Polarizability of microemulsion droplets

M. Richterová and V. Lisý

Department of Biophysics, P. J. Šafárik University,
Jesenná 5, 041 54 Košice, Slovakia

Abstract

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 and also the previous first-order calculations from the literature are corrected. 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 in the limit of small concentration of the droplets. An alternative simple derivation of the Kerr constant is also given assuming that the droplet in a weak electric field becomes a prolate ellipsoid. We consider both the case when the thickness of the surface layer is neglected and when the droplet is covered by a layer of nonzero thickness. The result differs significantly from that used in the literature to describe the Kerr-effect measurements on droplet microemulsions. Due to the difference the bending rigidity constant of the layer should be increased about two times in comparison with the value found in the original experiments.

1 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 thermodynamic 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 modules \( \kappa \) and \( \pi \), respectively, the spontaneous curvature \( C_s \), the surface tension coefficient \( \alpha \), and the equilibrium radius of the droplet, \( R_0 \). In addition, the free energy of the droplet is determined by the pressure difference \( \Delta p \) (pressure inside the droplet minus outside). In real microemulsions there is some distribution of the droplets in radii. The polydispersity of this distribution, \( \varepsilon \), can be regarded as a microemulsion parameter instead of \( \Delta p \) [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 even for the same microemulsion systems. For example, there is some one order difference in the bending rigidity $\kappa$ determined from the Kerr-effect measurements \cite{8} and the neutron scattering associated with spin echoes \cite{7} (for a more discussion see Ref. \cite{8}). We have shown in our recent paper \cite{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. \cite{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 \cite{7,9,10} but larger than possessed by the spinning drop measurements \cite{11}, the Kerr effect \cite{6} or a combination of dynamic light and neutron scattering \cite{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 $\alpha_{ik}$ of a microemulsion droplet, such experiments like the Kerr effect or the polarized and depolarized scattering of light could be described. They 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 \cite{14} the polarizability of an ellipsoid is evaluated. In that work the shape fluctuations have not been considered and, as shown below, the surface free energy found there is not correct. In Ref. \cite{15} the fluctuations of a spherical droplet are considered, however, also 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 diagonal polarizability tensor components. In the next section a brief phenomenological theory of the shape fluctuations of droplets is given. In the third section the polarizability tensor $\alpha_{ik}$ 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 the subsequent section a simple derivation of the Kerr constant is given assuming that in a weak electric field the fluid droplet becomes a prolate ellipsoid with small eccentricity. The derivation is done both for the case when the thickness of the surface layer of the droplet is negligible and when the droplet is covered by a membrane with nonzero thickness. The result differs significantly from that known in the literature \cite{14}. Due to the difference the bending rigidity constant should be increased about two times in comparison with the value found in the original experiments \cite{14}. In Conclusion, the obtained results and possible improvements of the theory are discussed.
2 Shape fluctuations of spherical droplets

Consider a flexible droplet taking 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,

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

where

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

with $m = -l, -l + 1, \ldots, l$, and $0 \leq l$. When $l = 0$ or 1, the coefficients $u_{lm}$ can be expressed as quadratic combinations of the rest of expansion coefficients, e.g.

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

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 translational motion of the droplet as a whole. The necessary time correlation functions are as follows:

$$\langle u_{l0}(0) u_{l0}(t) \rangle = \frac{k_BT}{\alpha l R_0^2 (l + 2)(l - 1)} \exp(-\Gamma_l t),$$

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

Here, $\alpha = \sigma + C_s^2\kappa/2$ ($\sigma$ is the microscopic interfacial tension [4]). The decay rates $\Gamma_l$ 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 $\Gamma_l$ 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

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

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

$$\varepsilon = \frac{k_BT}{8\pi(2\kappa + \pi)}.$$ 

Here, for simplicity, the two-phase coexistence is assumed, when $\alpha = (2\kappa + \pi)R_m^{-2} = \kappa C_s/R_m$. For small $\varepsilon$ the distribution (6) 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 $\sim \exp(-1/2\varepsilon)$. 

