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**POLARIZABILITY OF FLUID DROPLETS
AND THE KERR EFFECT ON MICROEMULSIONS**

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I. INTRODUCTION

Microemulsions are formed after the addition of surface-active molecules into the mixture of two immiscible fluids (oil and water). The surfactants are spread at the oil-water interface as a dense monolayer. The properties of the layer determine the phase behavior and thermodynamical stability of microemulsions [1]. Within the Canham-Helfrich concept of interfacial elasticity [2,3], the surfactant monolayer is characterized by the bending and saddle-splay moduli κ and $\bar{\kappa}$, respectively, the spontaneous curvature C_s , the surface tension coefficient α , and the equilibrium radius of the droplet, R_0 . In addition, the free energy of the droplet is determined by the pressure difference Δp (pressure inside the droplet minus outside). In real microemulsions there is some distribution of the droplets in radii. The polydispersity of this distribution, ε , can be regarded as a microemulsion parameter instead of Δp [4]. The number of these basic parameters lowers in the case when the microemulsion is in the state of the so called two-phase coexistence (with the excess amount of the dispersed droplet phase) [4]. The determination of the above parameters has been attempted by a number of experimental techniques [5]. However, different experimental methods yield very different values of the parameters for the same microemulsion systems. For example, there is some one order difference in the bending rigidity κ determined from the Kerr-effect measurements [6] and the neutron scattering associated with spin echoes [7] (for a more discussion see Ref. [8]). We have shown in our recent paper [8] that the interpretation of the neutron and light scattering experiments does not correspond to the reality. In particular, the thermal droplet fluctuations in the shape are not appropriately taken into account in the description of these experiments. In Ref. [8] we calculated the intermediate scattering function that is used to describe the scattering from dilute microemulsion and emulsion solutions. The theory consistently takes into account the droplet shape fluctuations to the second order in the fluctuation amplitudes. Comparing the theory and experimental data from the literature, we have found the microemulsion parameters to be in a notable disagreement with the values determined in the original experimental works operating with

the previous theories that do not take (or take not appropriately) into account the droplet fluctuations. So, the bending rigidities that we have extracted from the experiments are significantly lower than the values found in the neutron spin-echo experiments [7,9,10] but larger than possessed by the spinning drop measurements [11], the Kerr effect [6] or a combination of dynamic light and neutron scattering [12,13]. It would be thus useful to have adequate theoretical description of the different experimental probes of microemulsions.

In the present work the polarizability of a spheroidal droplet is evaluated. Having a model for the polarizability tensor α_{ik} of a microemulsion droplet, such experiments could be described like the Kerr effect or the polarized and depolarized scattering of light, which could serve as alternative probes of the droplet shape fluctuations and thus of the microemulsion parameters. Similar calculations can be already found in the literature. In the paper [14] the polarizability of an ellipsoid is evaluated, however, the shape fluctuations have not been considered. In Ref. [15] the fluctuations of a spherical droplet are considered, however, those calculations should be corrected. Moreover, they are carried out only to the first order in the fluctuation amplitudes that is insufficient in some cases when the observed quantities are represented by the products of the polarizability tensor components. In the next section a brief phenomenological theory of the shape fluctuations of droplets is given. In Section III the polarizability tensor α_{ik} is found to the second order in the fluctuations. Then it is applied to the description of the Kerr effect on microemulsion and the scattering of light. In Conclusion, the obtained results and necessary improvements of the theory are discussed.

II. SHAPE FLUCTUATIONS OF SPHERICAL DROPLETS

Consider a flexible droplet having a spherical shape in equilibrium. The fluid of the droplet is assumed to be incompressible and the equivalent-volume radius of the droplet is R_0 . The instantaneous shape of the deformed droplet can be described by the deviation of its radius from R_0 , in spherical harmonics,

$$f(\vartheta, \varphi) = R(\vartheta, \varphi)/R_0 - 1, \quad (1)$$

where

$$f(\vartheta, \varphi) = \sum_{l,m} u_{lm}(t) Y_{lm}(\vartheta, \varphi), \quad (2)$$

with $m = -l, -l + 1, \dots, l$, and $0 \leq l < l_{max} \sim R_0/a$, a being a typical molecular diameter. It is assumed that the fluctuations are small, $|f| \ll 1$. For what follows we need the correlation functions of the complex expansion coefficients u_{lm} , $u_{lm}^* = (-1)^m u_{l,-m}$. The shape fluctuations with different numbers l and m are uncorrelated,

$$\langle u_{lm}^* u_{l'm'} \rangle = \delta_{ll'} \delta_{mm'} \langle u_{lm} u_{lm}^* \rangle, \quad (3)$$

and $\langle u_{lm} \rangle = 0$ for $l > 1$ [16,17]. When $l = 0$ or 1, the coefficients u_{lm} can be expressed as quadratic combination of the rest of expansion coefficients, e.g.

