We separate in (43) the terms that diverge at $x=0$ and $x=l$. Substitution in (32) leads to

$$f(l_1,l_2)=(\omega_0\gamma_{\rm str}/2\varepsilon)(C-C^{-1})\,{\rm Li}_2(-C)(l_1^{-2}-l_2^{-2}), \tag{44}$$

where[8]

$${\rm Li}_n(x)=\sum_{k=1}^{\infty}x^k k^{-n}.$$

For $n=2$ and $x=-C$, accurate to 10–20%, we have ${\rm Li}_2(-C)\approx -C$ and

$$f(l_1,l_2)=\frac{2\omega_0\gamma_{\rm str}}{(\varepsilon+1)^2}\left(\frac{1}{l_1^2}-\frac{1}{l_2^2}\right). \tag{45}$$

From (29) we have in this case

$$\gamma_{\rm str}=\frac{1}{16\pi^2}\left(\rho\frac{\partial\varepsilon}{\partial\rho}\right)_T^2\beta_T \tag{46}$$

(β_T is the isothermal compressibility of the liquid) and for a plane wave we get ultimately

$$f(l_1,l_2)=\frac{\omega_0}{8\pi^2(\varepsilon+1)^2}\left(\rho\frac{\partial\varepsilon}{\partial\rho}\right)_T^2\beta_T(l_1^{-2}-l_2^{-2}). \tag{47}$$

For typical simple liquids $\omega_0\sim 2\cdot 10^{16}$, $\varepsilon\sim 2$, $(\rho\partial\varepsilon/\partial\rho)_T\sim 1$, $\beta_T\sim 10^{-9}$ (in CGS) and for l_1,l_2 and $f(l_1,l_2)$ in Å we have

$$f(l_1,l_2)\sim 30(l_1^{-2}-l_2^{-2}). \tag{48}$$

At l_1, $l_2\sim 50-100$, as follows from (34), the contribution to the capacitance or to the measured DC turns out to be $\sim 10^{-2}-10^{-4}\%$, which can be readily observed in experiment. The entire effect is governed here by the function D^{+}.

For a liquid in a gap between identical solids we have $f(l_1,l_2)=0$. The discussed effect exists also if the solids are different.

3.3 Nonpolar liquids consisting of anisotropic molecules

In such liquids, the greater part of the intensity of the molecular scattering of light goes into deopolarized scattering (85% for liquid CS_2). It can therefore be assumed that the orientational contribution to $f(l_1,l_2)$ exceeds the striction contribution and from (27) and (25) we get

$$\Delta\varepsilon_{xx}^{V}(x,l)=\frac{8\pi}{3}T\sum_{n=0}^{\infty}\gamma_{or}(0,i\xi_n,i\xi_n)$$
$$\times[2D_{xx}(x,x;\xi_n)-D_{yy}(x,x;\xi_n)$$
$$-D_{zz}(x,x;\xi_n)]. \tag{49}$$

Changing to thin films and substituting the functions (34), we get

$$\Delta\varepsilon_{xx}^{V}(x,l)=-\frac{4}{3}\int_0^{\infty}d\xi\,\frac{\gamma_{or}(0,i\xi,i\xi)}{\varepsilon(i\xi)}\int_0^{\infty}\frac{q\,dq}{p}\frac{q^2}{\overline{\Delta}}(6+\overline{Q}). \tag{50}$$

The molecules of the considered liquids have anisotropic polarizability the their dipole moments are equal to zero. Therefore, just as in the preceding case, the functions $\varepsilon(i\xi)$ and $\gamma_{or}(0,i\xi,i\xi)$ differ insignificantly from the static values all the way to electron frequencies and

$$\int_0^{\infty}d\xi\,\frac{\gamma_{or}(0,i\xi,i\xi)}{\varepsilon(i\xi)}=\frac{\omega_0\gamma_{or}}{\varepsilon}. \tag{51}$$