\[3\]
For dense microemulsions the interaction between the droplets should be taken into account. This is still an open question since it seems that the droplets do not interact like hard spheres \cite{20, 21}. Most often dilute solutions of droplets are studied assuming that 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 $\alpha_l$ from Eq. (5). 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 $2k_BTF(\Phi)$, where for small volume fractions $\Phi$ of the droplets $F \approx \ln \Phi - 1$. The mean quadrature of the amplitude of fluctuations does not explicitly depend on the function $F$,

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

3 Polarizability of a droplet

As mentioned in Introduction, the polarizability of a fluctuating droplet was already evaluated by Borkovec and Eicke \cite{15}. However, that work should be corrected in some points. The authors calculate the polarizability for a fluid droplet of infinite dielectric constant $\varepsilon$ 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 $\varepsilon$ 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 \cite{22}. In general, such a reasoning is not correct. In particular, it is not applicable in our problem of finding the polarizability tensor $\alpha_{ik}, i, k = x, y, z,$ of a droplet, since $\alpha_{ik}$ 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 $\varepsilon_i$ and the outer medium is characterized by the constant $\varepsilon_e$. 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 $\Phi$ inside and outside the droplet, together with the boundary conditions at the interface between the two medii,

$$\Phi^{(i)} = \Phi^{(e)}, \quad \varepsilon D^{(i)}_n = D^{(e)}_n, \quad \text{at} \quad r = R_0(1 + f), \quad (9)$$

where $D_n$ is the normal component of electric induction, $\varepsilon = \varepsilon_i/\varepsilon_e$, 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

$$\Phi^{(i)} = -\frac{3}{\varepsilon + 2}r \cos \vartheta + r \sum_M b^{(z)}_M Y_{1M},$$

$$\Phi^{(e)} = -r \cos \vartheta + \frac{\epsilon - 1}{\epsilon + 2}r^{-2} \cos \vartheta + r^{-2} \sum_M a^{(e)}_M Y_{1M}, \quad (10)$$
where we temporarily reduced the variables by replacing \( r/R_0 \rightarrow r \) and \( \Phi/E_0R_0 \rightarrow \Phi \). 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 \( a^{(z)}_M \) and \( b^{(z)}_M \). Only the dipole field is considered. To satisfy the second boundary condition in Eqs. (9) one has first to find the normal vector to the deformed droplet interface. The normal is defined through the vectors \( \vec{r}_\theta = \partial_\theta \vec{r} \) and \( \vec{r}_\varphi = \partial_\varphi \vec{r} \), using Eq. (1),

\[
\vec{n} = \frac{\vec{r}_\theta \times \vec{r}_\varphi}{(\vec{r}_\theta \times \vec{r}_\varphi)^2}.
\]

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

\[
\vec{n} \vec{\nabla} \Phi = (\vec{\nabla} \Phi)_r \{ 1 - \frac{1}{2} \left[ (\frac{\partial f}{\partial \theta})^2 + \sin^{-2} \vartheta (\frac{\partial f}{\partial \varphi})^2 \right] \}
+ (\vec{\nabla} \Phi)_\varphi (f - 1) \frac{\partial f}{\partial \theta} + \sin^{-1} \vartheta (\vec{\nabla} \Phi)_\theta (f - 1) \frac{\partial f}{\partial \varphi}.
\]

When \( \Phi^{(z)} \) and \( \Phi^{(e)} \) from Eqs. (10) are substituted in Eq. (12), the second boundary condition from Eq. (9) becomes

\[
\epsilon \sum_M b^{(z)}_MY_{1M} = -2 \sum_M a^{(z)}_MY_{1M} + 3 \epsilon \frac{1}{\epsilon + 2} [2f \cos \vartheta + \frac{\partial f}{\partial \vartheta} \sin \vartheta].
\]

Together with the condition of continuity of the potential,

\[
\sum_M b^{(z)}_MY_{1M} = \sum_M a^{(z)}_MY_{1M} - 3 \epsilon \frac{1}{\epsilon + 2} f \cos \vartheta,
\]