$$u_{00} = -(4\pi)^{-1/2} \sum_{l>1,m} |u_{lm}|^2, \quad (4)$$

that is a consequence of the constraint on the droplet volume (the $l = 0$ mode corresponds to the overall "breathing" of the droplet). Analogously, the $l = 1$ mode corresponds (to the second order in u) to the translational motion of the droplet as a whole. The necessary time correlation functions are as follows:

$$\langle u_{l0}(0) u_{l0}(t) \rangle = \frac{k_B T}{\alpha_l R_0^2 (l+2)(l-1)} \exp(-\Gamma_l t), \quad (5)$$

$$\alpha_l = \alpha - 2\kappa C_s / R_0 + \kappa l(l+1) / R_0. \quad (6)$$

Here, $\alpha = \sigma + C_s^2 \kappa / 2$ (σ is the microscopic interfacial tension [4]). The decay rates Γ_l can be found in our previous paper [18] where the shape fluctuations of compressible surface layers have been studied in detail (it is generally believed that the surfactant monolayer behaves like an almost incompressible two-dimensional fluid; for Γ_l in the limit of incompressible layers see also Ref. [19]).

Finally, the distribution of the droplets in radii as it follows from the phenomenological theory of the droplet formation [4] is

$$f(R_0) \propto \exp[-\frac{1}{2\varepsilon}(1 - \frac{R_0}{R_m})^2], \quad (7)$$

where R_m is the mean radius of the droplets. The generalized Laplace condition [4] relates the polydispersity ε to the characteristics of the layer,

$$\varepsilon = \frac{k_B T}{8\pi(2\kappa + \bar{\kappa})}. \quad (8)$$

Here, for simplicity, the two-phase coexistence is assumed, when $\alpha = (2\kappa + \bar{\kappa})R_m^{-2} = \kappa C_s/R_m$. For small ε the distribution (7) has a sharp maximum around R_m , $\langle R_0 \rangle \approx R_m$, and $\langle (R_0 - R_m)^2 \rangle \approx \varepsilon R_m^2$, neglecting small terms $\sim \exp(-1/2\varepsilon)$.

For dense microemulsions the interaction between the droplets should be taken into account. This is still an open question since the droplets do not interact like hard spheres [20,21]. Most often dilute solutions of droplets are studied when the effect of interaction is negligible. The influence of the entropy of dispersion should be also included into the consideration. It will change the polydispersity and the quantity α_l from Eq. (6). There is no agreement in the literature as to the concrete expression for the entropy. Within the random mixing approximation one should add to the denominator in Eq. (7) a quantity $2k_B T F(\Phi)$, where for small volume fractions Φ of the droplets $F \approx \ln \Phi - 1$. The mean quadrate of the amplitude of fluctuations does not explicitly depend on the function F ,

$$\langle u_{l0}^2 \rangle = \{(l-1)(l+2)[\frac{\kappa}{k_B T} l(l+1) - \frac{1}{8\pi\varepsilon}]\}^{-1}. \quad (9)$$

III. POLARIZABILITY OF A DROPLET

As mentioned in Introduction, the polarizability of a fluctuating droplet was already evaluated by Borkovec and Eicke [15]. However, that work should be corrected in many aspects. First, the authors calculate the polarizability for a fluid droplet of infinite dielectric constant ϵ in vacuum. One finds a number of errors in these calculations. Then the authors remark that the dipole field generated by a droplet of infinite ϵ in vacuum is the same as the dipole field generated by an ellipsoid. Based on this observation, they write the result

for a droplet with a finite dielectric constant in a dielectric medium simply using the known result for a dielectric ellipsoid with small eccentricities [22]. In general, such a reasoning is flawed. In particular, it is incorrect in our problem of finding the polarizability tensor α_{ik} , $i, k = x, y, z$, of a droplet, since α_{ik} should be in general calculated at least to the second order in the fluctuations. This follows from the fact that the observed quantities correspond to the products of the polarizability tensor components. Below the polarizability is evaluated up to the second order in the fluctuation amplitudes.

