PHYSICAL REVIEW E **83**, 041705 (2011)

Frederiks transition in ferroelectric liquid-crystal nanosuspensions

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(Received 5 August 2010; revised manuscript received 9 November 2010; published 8 April 2011)

We construct a theoretical model of the dielectric properties of a ferroelectric LC nanosuspension (FLCNS), using a generalized Maxwell-Garnett picture. The theory supposes that an FLCNS may as a first approximation be considered as a complex homogeneous dielectric ceramic, thus neglecting positional correlations of the colloidal particles. The FLCNS then consists of an anisotropic matrix with a very low concentration ($<1\%$ by volume) of impurity particles. The impurity particles possess both shape and dielectric anisotropy, as well as a permanent electric polarization and strong liquid-crystal director anchoring on the particle surface. We show that the effective dielectric properties for capacitance properties and for effective liquid-crystal free energies do not coincide. We calculate the effect of doping a liquid crystal with ferroelectric impurities on the Frederiks transition. The theory takes account of inclusion shape, dielectric susceptibility, and local field effects. We neglect the possibility of dielectric particle chaining, which appears experimentally not to occur in general. Our calculations suggest, in qualitative agreement with experiment, that doping a nematic liquid crystal with ferroelectric particles, even at very low particle concentration, can in some cases significantly decrease the electric Frederiks threshold field.

DOI: 10.1103/PhysRevE.83.041705 PACS number(s): 61.30.Gd, 77.84.Nh

I. INTRODUCTION

Colloidal suspensions—dispersions of small solid particles in a host liquid consisting of small molecules—dominate our daily lives. Examples of such suspensions include milk, liquid medicines, shampoo, paint, and ink. More recently, some of the new e-book displays involve charged particles suspended in a host liquid moving in an AC electric field. Likewise, as is well known, liquid crystals have given birth to a widely used display technology. It is not unnatural to combine the physics behind two of the more widespread display technologies, and inquire whether there is possible further technological potential in colloidal systems with a liquid-crystalline host.

Some perspectives on this subject were explored in a wide-ranging review article by Stark [1] in 2001. It turns out that not only are there possible technological applications, but the basic physics itself involves some new concepts. A particular focus of interest has been the often complex director configuration close to the colloidal particle, involving a complicated liquid-crystalline defect structure. In such cases the light-scattering induced by complex inhomogeneous order parameter structures dominates that due to simple impurity-host refractive index contrast. The light scattering changes dramatically the optical signature of the liquid crystal, even at very low colloidal concentration. The consequence is that such impure liquid crystals are useless in conventional display devices.

Notwithstanding this dismal prognosis, in recent years there do seem to have been two particular areas of display-oriented research which have been particularly fruitful in terms of combining colloid science and liquid crystals. The suggestion in 1970 by Brochard and de Gennes [2], according to which colloidal particles with a permanent magnetic moment would cause coupling of local moments and the nematic director, has stimulated a vigorous research program. These systems are known as *ferronematics*, and further work, both experimental [3–7] and theoretical [8,9], seems to confirm the picture predicted by Brochard and de Gennes. Despite encouraging early results, however, the goal of a low-magnetic field switchable cell still seems far off.

A system analogous to this, but in which potentially much more dramatic effects might be expected, involves ferroelectric rather than ferromagnetic colloidal particles. Such systems were first fabricated by Reznikov *et al.* [10], examined in detail by Li *et al.* [11], and have been the subject of considerable subsequent work [12–22]. These systems are the subject of this paper.

The key facts about these ferroelectric liquid-crystalline colloids are as follows. In particular, the colloidal particles are extremely small, sufficiently so that the anchoring effects due to the colloidal surface average, rather than antagonize. Thus they do not scatter light in the manner described above, and are therefore essentially invisible. At low concentrations, at least in some cases, these submicron colloids appear similar to a pure liquid crystal. Furthermore, in these suspensions the dielectric response is strongly enhanced, even at low concentration of dissolved particles. This leads to higher values of effective dielectric functions of such colloidal suspensions, in comparison with those of the analogous pure liquid crystals [10,11].

The anchoring mechanism seems to permit the intrinsic properties of the colloidal particles to influence the global properties of the liquid-crystal host matrix. One striking feature is that often in such systems, the temperature of the isotropic-nematic phase transition is increased. The effect is that for a given temperature, the degree of nematic order is higher than in the pure system [11,22]. Hence one might reasonably expect that the Frank-Oseen elastic constants (which are roughly proportional to square of the order parameter) would also increase.

A measurable consequence of the increased elastic constant should be, at least according to naive theory, an increase in the Frederiks threshold voltage. The experiments however, do

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not confirm this apparently robust prediction. Sometimes the Frederiks threshold indeed increases, but depending on subtle details of nanocolloid preparation the threshold voltage often rather exhibits an unexpected significant decrease [10,12,23].

We note that the magnitude of the Frederiks threshold voltage is fundamental to operation of many liquid-crystal devices. If the Frederiks threshold voltage reductions could be reliably replicated, this would have significant implication for the manufacture of very low-power LCDs and other liquid-crystalline devices. It also turns out that the ferroelectric liquid-crystalline colloids appear to be promising materials for use in a nonlinear optics setting.

This paper provides a theory of this phenomenon. In a previous paper [19], we provided a simple model of the Frederiks threshold voltage decrease. This paper presents a more sophisticated version of that theory. We do so partly because the previous model is theoretically unsatisfactory, and might only be expected to give rough trends. A further motivation is that in the intervening period, there has been significant further experimental work on ferroelectric liquid-crystalline colloids, concentrating not only on the Frederiks threshold, but also more generally on aspects of the material dielectric response [12,13,18]. Key extra input to the present work also comes from previous work by one of us [21], in which the effective dielectric constants in ferroelectric liquid-crystal nanosuspensions are discussed in the context of a tensor effective medium theory.

The plan of the paper is as follows. In Sec. II we introduce the basic model which combines important features of the properties of liquid-crystal and dielectric ceramics. Then in Sec. III we develop the relevant theory. The key properties of the theory are matrices which connect the bulk electric field to the fields inside the liquid crystal and the polarized inclusions, as well as to the corresponding displacement fields. This section also determines an expression for the effective coupling between the electric field and the local liquid-crystal director, and hence derives an expression for the corresponding change in the Frederiks threshold field. In Sec. IV we present some numerical results which follow from the theory, and make some comparison with experiments. In Sec. V we make a comprehensive discussion of the results and draw some conclusions from the paper. We make a comparison of the present theory with our earlier version [19], and discuss the differences. This section also tries to fit the calculation into a broader theoretical framework, assess its advantages and disadvantages, and point out where problems still remain. Some algebraically complicated but conceptually straightforward calculations from Sec. III have been relegated to the Appendix.

II. MODEL

We consider a suspension of ferroelectric particles, with anisotropic polarizability, embedded in a liquid-crystalline medium, and occupying a fraction f of the total volume. The cell geometry is shown in Fig. 1. We suppose the particles to be of spheroidal shape (i.e., ellipsoidal with two equivalent semiaxes). The principal axes of the anisotropic permittivity tensor of the particles coincide with the principal axes of the particle spheroid. The dipole moment per unit volume within a ferroelectric particle (i.e., permanent polarization) is d. We also suppose that there are strong forces aligning the principal axis of a particle with the local liquid-crystal director. If we define $\mathbf{P}_P$ as the mean permanent dipole moment per unit volume of particle (i.e., the polarization within the particles due to the permanent moments) and that these forces are sufficiently strong that we may suppose that the vectors $\mathbf{P}_P$ and $\mathbf{n}$ are aligned. We discuss the merits of this rather strong assumption at the end of the paper. However, we can note that this condition is precisely that assumed by Brochard and de Gennes [2] in their first study of the ferronematic systems, which are, as we have seen, the magnetic analog of the systems discussed here.

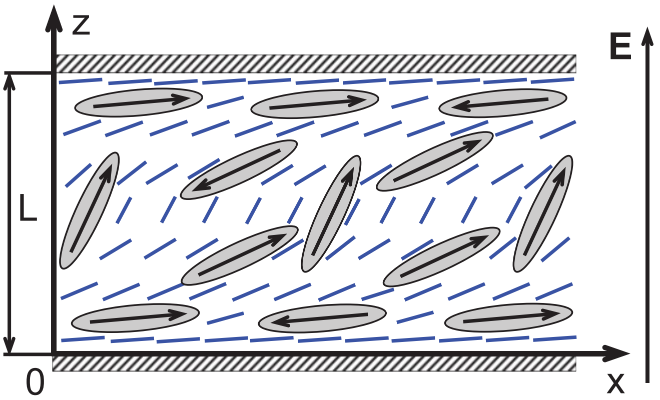

FIG. 1. (Color online) Cell geometry for ferroelectric nanosuspension. The cell is in the x-y plane. The perpendicular z direction ($0 < z < L$) defines distances across the cell. The liquid-crystal director is in the x-z plane and is defined by an angle θ where $\mathbf{n} = (\cos\theta, 0, \sin\theta)$. We suppose homogeneous anchoring conditions (i.e., director in x direction, $\theta = 0$). The lines represent liquid-crystal director fields, and the black arrows represent typical individual particle dipole moments. In our model, the colloidal nanoparticle moments are aligned parallel or antiparallel to the particle principal axes. In general the number of parallel and antiparallel dipole moments do not balance.

Inside the inhomogeneous medium, in general, the electric fields and electric displacements vary from place to place. We distinguish the local electric fields inside the particles and those inside the nematic liquid crystal. We average these electric and displacement fields over volumes which are small, in the spirit of continuum theory. The key electric fields in the theory are $\mathbf{E}_{LC}$ and $\mathbf{E}_P$, the averaged electric fields in the liquid crystal and ferroelectric particles, respectively, as well as the average field $\mathbf{E}$ in the whole medium.

