Kerr constant of vesicle-like droplets

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Abstract

The Kerr effect on vesicle-like droplets is described. We give a simple derivation of the
Kerr constant for a dielectric fluid droplet immersed in another fluid, assuming that the
droplet in an electric field becomes a prolate ellipsoid. The Kerr constant is evaluated
also for a droplet covered by a membrane of finite thickness. The latter result differs
significantly from the result by E. van der Linden et al. [Physica A 156, 130 (1989)].
Due to the difference the bending rigidity constant of the surface layer extracted from
their experiments on droplet microemulsions should be increased about two times.

Introduction

The vesicle \[1, 2, 3\] is a closed surface of the lipid-bilayer membrane. It is enclosed by a fluid
and, in general, is filled inside with another fluid. The membrane is several nm in thickness
and exists as a biological membrane. A cell, typically \(\sim 10\) nm in diameter, itself can be re-
garded as a vesicle, and usually contains intracellular vesicles as organelles. Artificial vesicles,
called liposomes, can carry drugs in their interior, and are used in the experimental biology
and pharmacology. Within the phenomenological “biologically inspired” physical models the
formation (thermodynamics) and the dynamics of vesicles are described neglecting the mem-
brane thickness when compared to its radius. In such an approach also the microemulsion
droplets coated with a surfactant monolayer film can be studied simultaneously. We shall
refer to all the mentioned fluid droplets as to vesicle-like droplets. Their surface membranes
or films can be in the frame of the Canham-Helfrich model of interfacial elasticity \[4, 5\]
characterized by a few parameters: the bending and saddle splay modules \(\kappa\) and \(\bar{\kappa}\), the spontan-
eous curvature radius \(R_s\), the surface tension coefficient \(\sigma\), and the equilibrium radius \(R\).
The determination of these constants has been attempted by several macroscopic and micro-
scopic methods. However, different techniques yield very different parameters of the surface
shells \[6\]. It is thus important to have adequate theoretical description of the experimental
techniques that could serve as alternative probes of the vesicle membrane properties.
With this aim, in the present work the theory of the Kerr effect on vesicle-like droplets is de-
veloped. We give a simple derivation of the Kerr constant for a fluid droplet having a spherical
shape in equilibrium. First we assume that the membrane thickness is negligible if compared
to the vesicle radius. Placing such a droplet in a constant electric field, the vesicle becomes a prolate ellipsoid. For small eccentricity of such an ellipsoid the free energy of the droplet is found. Then, using the known expressions for the dipole moment of the ellipsoid, the optical polarizabilities are calculated. This allows us to determine the difference in refractive indices parallel and perpendicular to the external field and thus to find the Kerr constant. In a similar way the calculations are generalized to the droplets with finite thickness of the surface membrane. Here we use the results due to Van der Linden et al. However, our correction of the surface free energy found in that work leads to a significantly different expression for the Kerr constant. Comparing our result with the experiment on a droplet microemulsion, we estimate the bending rigidity constant of the droplet to be about two times larger than the value determined in the original work.

The Kerr effect on a fluid droplet

Consider a flexible dielectric droplet taking a spherical shape in equilibrium, immersed in another fluid. The fluid of the droplet is assumed to be incompressible. When such a droplet of the radius \( R \) 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 \( e = \sqrt{1 - b^2/a^2} \),

\[
a = R(1 + e^2/3), \quad b = c = R(1 - e^2/6).
\] (1)

Within the Helfrich model of interfacial elasticity \([4, 5]\) the free energy of such an ellipsoid (without the electrostatic energy) is \([8]\)

\[
F = -\Delta p V + \sigma A + \int dA\left[\frac{\kappa}{2}(c_1 + c_2 - 2/R_s)^2 + \kappa c_1 c_2\right].
\] (2)

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

\[
F = F_0 + \frac{8\pi}{45} \epsilon^4 R^2 (\alpha - \frac{4\kappa}{RR_s} + \frac{6\kappa}{R^2}),
\] (3)

where \( F_0 \) is for the sphere, and \( \alpha = \sigma + 2\kappa/R^2 \) is now the macroscopic surface tension for the plane interface. The full free energy is obtained adding the energy of the ellipsoid in the electric field \( E_0 \). Let the dielectric constant of the ellipsoid is \( \epsilon^{(i)} \), and that of its exterior \( \epsilon^{(e)} \), denoting \( \epsilon = \epsilon^{(i)}/\epsilon^{(e)} \). Then the electrostatic energy is \([1]\)

\[
F_{el} = -\frac{V \epsilon^{(e)}}{8\pi} \frac{\epsilon - 1}{\epsilon + 1} \frac{1}{\epsilon^{(e)}(\epsilon - 1)} E_0^2.
\] (4)