Consider a spheroidal droplet whose shape is described by Eq. (1). The dielectric constant of the droplet is ϵ_i and the outer medium is characterized by a constant ϵ_e . To find the polarizability of the droplet, one has to calculate the electric field generated by the droplet in an external electrostatic field \vec{E}_0 . This means to solve the Laplace equation for the potential Φ inside and outside the droplet, together with the boundary conditions at the interface between the two media,

$$\Phi^{(i)} = \Phi^{(e)}, \quad \epsilon D_n^{(i)} = D_n^{(e)}, \quad \text{at} \quad r = R_0(1 + f), \quad (10)$$

where D_n is the normal component of electric induction, $\epsilon = \epsilon_i/\epsilon_e$, and the indices i and e refer to the interior and exterior of the droplet. At infinity the resulting electric intensity becomes \vec{E}_0 . Let the initial field is oriented along the axis z . We then search for the solution in the form

$$\begin{aligned} \Phi^{(i)} &= -\frac{3}{\epsilon + 2}r \cos \vartheta + r \sum_M b_M^{(z)} Y_{1M}, \\ \Phi^{(e)} &= -r \cos \vartheta + \frac{\epsilon - 1}{\epsilon + 2}r^{-2} \cos \vartheta + r^{-2} \sum_M a_M^{(z)} Y_{1M}, \end{aligned} \quad (11)$$

where we temporarily reduced the variables by replacing $r/R_0 \rightarrow r$ and $\Phi/E_0 R_0 \rightarrow \Phi$. That is, the field is represented by a potential due to a perfect sphere plus a small addition due to the distortion from the spherical shape. Such a deformation is described by the terms containing small coefficients $a_M^{(z)}$ and $b_M^{(z)}$. Only the dipole field is considered. To satisfy the second boundary condition in Eq. (10) one has first to find the normal vector to

the deformed droplet interface. The normal is defined through the vectors $\vec{r}_\vartheta = \partial_\vartheta \vec{r}$ and $\vec{r}_\varphi = \partial_\varphi \vec{r}$, using Eq. (1),

$$\vec{n} = \frac{\vec{r}_\vartheta \times \vec{r}_\varphi}{(\vec{r}_\vartheta \times \vec{r}_\varphi)^2}. \quad (12)$$

Performing the calculation we obtain, to the second order in small f ,

$$\begin{aligned} \vec{n} \vec{\nabla} \Phi &= (\vec{\nabla} \Phi)_r \left\{ 1 - \frac{1}{2} [(\partial_\vartheta f)^2 + \sin^{-2} \vartheta (\partial_\varphi f)^2] \right\} \\ &+ (\vec{\nabla} \Phi)_\vartheta (f - 1) \partial_\vartheta f + \sin^{-1} \vartheta (\vec{\nabla} \Phi)_\varphi (f - 1) \partial_\varphi f. \end{aligned} \quad (13)$$

When $\Phi^{(i)}$ and $\Phi^{(e)}$ from Eq. (11) are substituted in Eq. (13), the second boundary condition from Eq. (10) becomes

$$\epsilon \sum_M b_M^{(z)} Y_{1M} = -2 \sum_M a_M^{(z)} Y_{1M} + 3 \frac{\epsilon - 1}{\epsilon + 2} [2f \cos \vartheta + \partial_\vartheta f \sin \vartheta]. \quad (14)$$

Together with the condition of continuity of the potential,

$$\sum_M b_M^{(z)} Y_{1M} = \sum_M a_M^{(z)} Y_{1M} - 3 \frac{\epsilon - 1}{\epsilon + 2} f \cos \vartheta, \quad (15)$$

one obtains, to the first order in f , the following equation for the determination of the coefficients $a_M^{(z)}$:

$$\sum_M a_M^{(z)} Y_{1M} = 3 \frac{\epsilon - 1}{\epsilon + 2} \left[f \cos \vartheta + \frac{1}{\epsilon + 2} \partial_\vartheta f \sin \vartheta \right]. \quad (16)$$