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

\[
\sum_M a^{(z)}_MY_{1M} = 3 \epsilon \frac{1}{\epsilon + 2} [f \cos \vartheta + \frac{\sin \vartheta \partial f}{\epsilon + 2 \partial \vartheta}].
\]

Multiplying this equation by \( Y_{1M} \) and integrating over all angles \( \vartheta \) and \( \varphi \), one obtains the desired coefficients \( a^{(z)}_M \). 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 \( (l100 | 10) \) 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 \( \vartheta \) (the second term in Eq. (15)). We thus have only the spherical harmonics of order 1 and 2 so that the integration is performed in elementary functions. In this way we find from Eqs. (14) and (15)

\[
a^{(z)}_M = \frac{3}{\sqrt{5}} \left( \frac{2}{\sqrt{3}} \delta_{M0} + \delta_{M1} + \delta_{M1-1} \right) \left( \frac{\epsilon - 1}{\epsilon + 2} \right)^2 u_{2M}, \quad b^{(z)}_M = -\frac{3}{\epsilon - 1} a^{(z)}_M.
\]

Quite similarly the response of the droplet can be considered when the external field is oriented along the axes \( x \) and \( y \). In Eqs. (10) 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 \( a^{(z)}_M \) we obtained

\[
a^{(x)}_0 = \frac{3}{\sqrt{10}} \frac{(\epsilon - 1)^2}{(\epsilon + 2)} (u_{2,1} - u_{21}), \quad a^{(x)}_{\pm1} = \pm \frac{3}{\sqrt{10}} \frac{(\epsilon - 1)^2}{(\epsilon + 2)} (u_{20} - \sqrt{6}u_{2,\pm2}),
\]

\[
a^{(y)}_0 = -i \frac{3}{\sqrt{10}} \frac{(\epsilon - 1)^2}{(\epsilon + 2)} (u_{2,1} + u_{21}), \quad a^{(y)}_{\pm1} = -i \frac{3}{\sqrt{10}} \frac{(\epsilon - 1)^2}{(\epsilon + 2)} (u_{20} + \sqrt{6}u_{2,\pm2}).
\]

The relation between the coefficients \( b^{(i)}_M \) and \( a^{(i)}_M \) is the same as for \( i = z \) in Eq. (16). 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 coefficients as \( a_M \rightarrow a_M + \Delta_M \) and \( b_M \rightarrow b_M + \delta_M \), where \( \Delta \) and \( \delta \) are of the second order in the amplitudes \( u \). Substituting the solutions (10) in Eqs. (9) using (12), the two boundary conditions are obtained for the unknown corrections \( \Delta \) and \( \delta \). Combining the two equations we obtain

\[
\sum_M \Delta^{(z)}_MY_{1M} = \frac{2\epsilon - 3}{\epsilon - 1} \sum_M a^{(z)}_M fY_{1M} - \frac{4\epsilon - 1}{(\epsilon - 1)(\epsilon + 2)} \sum_M a^{(z)}_M \left[ \frac{\partial Y_{1M}}{\partial \vartheta} \frac{\partial f}{\partial \vartheta} + \frac{1}{\sin^2 \vartheta} \frac{\partial Y_{1M}}{\partial \varphi} \frac{\partial f}{\partial \varphi} \right] + 3 \frac{(\epsilon - 1)(\epsilon + 4)}{(\epsilon + 2)^2} f^2 \cos \vartheta - 6 \frac{\epsilon - 1}{\epsilon + 2} \sin \vartheta \frac{f\partial f}{\partial \vartheta} + 3 \frac{\epsilon - 1}{\epsilon + 2} u_{00} Y_{00} \cos \vartheta.
\]