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

\[
F_{el} \approx -\frac{R^3}{2} \frac{\epsilon^{(e)}}{\epsilon + 2} \frac{\epsilon - 1}{\epsilon + 2} [1 + \frac{2\epsilon - 1}{3\epsilon + 2} ] E_0^2.
\] (5)
Minimalizing the full free energy with respect to the eccentricity we find

\[ e^2 = \frac{9\epsilon^{(e)}}{16\pi} \left( \frac{\epsilon - 1}{\epsilon + 2} \right)^2 (\alpha - \frac{4\kappa}{RR_s} + \frac{6\kappa}{R^2} - 1) R^2_0. \]  

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 \[9\],

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

with \( n \) being the relative refractive index \( n = n^{(i)}/n^{(e)} \). The difference in the refractive indices parallel and perpendicular to the field is \[10\],

\[ n_{\parallel} - n_{\perp} \approx 2\pi n^{(e)} \rho (\alpha_{\parallel}^{opt} - \alpha_{\perp}^{opt}) \]  

\((n^{(e)} \approx n_0)\) is the refractive index of the microemulsion when the number of droplets per unit volume, \( \rho \), is small). Using instead of \( \rho \) the volume fraction of the droplets, \( \Phi \), we thus have

\[ n_{\parallel} - n_{\perp} \approx \frac{9}{10} n_0 \left( \frac{n^2 - 1}{n^2 + 2} \right)^2 \Phi e^2. \]  

The Kerr constant is defined as

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

Substituting here the eccentricity from Eq.(6), we finally obtain

\[ K = \frac{81}{160\pi R n_0^{(e)} \left( \frac{\epsilon - 1}{\epsilon + 2} \right)^2 (\frac{n^2 - 1}{n^2 + 2})^2 (\alpha - \frac{4\kappa}{RR_s} + \frac{6\kappa}{R^2} - 1). \]  

Note that if the entropy of mixing \[11\] is taken into account, \(-kTF(\Phi)/(4\pi R^2)\) where \( F(\Phi) \approx \ln \Phi - 1 \) for small \( \Phi \), should be added into the last term of Eq.(11) \[3\]. For the case of two-phase coexistence in microemulsions \[8\] Eq.(11) significantly simplifies since then \( R/R_s = (2\kappa + \pi)/2\kappa \) and \( \alpha = 2\kappa/RR_s \).

The Kerr effect on a droplet 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.(7) for the polarizabilities of the ellipsoid, taking into account the size of the surface shell. Such expressions have been found in the work \[4\]. Following that work we assume the vesicle water 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 that corresponds to the experiments \[7\]. A generalization to other, more complicated cases, is straightforward; the
corresponding formulae for the polarizabilities can be found in the work [7]. 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 $\epsilon_\parallel$, characterizing the orthogonal (to the surface) components of the dielectric constant, and by $\epsilon_\perp$ for the parallel components. Both $\epsilon_\parallel$ and $\epsilon_\perp$ 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 [7]:

$$
\alpha_\parallel = \frac{R_w^3}{\epsilon_w + 2\epsilon_o} \left[ 1 + 3ae^2 \frac{\epsilon_w - \epsilon_o}{\epsilon_w + 2\epsilon_o} \right] + \frac{R_w^2 D_e}{(\epsilon_w + 2\epsilon_o)^2} \frac{3\epsilon_o}{\epsilon_w + 2\epsilon_o} 
$$

$$
\times \left\{ \frac{1}{\epsilon_o} - \frac{1}{\epsilon_\parallel} \right\} \left[ 1 + 2ae^2 \frac{\epsilon_w - 7\epsilon_o}{\epsilon_w + 2\epsilon_o} \right] + 2(\epsilon_\perp - \epsilon_o) \left[ 1 + 2ae^2 \frac{4\epsilon_w - \epsilon_o}{\epsilon_w + 2\epsilon_o} \right],
$$

(12)