Multiplying this equation by Y_{1M} and integrating over all angles ϑ and φ , one obtains the desired coefficients $a_M^{(z)}$. This can be easily done expressing the products $Y_{lm} Y_{1m'}$ that appear in the integrals through sums of spherical harmonics. These sums always contain the Clebsch-Gordan coefficients ($1100 \mid 10$) [23] that are nonzero only for $l = 0$ or $l = 2$. The $l = 0$ mode is excluded since it gives corrections of the second order in u_{lm} or becomes zero when differentiated with respect to ϑ (the second term in Eq. (16)). We have thus only the spherical harmonics of order 1 and 2 so that the integration is easily performed in elementary functions. In this way we find from Eqs. (15) and (16)

$$a_M^{(z)} = \frac{3}{\sqrt{5}} \left(\frac{2}{\sqrt{3}} \delta_{M0} + \delta_{M1} + \delta_{M,-1} \right) \left(\frac{\epsilon-1}{\epsilon+2} \right)^2 u_{2M}, \quad b_M^{(z)} = -\frac{3}{\epsilon-1} a_M^{(z)}. \quad (17)$$

Quite similarly the response of the droplet can be considered when the external field is oriented along the axes x and y . In Eqs. (11) one has just to replace $z = r \cos \vartheta$ by $x = r\sqrt{2\pi/3}(Y_{1,-1} - Y_{11})$ and $y = ir\sqrt{2\pi/3}(Y_{1,-1} + Y_{11})$, and repeat the calculations. Instead of the coefficients $a_M^{(z)}$ we obtained

$$a_0^{(x)} = \frac{3}{\sqrt{10}} \left(\frac{\epsilon-1}{\epsilon+2} \right)^2 (u_{2,-1} - u_{21}), \quad a_{\pm 1}^{(x)} = \pm \sqrt{\frac{3}{10}} \left(\frac{\epsilon-1}{\epsilon+2} \right)^2 (u_{20} - \sqrt{6}u_{2,\pm 2}), \quad (18)$$

$$a_0^{(y)} = -i \frac{3}{\sqrt{10}} \left(\frac{\epsilon-1}{\epsilon+2} \right)^2 (u_{2,-1} + u_{21}), \quad a_{\pm 1}^{(y)} = -i \sqrt{\frac{3}{10}} \left(\frac{\epsilon-1}{\epsilon+2} \right)^2 (u_{20} + \sqrt{6}u_{2,\pm 2}). \quad (19)$$

The relation between the coefficients $b_M^{(i)}$ and $a_M^{(i)}$ is the same as for $i = z$ in Eq. (17). The set of the obtained coefficients a_M and b_M fully determines the dipolar field of a droplet in the first approximation in the droplet fluctuations. To find the second-order correction to this solution, we act in the following way. We represent the searched coefficient as $a_M \rightarrow a_M + \Delta_M$ and $b_M \rightarrow b_M + \delta_M$, where Δ and δ are of the second order in the amplitudes u . Substituting the solution (11) in Eq. (10) using (13), the two boundary conditions are obtained for the unknown corrections Δ and δ . Combining the two equations we obtain

$$\begin{aligned} \sum_M \Delta_M^{(z)} Y_{1M} &= \frac{2\epsilon-3}{\epsilon-1} \sum_M a_M^{(z)} f Y_{1M} - \frac{4\epsilon-1}{(\epsilon-1)(\epsilon+2)} \sum_M a_M^{(z)} [\partial_\vartheta Y_{1M} \partial_\vartheta f + \frac{1}{\sin^2 \vartheta} \partial_\varphi Y_{1M} \partial_\varphi f] \\ &\quad - 3 \frac{(\epsilon-1)(\epsilon+4)}{(\epsilon+2)^2} f^2 \cos \vartheta - 6 \frac{\epsilon-1}{(\epsilon+2)^2} \sin \vartheta f \partial_\vartheta f + 3 \frac{\epsilon-1}{\epsilon+2} u_{00} Y_{00} \cos \vartheta. \end{aligned} \quad (20)$$