Consider a liquid in a planar gap. Using the estimates obtained above for W_1 and $\overline{W}_1$, we get

$$\Delta\varepsilon_{xx}^{V}(x,l)=\frac{4}{3}\frac{\omega_0\gamma_{or}}{\varepsilon}\int_0^{\infty}p^2\,dp\,\frac{e^{2p(l-x)}+e^{2px}+6}{e^{2pl}-1}. \tag{52}$$

We introduce the function

$$\xi(3,a)=\frac{1}{a^3}+\sum_{k=1}^{\infty}\frac{1}{(k+a)^3}=\frac{1}{a^3}+\varphi(a) \tag{53}$$

and rewrite (52) in the form

$$\Delta\varepsilon_{xx}^{V}(x,l)=\frac{\omega_0\gamma_{or}}{3\varepsilon l^3}\left[\xi\left(3,\frac{x}{l}\right)+\xi\left(3,\frac{l-x}{l}\right)+6\xi(3)\right]. \tag{54}$$

The function $\varphi(a)$ in (53) is bounded in the interval $a\in(0,1)$, and it is possible to separate in (54) the singular and regular parts:

$$\Delta\varepsilon_{xx}^{V}(x,l)=\frac{\omega_0\gamma_{or}}{3\varepsilon}\left[x^{-3}+(l-x)^{-3}+l^{-3}\varphi\left(\frac{x}{l}\right)\right.$$
$$\left.+l^{-3}\varphi\left(\frac{l-x}{l}\right)+\frac{6\xi(3)}{l^3}\right]. \tag{55}$$

Substitution in (32) leads to

$$f(l_1,l_2)={}^2/_3\,\omega_0\gamma_{op}\xi(3)(l_1^{-2}-l_2^{-2}). \tag{56}$$

The dependence on l_1 and l_2 does not differ from that in (47). The effect is completely determined by the function $D^{(-)}$.

For carbon disulfide we have $\varepsilon = 2.6, \omega_0 \sim 1.5 \cdot 10^{16}$, $\gamma_{or} \sim 0.8 \cdot 10^{-11}$, and for a gap filled with liquid carbon disulfide we obtain

$$f(l_1, l_2) \sim 110 (l_1^{-2} - l_2^{-2}). \tag{57}$$

The effect is several times larger than the one described above for simple liquids.

We now carry out the calculation for films of the considered liquids. We obtain in lieu of (53)

$$\Delta\varepsilon_{xx}^V (x,l) = \frac{4}{3} \frac{\omega_0 \gamma_{or}}{\varepsilon} \int_0^\infty p^2 \, dp \frac{e^{2p(l-x)} - Ce^{2px} - 6C}{e^{2pl} + C}. \tag{58}$$

Separating, just as for a liquid in a gap, the singular contributions in the integral (29), we get

$$f(l_1,l_2) = \frac{\omega_0 \gamma_{or}}{3\varepsilon} \left[-6\mathrm{Li}_3(-C) + \frac{1}{2} (C - C^{-1}) \mathrm{Li}_2(-C) \right] \times (l_1^{-2} - l_2^{-2}). \tag{59}$$

Using again the estimate $\mathrm{Li}_n(-C) \approx -C$, we get as a result

$$f(l_1,l_2) = \frac{\omega_0 \gamma_{or}}{3\varepsilon} \left[\frac{6(\varepsilon - 1)}{\varepsilon + 1} + \frac{2\varepsilon}{(\varepsilon+1)^2} \right] (l_1^{-2} - l_2^{-2}). \tag{60}$$

For carbon disulfide we have

$$f(l_1, l_2) \sim 50 (l_1^{-2} - l_2^{-2}). \tag{61}$$

3.4. Polar liquids

In such liquids, $\gamma_{or}(0, i\xi, i\xi)$ can be divided into two terms, γ_{or}^d and γ_{or}^a. The first is generated by the dipole moments of the molecules, is large at low frequencies, and vanishes rapidly at frequencies exceeding those of the dipole relaxation. The term γ_{or}^a is determined by the anisotropic polarizability of the molecules and remains practically constant at all frequencies all the way to electronic.[9] Its contribution to $f(l_1,l_2)$ was investigated above and can be added to the now-considered contribution γ_{or}^d.