We remark here that the word “average” here (and elsewhere in the paper) must be interpreted as meaning “averaged over a suitably small volume.’ This is because a liquid-crystal cell is itself a macroscopically inhomogeneous object, whose (average) properties change across the cell. There is supposed to be a suitable separation of scales between these changes across the liquid-crystal cell, which are treated by a continuum theory, and local medium properties, discussed using an effective medium theory.

Subject to the clarification in the last paragraph, there are also electric displacements associated with each of these electric fields. Within a mean field theory in which the colloid particles are dilute, well-separated, and uncorrelated in position, these quantities are related as follows [21]:

$$\mathbf{E} = (1-f)\mathbf{E}_{LC} + f\mathbf{E}_P, \tag{1a}$$

$$\mathbf{D} = \mathbf{D}_0 + f\mathbf{P}_P = (1-f)\mathbf{D}_{LC} + f\mathbf{D}_P + f\mathbf{P}_P. \tag{1b}$$

The quantities $\mathbf{D}$, $\mathbf{D}_0$, $\mathbf{D}_{LC} = \varepsilon_0\hat{\varepsilon}^{LC}\mathbf{E}_{LC}$, and $\mathbf{D}_P = \varepsilon_0\hat{\varepsilon}^{P}\mathbf{E}_P$ are defined, respectively, as the mean displacement field, the contribution to the mean displacement field resulting from induced polarization effects, the mean displacement field in the liquid crystal, and the mean-induced displacement field in the ferroelectric particles. We note that our definition of the displacement field $\mathbf{D}_P$ inside the colloidal particles only includes the induced polarization, but does not include the permanent polarization (contrary to the convention of, e.g., Landau and Lifshitz [24]). In our treatment we find it convenient to separate the mean permanent polarization term $\mathbf{P}_P$ from the induced displacement fields.

In addition, we introduce a further relevant electric field $\mathbf{E}_P^0$, which does not appear in Eq. (1a). This is the electric field that orients the permanent polarization of the particles. This differs from the electric field $\mathbf{E}_P$ in that it does not include the field due to the permanent polarization inside the particles themselves. We discuss this term in more detail below.

In order to calculate the permanent polarization $\mathbf{P}_P$, we recall the strong anchoring condition that the ferroelectric particles be aligned only parallel or antiparallel to the local liquid crystal director. Then let ρ_+ and ρ_- be the fractions of ferroelectric particles aligned, respectively, parallel and antiparallel to the local nematic director $\mathbf{n}$. The mean particle permanent polarization $\mathbf{P}_P$ now takes the form

$$\mathbf{P}_P = d\mathbf{n}(\rho_+ - \rho_-). \tag{2}$$

The free-energy functional for the suspension now includes electric and orientational entropy terms, as well as the conventional nematic elastic terms. The functional is homogeneous in the xy directions within the cell, and the form we present technically represents free energy per unit area of the cell. We obtain

$$\mathcal{F} = \mathcal{F}_{\text{el}} + \mathcal{F}_E + \mathcal{F}_{\text{entr}}, \tag{3}$$

where

$$\mathcal{F}_{\text{el}} = \frac{1}{2}\int_0^L \{K_1(\nabla\cdot\mathbf{n})^2 + K_2(\mathbf{n}\cdot\nabla\times\mathbf{n})^2 + K_3[\mathbf{n}\times\nabla\times\mathbf{n}]^2\}dz, \tag{4a}$$

$$\mathcal{F}_E = -\frac{1}{2}\int_0^L (1-f)\mathbf{D}_{LC}\cdot\mathbf{E}_{LC}\,dz - \frac{1}{2}\int_0^L f\mathbf{D}_P\cdot\mathbf{E}_P\,dz - \int_0^L f\mathbf{P}_P\cdot\mathbf{E}_P^0\,dz, \tag{4b}$$

$$\mathcal{F}_{\text{entr}} = \int_0^L f\frac{k_BT}{v}\{\rho_+\ln\rho_+ + \rho_-\ln\rho_-\}dz. \tag{4c}$$

$\mathcal{F}_{\text{entr}}$ is the standard free energy associated with the orientational degrees of freedom of the polarization directions of ferroelectric particles, and v is the volume of an individual particle. The field $\mathbf{E}_P^0$ in Eq. (4b) was discussed above, and is the contribution from the electric field from all sources other than the depolarization field due to the permanent polarization of the particular particle under consideration. It does not include the self-field effects of a permanently polarized nanoparticle, which must not appear in the correct formulation of the electrostatic energy.

The equilibrium configuration is found by minimizing the total free energy functional Eq. (3) subject to the applied voltage across the cell:

$$V = \int_0^L E_z dz. \tag{5}$$

The electric contribution to the free energy $\mathcal{F}_E$ in Eq. (4b) takes an intuitively sensible form. However, it can also be derived explicitly [19], by using Eqs. (1a) and (1b) to average the standard form in which this energy appears in textbooks [24,25]:

$$\mathcal{F}_E = -\frac{1}{2}\int_0^L \mathbf{D_0}\cdot\mathbf{E}\,dz - \int_0^L \mathbf{P}\cdot\mathbf{E}_P^0\,dz, \tag{6}$$

where as before $\mathbf{D}_0$ is the suspension field-induced displacement field and $\mathbf{P} = f\mathbf{P}_P$ represents the permanent polarization inside the colloidal suspension.

III. THEORY

A. Particle permanent polarization

We first need to obtain the explicit expression for the particle permanent polarization $\mathbf{P}_P$. In what follows, we minimize the free-energy functional Eq. (3) with respect to particle orientation fractions $\rho_\pm$, subject to the constraint $\rho_+ + \rho_- = 1$. The resulting particle orientational distribution takes the form:

$$\rho_\pm = \frac{\exp\left[\pm dv\beta\left(\mathbf{n}\cdot\mathbf{E}_P^0\right)\right]}{\exp\left[dv\beta\left(\mathbf{n}\cdot\mathbf{E}_P^0\right)\right] + \exp\left[-dv\beta\left(\mathbf{n}\cdot\mathbf{E}_P^0\right)\right]}, \tag{7}$$

where $\beta = \dfrac{1}{k_BT}$.

We also assume that ferroelectric particles are small enough, and the applied fields are small as well, so that

$$dv\beta\left(\mathbf{n}\cdot\mathbf{E}_P^0\right) \ll 1. \tag{8}$$

This condition implies that typical energies associated with the orientation of the permanent electric dipoles of the nanoparticles are small by comparison with thermal energy k_BT. In the calculations presented in this paper, this quantity usually does not exceed 0.5, and the assumption is valid. In general, however, the condition may be violated, and in a more general theory, it may need to be relaxed. Using Eqs. (2), (7), (8), the particle polarization resulting from permanent dipoles now reduces to

$$\mathbf{P}_P \approx d^2v\beta\mathbf{n}\left(\mathbf{n}\cdot\mathbf{E}_P^0\right) \equiv \varepsilon_0\nu\mathbf{n}\left(\mathbf{n}\cdot\mathbf{E}_P^0\right), \tag{9}$$

where the dimensionless parameter $\nu = d^2v\beta/\varepsilon_0$ describes the ratio of the electric interaction energy of two adjacent dipoles to thermal energy. In our case, $\nu \sim 10^3$–10^5.

B. Effective permittivity

The goal of this subsection is to derive an expression for the effective permittivity tensor for liquid-crystal-based suspensions. This is defined by

$$\mathbf{D} = \hat{\tilde{\varepsilon}}\mathbf{E}. \tag{10}$$

The first stage of the calculation requires specific relationships between the average applied field $\mathbf{E}$ and the local fields $\mathbf{E}_{LC}$, $\mathbf{E}_P$, and $\mathbf{E}_P^0$. For suitably defined small fields (although the fields will be large in an absolute sense), this is linear (see, e.g., [21]):

$$\mathbf{E}_P^0 = \hat{T}^0\mathbf{E}_{LC}, \tag{11a}$$

$$\mathbf{E}_P = \hat{T}\mathbf{E}_{LC}, \tag{11b}$$

$$\mathbf{E}_{LC} = \hat{T}^{LC}\mathbf{E}. \tag{11c}$$

The quantities $\hat{T}^0$, $\hat{T}$, and $\hat{T}^{LC}$ are tensors, indicating that the fields $\mathbf{E}_{LC}$, $\mathbf{E}_P$, and $\mathbf{E}_P^0$ are not necessarily parallel. In a scalar theory, they reduce to coefficients. The standard procedure for the description of effective medium theories of dielectric behavior in heterogeneous media goes back to Maxwell-Garnett [26] in 1904. This approach supposes that these quantities can be calculated by considering a single inclusion in the host medium [27,28]. Other workers have considered the dielectric effect of inclusions with a permanent polarization, but without including anisotropy effects [24,29] or alternatively without a permanent polarization, but including anisotropy [28,30].

We now generalize this approach so that both permanent polarization of the colloidal particles and anisotropy effects are included. We thus calculate the transformation matrices by considering a host anisotropic liquid-crystal medium with dielectric permittivity tensor $\hat{\varepsilon}^{LC}$, and a single spheroidal particle with dielectric permittivity tensor $\hat{\varepsilon}^P$, but now also with a permanent polarization $\mathbf{P}_P$, placed inside this medium.

A key result links the mean liquid-crystal electric field $\mathbf{E}_{LC}$, the mean particle electric field $\mathbf{E}_P$, and the mean polarization $\mathbf{P}_P$. This is

$$\hat{\varepsilon}^{LC}\mathbf{E}_{LC} = [\hat{\varepsilon}^{LC} + \hat{\tilde{\mu}}(\hat{\varepsilon}^P - \hat{\varepsilon}^{LC})]\mathbf{E}_P + \hat{\tilde{\mu}}\mathbf{P}_P/\varepsilon_0, \tag{12}$$

where $\hat{\tilde{\mu}}$ is the so-called *depolarization tensor* [24] of a dielectric spheroid in an anisotropic medium. We postpone the details of the calculation to the Appendix.