Here, \( a^{(z)}_M \) are from Eq. (16). 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 \( \Phi \) 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. (19). By this way we obtain the solution to Eq. (19) in a simplified form that however gives correct contributions to the averaged quantities of the second order in the fluctuations:

\[
\Delta^{(z)}_{\pm1} = 0, \quad \Delta^{(z)}_0 \equiv \Delta = -\sqrt{\frac{3}{\pi}} \frac{\epsilon - 1}{(\epsilon + 2)^2} \frac{1}{3} \left( \frac{\epsilon + 1}{\epsilon + 2} \right) u_{20}^2 + (\epsilon + 3) \sum_{l>2} (2l + 1) u_{l0}^2.
\]

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:

\[
\Delta^{(x)}_0 = 0, \quad \Delta^{(x)}_{\pm1} = \mp \frac{1}{\sqrt{2}} \Delta, \quad \Delta^{(y)}_0 = 0, \quad \Delta^{(y)}_{\pm1} = \frac{i}{\sqrt{2}} \Delta.
\]

Now it is easy to obtain the polarizability tensor components, that is the main purpose of the paper. Writing the solution (10) for \( \Phi^{(e)} \) through the cartesian coordinates \( x, y, z \), from the expression for the dipole field \( \Phi^{(e)} = \frac{d}{r^3} \), the \( x, y, z \) components of the dipole moment are

\[
\overrightarrow{d} = E_0 R_0^3 \left\{ \frac{3}{8\pi} (a^{(z)}_{l-1} - a^{(z)}_1), -i \frac{3}{8\pi} (a^{(z)}_{l-1} + a^{(z)}_1), \frac{\epsilon - 1}{\epsilon + 2} + \sqrt{\frac{3}{4\pi}} a^{(z)}_0 \right\}.
\]
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. (16) and (21), one obtains the polarizability tensor components \( \alpha_{iz}, i = x, y, z \) in the laboratory frame. Analogously the rest of the components of the tensor \( \alpha_{ik} \) is obtained with the use of Eqs. (17), (18), and (21). The result is as follows:

\[
\begin{align*}
\alpha_{xy} &= \alpha_{yx} = -\frac{3}{2} R_0^3 \frac{\epsilon - 1}{\epsilon + 2} \left( u_{2,-2} - u_{22} \right), \\
\alpha_{xz} &= \alpha_{zx} = \frac{3}{2} R_0^3 \frac{\epsilon - 1}{\epsilon + 2} \left( u_{2,-1} - u_{21} \right), \\
\alpha_{yz} &= \alpha_{zy} = -\frac{3}{2} R_0^3 \frac{\epsilon - 1}{\epsilon + 2} \left( u_{2,-1} + u_{21} \right), \\
\alpha_{xx} &= R_0^3 \frac{\epsilon - 1}{\epsilon + 2} \left[ 1 + \frac{3}{2} \frac{\epsilon - 1}{10\pi \epsilon + 2} u_{2,-2} + \sqrt{\frac{2}{3}} u_{20} - \tilde{\Delta} \right], \\
\alpha_{yy} &= R_0^3 \frac{\epsilon - 1}{\epsilon + 2} \left[ 1 - \frac{3}{2} \frac{\epsilon - 1}{10\pi \epsilon + 2} u_{2,-2} + \sqrt{\frac{2}{3}} u_{20} - \tilde{\Delta} \right], \\
\alpha_{zz} &= R_0^3 \frac{\epsilon - 1}{\epsilon + 2} \left[ 1 + \frac{3}{ \sqrt{5\pi} \epsilon + 2} u_{20} - \tilde{\Delta} \right], \\
\alpha_{ik} &= \frac{1}{2} \sqrt{\frac{3\epsilon + 2}{\pi \epsilon - 1}} \Delta,
\end{align*}
\]