Here, $a_M^{(z)}$ are from Eq. (17). There is no need to search for the full solution of this equation. All experimentally observed quantities that we construct using the solution for the potential Φ have to be in the final step averaged over the fluctuations u . Having this in mind, and since we are interested in the solution correct to the second order in the fluctuations, we can perform the averaging already in Eq. (20). By this way we obtain the solution to Eq. (20) in a simplified form that however gives correct contributions to the averaged quantities of the second order in the fluctuations:

$$\Delta_{\pm 1}^{(z)} = 0, \quad \Delta_0^{(z)} \equiv \Delta = -\sqrt{\frac{3}{\pi}} \frac{\epsilon - 1}{(\epsilon + 2)^2} \left[3 \frac{(\epsilon + 1)(\epsilon + 11)}{\epsilon + 2} u_{20}^2 + (\epsilon + 3) \sum_{l>2} (2l + 1) u_{l0}^2 \right]. \quad (21)$$

Analogously, quadratic corrections can be obtained in the cases when the external field is oriented along the axes x and y . The change of the corresponding coefficients a_M is as follows:

$$\Delta_0^{(x)} = 0, \quad \Delta_{\pm 1}^{(x)} = \mp \frac{1}{\sqrt{2}} \Delta, \quad \Delta_0^{(y)} = 0, \quad \Delta_{\pm 1}^{(y)} = \frac{i}{\sqrt{2}} \Delta. \quad (22)$$

Now it is easy to obtain the polarizability tensor components, that is the main purpose of the paper. Writing the solution (11) for $\Phi^{(e)}$ through the cartesian coordinates x, y, z , from the expression for the dipole field $\Phi^{(e)} = \vec{d} \vec{r} / r^3$, the x, y, z components of the dipole moment are

$$\vec{d} = E_0 R_0^3 \left\{ \sqrt{\frac{3}{8\pi}} (a_{-1}^{(z)} - a_1^{(z)}), -i \sqrt{\frac{3}{8\pi}} (a_{-1}^{(z)} + a_1^{(z)}), \frac{\epsilon - 1}{\epsilon + 2} + \sqrt{\frac{3}{4\pi}} a_0^{(z)} \right\}, \quad (23)$$

where the proper dimension is recovered. Comparing this expression with the definition of the polarizability,

$$d_i = \sum_k \alpha_{ik} E_{0k},$$

and using Eqs. (17) and (22), one obtains the polarizability tensor components α_{iz} , $i = x, y, z$ in the laboratory frame. Analogously the rest of the components of the tensor α_{ik} is obtained with the use of Eqs. (18), (19), and (22). The result is as follows:

$$\begin{aligned} \alpha_{xy} = \alpha_{yx} &= -i \frac{3}{2} \sqrt{\frac{3}{10\pi}} R_0^3 \left(\frac{\epsilon - 1}{\epsilon + 2} \right)^2 (u_{2,-2} - u_{22}), \\ \alpha_{xz} = \alpha_{zx} &= \frac{3}{2} \sqrt{\frac{3}{10\pi}} R_0^3 \left(\frac{\epsilon - 1}{\epsilon + 2} \right)^2 (u_{2,-1} - u_{21}), \\ \alpha_{yz} = \alpha_{zy} &= -i \frac{3}{2} \sqrt{\frac{3}{10\pi}} R_0^3 \left(\frac{\epsilon - 1}{\epsilon + 2} \right)^2 (u_{2,-1} + u_{21}), \\ \alpha_{xx} &= R_0^3 \frac{\epsilon - 1}{\epsilon + 2} \left[1 + \frac{3}{2} \sqrt{\frac{3}{10\pi}} \frac{\epsilon - 1}{\epsilon + 2} (u_{2,-2} + u_{22} - \sqrt{\frac{2}{3}} u_{20}) - \tilde{\Delta} \right], \\ \alpha_{yy} &= R_0^3 \frac{\epsilon - 1}{\epsilon + 2} \left[1 - \frac{3}{2} \sqrt{\frac{3}{10\pi}} \frac{\epsilon - 1}{\epsilon + 2} (u_{2,-2} + u_{22} + \sqrt{\frac{2}{3}} u_{20}) - \tilde{\Delta} \right], \end{aligned}$$

$$\alpha_{zz} = R_0^3 \frac{\epsilon - 1}{\epsilon + 2} \left[1 + \frac{3}{\sqrt{5\pi}} \frac{\epsilon - 1}{\epsilon + 2} u_{20} - \tilde{\Delta} \right], \quad \tilde{\Delta} \equiv -\frac{1}{2} \sqrt{\frac{3}{\pi}} \frac{\epsilon + 2}{\epsilon - 1} \Delta, \quad (24)$$

