Kerr Constant of Vesicle-Like Droplets

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Abstract. The Kerr effect on vesicle-like droplets (vesicles, cells or emulsion droplets) is described. We give a derivation of the Kerr constant for a dielectric fluid droplet immersed in another fluid, assuming that the droplet in a weak electric field becomes a prolate ellipsoid. The Kerr constant is evaluated also for a droplet covered by a membrane of nonzero thickness. Comparing the theory with the experiment on droplet microemulsions from the literature, the bending rigidity constant of the surface layer is estimated.

Key words: interfacial elasticity, Kerr effect, microemulsion droplets, polarizability, refractive indices, spherical membranes, surface bending rigidities, vesicles

1. 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 ~ 10 nm in diameter, itself can be regarded 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 membrane thickness when compared to its radius. In such an approach also the emulsion or 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 κ and $\bar{\kappa}$, the spontaneous curvature radius R_s , the surface tension coefficient σ , and the equilibrium radius R . The determination of these constants has been attempted by several macroscopic and microscopic methods. However, as discussed in Ref. [6], different techniques yield very different parameters of the surface shells. 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 developed. We give a simple derivation of the Kerr constant for a fluid droplet having a spherical shape in equilibrium. First we consider the case when the membrane thickness is negligible if compared to the vesicle radius. We assume that 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 of Ref. [7]. However, our expression for the surface free energy differs from that found in [7], which leads to a significantly different formula for the Kerr constant. As a consequence, our estimate for the bending rigidity constant of the droplet from the experiment [7] on a droplet microemulsion is notably larger than the value determined in the original work.

2. 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 $e = \sqrt{1 - b^2/a^2}$,

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

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

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

Here V is the (constant) volume of the droplet, Δp is the pressure inside minus outside the droplet, and σ 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

$$F = F_0 + \frac{8\pi}{45} e^4 R^2 \left(\alpha - \frac{4\kappa}{RR_s} + \frac{6\kappa}{R^2} \right), \quad (3)$$

where F_0 is for the sphere, and $\alpha = \sigma + 2\kappa/R_s^2$ is now the macroscopic surface tension for the plane interface. The modulus $\bar{\kappa}$ is not explicitly seen in this expression; due to the Gauss-Bonnet theorem [3] it enters F_0 as a topologically invariant term $4\pi\bar{\kappa}$. The full free energy is obtained by 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 [9]

$$F_{el} = -\frac{V\epsilon^{(e)}}{8\pi} \frac{\epsilon - 1}{1 + n^{(z)}(\epsilon - 1)} E_0^2. \quad (4)$$

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

$$F_{el} \approx -\frac{R^3}{2} \epsilon^{(e)} \frac{\epsilon - 1}{\epsilon + 2} \left[1 + \frac{2}{5} \frac{\epsilon - 1}{\epsilon + 2} e^2\right] E_0^2. \quad (5)$$

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

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

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],

$$\alpha_{\perp}^{opt} \approx \frac{3V}{4\pi} \frac{n^2 - 1}{n^2 + 2} \left[1 - \frac{e^2}{5} \frac{n^2 - 1}{n^2 + 2}\right], \quad \alpha_{\parallel}^{opt} \approx \frac{3V}{4\pi} \frac{n^2 - 1}{n^2 + 2} \left[1 + \frac{2e^2}{5} \frac{n^2 - 1}{n^2 + 2}\right] \quad (7)$$

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],

$$n_{\parallel} - n_{\perp} \approx 2\pi n^{(e)} \rho (\alpha_{\parallel}^{opt} - \alpha_{\perp}^{opt}) \quad (8)$$

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

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

The Kerr constant is defined as

$$K = \frac{n_{\parallel} - n_{\perp}}{E_0^2 \Phi}. \quad (10)$$

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

$$K = \frac{81}{160\pi} R n_0 \epsilon^{(e)} \left(\frac{\epsilon - 1}{\epsilon + 2}\right)^2 \left(\frac{n^2 - 1}{n^2 + 2}\right)^2 \left(\alpha - \frac{4\kappa}{RR_s} + \frac{6\kappa}{R^2}\right)^{-1}. \quad (11)$$

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 Φ , should be added into the last term of Eq.(11) [6]. For the case of two-phase coexistence in microemulsions [8] Eq.(11) significantly simplifies since then $R/R_s = (2\kappa + \bar{\kappa})/2\kappa$ and $\alpha = 2\kappa/R R_s$.