(23)

where \( \Delta \) is introduced in Eq. (20). 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 \( a = R_0 [1 + (e_x^2 + e_y^2)/6], b = R_0 [1 + (e_y^2 - 2e_z^2)/6], \) and \( c = R_0 [1 + (e_z^2 - 2e_x^2)/6], \) where the eccentricities \( e_x \) and \( e_y \) are \( e_x^2 = \sqrt{15/2\pi(-u_{22} + \sqrt{3/2u_{20}})}, \) and \( e_y^2 = \sqrt{15/2\pi+3/2u_{20}}), \) 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, \( n^{(i)} = R_0^3/3\alpha_{ii}, i = x, y, z, \) are \( 3n^{(x)} = 1 - (3/\sqrt{5\pi})u_{20}, 3n^{(y)} = 1 + (3/\sqrt{5\pi})u_{20} + \sqrt{6u_{22}}, \) and \( 3n^{(z)} = 1 + (3/2\sqrt{5\pi})u_{20} + \sqrt{6u_{22}}, \) 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) \( \langle d \rangle = \frac{d_{\text{spin}}}{1 - \langle \tilde{\Delta} \rangle} \parallel \) 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 (10) for \( \Phi^{(i)}, \) that gives \( \langle E_x \rangle = \langle E_y \rangle = 0, \langle E_z \rangle = 3E_0/(\epsilon+2) - E_0 \sqrt{3/4\pi} \langle b^{(z)} \rangle, \) where \( \langle b^{(z)} \rangle = \langle b^{(z)} \rangle < 0 \) (if \( b \) is calculated to the second order in fluctuations) is easily found using Eq. (16) and the continuity of the potential.
4 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

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

where $\Phi$ is the volume fraction of the droplets and $n_e$ is the refractive index of the microemulsion continuous phase. Eq. (24) follows from the Lorentz-Lorenz formula simplified for the case of low $\Phi$ [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],

$$F - F_0 = -\frac{1}{8\pi} \int \bar{E} \Phi(\bar{D} - \epsilon_e \bar{E}) dV,$$

where $F_0$ is the free energy of the field without a dielectric body, and $\bar{E}$ is the field changed by the presence of the body. Equation (25) 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

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

(26)

Using the expansion $\exp[-(F - F_0)/k_B T]$ to the first order in $u_{20}$ and the polarizability tensor components from Eq. (23) (with $\epsilon = n^2 = (n_i/n_e)^2$ for the optical polarizabilities), we finally find the Kerr constant

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

(27)

This equation agrees with that obtained in [15]. Using the distribution (6), after the averaging over the droplet radii $R_0^3$ has to be replaced by $\langle R_0^3 \rangle \approx R_m^3 (1 + 3\varepsilon)$. The estimation of the bending rigidity value obtained from the experiments [3] (see also Ref. [25]) is $\kappa \approx 1k_B T$. For the discussion of this result see, however, Conclusion.

5 Depolarized scattering of light

The effects of polarization anisotropy are well revealed in the experiments on the depolarized scattering of light [26]. 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

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

(28)

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

$$I_{VV} = N\langle \alpha_{zz}^{\text{opt}}(0)\alpha_{zz}^{\text{opt}}(t) \rangle F_s(Q, t).$$  \hspace{1cm} (29)$$

Using Eq. (23), one finds

$$I_{VH} = \frac{27N}{20\pi}R_0^6\left(\frac{n^2-1}{n^2+2}\right)^4\langle u_{20}^2 \rangle \exp(-\Gamma_2 t)F_s(Q, t).$$  \hspace{1cm} (30)$$

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,

$$I_{VV} = NR_0^6\left(\frac{n^2-1}{n^2+2}\right)^2[1 + \frac{9}{5\pi}\left(\frac{n^2-1}{n^2+2}\right)^2\langle u_{20}^2 \rangle \exp(-\Gamma_2 t) - 2\langle \tilde{\Delta}(n) \rangle]F_s(Q, t).$$  \hspace{1cm} (31)$$

For the integral intensity of the scattering we have, in agreement with the formula for cylindrically symmetric molecules [20], $I_{VV} = I_{ISO} + \frac{4}{3}I_{VH}$, where $I_{ISO} = N\alpha^2$ is the isotropic part of the scattering determined by the trace $\alpha$ of the polarizability tensor, and is easily found from Eq. (23). One thus obtains for the depolarization ratio

$$\frac{I_{VH}}{I_{ISO}} = \frac{27}{20\pi}\left(\frac{n^2-1}{n^2+2}\right)^2\langle u_{20}^2 \rangle.$$  \hspace{1cm} (32)$$

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 $n_e \approx 1.37, n \approx 1, \sqrt{\varepsilon} \approx 0.12$, and $\kappa \approx 1k_B T$, the isotropic part of the scattering is determined by $I_{ISO} = NR_0^6(n^2-1)^2(n^2+2)^{-2}(1-2\langle \tilde{\Delta}(n) \rangle)\langle \tilde{\Delta} \rangle \approx 0.4$. 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.