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

$$
\alpha_\parallel \approx R_w^3 \left( 1 + \frac{2}{5} e^2 \right) + 3R_w^2 D_e \left[ 1 + \frac{4}{15} e^2 + 2\frac{\epsilon_o e_\parallel}{\epsilon_w} \left( 1 + \frac{16}{15} e^2 \right) \right].
$$

(13)

Using this expression we find the electrostatic part of the free energy of the ellipsoid, which is now instead of Eq.(4)

$$
F_{el} = -\frac{1}{2} \alpha_{\parallel o} E_0^2.
$$

(14)

Minimalizing the full free energy $F + F_{el}$, with $F$ from Eq.(3), the eccentricity is

$$
e^2 \approx \frac{9\epsilon_o R_w E_0^2}{16\pi} \left( \alpha - \frac{4\kappa}{R_w R_s} + \frac{6\kappa}{R_w^2} \right)^{-1} \left( 1 + 2\frac{D_e}{R_w} \right).
$$

(15)

From Eq.(8), rewriting the polarizabilities $\alpha_\parallel$ and $\alpha_\perp$ from Eq.(12) for the optical case simply changing the static dielectric constants by the squares of the refractive indices [7], we finally obtain

$$
n_\parallel - n_\perp \approx \frac{27}{40} R_w^4 \rho_m \epsilon_o (\alpha - \frac{4\kappa}{R_w R_s} + \frac{6\kappa}{R_w^2})^{-1} \left( 1 + 2\frac{D_e}{R_w} \right) \left\{ \left( \frac{n_o^2}{n_e^2 - n_\parallel^2} \right)^2 \right\}
$$

$$
+ \frac{2Dn_o^2}{R_w(n_o^4 + 2n_o^2)3} \left\{ n_w^2 \left( n_o^2 - n_\parallel^2 \right)^2 \left( n_w^4 - 7n_o^2 + 2 \left( n_\perp^2 - n_o^2 \right) \left( 4n_w^2 - n_o^2 \right) \right) \right\}.
$$

(16)

The difference between this result and the result by Van der Linden et al. [7] 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.(16) 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 [11]. 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 [7]. So, for a microemulsion droplet, the two radii can be comparable, e.g. in the case of the so-called two-phase coexistence we have $R_w/R_s = (2\kappa + \pi)/2\kappa$. 

4
In the paper [7] 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 different units used and the above discussed improvement of the theory, it is seen that this value of the rigidity constant is essentially underestimated. Really, let us express $[4]$ in Eq.(16)

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


where $\varepsilon$ is the polydispersity of the droplets in radii. Exactly this expression should be used in the analysis of the experimental data [7] that yielded the value $\kappa \approx 0.46kT$. Taking into account the polydispersity in the sample, one can see that the lower the polydispersity is, the higher value of $\kappa$ would be determined from the experiment. For example, for a typical polydispersity index $[12] \sqrt{\varepsilon} = 0.12$ one obtains $\kappa \approx 0.92kT$: a value two times larger than that found in Ref. [4] for the water-AOT-isooctane droplet microemulsion and very close to that determined from the Kerr effect measurements by Borkovec and Eicke [13, 12].

**Conclusion**

The Kerr effect measurements on vesicle-like droplets could in principle serve as an alternative (to such techniques like the static and dynamic neutron or light scattering) probe of the properties of the droplet surface membranes or films. In the present work the Kerr effect on dilute suspension of such (noninteracting) droplets has been described. We evaluated the Kerr constant of a fluid droplet immersed in another fluid assuming that the droplet in a constant weak electric field takes a shape of the prolate ellipsoid. This assumption is substantiated by the works [14, 15] where the flexible dielectric sphere in the electric field is considered coming from the Laplace equation for the electric potential with the appropriate boundary conditions. It was shown that in the lowest approximation the sphere undergoes ellipsoidal fluctuations and after the statistical averaging in the presence of the electric field the result for the Kerr constant is the same as for a prolate axisymmetric ellipsoid with small eccentricity. Following the work [7] we obtained a very different result for the Kerr constant that is due to the different expression found for the surface elastic energy of the droplet. As a result, the Kerr constant extracted from the experimental data [7] differs significantly, about two times, from the value determined in the original work. However, also this value should be considered with some 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 signal detected in the Kerr-effect measurements is very sensitive to the droplet radius, so it should be measured in the experiments with high precision together with the polydispersity of the droplets in radii, that was not determined in the described experiments at all. Finally, the recent investigation [16] suggests that a relevant theory of the electro-optical measurements on solutions of vesicle-like droplets 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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