

Local field effects and the field-dependent dielectric response of polymer dispersed liquid crystals

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An anisotropic version of the Maxwell Garnett approximation is applied for studying the dielectric properties of polymer dispersed liquid crystals containing bipolar liquid crystal droplets. This approach provides an explicit link between the droplet orientation distribution and the macroscopic response of the material. The electrostatic energy of the droplets is balanced with a strong anchoring elastic energy term for different initial orientation distributions. For aligned droplets we find a switching process whose sharpness depends on the initial orientation and a concentration dependent threshold field. For a planar distribution we find sharp transitions with a hysteresis loop whose width depends on the droplet concentration. For a random distribution the droplet reorientation is more gradual. The theory is also applied to the negligible elastic energy limit, recently observed at temperatures near the nematic-isotropic phase transition, where the droplets consist of bipolar nematic cores coated by isotropic liquid shells. This structural change within the droplets causes a considerable modification of the electro-optical properties. The Maxwell Garnett approach is used to calculate the dielectric response of this structure and reproduces all the main features of the experimental results.

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I. INTRODUCTION

Polymer dispersed liquid crystals (PDLCs) are inhomogeneous materials in which a liquid crystal (LC) is contained inside tiny droplets embedded in a polymer matrix. PDLC films of bipolar nematic LC droplets are of particular current interest for optical applications, ranging from switchable windows to active matrix projection displays (see, for example, [1,2]). These applications are based on the easy manipulation of the LC orientation inside the droplets by an externally applied electric field, thus modifying the electro-optical properties of the material. Typically, a PDLC film is sandwiched between conducting electrodes and is electrically driven to obtain the desired effect. Each application has its own electrical constraints on the power consumption, driving voltage, maximum current, and frequency of operation, which are determined by the dielectric properties of the film. These dielectric properties and their dependence on externally applied fields and the morphology of the material have been the subject of numerous experimental studies (some recent examples are [3–10]). In contrast, despite their inherent importance, very little theoretical work has been done to understand these issues. Wu, Erdmann, and Doane [11] studied the effect of an applied field on the director orientation of an isolated bipolar LC droplet. They calculated the electrostatic torque on the droplet using a simple approximation for the field inside it. Balancing this torque with an elastic torque, created by strong anchoring at the droplet walls, they obtained the field-dependent orientation of the director. This derivation leads to a relation between the switching voltage of a PDLC in which LC droplets are dilutely dispersed and some of its microscopic parameters. Kelly and Palfy-Muhoray [12] introduced a model that relates the dielectric response of PDLC films to external fields

via their effects on a hierarchy of orientation order parameters. In this model the LC droplets are approximated as isotropic inclusions with an averaged scalar dielectric coefficient, which depends on an internal order parameter. This approximation is then used to calculate the bulk dielectric coefficient of the film via the classical Maxwell Garnett formula [13] for a dispersion of isotropic inclusions in an isotropic host. Reshetnyak, Sluckin, and Cox [14] proposed an effective medium approach to calculate the dielectric tensor of a PDLC film. They too obtained an expression for the switching voltage of a very dilute PDLC, slightly different from that of [11]. In nondilute systems, they showed that this approach can be used to numerically calculate the dielectric tensor for a few initial orientation distributions of the bipolar droplets.

In this paper we present an alternative method for calculating the bulk effective dielectric response of PDLC films, based on a recent extension of the Maxwell Garnett approximation for mixtures of anisotropic inclusions (in our case the LC droplets) embedded in an isotropic host (the polymer) [15]. The Maxwell Garnett (MG) approximation [13], also known as the Clausius-Mossotti approximation, is one of the most widely used methods for calculating the bulk dielectric properties of inhomogeneous materials [16,17]. It is particularly useful when one of the components can be considered as a host in which inclusions of the other component are embedded, as is the case in PDLCs. We obtain an expression for the effective dielectric tensor of a PDLC that depends explicitly on the distribution of director orientations of the LC droplets. The field-dependent response of a PDLC film is calculated by relating this distribution to the magnitude of an externally applied low-frequency electric field. In the dilute limit this method leads, as expected, to results identical to those of the effective medium approach of [14]. In the nondilute case, we show that it gives an analytic solution for two interesting types of initial droplet orientation distributions, with switching fields that depend on the volume fraction of the LC droplets. For all other initial distributions it provides

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a simple scheme for a numerical calculation of the dielectric response. The MG approach may therefore be a useful tool for the interpretation of experimental results and the prediction of PDLC properties under various conditions.