6 A simple derivation of the Kerr constant

In this section we give a simple alternative derivation of the Kerr constant (27). First, consider a fluid droplet assuming that the thickness of the surface layer of the droplet is negligible if compared to its radius. When such a droplet of the radius $R_0$ is placed in a weak electric field $\vec{E}_0$ directed along the axis $z$, it becomes a prolate ellipsoid with the half-axes, to the second order of the small eccentricity $e = \sqrt{1-b^2/a^2},$

$$a = R_0(1+e^2/3), \quad b = c = R_0(1-e^2/6).$$  \hspace{1cm} (33)$$

Within the Helfrich model of interfacial elasticity [3, 4] the free energy of such an ellipsoid (without the electrostatic energy) is [4]

$$F = -\Delta p V + \sigma A + \int dA\left[\frac{\kappa}{2}(c_1 + c_2 - 2/R_s)^2 + \pi c_1 c_2 \right].$$  \hspace{1cm} (34)$$
Here $V$ is the (constant) volume of the droplet, $\Delta p$ is the pressure inside minus outside the droplet, and $\sigma$ is the microscopic surface tension. The integral over the surface $A$ of the ellipsoid yields the bending energy of the droplet. It is determined through the local curvatures $c_1$, $c_2$, and the spontaneous curvature radius $R_s$. Performing the integration over the ellipsoid, one finds

$$F = F_0 + \frac{8\pi}{45} R_0^4 (\alpha - \frac{4\kappa}{R_0 R_s} + \frac{6\kappa}{R_0^2}),$$

(35)

where $F_0$ is for the sphere, and $\alpha$ is now the macroscopic surface tension for the plane interface from Eq. (5). The full free energy is obtained adding the energy of the ellipsoid in the electric field $E_0$. The electrostatic energy is

$$F_{el} = -\frac{V \epsilon_e}{8\pi} \frac{\epsilon - 1}{1 + n^{(z)}(\epsilon - 1)} E_0^2.$$  

(36)

The depolarization coefficient is $n^{(z)} \approx [1 - 4(a - b)/5R_0]/3$, so that we have

$$F_{el} \approx -\frac{R_0^3 \epsilon_e}{2} \frac{\epsilon - 1}{\epsilon + 2} \left[1 + \frac{2 \epsilon - 1 - 2 e^2}{5 \epsilon + 2 e^2}\right] E_0^2.$$  

(37)

Minimalizing the full free energy with respect to the eccentricity we find

$$e^2 = \frac{9 \epsilon_e}{16\pi} \left(\frac{\epsilon - 1}{\epsilon + 2}\right)^2 (\alpha - \frac{4\kappa}{R_0 R_s} + \frac{6\kappa}{R_0^2})^{-1} R_0 E_0^2.$$  

(38)

To describe the Kerr birefringence, we now need the optical polarizabilities perpendicular $\alpha_{\perp}^{opt} = \alpha_{xx}^{opt}$ and parallel $\alpha_{\parallel}^{opt} = \alpha_{zz}^{opt}$ to the external field. They are obtained from the expressions for the dipole moment of the ellipsoid with small eccentricity 

$$\alpha_{\perp}^{opt} \approx \frac{3V n^2 - 1}{4\pi n^2 + 2} \left[1 - \frac{e^2 n^2 - 1}{5 n^2 + 2}\right], \quad \alpha_{\parallel}^{opt} \approx \frac{3V n^2 - 1}{4\pi n^2 + 2} \left[1 + \frac{2 e^2 n^2 - 1}{5 n^2 + 2}\right],$$  