The quantity $\mathbf{E}_P^0$ differs from $\mathbf{E}_P$ because it excludes the explicit effect of the particle permanent polarization. $\mathbf{E}_P^0$ can be expressed using a formula analogous to Eq. (12), but now putting $\mathbf{P}_P = 0$ (see, e.g., [28]). Thus

$$\hat{\varepsilon}^{LC}\mathbf{E}_{LC} = [\hat{\varepsilon}^{LC} + \hat{\tilde{\mu}}(\hat{\varepsilon}^P - \hat{\varepsilon}^{LC})]\mathbf{E}_P^0. \tag{13}$$

We now use Eqs. (12), (13) to find the components of the $\hat{T}$ matrices in Eqs. (11a)–(11c). Comparing Eq. (11a) with Eq. (13) yields a specific expression for $\hat{T}^0$:

$$\hat{T}^0 = [I + (\hat{\varepsilon}^{LC})^{-1}\hat{\tilde{\mu}}(\hat{\varepsilon}^P - \hat{\varepsilon}^{LC})]^{-1}. \tag{14}$$

To obtain $\hat{T}$, we substitute Eqs. (9) and (11a) into Eq. (12), obtaining

$$\hat{\varepsilon}^{LC}\mathbf{E}_{LC} = [\hat{\varepsilon}^{LC} + \hat{\tilde{\mu}}(\hat{\varepsilon}^P - \hat{\varepsilon}^{LC})]\mathbf{E}_P + \nu\hat{\tilde{\mu}}\mathbf{n}(\mathbf{n}\cdot\hat{T}^0\mathbf{E}_{LC}), \tag{15}$$

where the dimensionless quantity ν has been defined in Eq. (9). We then rewrite Eq. (15) in the form:

$$[\hat{\varepsilon}^{LC} + \hat{\tilde{\mu}}(\hat{\varepsilon}^P - \hat{\varepsilon}^{LC})]\mathbf{E}_P = [\hat{\varepsilon}^{LC} - \nu\hat{\tilde{\mu}}\hat{n}\hat{T}^0]\mathbf{E}_{LC}, \tag{16}$$

where $\hat{n}$ is the tensor which components are $n_{ij} = n_i n_j$. Comparing this equation with Eq. (11b) yields a formula for $\hat{T}$:

$$\hat{T} = [I + (\hat{\varepsilon}^{LC})^{-1}\hat{\tilde{\mu}}(\hat{\varepsilon}^P - \hat{\varepsilon}^{LC})]^{-1}[I - \nu(\hat{\varepsilon}^{LC})^{-1}\hat{\tilde{\mu}}\hat{n}\hat{T}^0], \tag{17}$$

We can now obtain the tensor $\hat{T}^{LC}$. Combining Eqs. (1a) and (11b) yields the following relationship between $\mathbf{E}$ and $\mathbf{E}_{LC}$:

$$\mathbf{E} = [1 - f + f\hat{T}]\mathbf{E}_{LC}. \tag{18}$$

Now comparing Eqs. (11c) and (18) yields an expression for matrix $\hat{T}^{LC}$:

$$\hat{T}^{LC} = [(1 - f)I + f\hat{T}]^{-1}. \tag{19}$$

The final step to obtain the effective permittivity tensor involves rewriting the displacement field (1b) in the form of $\hat{T}$ matrices:

$$\mathbf{D} = (1 - f)\varepsilon_0\hat{\varepsilon}^{LC}\hat{T}^{LC}\mathbf{E} + f\varepsilon_0\hat{\varepsilon}^P\hat{T}^P\mathbf{E} + f\varepsilon_0\nu(\hat{T}^{P0}\mathbf{E}\cdot\mathbf{n})\mathbf{n}, \tag{20}$$

where we have defined new matrices $\hat{T}^{P0} \equiv \hat{T}^0\hat{T}^{LC}$ and $\hat{T}^P \equiv \hat{T}\hat{T}^{LC}$. This equation can now be compared with definition of the effective dielectric permittivity in Eq. (10), to yield the following values for the components of the dielectric permittivity tensor $\hat{\tilde{\varepsilon}}$:

$$\tilde{\varepsilon}_\perp = (1 - f)\varepsilon_\perp^{LC}T_\perp^{LC} + f\varepsilon_\perp^P T_\perp^P, \tag{21a}$$

$$\tilde{\varepsilon}_\parallel = (1 - f)\varepsilon_\parallel^{LC}T_\parallel^{LC} + f\varepsilon_\parallel^P T_\parallel^P + f\nu T_\parallel^{P0}. \tag{21b}$$

The two effective permittivities of the suspension can now be obtained explicitly by substituting the $\hat{T}$-matrix components into Eqs. (21a) and (21b). We obtain

$$\tilde{\varepsilon}_\perp = \varepsilon_\perp^{LC} + f\frac{(\varepsilon_\perp^P - \varepsilon_\perp^{LC})\varepsilon_\perp^{LC}}{\varepsilon_\perp^{LC} + (1 - f)\tilde{\mu}_\perp(\varepsilon_\perp^P - \varepsilon_\perp^{LC})}, \tag{22a}$$

$$\tilde{\varepsilon}_\parallel = \varepsilon_\parallel^{LC} + f\frac{(\varepsilon_\parallel^P - \varepsilon_\parallel^{LC} + \nu)\varepsilon_\parallel^{LC} - (\varepsilon_\parallel^P - \varepsilon_\parallel^{LC})\nu\tilde{\mu}_\parallel T_\parallel^0}{\varepsilon_\parallel^{LC} + (1 - f)\tilde{\mu}_\parallel(\varepsilon_\parallel^P - \varepsilon_\parallel^{LC}) - f\nu\tilde{\mu}_\parallel T_\parallel^0}, \tag{22b}$$

where, from Eq. (14),

$$T_\parallel^0 = \frac{\varepsilon_\parallel^{LC}}{\varepsilon_\parallel^{LC} + \tilde{\mu}_\parallel(\varepsilon_\parallel^P - \varepsilon_\parallel^{LC})}.$$

C. Free-energy functional homogenization

Equations (22a), (22b) yield values for the effective permittivity tensor of the suspension. They can be measured in experiments given suitable boundary conditions. Alternatively, if the director profile were to be known, then this effective permittivity tensor allows, for example, a calculation of the capacitance of the nonuniform liquid-crystal layer. At first sight, it would seem reasonable to use these effective values in a calculation of the nematic director profile. The local free-energy density associated with a director $\mathbf{n}$ in an electric field $\mathbf{E}$ would then be $-\frac{1}{2}(\tilde{\varepsilon}_\parallel - \tilde{\varepsilon}_\perp)(\mathbf{E}\cdot\mathbf{n})^2$, by analogy with a similar calculation in a pure nematic.

However, detailed calculation shows that this is not the case. The effective permittivity as it appears in an energy expression is not the same quantity as the effective permittivity as directly measured. While this may be at first sight implausible, further reflection shows that in general in a nonuniform medium the spatial averages $\langle \mathbf{D} \cdot \mathbf{E} \rangle$, $\langle \mathbf{D} \rangle \cdot \langle \mathbf{E} \rangle$ will not be equal.

Combining Eq. (7) with the free-energy functional Eq. (3) involves some cancellation with $\mathcal{F}_E$ and yields the following free-energy functional:

$$\begin{aligned}\mathcal{F} &= \mathcal{F}_{\mathrm{el}} + \mathcal{F}_E + \mathcal{F}_{\mathrm{entr}} \\ &= \mathcal{F}_{\mathrm{el}} - \frac{1}{2}\int_0^L (1-f)\varepsilon_0 \hat{\varepsilon}^{LC} \mathbf{E}_{LC} \cdot \mathbf{E}_{LC}\, dz \\ &\quad - \frac{1}{2}\int_0^L f \varepsilon_0 \hat{\varepsilon}^{P} \mathbf{E}_P \cdot \mathbf{E}_P\, dz - \frac{f}{\beta v}\int_0^L \ln\big[\exp\big(dv\beta(\mathbf{n} \cdot \mathbf{E}_P^0)\big) \\ &\quad + \exp\big(-dv\beta(\mathbf{n} \cdot \mathbf{E}_P^0)\big)\big] dz. \end{aligned} \tag{23}$$

We now rewrite the free-energy functional Eq. (23), so that it takes a form analogous to that of a pure liquid-crystal free-energy functional, but with some modified coupling constants which represent the effect of doping. Using the inequality condition (8), we substitute Eq. (9) into the free-energy functional (23), thus eliminating the exponentials in this equation. We obtain the following quadratic form in the electric field for the free-energy functional:

$$\begin{aligned}\mathcal{F} &= \mathcal{F}_{\mathrm{el}} \\ &\quad - \frac{1}{2}\int_0^L (1-f)\varepsilon_0 \hat{\varepsilon}^{LC} \mathbf{E}_{LC} \cdot \mathbf{E}_{LC}\, dz \\ &\quad - \frac{1}{2}\int_0^L f\varepsilon_0 \hat{\varepsilon}^{P} \mathbf{E}_P \cdot \mathbf{E}_P\, dz - \frac{1}{2}\int_0^L f\varepsilon_0 \nu \big(\mathbf{n} \cdot \mathbf{E}_P^0\big)^2 dz \\ &\quad + \mathrm{const}\,. \end{aligned} \tag{24}$$

Substituting the local fields from Eqs. (11a),(11b),(11c) into the free-energy functional Eq. (24) now yields the following detailed form for the liquid-crystal free-energy functional:

$$\begin{aligned}\mathcal{F} &= \frac{1}{2}\int_0^L [K_1(\nabla \cdot \mathbf{n})^2 + K_3(\mathbf{n} \times \nabla \times \mathbf{n})^2]\, dz \\ &\quad - \frac{1}{2}\int_0^L \{(1-f)\varepsilon_0 \hat{\varepsilon}^{LC} \hat{T}^{LC}\mathbf{E} \cdot \hat{T}^{LC}\mathbf{E} + f\varepsilon_0 \hat{\varepsilon}^{P} \hat{T}^{P}\mathbf{E} \cdot \hat{T}^{P}\mathbf{E} \\ &\quad + f\varepsilon_0 \nu (\hat{T}^{P0}\mathbf{E} \cdot \mathbf{n})^2\} dz + \mathrm{const}\,, \end{aligned} \tag{25}$$

where $\hat{T}^{P0}, \hat{T}^{P}$ have been defined just below Eq. (20).