All the models described above assume strong planar anchoring at the droplet walls. A recent experimental study by Amundson demonstrated that this assumption is justified at relatively low temperatures, well below the nematic-isotropic transition inside the LC droplets [4]. Near the transition the droplets undergo an internal structural change accompanied by changes in the electro-optical properties. Amundson showed that in this temperature range (within 4–5 °C below the transition) the transition starts by creating a shell of isotropic liquid near the droplet walls. In this paper we will also apply an adaptation of the MG approach to mixtures of coated inclusions for calculating the bulk dielectric coefficient of a PDLC near the nematic-isotropic transition, based on the structural information from Amundson's experiments. The results obtained exhibit the main experimental features associated with the nematic-isotropic transition in PDLC films and demonstrate the usefulness of the MG approach for the description of PDLC properties in this regime.

The rest of the paper is organized as follows. The Maxwell Garnett approximation for suspensions of anisotropic inclusions is introduced in Sec. II, and explicit results are derived for uniaxial materials. In Sec. III, we discuss the reorientation of bipolar LC droplets in the presence of applied field and its effects on the dielectric response of PDLC films for a few different types of initial orientation distribution. The model is extended to systems of coated inclusions in Sec. IV, and applied to the discussion of PDLC dielectric properties near the nematic-isotropic transition. Finally, some brief conclusions are included in Sec. V.

II. DIELECTRIC RESPONSE OF MIXTURES OF ANISOTROPIC INCLUSIONS

An exact calculation of the effective properties of an inhomogeneous medium is in general an intractable problem. The literature on this subject therefore includes a wide variety of approximate schemes, each of which is appropriate for different types of composite microgeometries (see, for example, the review papers [16,17], and references therein). One of those, which is particularly useful for microgeometries in which a host material and isolated inclusions of other materials are clearly identified, is the Maxwell Garnett (MG) approximation. It involves an exact calculation of the field induced in the uniform host by a single spherical or ellipsoidal inclusion and an approximate treatment of its distortion by the electrostatic interaction between the different inclusions. This distortion is caused by the charge dipoles and higher multipoles induced in the other inclusions. The induced dipole moments cause the longest range distortions and their average effect is included in the MG approximation, which results in a uniform field inside all the inclusions. This approach has been extensively used for studying the properties of two-component mixtures in which both the host and the inclusions are isotropic materials with scalar dielectric coefficients. It has been shown to be exact to second order in the volume fraction of the inclusions and to second order in the dielectric contrast between the inclusions and the

host [17]. In addition, it was proved that it provides an exact solution for a geometry where the entire space is filled with coated spheres, each with identical ratio of inner to outer radius, such that one component is the core material (isolated inclusions) and the other is the coating material (the host). The microgeometry of PDLCs is clearly of this host-inclusions type and therefore the MG approach may be considered as particularly appropriate for the calculation of its macroscopic dielectric properties. In this paper, we use a variation of the MG approach [15] that is adapted for mixtures where the host is an isotropic material but the inclusions are made of an anisotropic component in which the direction of the dielectric tensor axes may vary from one inclusion to the other. The distribution of these directions significantly influences the bulk effective dielectric response of the material.

Consider a parallel plate condenser whose plates are large enough so that edge effects can be neglected. The condenser is filled by a homogeneous host with a scalar dielectric constant ϵ_p in which nonoverlapping spheres of an anisotropic component with a tensor dielectric coefficient $\tilde{\epsilon}_s$ are distributed randomly but uniformly. The orientation of the dielectric tensor differs from inclusion to inclusion, such that

$$\tilde{\epsilon}_s = R \tilde{\epsilon} R^T, \quad (1)$$

where $\tilde{\epsilon}$ is a diagonal tensor and R is the inclusion dependent rotation. Our aim in this section is to derive an expression for the bulk effective dielectric tensor of this mixture.

First we consider a single sphere $\tilde{\epsilon}_s$ immersed in the host ϵ_p . A voltage is applied between the condenser plates such that the volume averaged field in the system is E_0 . In this case, the electric field E_s and the displacement field $D_s = \tilde{\epsilon}_s E_s$ inside the inclusion are uniform and satisfy the exact relation

$$D_s + 2\epsilon_p E_s = 3\epsilon_p E_0. \quad (2)$$

The induced dipole moment of the sphere is

$$p_s = V_s \frac{D_s - \epsilon_p E_s}{4\pi} = V_s \frac{3\epsilon_p}{4\pi} \frac{\tilde{\epsilon}_s - \epsilon_p I}{\tilde{\epsilon}_s + 2\epsilon_p I} E_0, \quad (3)$$

where V_s is the volume of the sphere and I is the identity matrix. In this, and in the subsequent equations, the denominators should be understood as representing inverse matrices. From this it follows that if the medium contains a few such spheres, sufficiently far apart for their mutual interactions to be negligible, then the volume averaged polarization in the medium is

$$\langle P \rangle \equiv \frac{1}{V} \sum_s p_s = f \frac{3\epsilon_p}{4\pi} \left\langle \frac{\tilde{\epsilon}_s - \epsilon_p I}{\tilde{\epsilon}_s + 2\epsilon_p I} \right\rangle_R E_0, \quad (4)$$

where f is the volume fraction of the inclusions and $\langle \rangle_R$ denotes an average over the dielectric tensor orientations inside the inclusions.