(39)

with $n$ being the relative refractive index from Eq. (27). The difference in the refractive indices parallel and perpendicular to the field is

$$n_{\parallel} - n_{\perp} \approx \frac{9}{10} n_e \frac{n^2 - 1}{n^2 + 2} \Phi e^2.$$  

(40)

and the Kerr constant is

$$K = \frac{n_{\parallel} - n_{\perp}}{E_0^2 \Phi}.$$  

(41)

Substituting here the eccentricity from Eq. (38), we finally obtain

$$K = \frac{81}{160\pi} R_0 n_e \epsilon_e \left(\frac{\epsilon - 1}{\epsilon + 2}\right)^2 \frac{n^2 - 1}{n^2 + 2} \left(\alpha - \frac{4\kappa}{R_0 R_s} + \frac{6\kappa}{R_0^2}\right)^{-1},$$  

(42)

that agrees with Eqs. (27) and (4, 5). For the case of two-phase coexistence in microemulsions 

Eq. (42) significantly simplifies according to the formulas from Section 2.
7 The Kerr effect on droplets covered with a shell

The simple method used in the preceding section can be readily generalized for the description of the Kerr effect on the droplets covered with a vesicle membrane or a surfactant shell of nonzero thickness. To do this we need only the expressions that generalize Eqs. (39) for the polarizabilities of the ellipsoid, taking into account the size of the surface shell. Such expressions have been found in the work [14]. Following that work we assume the vesicle fluid core of radius $R_w$ to be characterized by the dielectric constant $\epsilon_w$, and the continuous phase of surrounding fluid by the constant $\epsilon_o$. For simplicity and in order to make a comparison with the experiment, we use $\epsilon_w \gg \epsilon_o$ which is true when $\epsilon_o$ stays for oil and $\epsilon_w$ for water, that corresponds to the experiments [14]. A generalization to other, more complicated cases, is straightforward; the corresponding formulae for the polarizabilities can be found in the work [14]. The surface shell can consist of two parts: a polar part which is characterized by the constant thickness $D$, and an apolar part of the thickness $D - D_e$. The polar part is described by the dielectric constant $\epsilon_\beta$, characterizing the orthogonal (to the surface) components of the dielectric constant, and by $\epsilon_\gamma$ for the parallel components. Both $\epsilon_\beta$ and $\epsilon_\gamma$ are large compared to $\epsilon_o$. The apolar part of the layer has the dielectric constant approximately the same as for the oil. Then the parallel component of the polarizability tensor of such an ellipsoid is as follows [14]:

$$\alpha_\parallel = \frac{3\epsilon_o}{\epsilon_w + 2\epsilon_o}[1 + 3a\epsilon^2\epsilon_w - \epsilon_o] + R_w^2D_e\frac{3\epsilon_o}{(\epsilon_w + 2\epsilon_o)^2} \epsilon_\gamma \approx \frac{1}{\epsilon_\beta}[1 + 2a\epsilon^2\epsilon_w - 7\epsilon_o] + 2(\epsilon_\gamma - \epsilon_o)[1 + 2a\epsilon^2\epsilon_w - 7\epsilon_o],$$

where $a = 2/15$. For $\alpha_\perp$ the same expression is valid but with $a = -1/15$. In the calculation of the eccentricity $e$ we use the above mentioned inequalities for the dielectric constants that gives

$$\alpha_\parallel \approx R_w^3(1 + \frac{2}{5}e^2) + 3R_w^2D_e[1 + \frac{4}{15}e^2 + 2\epsilon_\gamma/(1 + \frac{16}{15}e^2)].$$