Since $\omega_d \ll T$, we need retain in (49) only the term with $n = 0$, and we get for arbitrary l

$$\Delta\varepsilon_{xx}^V (x,l) = -\frac{4\pi}{3} T \gamma_{or}^d \frac{1}{\varepsilon} \int_0^\infty \frac{q\, dq}{p} \frac{q^2}{\bar{\Delta}} (6 + \bar{Q}). \tag{62}$$

For a liquid in a gap this leads to

$$\Delta\varepsilon_{xx}^V (x,l) = \frac{4\pi}{3\varepsilon} T \gamma_{or}^d \int_0^\infty p^2 \, dp \frac{e^{2p(l-x)} + e^{2px} + 6}{e^{2pl} - 1}. \tag{63}$$

Substitution in (32) leads to

$$f(l_1, l_2) = (2\pi/\varepsilon) \xi(3) T \gamma_{or}^d (l_1^{-2} - l_2^{-2}). \tag{64}$$

For nitrobenzene ($\varepsilon \sim 38$), $\gamma_{or}^d \sim 10^{-9}$ and $T \sim 4 \cdot 10^{-14}$, and for $f(l_1,l_2)$ in A we have

$$f(l_1, l_2) \sim 8 (l_1^{-2} - l_2^{-2}). \tag{65}$$

For a film, similarly,

$$\Delta\varepsilon_{xx}^V (x,l) = \frac{4\pi}{3\varepsilon} T \gamma_{or}^d \int_0^\infty p^2 \, dp \frac{e^{2p(l-x)} - Ce^{2px} - 6C}{e^{2pl} + C} \tag{66}$$

and

$$f(l_1, l_2) = \frac{1{,}8\pi}{\varepsilon} T \gamma_{or}^d (l_1^{-2} - l_2^{-2}). \tag{67}$$

For nitrobenzene (in view of its high DC) the result does not differ from that of the liquid in a gap:

$$f(l_1, l_2) \sim 6 (l_1^{-2} - l_2^{-2}). \tag{68}$$

The dipole contribution is thus small compared with determined by the anisotropic polarizability.

3.5. Birefringence in liquid films

Consider a thick liquid film ($l \gg 1/T$). In this case we can rewrite (27) in the form

$$\Delta\varepsilon_{ik}^V (x,l) = 4\pi T \sum_{n=0}^\infty \gamma_{ik,lm}^{or} (0, i\xi_n, i\xi_n) \xi_n^2 Dl_m(x, x; \xi_n). \tag{69}$$

From (25) we obtain then $\Delta\varepsilon_{ii}^V = 0$ and since $\Delta\varepsilon_{yy}^V = \varepsilon_{zz}^V$, it follows that $\Delta\varepsilon_{yy}^V = -\frac{1}{2} \Delta\varepsilon_{xx}^V$.

Let a beam of plane-parallel waves propagate along the film and let the angle between the polarization plane and the x axis be $\pi/4$. Assume that the wavelength is $\lambda \ll l$. A diaphragm placed ahead of the film prevents the beam from propagating near the film boundaries, where the geometric-optics conditions are violated. On emerging from a film of length L, the phase shift between the extraordinary and ordinary rays is given by the relation[7]

$$\Delta\varphi = \frac{\omega L}{c} \left[(\varepsilon + \Delta\varepsilon_{xx}^V)^{1/2} - (\varepsilon + \Delta\varepsilon_{yy}^V)^{1/2} \right], \tag{70}$$

where $\omega = 2\pi c / \lambda \varepsilon^{1/2}$ and c is the speed of light. Using the foregoing relation between $\Delta\varepsilon_{xx}^V$ and $\Delta\varepsilon_{yy}^V$ we can transform the latter into

$$\Delta\varphi = (3\pi L / 2\lambda\varepsilon) \Delta\varepsilon_{xx}^V, \tag{71}$$

where $\Delta\varepsilon_{xx}^V$ is the mean value of the function $\Delta\varepsilon_{xx}^V (x,l)$ over the beam width. The result of the averaging depends substantially on the location and dimensions of the film region over which the average is taken.