The bulk effective dielectric tensor can be defined by the ratio between the volume averaged displacement field $D_0 = \langle D \rangle$ and the volume averaged electric field $E_0 = \langle E \rangle$. The volume averaged displacement field is easily calculated by

$$D_0 = \epsilon_p E_0 + 4\pi \langle P \rangle = \left[I + 3f \left\langle \frac{\tilde{\epsilon}_s - \epsilon_p I}{\tilde{\epsilon}_s + 2\epsilon_p I} \right\rangle_R \right] \epsilon_p E_0. \quad (5)$$

The bulk effective dielectric tensor is therefore

$$\tilde{\epsilon}_e = \epsilon_p I + 3f \epsilon_p \left\langle \frac{\tilde{\epsilon}_s - \epsilon_p I}{\tilde{\epsilon}_s + 2\epsilon_p I} \right\rangle_R. \quad (6)$$

This result, ignoring the interaction between the different inclusions, is usually called the dilute limit and is valid to first order in the volume fraction of the inclusions.

The electrostatic interaction between the inclusions is negligible only in mixtures where the volume fraction of the inclusions is small. In all other cases it should be taken into account when calculating the dielectric properties of the system. This is easily done in the Maxwell Garnett approximation, where the average field acting on each inclusion is considered to be not the applied field E_0 but the well known Lorentz local field [16]. Using this correction, the dipolar interaction between the inclusions is taken into account in an averaged way. A simple method to calculate this correction, usually referred to as the excluded volume approach, was proposed by Bragg and Pippard [18]. The average field acting on an inclusion, in a mixture that is not too dense, is the average field in the host medium E_{ex} . The difference between E_{ex} and E_0 is due to the correlations between positions of different spheres that arise from the prohibition of overlap between them [18]. Substituting E_{ex} for E_0 in Eq. (2), we find that the field inside the inclusion satisfies the relation

$$D_s + 2\epsilon_p E_s = 3\epsilon_p E_{ex}. \quad (7)$$

The averaged field over the entire system, inside and outside the inclusions, must still be E_0 . This leads to a simple relation between the average fields in the host and in the inclusions

$$f \langle E_s \rangle + (1-f) E_{ex} = E_0, \quad (8)$$

where the angular brackets denote a volume average inside the inclusions. Substituting E_s from Eq. (7) we solve for E_{ex} and find

$$E_{ex} = \frac{E_0}{(1-f) + 3f \epsilon_p \langle (\tilde{\epsilon}_s + 2\epsilon_p I)^{-1} \rangle_R}. \quad (9)$$

The induced dipole moment of a single spherical inclusion is

$$P_s = \frac{V_s}{4\pi} \frac{\tilde{\epsilon}_s - \epsilon_p I}{\tilde{\epsilon}_s + 2\epsilon_p I} \frac{3\epsilon_p E_0}{(1-f) + 3f \epsilon_p \langle (\tilde{\epsilon}_s + 2\epsilon_p I)^{-1} \rangle_R}, \quad (10)$$

which, in contrast to the dilute case, depends not only on the dielectric tensor of the inclusion but on an average of the polarization field of all the other inclusions in the system. The volume averaged polarization is

$$\langle P \rangle = \frac{f}{4\pi} \left\langle \frac{\tilde{\epsilon}_s - \epsilon_p I}{\tilde{\epsilon}_s + 2\epsilon_p I} \right\rangle_R \frac{3\epsilon_p E_0}{(1-f) + 3f \epsilon_p \langle (\tilde{\epsilon}_s + 2\epsilon_p I)^{-1} \rangle_R}, \quad (11)$$

which leads to the bulk effective dielectric tensor

$$\tilde{\epsilon}_e = \epsilon_p I + 3f \epsilon_p \left\langle \frac{\tilde{\epsilon}_s - \epsilon_p I}{\tilde{\epsilon}_s + 2\epsilon_p I} \right\rangle_R \times \frac{1}{(1-f) + 3f \epsilon_p \langle (\tilde{\epsilon}_s + 2\epsilon_p I)^{-1} \rangle_R}. \quad (12)$$

This is the Maxwell Garnett result for mixtures of anisotropic inclusions. It depends on the type of anisotropy of the tensor $\tilde{\epsilon}_s$ and on the orientation distribution function of the rotation matrices R .