We now recall that the $\hat{T}$ matrices are diagonal in the reference frame of the particle. The $\hat{T}$ matrices can then in general be represented in the following general form:

$$T_{ij} = T_\perp \delta_{ij} + T_a n_i n_j, \tag{26}$$

where $T_a = T_\parallel - T_\perp$. Using Eq. (26), we now rewrite the functional (25) in general vector form, obtaining

$$\begin{aligned}\mathcal{F} &= \frac{1}{2}\int_0^L [K_1(\nabla \cdot \mathbf{n})^2 + K_3(\mathbf{n} \times \nabla \times \mathbf{n})^2]\, dz \\ &\quad - \frac{1}{2}\int_0^L \{\varepsilon_0 \varepsilon_{\perp\,\mathrm{eff}} \mathbf{E}^2 + \varepsilon_0 \varepsilon_{a\,\mathrm{eff}} (\mathbf{n} \cdot \mathbf{E})^2\} dz + \mathrm{const}\,. \end{aligned} \tag{27}$$

This expression now uses effective dielectric constants for the suspension defined by

$$\varepsilon_{\perp\,\mathrm{eff}} \equiv (1-f)\varepsilon_\perp^{LC}(T_\perp^{LC})^2 + f\varepsilon_\perp^{P}(T_\perp^{P})^2, \tag{28a}$$

$$\begin{aligned}\varepsilon_{a\,\mathrm{eff}} &\equiv (1-f)(\varepsilon_\parallel^{LC}(T_\parallel^{LC})^2 - \varepsilon_\perp^{LC}(T_\perp^{LC})^2) \\ &\quad + f(\varepsilon_\parallel^{P}(T_\parallel^{P})^2 - \varepsilon_\perp^{P}(T_\perp^{P})^2) + f\nu(T_\parallel^{P0})^2. \end{aligned} \tag{28b}$$

Finally, substituting in the explicit $\hat{T}$-matrix components into Eqs. (28a) and (28b), we obtain explicit expressions for a new set of effective dielectric constants which occur in the homogenized free energy. These are

$$\varepsilon_{\perp\,\mathrm{eff}} = \varepsilon_\perp^{LC} + f\frac{(\varepsilon_\perp^{P} - \varepsilon_\perp^{LC})\varepsilon_\perp^{LC}}{\varepsilon_\perp^{LC} + (1-f)\tilde{\mu}_\perp(\varepsilon_\perp^{P} - \varepsilon_\perp^{LC})} \cdot \frac{\varepsilon_\perp^{LC} + (1-f)\tilde{\mu}_\perp^2(\varepsilon_\perp^{P} - \varepsilon_\perp^{LC})}{\varepsilon_\perp^{LC} + (1-f)\tilde{\mu}_\perp(\varepsilon_\perp^{P} - \varepsilon_\perp^{LC})}, \tag{29a}$$

$$\begin{aligned}\varepsilon_{\parallel\,\mathrm{eff}} &= \varepsilon_\parallel^{LC} + f\varepsilon_\parallel^{LC}\frac{[\varepsilon_\parallel^{LC} + \tilde{\mu}_\parallel(\varepsilon_\parallel^{P} - \varepsilon_\parallel^{LC}) - \varepsilon_\parallel^{LC}(1 - \nu\tilde{\mu}_\parallel T_\parallel^0/\varepsilon_\parallel^{LC})]}{\varepsilon_\parallel^{LC} + (1-f)\tilde{\mu}_\parallel(\varepsilon_\parallel^{P} - \varepsilon_\parallel^{LC}) - f\tilde{\mu}_\parallel T_\parallel^0} \\ &\quad - f(\varepsilon_\parallel^{LC})^2\frac{(1 - \nu\tilde{\mu}_\parallel T_\parallel^0/\varepsilon_\parallel^{LC})[\varepsilon_\parallel^{LC} + \tilde{\mu}_\parallel(\varepsilon_\parallel^{P} - \varepsilon_\parallel^{LC}) - \varepsilon_\parallel^{P}(1 - \nu\tilde{\mu}_\parallel T_\parallel^0/\varepsilon_\parallel^{LC})] + f\nu(\varepsilon_\parallel^{LC})^2}{[\varepsilon_\parallel^{LC} + (1-f)\tilde{\mu}_\parallel(\varepsilon_\parallel^{P} - \varepsilon_\parallel^{LC}) - f\nu\tilde{\mu}_\parallel T_\parallel^0]^2}. \end{aligned} \tag{29b}$$

D. Frederiks transition voltage

We now use the formulas of the last subsection to calculate the Frederiks transition voltage. The free-energy functional is minimized with respect to director configuration, subject to given applied voltage V [i.e., constraint Eq. (5)]. The threshold voltage is then the voltage at which the initial liquid-crystal configuration becomes unstable.

The Frederiks threshold can be obtained from the functional Eq. (27) in the limit of small $\theta(z)$. We recall from Sec. II that $\hat{\mathbf{n}} = (\cos\theta, 0, \sin\theta)$; in this limit the elastic term reduces to $\frac{1}{2}K_1(\frac{d\theta}{dz})^2$. Calculation of the Frederiks threshold in conventional nematic liquid crystals is a standard problem [31]. The only new element in our case involves the explicit calculation of $\varepsilon_{\perp\,\mathrm{eff}}$ and $\varepsilon_{a\,\mathrm{eff}}$. In the limit $\theta \to 0$ Eq. (27) reduces to

$$\mathcal{F} = \frac{1}{2}\int_0^L \left\{ K_1\theta'^2 - \varepsilon_0\varepsilon_{a\,\mathrm{eff}}\left(\frac{V}{L}\right)^2 \theta^2 \right\} dz + \mathrm{const}\,, \tag{30}$$

where only terms up to second order in θ have been included, and in this limit it is still possible to replace E_z by $\frac{V}{L}$.

It is now straightforward to show that the Frederiks transition threshold voltage is given by

$$V_{\mathrm{thr}} = \pi\sqrt{\frac{K_1}{\varepsilon_0\varepsilon_{a\,\mathrm{eff}}}}. \tag{31}$$

TABLE I. Table of parameters.

Parameter	Value	Description
P	6μC cm^{-2}	Estimated particle permanent polarization
$\varepsilon_\perp^P$	10	(in $Sn_2P_2S_6$)
$\varepsilon_\parallel^P$	1000	(in $Sn_2P_2S_6$)
f	$3 \times 10^{-3} = 0.3\%$	Particle volume fraction in suspension
v	10^{-25}m^3	Volume of particle
$\varepsilon_\perp^{LC}$	7.0	(in 5CB)
$\varepsilon_\parallel^{LC}$	18.5	(in 5CB)
$a = b$	variable	Minor semiaxis of particle
c	variable	Major semiaxis of particle

IV. RESULTS

A. Parameter values

In our examples, we use parameters appropriate to thiohypodiphosphate ($Sn_2P_2S_6$) ferroelectric particles [10], in a LC matrix made from 5CB (Merck). The parameters, and their meanings are shown in Table I. Our calculations include effects of both polarization and anisotropy.

We note that the permanent polarization of bulk $Sn_2P_2S_6$ $d = 14\ \mu$C cm^{-2} [32]. Nanoparticle surface effects, such as lack of a local surface field and ionic effects due to adsorbed surfactant, would reduce this. To take account of this, in our calculation we use a value of $d = 6\mu$C cm^{-2} (see top row). By comparison, Lopatina and Selinger [22] have used the slightly lower figure of 4 μC cm^{-2}.

We now estimate the expansion parameter $dv\beta(\mathbf{n}\cdot\mathbf{E}_P^0)$, which occurs in Eq. (8). For our theory to be valid, this quantity must be less than unity. We suppose a typical cell thickness $L = 10\ \mu$m, at temperature $T = 20^\circ$ C $= 293^\circ$ K. Other typical parameter values are shown in Table I. We estimate the maximum field that orients particle permanent polarization E_P^0 to be of the same order as the Frederiks transition threshold $E_{FT} = \frac{\pi}{L}\sqrt{\frac{K_1}{\varepsilon_0\varepsilon_a^{LC}}} \simeq 7.88 \times 10^4$ Vm^{-1}. The relevant expansion parameter in Eq. (8) now takes the value

$$dv\beta E_P^0 \simeq dv\beta\frac{\pi}{L}\sqrt{\frac{K_1}{\varepsilon_0\varepsilon_a^{LC}}} \simeq 0.1. \qquad (32)$$

Thus in this case the inequality (8) is satisfied.

We note that a particle volume $v = 10^{-25}$ m^3 corresponds (in the case of spherical particles) to a particle diameter ~6 nm. By comparison, Cook *et al.* [33] state that their particle diameter is ~9 nm, increasing the value of this parameter from ~0.1 to ~0.45, but not violating the inequality Eq. (8). But the present theory should be applied cautiously. There are cases in which particles are large, or the electric field is high, and condition (8) is violated. One such case occurs in the experiments of Blach *et al.* [12], for which the particle diameter is ~150 nm.