where Δ is introduced in Eq. (21). In the first approximation with respect to the account of fluctuation our expressions correct those from Ref. [15] where there were found for $\epsilon \rightarrow \infty$. The dipole moment induced by an external field is the same as the dipole moment of an ellipsoid with the main half-axes $a = R_0[1 + (e_x^2 + e_y^2)/6]$, $b = R_0[1 + (e_y^2 - 2e_x^2)/6]$, and $c = R_0[1 + (e_x^2 - 2e_y^2)/6]$, where the eccentricities e_x and e_y are $e_x^2 = \sqrt{15/2\pi}(-u_{22} + \sqrt{3/2}u_{20})$, and $e_y^2 = \sqrt{15/2\pi}(u_{22} + \sqrt{3/2}u_{20})$, in the frame connected with the droplet and with the axes along the main axes of the ellipsoid. The depolarization coefficients of such an ellipsoid, $n^{(i)} = R_0^3/3\alpha_{ii} - 1(\epsilon - 1)$, $i = x, y, z$, are $3n^{(x)} = 1 - (3/\sqrt{5\pi})u_{20}$, $3n^{(y)} = 1 + (3/2\sqrt{5\pi})(u_{20} + \sqrt{6}u_{22})$, and $3n^{(z)} = 1 + (3/2\sqrt{5\pi})(u_{20} - \sqrt{6}u_{22})$, that follows from the general formula for the dipole moment of an ellipsoid placed in an external field parallel to the axis i [22]. The contributions of the second order of the fluctuation amplitudes change only the diagonal components of the polarizability tensor. Thus the polarizability anisotropy, that is reflected e.g. in the Kerr effect, is determined solely by the ellipsoidal fluctuations (the $l = 2$ modes, as already pointed out in Ref. [15]). The higher order terms are determined by all kinds of the droplet vibrations with $l > 1$. Outside the droplet the resulting electric field is a sum of the applied field and a field of an electric dipole in the origin with a dipole moment (when averaged over the fluctuations) $\langle d \rangle = d_{sph}[1 - \langle \tilde{\Delta} \rangle]$ parallel to the applied field. Inside the droplet the mean field is oriented along \vec{E}_0 and its absolute value is larger than that of a perfect sphere. This follows from the solution (11) for $\Phi^{(i)}$, that gives $\langle E_x \rangle = \langle E_y \rangle = 0$, $\langle E_z \rangle = 3E_0/(\epsilon + 2) - E_0\sqrt{3/4\pi}\langle b_0^{(z)} \rangle$, where $\langle b_0^{(z)} \rangle = \langle \delta_0^{(z)} \rangle < 0$ (if b is calculated to the second order in fluctuations) is easily found using Eq. (17) and the continuity of the potential.

IV. THE KERR EFFECT

The obtained polarizability of a droplet can be used for a simplest description of the Kerr effect on droplet microemulsions. When the droplet is placed in an electric field, the difference between the refractive indices n_{\parallel} parallel and n_{\perp} perpendicular to the field can be expressed in terms of the optical polarizabilities as

$$\Delta n \equiv n_{\parallel} - n_{\perp} \approx \frac{3}{2R_0^3} n_e \Phi (\alpha_{\parallel}^{opt} - \alpha_{\perp}^{opt}), \quad (25)$$

where Φ is the volume fraction of the droplets and n_e is the refractive index of the microemulsion continuous phase. Eq. (25) follows from the Lorentz-Lorenz formula simplified for the case of low Φ [24]. To obtain the statistically averaged quantity $\langle \Delta n \rangle$, we use the full free energy of a dielectric body in an electric field [22],

$$F - F_0 = -\frac{1}{8\pi} \int \vec{E}_0 (\vec{D} - \epsilon_e \vec{E}) dV, \quad (26)$$

where F_0 is the free energy of the field without a dielectric body, and \vec{E} is the field changed by the presence of the body. Equation (26) is especially suitable since we have to integrate only within the volume of the droplet. Finding the electric intensity inside the droplet and performing the integration, one obtains

$$F - F_0 = -\epsilon_e \frac{\epsilon - 1}{\epsilon + 2} \frac{R_0^3 E_0^2}{2} \left[1 + \frac{3}{\sqrt{5\pi}} \frac{\epsilon - 1}{\epsilon + 2} u_{20} \right]. \quad (27)$$