3. 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 [7]. Following that work we assume the vesicle water core of radius R_w to be characterized by the dielectric constant ϵ_w , and the continuous phase of surrounding fluid by the constant ϵ_o . For simplicity and in order to make a comparison with the experiment, we use $\epsilon_w \gg \epsilon_o$, which 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_ϵ , and an apolar part of the thickness $D - D_\epsilon$. The polar part is described by the dielectric constant ϵ_β , characterizing the orthogonal (to the surface) components of the dielectric constant, and by ϵ_γ for the parallel components. Both ϵ_β and ϵ_γ are large compared to ϵ_o . The apolar part of the layer has the dielectric constant approximately the same as for the solvent. Then the parallel component of the polarizability tensor of such an ellipsoid is as follows [7]:

$$\alpha_{\parallel} = R_w^3 \frac{\epsilon_w - \epsilon_o}{\epsilon_w + 2\epsilon_o} [1 + 3ae^2 \frac{\epsilon_w - \epsilon_o}{\epsilon_w + 2\epsilon_o}] + R_w^2 D_\epsilon \frac{3\epsilon_o}{(\epsilon_w + 2\epsilon_o)^2} \times \{ \epsilon_w^2 (\frac{1}{\epsilon_o} - \frac{1}{\epsilon_\beta}) [1 + 2ae^2 \frac{\epsilon_w - 7\epsilon_o}{\epsilon_w + 2\epsilon_o}] + 2(\epsilon_\gamma - \epsilon_o) [1 + 2ae^2 \frac{4\epsilon_w - \epsilon_o}{\epsilon_w + 2\epsilon_o}] \}, \quad (12)$$

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

$$\alpha_{\parallel} \approx R_w^3 (1 + \frac{2}{5}e^2) + 3R_w^2 D_\epsilon [1 + \frac{4}{15}e^2 + 2\frac{\epsilon_o \epsilon_\gamma}{\epsilon_w^2} (1 + \frac{16}{15}e^2)]. \quad (13)$$

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

$$F_{el} = -\frac{1}{2} \alpha_{\parallel} \epsilon_o E_0^2. \quad (14)$$

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

$$e^2 \approx \frac{9\epsilon_o R_w E_0^2}{16\pi} (\alpha - \frac{4\kappa}{R_w R_s} + \frac{6\kappa}{R_w^2})^{-1} (1 + 2\frac{D_\epsilon}{R_w}). \quad (15)$$

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

$$\begin{aligned} \frac{n_{\parallel} - n_{\perp}}{E_0^2} \approx & \frac{27}{40} R_w^4 \rho n_o \epsilon_o \left(\alpha - \frac{4\kappa}{R_w R_s} + \frac{6\kappa}{R_w^2} \right)^{-1} \left(1 + 2 \frac{D_{\epsilon}}{R_w} \right) \left(\frac{n_w^2 - n_o^2}{n_w^2 + 2n_o^2} \right)^2 \\ & + \frac{2Dn_o^2}{R_w(n_w^2 + 2n_o^2)^3} [n_w^4(n_o^{-2} - n_{\beta}^{-2})(n_w^2 - 7n_o^2) + 2(n_{\gamma}^2 - n_o^2)(4n_w^2 - n_o^2)] \end{aligned} \quad (16)$$

The difference between this result and the result [7] is significant. This is because of the difference in the surface energy of the deformed droplet in the electric field: in Ref. [7] in the first bracket in Eq.(16) there is 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 $R_w/R_s \approx (2\kappa + \bar{\kappa})/2\kappa$.

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 above discussed improvement of the theory, it can be shown that this value of the rigidity constant is essentially underestimated. Really, in our paper [6] we have related the surface parameters to the polydispersity of the droplets in radii, ε , by the following expression:

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

Applying this formula to Eq.(16), one can see that the lower the polydispersity is, the higher value of κ would be determined from the experiment. For example, for a typical polydispersity index [12] $\sqrt{\varepsilon} = 0.12$ one obtains from the experiment [7] $\kappa \approx 0.92kT$: a value two times larger than that originally found for the water-AOT-isooctane droplet microemulsion [7] and close to that determined from the Kerr effect measurements by Borkovec and Eicke [12, 13]. Notice that the consideration of the polydispersity in the sample is important in the analysis of experimental data. The expressions found for the Kerr constant have to be averaged over the distribution of the droplets in radii that was not done in the cited works. The necessary formulae can be found in Refs. [6, 8].

4. 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 [6]) 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. The sphere fluctuated in the shape. It was shown that 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. In this work, 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 estimated from the experimental data [7] notably differs, about two times, from the value determined in the original work. However, also this value should be considered with some reserve. 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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