B. Unpolarized particles

We first present results of calculations including hypothetical unpolarized particles whose dielectric properties are identical to those of $Sn_2P_2S_6$. Figures 2 and 3 show results, respectively, for the perpendicular and parallel components of the dielectric tensor, as a function of particle volume fraction f in the low-f regime where our calculations may have some validity. We also show in the same figures the so-called Weiner bounds [34,35], which delineate the region in which the effective medium properties may occur for *any* mixture with this ratio of materials. The upper bound corresponds to the (volume-fraction-weighted) arithmetic mean dielectric function, while the lower bound corresponds to the harmonic mean of the dielectric function.

Each of Figs. 2 and 3 shows two separate curves, in addition to the Weiner bounds. One of these corresponds to the dielectric function itself (i.e., the calculation of Sec. III B). The second plot corresponds to the effective dielectric constants to be used in an energy calculation (i.e., Sec. III C), which is to be used, for example, in calculations of the Frederiks threshold. This difference can be significant, even at very low f, particularly for $\varepsilon_{\parallel\,\mathrm{eff}}$. Gratifyingly, the calculated quantities do fall within the Weiner limits.

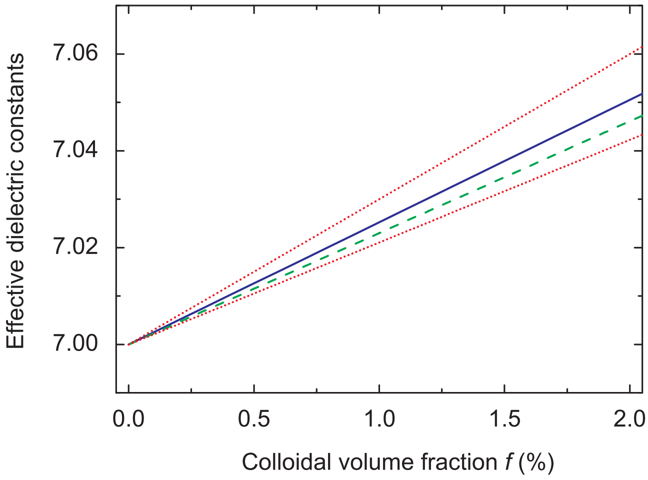

FIG. 2. (Color online) Perpendicular effective permittivities as a function of particle volume fraction f, for spherical dielectric particles, as discussed in text. $\tilde{\varepsilon}_\perp$ (full line) and $\varepsilon_{\perp\,\mathrm{eff}}$ (dashed line) are the effective perpendicular dielectric tensor components associated respectively with capacitance and energy calculations. The dotted lines are the Weiner limits described in the text.

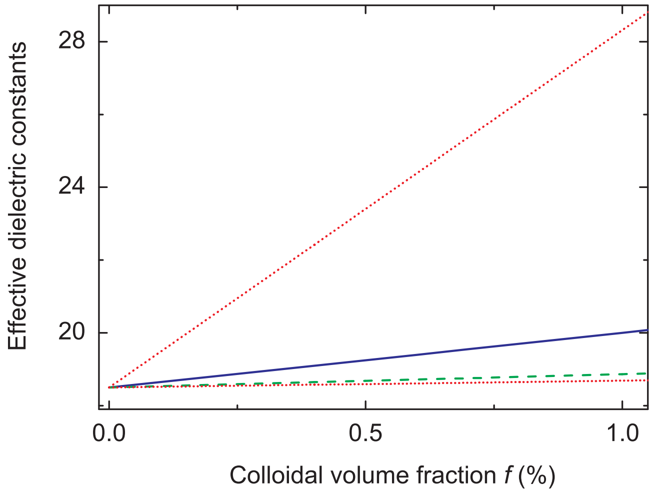

FIG. 3. (Color online) As for Fig. 2, but now showing parallel effective permittivities, also as discussed in text. Dotted lines: Weiner limits; full line: dielectric function; dashed line: effective dielectric component for energy calculations.

C. Ferroelectric particles

In Fig. 4 we show results for the full parallel components of the effective dielectric constant, but now also including the effect of the permanent dipoles. In order to make sensible comparisons, we assume as in Figs. 2 and 3, that the particle properties have not changed. The graphs include both $\tilde{\varepsilon}_{\parallel}$ (the "measurable" permittivity) and $\varepsilon_{\parallel\,\mathrm{eff}}$ (the quantity appearing in the energy functional). The permanent polarization does not enter the expression for the analogous perpendicular components.

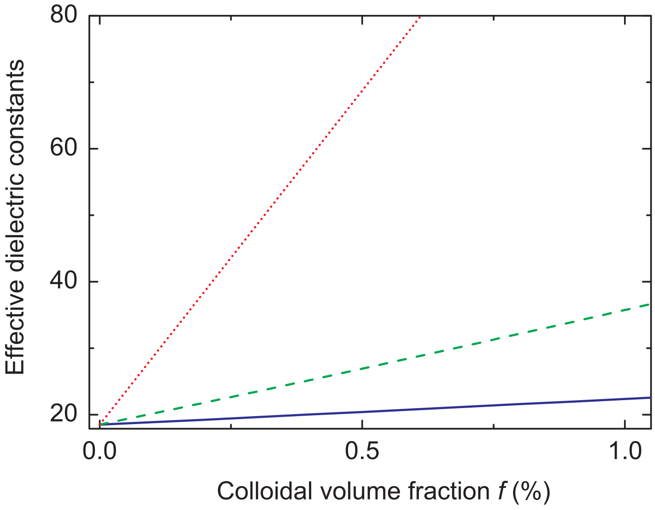

FIG. 4. (Color online) Effective permittivities $\tilde{\varepsilon}_{\parallel}$ (direct measurement: full line) and $\varepsilon_{\parallel\,\mathrm{eff}}$ (energy functional: dashed line), as a function of particle volume fraction f. Dotted line: predictions of our analogous 2006 theory [19].

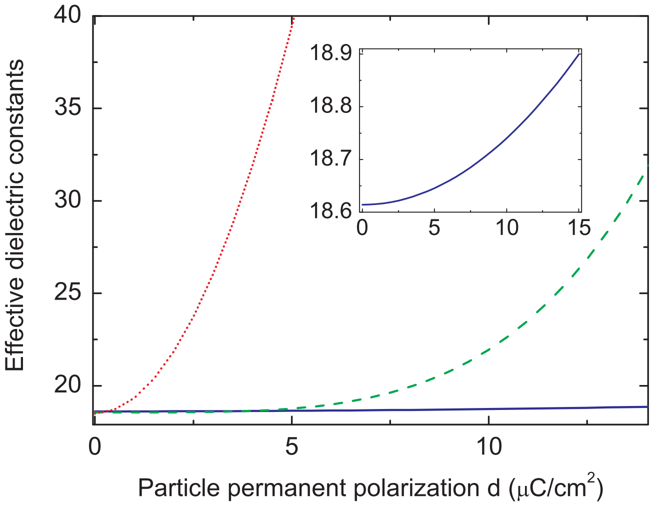

FIG. 5. (Color online) Effective (parallel) permittivities $\tilde{\varepsilon}_{\parallel}$ (direct measurement: full line) and $\varepsilon_{\parallel\,\mathrm{eff}}$ (energy functional: dashed line) as a function of particle permanent polarization d. Dotted line: 2006 theory [19]. Inset: direct measurement on a finer scale.

For comparison we have also included results from the cruder effective medium theory in our previous paper [19]. We note the dramatic difference (of the order of a factor of 2) between numerical values coming from the two different expressions for the parallel permittivity. Our previous paper predicts a numerically much larger value than either of these plots. Part of this discrepancy can be put down to a poor treatment of depolarization factors, presumed unity in our previous work.

In Fig. 5 we examine the explicit effect of increasing the colloidal particle dipole moment, at fixed particle shape and volume fraction. The predicted effect seems small by comparison with our 2006 theory. However, the quantity appearing in the energy functional lies between the result of our 2006 theory and the current theory.

In Fig. 6, we make an analogous study of the effect of particle shape, by changing the semiaxis ratio a/c at fixed particle volume v and fixed volume fraction f, subject to fixed particle polarization d. Thus $a/c = 1$ corresponds to a spherical particle, whereas $a/c \ll 1$ corresponds to a needle-shaped particle. The effect on the perpendicular component of the permittivity is negligible, and we do not show it. However, the effect on the parallel component is noticeable, although for the physical parameters we are using not dramatic until $a/c \ll 1$, i.e., the particle is strongly needle-like.

D. Frederiks transition

Finally we turn to predictions for the Frederiks threshold from Sec. III D. In Fig. 7 we show predictions for the dependence of the Frederiks threshold for spherical ferroelectric particles as a function of nanosuspension volume fraction, normalizing with respect to the Frederiks threshold voltage $V_{\mathrm{thr}}^{\mathrm{pure}}$ of pure liquid crystal. The effect is not as large that predicted in our 2006 theory [19]. Nevertheless, using the same set of model parameters, we predict a decrease of the order of a factor of 2, for volume concentrations of the order of 2%, which we regard as significant. For comparison we also show in this figure the normalized Frederiks threshold voltage for hypothetical unpolarized particles with the same dielectric properties. Here there is also some decrease in the threshold voltage. However, the results demonstrate conclusively that the main factor responsible for the significant threshold

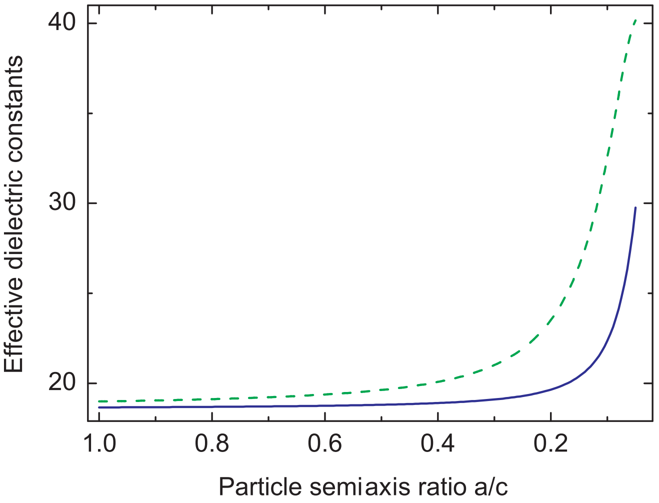

FIG. 6. (Color online) Effective (parallel) permittivities $\tilde{\varepsilon}_{\parallel}$ (direct measurement: full line) and $\varepsilon_{\parallel\,\mathrm{eff}}$ (energy functional: dashed line), as a function of particle shape parameter a/c, for polarized particles, using polarization parameters for $Sn_2P_2S_6$.