Using the expansion $\exp[-(F - F_0)/k_B T]$ to the first order in u_{20} and the polarizability tensor components from Eq. (24) (with $\epsilon = n^2 = (n_i/n_e)^2$ for the optical polarizabilities), we finally find the Kerr constant

$$K = \frac{\langle \Delta n \rangle}{E_0^2 \Phi} = \frac{81}{40\pi} \frac{R_0^3 n_e \epsilon_e}{k_B T} \left(\frac{\epsilon - 1}{\epsilon + 2} \right)^2 \left(\frac{n^2 - 1}{n^2 + 2} \right)^2 \langle u_{20}^2 \rangle. \quad (28)$$

This equation surprisingly agrees with that obtained in [15]. Using the distribution (7), after the average over the droplet radii R_0^3 has to be replaced by $\langle R_0^3 \rangle \approx R_m^3 (1 + 3\epsilon)$. The estimation of the bending rigidity value obtained from the experiments [6] (see also Ref. [26]) is $\kappa \approx 1k_B T$. For the discussion of this result see, however, Conclusion.

V. DEPOLARIZED SCATTERING OF LIGHT

The effects of polarization anisotropy are well revealed in the experiments on the depolarized scattering of light [25]. Let the scattered field is propagating in the x direction, and the initial field has a polarization $\vec{n}_i = \hat{z}$. Then the intensity of the depolarized light ($\vec{n}_f = \hat{y}$) is

$$I_{VH} = N \langle \alpha_{yz}^{opt}(0) \alpha_{yz}^{opt}(t) \rangle F_s(Q, t). \quad (29)$$

Here, F_s is the self-diffusion correlation function of the droplet, Q is the wave-vector transfer at the scattering, N is the number of droplets in the scattering volume, and $\langle \rangle$ denotes the thermal equilibrium average over the ensemble of droplets in the absence of any field. The polarized component of the scattered light is

$$I_{VV} = N \langle \alpha_{zz}^{opt}(0) \alpha_{zz}^{opt}(t) \rangle F_s(Q, t). \quad (30)$$

Using Eq. (24), one finds

$$I_{VH} = \frac{27N}{20\pi} R_0^6 \left(\frac{n^2 - 1}{n^2 + 2} \right)^4 \langle u_{20}^2 \rangle \exp(-\Gamma_2 t) F_s(Q, t). \quad (31)$$

This expression differs from the equation found in Ref. [15] that contains an extra factor n_e^4 . Analogously the intensity of the polarized scattering can be found,

$$I_{VV} = N R_0^6 \left(\frac{n^2 - 1}{n^2 + 2} \right)^2 \left[1 + \frac{9}{5\pi} \left(\frac{n^2 - 1}{n^2 + 2} \right)^2 \langle u_{20}^2 \rangle \exp(-\Gamma_2 t) - 2 \langle \tilde{\Delta}(n) \rangle \right] F_s(Q, t). \quad (32)$$

For the integral intensity of the scattering we have, in agreement with the formula for cylindrically symmetric molecules [25], $I_{VV} = I_{ISO} + \frac{4}{3} I_{VH}$, where $I_{ISO} = N\alpha^2$ is the isotropic part of the scattering determined by the trace α of the polarizability tensor, and is easily found from Eq. (24). One thus obtains for the depolarization ratio

$$\frac{I_{VH}}{I_{ISO}} = \frac{27}{20\pi} \left(\frac{n^2 - 1}{n^2 + 2} \right)^2 \langle u_{20}^2 \rangle. \quad (33)$$

The account for the second-order terms in fluctuations is necessary in the determination of the polarized and isotropic scattering. For example, for the system studied in Ref. [6]

(water - AOT - n-hexane microemulsion) with the parameters $n_e \approx 1.37$, $n \approx 1$, $\sqrt{\epsilon} \approx 0.12$, and $\kappa \approx 1k_B T$, the isotropic part of the scattering is determined by $I_{ISO} = NR_0^6(n^2 - 1)^2(n^2 + 2)^{-2}(1 - 2\langle\tilde{\Delta}\rangle)$ with $\langle\tilde{\Delta}\rangle \approx 0.4$. In $\langle\tilde{\Delta}\rangle$ itself the account for the $l > 2$ modes is important: it represents about 1/3 of the $l = 2$ contribution. Unfortunately, we have no knowledge about experiments where the depolarized and polarized light scattering on microemulsions were measured.