The diaphragm cuts out a region of film from an interval $(\delta, l - \delta)$. Assume that $l > \delta \gg 1/T$. We consider a wide beam ($\delta / l \ll 1$) and a narrow one (δ close to $l/2$). In the considered region we have $x \gg 1/T$ and it suffices to retain in (69) only the term with $n = 0$. Expressions (34) and (35) lead to

$$\Delta\varepsilon_{xx}^V (x,l) = (\pi T \gamma_{or} / \varepsilon) [x^{-3} + (l - x)^{-3}].$$

Averaging over the beam width leads to the following phase shifts: for a wide beam

$$\Delta\varphi \approx 3\pi^2 LT (\gamma_{or} / 2\lambda\varepsilon^2)(1 / l\delta^2),$$

and for a narrow one

$$\Delta\varphi \approx 6\pi^2 LT (\gamma_{or} / \lambda\varepsilon^2)(1 / l^3).$$

In the former case the phase shift decreases like $1/l$ with increase of the film thickness. The high accuracy of phase-shift measurement methods makes it possible to observe the proposed effects for wide beams.

§4. CONCLUSION

The arguments advanced above indicate that the DC of an inhomogeneous liquid with weak nonlinearity is increased by long-range forces. The contribution of these forces, at distances from the inhomogeneity boundaries much larger than the atomic dimensions, is inhomogeneous, anisotropic, and depends on the size and shape of the inhomogeneity. In the assumed phenomenological model this contribution is determined by the interaction of the long-wave photons with the long-wave scalar and tensor modes of the liquid. The possible manifestations of the results obtained for the DC can be indicated, notwithstanding their asymptotic character. Thus, in planar films the function describing to the difference between the average DC of the films differs from zero, and birefringence induced by an inhomogeneous long-wave fluctuation field can be observed in sufficiently thick films. The magnitudes of the effects depend on the film thicknesses. Numerical estimates point to the feasibility of observing these effects.

The authors thank A. F. Andreev, D. E. Khmel'nitskiĭ, and A. M. Dyugaev for a helpful discussion of the work.

[1] I. E. Dzyaloshinskiĭ and L. P. Pitaevskiĭ, Zh. Eksp. Teor. Fiz. **36**, 1797 (1959) [Sov. Phys. JETP **9**, 1282 (1969)]. I. E. Dzyaloshinskiĭ, L. P. Pitaevskiĭ, and E. M. Lifshitz, Usp. Fiz. Nauk **73**, 381 (1961) [Sov. Phys. Usp. **4**, 153 (1961)].

[2] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media*, Pergamon, 1984.

[3] G. I. Salistra, Zh. Eksp. Teor. Fiz. **87**, 1713 (1984) [Sov. Phys. JETP **60**, 984 (1984)].

[4] D. N. Zubarev, *Nonequilibrium Statistical Thermodynamics*, Plenum, 1974.

[5] J. M. Luttinger, Phys. Rev. **135**, 1505 (1964).

[6] G. I. Salistra, Zh. Eksp. Teor. Fiz. **53**, 258 (1967) [Sov. Phys. JETP **26**, 173 (1968)].

[7] M. V. Vol'kenshteĭn, Molecular Optical [in Russian], Nauka, 1971.

[8] A. P. Prudnikov, Yu. A. Brychkov, and O. I. Marichev, Integrals and Series. Elementary Functions [in Russian], Nauka, 1981.

[9] M. V. Vuks, Electrical and Optical Properties of Molecules in Condensed Media [in Russian] Leningrad Univ. Press, 1984.

Translated by J. G. Adashko