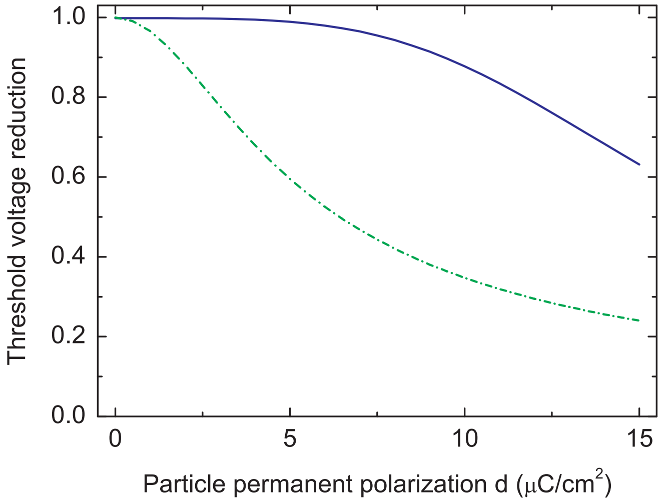

FIG. 8. (Color online) Dependence of Frederiks threshold voltage $V_{\mathrm{thr}}/V_{\mathrm{thr}}^{\mathrm{pure}}$ on particle permanent polarization d. Spherical dielectric particles at fixed particle volume fraction $f = 0.3\%$. Full line: present theory. Dashed line: 2006 theory.

voltage decrease is connected with the particle permanent polarization.

In Fig. 8 we make an analogous study of the specific effect of particle permanent polarization d for spherical particles at fixed volume fraction $f = 0.3\%$. V_{thr} decreases monotonically with d. As in Fig. 7, the effect is less marked than in our 2006 theory (also shown for comparison), but even at $f = 0.3\%$, there is a noticeable effect.

Figure 9 shows the effect of inclusion shape, keeping other relevant properties constant. We take account of shape by changing the semiaxis ratio a/c. As in Fig. 6, $a/c = 1$ corresponds to a spherical particle, whereas $a/c \ll 1$ corresponds to a needle-shaped spheroidal particle. From the point of view of dielectric properties, this calculation corresponds to changing the depolarization factors, which can be strongly dependent on particle shape. By comparison we observe that our 2006 theory [19] can only take account of particle shape in an ad hoc fashion.

The 2006 theory predicts a larger threshold voltage decrease than the current theory. For the physical parameters we use, the shape effect is only noticeable for $a/c \ll 1$, i.e., when the particle is strongly needle-like. This is also true for nonpolarized inclusions, but in this case the effect is anyway much smaller.

Finally we recall the distinction we have made between the effective permittivities to be used in energy minimization (and hence to predict the Frederiks threshold), and the effective permittivity to be used when calculating the dielectric response.

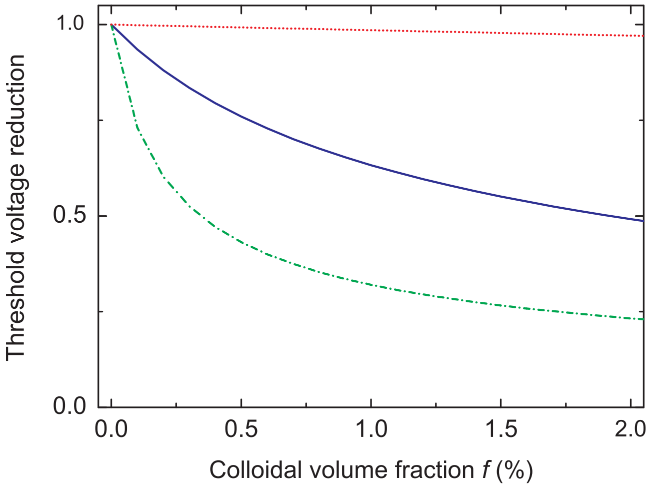

FIG. 7. (Color online) Frederiks threshold voltage $V_{\mathrm{thr}}/V_{\mathrm{thr}}^{\mathrm{pure}}$ as a function of particle volume fraction f, for spherical dielectric particles, as discussed in text. Full line: present theory. Dashed line: 2006 theory. Dotted line: nonpolarized dielectric nanoparticles.

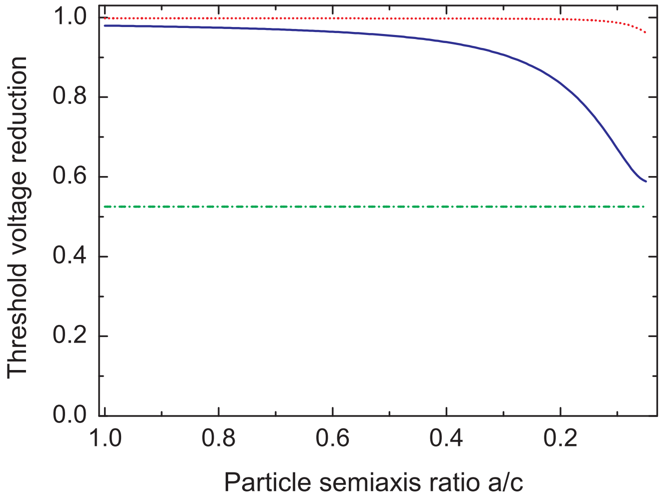

FIG. 9. (Color online) Dependence of Frederiks threshold voltage $V_{\mathrm{thr}}/V_{\mathrm{thr}}^{\mathrm{pure}}$ on particle shape, as represented by semiaxis ratio a/c. Other relevant parameters given in Table I. Full line: present theory. Dashed line: 2006 theory. Dotted line: present theory with nonpolarized dielectric nanoparticles.

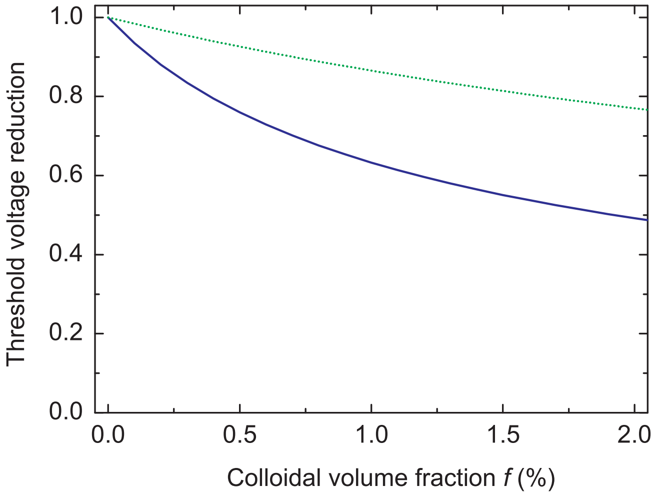

FIG. 10. (Color online) Comparison of "dielectric" and "free energy" routes to the calculation of the reduction in Frederiks threshold, as a function of particle volume fraction f, as discussed in the text. Other relevant properties as given in Table I. Full line: permittivity tensor given by $\hat{\varepsilon}_{\rm eff}$, i.e., free-energy functional permittivity ("correct procedure"). Dotted line: permittivity tensor given by $\hat{\hat{\varepsilon}}$, i.e., direct measurement permittivity ("incorrect procedure").

In Fig. 10, we examine the effect of making this distinction, by explicitly comparing the Frederiks threshold predictions calculated by what we believe is the correct criterion (from Sec. III C), and those calculated using an incorrect criterion (from Sec. III B). The difference between the predictions as a function of colloidal volume fraction, otherwise using physical parameters from Table I, is quite striking. Use of an inappropriate effective medium tensor would predict a considerably smaller effect, by factors of between 2.5 and 5.

V. CONCLUSIONS

A. General considerations

In this paper we have introduced a tensor effective medium theory for a system containing ferroelectric nanoparticles in a liquid-crystal suspension. Such systems have been the focus of much research in recent years, because thermodynamic, dielectric, and potential device properties of such systems seem to show extreme sensitivity to very low ferroparticle volume concentrations. A theory describing dielectric properties is a major priority in order that further progress may be made in device applications, and presents interesting new challenges in the context of the general theory of inhomogeneous dielectric media.

An important point, at which our theory starts, is the assumption that the particles are supposed to align perfectly with the local nematic director. This point, although plausible, is not at all obvious. We first give a brief justification of this postulate.