VI. CONCLUSION

In the present work the polarizability of a droplet has been calculated. It was assumed that the shape of the droplet fluctuates in time and the result for the polarizability was obtained to the second order in the amplitudes of these fluctuations. This could be important when the relevant quantities are expressed through the correlation functions of the diagonal components of the polarizability tensor, like in the scattering of light. Of course, the account for the second order in fluctuations is unnecessary when the polarizability anisotropy is responsible for the measured effect. We proceeded from the solution of the Laplace equation for a fluctuating droplet with a finite dielectric constant in a dielectric medium. We have corrected the expressions for the polarizability found in Ref. [15] where it was calculated to the first order in the fluctuations and for a droplet with infinite dielectric constant in vacuum. The obtained formulae were applied to the description of the Kerr effect and the depolarized and polarized scattering of light. The expression for the specific Kerr constant is the same as in Ref. [15], a significant difference has been found in the expressions for the intensity of the scattered light. A comparison of the theoretical results with the Kerr-effect experiment on microemulsions gave an estimation of the bending rigidity constant of about $1k_B T$ for microemulsions consisting of droplets with relatively large radii [6]. However, this estimation should be considered with serious doubts. First, the experimental error in obtaining the Kerr constant by extrapolation of the data to zero concentration of the droplets is large so that the estimation is not very reliable. The radius of the droplet was

determined by standard dynamic light scattering (DLS) experiments. It is known that the DLS technique is rather problematic in the determination of microemulsion characteristics (see the discussion in Ref. [8]), especially it concerns the radius of the droplets. It is always larger than the radius obtained from other techniques like the scattering of neutrons. Since the signal measured in the Kerr-effect experiments is very sensitive to the radius, it should be determined with a high precision. Moreover, the polydispersity of the droplet distribution in radii becomes very important. In the work [6] it was first assumed for the polydispersity that $\sqrt{\varepsilon}$ (from small-angle neutron scattering experiments by other authors) varies from about 0.25 to 0.30. In Erratum to Ref. [6] the value for $\sqrt{\varepsilon}$ was changed to about 0.12 (based on reports from the literature on experiments using light scattering techniques). To our opinion, all the characteristics should be determined in one series of experiments on the same system. From available techniques the small-angle neutron scattering seems to be the method in which the basic characteristics of the microemulsion droplets are well fixed. Other experimental techniques, like the Kerr-effect measurements or light scattering methods, could serve as alternative probes for these characteristics. For these purposes, however, the description of the methods should be improved in comparison with the approach presented in this communication. On the basis of our analysis of the DLS experiments [8], we propose that on the first place the inclusion of the finite thickness of the surfactant layer, with dielectric and optical properties different from its environment, is needed.

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Лисы В.

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Поляризуемость жидких капель и эффект Кэрра
на микроэмульсиях

Рассмотрены сфероидальные жидкие капли, находящиеся в другой жидкости. С учетом тепловых флуктуаций формы капель рассчитана их поляризуемость до второго порядка по амплитудам флуктуаций. Найдены корреляционные функции компонентов тензора поляризуемости. С их помощью описаны поляризованное и деполяризованное рассеяние света и эффект Кэрра на микроэмульсиях. Из сравнения результатов теории и литературных данных по измерению константы Кэрра оценивается изгибная жесткость монослоя сурфактанта, разделяющего фазы масла и воды в капельных микроэмульсиях.

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Lisy V.

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Polarizability of Fluid Droplets and the Kerr Effect
on Microemulsions

Spheroidal fluid droplets immersed in another fluid and thermally fluctuating in the shape are considered. The polarizability of the droplet is evaluated up to the second order in the fluctuation amplitudes. The correlation functions of the polarizability tensor components are found and used to describe the polarized and depolarized scattering of light, and the Kerr effect on microemulsions. By comparison of the theoretical results with the Kerr constant measurements from the literature, we estimate the bending rigidity of the surfactant monolayer that separates the oil and water phases in droplet microemulsions.

The investigation has been performed at the Bogoliubov Laboratory of Theoretical Physics, JINR.

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