Using this expression we find the electrostatic part of the free energy of the ellipsoid, which is now instead of Eq. (36)

$$F_{el} = -\frac{1}{2}\alpha_\parallel\epsilon_oE_0^2.$$

Minimalizing the full free energy $F + F_{el}$, with $F$ from Eq. (35), the eccentricity is

$$e^2 \approx \frac{9}{16\pi}\epsilon_oR_wE_0^2\alpha_2^{-1}(1 + 2\frac{D_e}{R_w}),$$

where $\alpha_2$ is from Eq. (5) with $R_0 = R_s$. From Eq. (40), rewriting the polarizabilities $\alpha_\parallel$ and $\alpha_\perp$ from Eq. (43) for the optical case simply changing the static dielectric constants by the squares of the refractive indices [14], we finally obtain

$$\frac{n_\parallel - n_\perp}{E_0^2} \approx \frac{27}{40}R_w^4\epsilon_o(\alpha - \frac{4\kappa}{R_wR_s} + 6\kappa\frac{D_e}{R_w})^{-1}(1 + 2\frac{D_e}{R_w})(\frac{n_o^2 - n_\beta^2}{n^2 + 2n_\gamma^2}$$

$$+ \frac{2Dn_o^2}{R_w(n_o^2 + 2n_\gamma^2)^3}[n_w(4n_w^2 - n_o^2)n_w - 7n_o^2 + 2(n^2 - n_o^2)(4n_w^2 - n_o^2)],$$

where $n_w$ is from Eq. (41).
The difference between this result and the result by Van der Linden et al. [14] is significant. This is because of the difference in the surface energy of the deformed droplet in the electric field: they have in the first bracket in Eq. (47) only the term $6\kappa/R_w^2$. The rest terms are, however, not negligible if compared with this one: for a detailed discussion we can refer, e.g., to the work [27]. Neglecting the surface energy associated with the surface tension is justified only for an absolutely free vesicle membrane with identical fluids inside and outside it, but not in other cases. As well, in general one cannot assume $R_w/R_s \ll 1$ and drop out the corresponding terms as it was done in [14]. So, for a microemulsion droplet, the two radii can be comparable, e.g. in the case of two-phase coexistence we have $R_w/R_s \approx (2\kappa + \pi)/2\kappa$. In the paper [14] a detailed comparison between the theory and the Kerr effect experiment was done from which the value $\kappa \approx 0.46kT$ has been extracted. Taking into account the above discussed improvement of the theory, it is seen that this value of the rigidity constant is essentially underestimated. Really, let us express $[8]$ in Eq. (47)

$$\frac{\alpha R_w^2}{6} - \frac{2\kappa R_w}{3R_s} + \kappa \approx \left(\frac{\kappa}{kT} - \frac{1}{48\pi \varepsilon}\right) kT,$$

(48)

where $\varepsilon$ is the polydispersity of the droplets in radii. Exactly this expression should be used in the analysis of the experimental data [14] that yielded the value $\kappa \approx 0.46kT$. One can see that the lower the polydispersity in the sample is, the higher value of $\kappa$ would be determined from the experiment. For example, for a typical polydispersity index [25] $\sqrt{\varepsilon} = 0.12$ one obtains $\kappa \approx 0.92kT$: a value two times larger than that found in Ref. [14] for the water - AOT - isooctane droplet microemulsion and very close to that determined from the Kerr effect measurements by Borkovec and Eicke [1, 25].

8 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 the 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. [13] 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. [13], a significant difference has been found in the expressions for the intensity of the scattered light. We also gave a simple alternative derivation of the Kerr constant for the case when the thickness of the surface layer can be neglected and when it is nonzero. The latter result corrects that from Ref. [13]. A comparison of the theoretical results with the Kerr-effect experiment on microemulsions gave an estimation of the bending rigidity constant of about $1k_BT$ for microemulsions consisting of droplets with relatively large radii [3, 14]. 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. In Ref. [1] 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. [2], 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 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 Ref. [3] the polydispersity was not determined at all. 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, a question concerning the role of the interaction between the droplets in microemulsion should be solved. We note this problem since according to the recent investigation [28] a relevant theory of the electro-optical measurements on microemulsions should incorporate many-particle correlations even in the case of small concentrations of the droplets. It appears that long-range anisotropic density correlations resulting from dipolar interactions have to be taken into account in a generalization of the simple single-body theory presented here.

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