There are several possibilities for mutual arrangement of the spontaneous polarization of a ferroelectric particle with respect to the liquid-crystal director in the absence of an external electric field. The liquid crystal is a uniaxial anisotropic dielectric medium, with principal axis parallel to the director. The liquid-crystal host can in principle possess either positive or negative dielectric anisotropy. Here, we suppose that it has positive anisotropy. A further key assumption is to consider the case in which the ferroelectric nanoparticles are sufficiently small not to disturb the director in their neighborhood. We remark that most studies of liquid-crystal colloids (see, e.g., Stark [1]) do not consider this limit, and in this case the defect structure in the neighborhood is important. But here there is no defect structure. A similar assumption was used by Lopatina and Selinger [22], but it is in any case implicit in the lack of turbidity observed in the experiments on these materials. We now assert that in this limit, at zero externally applied electric field, it is energetically favorable for the particle spontaneous polarization to be aligned either parallel or antiparallel to the director. A more detailed calculation will be published elsewhere, but a semiquantitative estimate can be established as follows.

Place at the origin a ferroelectric particle with dipole $\mathbf{p} = \mathbf{d}v$, where $d = |\mathbf{d}|$ is the ferroelectric polarization and v is its volume [see Eq. (2)]. In an isotropic medium the field produced by dipole $\mathbf{p}$ at a point $\mathbf{r}$ is

$$\bar{\mathbf{E}}(\mathbf{r}) = \frac{v}{4\pi\epsilon_0 r^5}[\mathbf{d}r^2 - 3(\mathbf{d}\cdot\mathbf{r})\mathbf{r}]. \tag{33}$$

The electrostatic energy associated with the ferroparticle is then

$$U_{\rm es-fp} = \frac{1}{2}\int_V \mathbf{D}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r})dV, \tag{34}$$

where the electric displacement $\mathbf{D} \sim \epsilon_0\epsilon_{LC}\mathbf{E}$, the integral is taken outside the particle, and ϵ_{LC} is an effective liquid-crystal dielectric constant. Then evaluating this explicitly yields

$$U_{\rm es-fp} = \frac{v^2\epsilon_{LC}}{32\pi^2\epsilon_0}\int_V \frac{1}{r^{10}}[\mathbf{d}r^2 - 3(\mathbf{d}\cdot\mathbf{r})\mathbf{r}]^2 dV \sim 10^{-15}\ \text{Joules}. \tag{35}$$

This evaluation of the total electrostatic energy in the isotropic system becomes an estimate of the energy in an anisotropic system, but is nevertheless reliable. However, in the anisotropic liquid crystal, the electrostatic energy will now depend on the external director $\mathbf{n}$. Given the rather large degree of dielectric anisotropy in the liquid crystal even close to T_{NI}, we expect that at the order of magnitude of the anisotropic contribution will be comparable to its total value. We note that $\frac{U_{\rm es-fp}}{k_BT} \sim 10^4$, which is a very large number. The conclusion is that even if the anisotropic part of the electrostatic energy is a really rather small fraction, the relevant Boltzmann factor enforcing alignment will still be sufficiently large a number to require the ferroelectric particles to align rather closely (parallel or antiparallel) to the local director.

The relevant nondimensional quantity is just the quantity $\nu = \frac{d^2v}{k_BT\epsilon_0} \sim 10^4$ introduced in Sec. III A, which originally quantified the ratio of the electrostatic interaction between two dipoles to the thermal energy. Here, remarkably, it turns out also to refer to the effective anchoring energy of the dipole to the local director.

A particularly interesting feature of this calculation is that this anchoring is principally electrostatically enforced. We have made reference earlier in this paper to ferronematics, which are the analogous magnetic systems [2–4,8,9]. In these systems the nematic director is also coupled to the local dipolar order. But in the ferronematics, the coupling is steric or due to dispersion forces and are much weaker than in the ferroelectric case. Thus strong departures from mutual local alignment can in principle be expected under some circumstances. By contrast, here in the ferroelectrics, it seems very unlikely indeed. In this sense these systems conform quite closely to the (incorrect) assumptions made about dipolar-director coupling made by Brochard and de Gennes [2].

We note that an *a priori* plausible alternative assumption would be that the dipoles order along the direction of the external field. In this case we might take the Frederiks threshold field as a typical field. However, the electrostatic energy associated with this interaction is almost five orders of magnitude lower than that associated with the fields due to the dipoles alone, and can thus to lowest order be neglected. This is not to say that the external fields cannot reorient the dipoles. Rather it asserts that of such reorientation takes place, then the dipolar reorientation must also be accompanied by director reorientation.

In addition, the theory is complicated because the suspension is itself anisotropic, the colloidal particles are anisotropic in shape with anisotropic electrostatic properties, and the interaction between the two contains both electrostatic and nonelectrostatic components. As such, it is rather difficult to reduce the theory to its key components, and draw out its key predictions using intuitive arguments. A full theory would no doubt be even more complicated.

An important qualitative and somewhat surprising conclusion of the theory is that the concept of "effective permittivity" is not well defined. We derive two sets of effective permittivity tensors. One of these is used simply to derive the dielectric properties, such as would be measured in a capacitance experiment. A second set is used in a free-energy calculation to predict the dependence of the Frederiks threshold voltage on ferroelectric particle concentration. The distinction between the two is not merely academic, but should lead to measurable consequences.

The deep reason for the existence of this distinction is hinted at in Sec. III C. The average displacement $\mathbf{D}$ defines the effective permittivity. But electrostatic energies come from the product $<\mathbf{D}\cdot\mathbf{E}>$, and this also defines an effective permittivity. However in a complex microscopically inhomogeneous medium $<\mathbf{D}\cdot\mathbf{E}>\neq<\mathbf{D}>\cdot<\mathbf{E}>$. The product of the means of two quantities is not in general the same thing as the mean of a product of the same quantities. But the mean electrostatic energy is a well-defined quantity. In order to reconcile the apparent contradiction, two different permittivities must be introduced, one when considering energies (or other quadratic properties), and another when considering capacitances (or other linear properties).

The present theory is only a zero frequency treatment of dielectric response. We do not treat at all finite frequency. However, we may conjecture that many of the principal features are retained at low frequency. At this stage, even the characteristic magnitudes are unclear. At sufficiently high frequencies the rotational inertia of the dipoles must play a role, and then for a full treatment the assumption of strong coupling between the director and the dipole directions must be relaxed.

B. Specific applications

Our theory unambiguously predicts a reduction in the Frederiks threshold voltage as a function of ferroparticle concentration. The reductions are quite large: of the order of a factor of 2 for particle volume concentrations of the order of a few %. Using an inappropriate set of effective medium parameters leads to significantly different predictions. Qualitatively, our results are consistent with many recent experiments [10], although not always consistently so. A usual experiment for determining the splay elastic constant involves a measurement of the Frederiks threshold voltage. But the shift in the Frederiks threshold does not mark a dramatic shift in the splay elastic constant, but is an effective dielectric phenomenon. Our theory suggests that if the Frederiks threshold in a ferroparticle liquid-crystal system *increases*, then there is extra new physics in addition.

The present theory replaces a previous theory, published in 2006 [19], which contained some of the same physics, but dealt with the complicated tensor electrostatics in a much less sophisticated fashion. This theory, however, was much less complicated and easier to use. The results of that theory were qualitatively similar, but quantitatively different, from the predictions of the present theory. A key element omitted from that theory was an independent method of determining depolarization factors. Equivalently the self-field effects of a ferroparticle in a dielectric medium were lumped together in a phenomenological parameter λ. In our 2006 theory we simply put this parameter equal to unity. We have continued to do this in the comparisons presented in the present paper. But in fact it is possible to use the present theory to evaluate the parameter λ in our 2006 paper, thus enabling some of the qualitative insights in a simpler approach to be preserved.

In Fig. 11, we compare the predictions of the 2006 theory against the current theory for the dependence of the Frederiks threshold voltage on particle concentration. The figure shows that, for spherical particles and other parameters fixed in

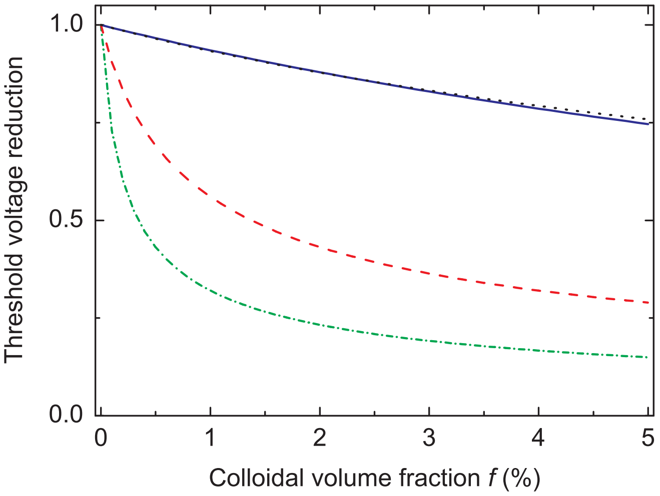

FIG. 11. (Color online) Plots of Frederiks threshold against particle volume fraction f. Solid line: Current theory. Dotted line: 2006 theory with $\lambda = 0.13$. Dashed line: 2006 theory with $\lambda = 0.5$. Dot-dash line: 2006 theory with $\lambda = 1$. Current theory agrees well with 2006 theory with $\lambda = 0.13$.

Table I, the current theory compares very well with the 2006 theory, subject to $\lambda = 0.13$. We not, however, at this stage have an analytic treatment of this problem, and the deep reason for this coincidence is at this stage unclear.

There is a need for further experiments, analytic theory, and computational modeling in ferroparticle liquid crystal colloids. The need for an advanced theory is highlighted by problems encountered by Blach *et al.* [12]. These authors have carried out careful electro-optical studies of a liquid-crystalline system with 4% by volume of ferroelectric colloidal particles of 150 nm diameter. Blach *et al.* find that their results are not numerically in accord with our 2006 paper [19]. However, by contrast with results by Glushchenko *et al.* [36], a reduction in the Frederiks threshold is nevertheless observed in the presence of ferroelectric particles. We would remark that unfortunately these experiments do not satisfy the key condition in Eq. (8) that $d v \beta(\mathbf{n} \cdot \mathbf{E}_p^0) < 1$ close to the Frederiks threshold, and hence neither [19] nor the present paper can be used quantitatively. However, it is possible that some suitable nonlinear extension of the theory might apply.

Furthermore, the connection between the 2006 theory and the present theory remains unclear. It may be that the close agreement for one prediction of the theory is a numerical coincidence, and not robust with respect to changes in particle shape and other parameters. Preliminary analysis has not so far yielded any conclusion on this question. In a more general context a number of workers, most notably Fu, Resca, and coworkers [29,37–39], have studied effective medium theories analogous to those which we have addressed, but including details of the positional and orientational correlations between the inclusions, and it may be that progress is possible in this direction as well.

In addition, the present theory assumes that the ferroparticles are uniformly distributed. Equivalently, it represents the liquid crystal as a ceramic, and draws its inspiration from dielectric theories of ceramics. Positional, as opposed to orientational, dielectric ferroparticle response is neglected. It would be of interest to try to model such a system computationally, solving the relevant electrostatic equations numerically. As far as we are aware, such modeling has not been attempted for systems of the kind of complexity under discussion here. We believe, however, that in principle, nontrivial computational modeling of these systems may now be computationally feasible. Such studies would give a firmer theoretical basis to the present calculations and other calculations in the same genre.

In addition, however, theoretical considerations based on statistical mechanical theories of dipolar particles [40] strongly indicate that at the volume concentrations at which experiments are carried out, the ferroelectric dipoles should form almost unbreakable chains. The key nondimensional parameter is the quantity ν, discussed above in the context of dipolar-director anchoring. Thus positional ordering is expected in addition to the orientational ordering. But such chains have not been observed. Indeed, in at least one so-far-unreported experiment [41] low angle x-ray scattering experiments seem explicitly to *exclude* chain formation. Why this would be the case is at the moment a mystery. In the presence of chains a new theoretical approach would be necessary, and the present considerations would at least partially be invalidated. So further investigation of this aspect of the problem is of great importance.

ACKNOWLEDGMENTS

This work was partially supported by NATO Grant No. CBP-.NUKR.CLG.981968 “Electro-optics of heterogeneous liquid crystal systems,’ by STCU (Ukraine) Grant No. 5205, by EOARD grant no. 078001, and Joint Slovenian-Ukrainian M 86-2009. We are grateful to our colleagues G. Cook (Dayton, Ohio, USA), D. R. Evans (Dayton, Ohio, USA), M. Kaczmarek (Southampton, UK), A. Glushchenko (Colorado Springs, USA), M.A. Osipov (Glasgow, UK), Yu. Reznikov (Kiev, Ukraine), J. V. Selinger (Kent, Ohio, USA), R.C. Richardson (Bristol, UK), P. I. C. Teixeira (Lisbon, Portugal), and J. L. West (Kent State, Ohio, USA) for useful conversations. We thank Irena Drevenšek Olenik and Samo Kralj for hosting a visit by VYR and TJS to Ljubljana where this paper was completed.

APPENDIX: DIELECTRIC ELLIPSOID PROBLEM

In this appendix we summarize ideas concerning the depolarization factors associated with inclusions in a dielectric medium, and which enter in Eq. (12).

In order to do this, we use ideas from Jones [30] and Sihvola [42] to derive the relation between local fields of an aligned anisotropic spheroid with a permanent electric dipole embedded in an anisotropic dielectric host.

Let us assume provisionally that the medium which the dielectric ellipsoid is placed is a vacuum. At an inner point of a uniformly polarized ellipsoid there is an electric field, known as the depolarization field [24]. This is given by the following expression: [30]

$$\mathbf{E}_d = -\hat{\mu}\mathbf{P}/\varepsilon_0, \tag{A1}$$

where $\mathbf{P}$ is the ellipsoid polarization and $\hat{\mu}$ is the depolarization tensor. This tensor is diagonal in the ellipsoidal reference frame, i.e. when the coordinate axes are parallel to the main ellipsoid axes:

$$\hat{\mu} = \begin{pmatrix} \mu_x & 0 & 0 \\ 0 & \mu_y & 0 \\ 0 & 0 & \mu_z \end{pmatrix}, \tag{A2}$$

where μ_x, μ_y, μ_z are known as depolarizing factors.

For a spheroid ($a = b < c$ or $a = b > c$) the depolarization tensor is given by [24]

$$\hat{\mu} = \begin{pmatrix} \mu_\perp & 0 & 0 \\ 0 & \mu_\perp & 0 \\ 0 & 0 & \mu_\parallel \end{pmatrix}, \tag{A3}$$

with

$$\begin{aligned} \mu_\parallel &= \frac{1-e^2}{e^3}(\operatorname{arctanh} e - e), \\ \mu_\perp &= \frac{1}{2}(1-\mu_\parallel), \end{aligned} \tag{A4}$$

and where $\mu_\parallel$ and $\mu_\perp$ are the depolarizing factors for a prolate spheroid with eccentricity $e = \sqrt{1 - a^2/c^2}$. For an oblate spheroid, the analogous expressions are

$$\begin{aligned}\mu_\parallel &= \frac{1+e^2}{e^3}(e - \arctan e),\\ \mu_\perp &= \frac{1}{2}(1-\mu_\parallel),\end{aligned} \tag{A5}$$

where $e = \sqrt{a^2/c^2 - 1}$.

The uniform field inside the ellipsoid $\mathbf{E}_P$ produces induced polarization

$$\mathbf{P}_{\hat{\varepsilon}^P} = \varepsilon_0(\hat{\varepsilon}^P - 1)\mathbf{E}_P. \tag{A6}$$

If the ellipsoidal particles also possess a permanent polarization $\mathbf{P}_P$, then the total polarization of the ellipsoid is

$$\mathbf{P} = \mathbf{P}_{\hat{\varepsilon}^P} + \mathbf{P}_P = \varepsilon_0(\hat{\varepsilon}^P - 1)\mathbf{E}_P + \mathbf{P}_P. \tag{A7}$$

Combining Eqs. (A1) and (A7), we can now derive the internal electric field produced by this total ellipsoid polarization:

$$\mathbf{E}_d = -\hat{\mu}(\hat{\varepsilon}^P - 1)\mathbf{E}_P - \hat{\mu}\mathbf{P}_P/\varepsilon_0. \tag{A8}$$

The total field $\mathbf{E}_P$ inside the dielectric ellipsoid is given by the sum of the uniform external field $\mathbf{E}$ and the field $\mathbf{E}_d$ due to the polarization of the spheroid:

$$\mathbf{E}_P = \mathbf{E}_d + \mathbf{E}. \tag{A9}$$

This yields the following equation for the external field:

$$\mathbf{E} = [1 + \hat{\mu}(\hat{\varepsilon}^P - 1)]\mathbf{E}_P + \hat{\mu}\mathbf{P}_P/\varepsilon_0. \tag{A10}$$

In our case, however, the ellipsoid is placed not in a vacuum, but in the nematic liquid crystal host with dielectric permittivity tensor $\hat{\varepsilon}^{LC}$. We can thus modify Eq. (A10) by replacing ε_0 by $\varepsilon_0\hat{\varepsilon}^{LC}$, while maintaining $\hat{\varepsilon}^P$, thus obtaining:

$$\hat{\varepsilon}^{LC}\mathbf{E}_{LC} = [\hat{\varepsilon}^{LC} + \hat{\tilde{\mu}}(\hat{\varepsilon}^P - \hat{\varepsilon}^{LC})]\mathbf{E}_P + \hat{\tilde{\mu}}\mathbf{P}_P/\varepsilon_0. \tag{A11}$$

Particular cases of this formula have been derived, for example, by Landau [24] and Sihvola [28].

In Eq. (A11), we have used a modified depolarization tensor $\hat{\tilde{\mu}}$. It is modified as a result of the anisotropy of the external medium. Sihvola [42] has demonstrated a procedure to take account of this anisotropy.

The procedure involves an affine transformation to the external medium in such a way that the Laplace equation holds for the potential in the transformed space. After the transformation, the spheroidal surface of the inclusion will in general now be ellipsoidal. But in our case, the spheroidal particles are aligned with the principal axis of the host medium. As a result, even after transformation, the particle shape remains spheroidal, but with modified semiaxes:

$$\tilde{a}_i = \frac{a_i}{\sqrt{\varepsilon_i^{LC}}}, \quad i = \perp\,,\ \parallel\,. \tag{A12}$$

The modified depolarization coefficient tensor $\hat{\tilde{\mu}}$ is calculated then using the well-known formulas (A4)–(A5), but now with a modified eccentricity.

For a prolate spheroid, we obtain

$$\begin{aligned}\tilde{\mu}_\parallel &= \frac{1-e'^2}{e'^3}(\operatorname{arctanh} e' - e'),\\ \tilde{\mu}_\perp &= \frac{1}{2}(1-\tilde{\mu}_\parallel),\end{aligned} \tag{A13}$$

$e' = \sqrt{1 - \frac{\varepsilon_\parallel^{LC}a^2}{\varepsilon_\perp^{LC}c^2}}$. For an oblate spheroid, the analogous expressions are

$$\begin{aligned}\tilde{\mu}_\parallel &= \frac{1+e'^2}{e'^3}(e' - \arctan e'),\\ \tilde{\mu}_\perp &= \frac{1}{2}(1-\tilde{\mu}_\parallel),\end{aligned} \tag{A14}$$

where $e' = \sqrt{\frac{\varepsilon_\parallel^{LC}a^2}{\varepsilon_\perp^{LC}c^2} - 1}$.

Formulas (A13), (A14) are required for explicit calculations of the dielectric properties of the liquid-crystal media, as discussed in Eq. (12) and the subsequent development.

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