A. Mixtures of uniaxial inclusions

The nematic LC droplets in a PDLC are usually arranged in a bipolar configuration. This configuration is insensitive to an externally applied electric field. The only effect of an imposed field is to rotate the bipolar axis of the droplet to a new direction more closely aligned with the field [11]. It is therefore reasonable to describe the LC droplet as a uniaxial dielectric material where the dielectric coefficient obtains one value along one preferred direction and another value in all perpendicular directions. The dielectric tensor of such a material is

$$\tilde{\epsilon} = \begin{pmatrix} \epsilon_{\perp} & 0 & 0 \\ 0 & \epsilon_{\perp} & 0 \\ 0 & 0 & \epsilon_{\parallel} \end{pmatrix} \quad (13)$$

in the coordinate system defined by the dielectric axis parallel to the droplet director. It should be noted that ϵ_{\perp} and ϵ_{\parallel} are effective values obtained by averaging the actual LC dielectric tensor over the nonuniform local director field inside the droplet [14]. For a mixture of many such inclusions, embedded in an isotropic host, it is convenient to define the coordinate system such that the external field E_0 is applied in the positive z direction. In this coordinate system the dielectric tensor of each inclusion may be written explicitly as

$$\tilde{\epsilon}_s = R_{\theta\phi} \tilde{\epsilon} R_{\theta\phi}^T = \epsilon_{\perp} I + \alpha \begin{pmatrix} \cos^2 \phi \sin^2 \theta & \cos \phi \sin \phi \sin^2 \theta & \cos \phi \cos \theta \sin \theta \\ \cos \phi \sin \phi \sin^2 \theta & \sin^2 \phi \sin^2 \theta & \sin \phi \cos \theta \sin \theta \\ \cos \phi \cos \theta \sin \theta & \sin \phi \cos \theta \sin \theta & \cos^2 \theta \end{pmatrix}, \quad (14)$$

where $\alpha \equiv \epsilon_{\parallel} - \epsilon_{\perp}$ and θ and ϕ are the orientation angles from the z axis. Substituting this in Eq. (6) we find an explicit expression for the bulk effective dielectric tensor of a dilute PDLC, depending on the distribution of the orientation angles θ and ϕ ,

$$\tilde{\epsilon}_e = \epsilon_p I + \frac{3f\epsilon_p \tilde{A}}{(\epsilon_{\perp} + 2\epsilon_p)(\epsilon_{\parallel} + 2\epsilon_p)}, \quad (15)$$

where

$$\tilde{A} = \begin{pmatrix} \delta - 3\alpha\epsilon_p \langle \cos^2 \theta + \sin^2 \phi \sin^2 \theta \rangle & \frac{3\alpha\epsilon_p}{2} \langle \sin 2\phi \sin^2 \theta \rangle & \frac{3\alpha\epsilon_p}{2} \langle \cos \phi \sin 2\theta \rangle \\ \frac{3\alpha\epsilon_p}{2} \langle \sin 2\phi \sin^2 \theta \rangle & \delta - 3\alpha\epsilon_p \langle \cos^2 \theta + \cos^2 \phi \sin^2 \theta \rangle & \frac{3\alpha\epsilon_p}{2} \langle \sin \phi \sin 2\theta \rangle \\ \frac{3\alpha\epsilon_p}{2} \langle \cos \phi \sin 2\theta \rangle & \frac{3\alpha\epsilon_p}{2} \langle \sin \phi \sin 2\theta \rangle & \delta - 3\alpha\epsilon_p \langle \sin^2 \theta \rangle \end{pmatrix},$$

and $\delta \equiv (\epsilon_{\perp} + 2\epsilon_p)(\epsilon_{\parallel} - \epsilon_p)$. In the MG approximation we find similarly, from Eq. (12),

$$\tilde{\epsilon}_e = \epsilon_p I + \frac{3f\epsilon_p \tilde{A}}{(\epsilon_{\perp} + 2\epsilon_p)(\epsilon_{\parallel} + 2\epsilon_p)} \left[1 - f + \frac{3f\epsilon_p \tilde{B}}{(\epsilon_{\perp} + 2\epsilon_p)(\epsilon_{\parallel} + 2\epsilon_p)} \right]^{-1}, \quad (16)$$

where \tilde{A} is as defined above and

$$\tilde{B} = \begin{pmatrix} \epsilon_{\perp} + 2\epsilon_p + \alpha \langle \cos^2 \theta + \sin^2 \phi \sin^2 \theta \rangle & -\frac{\alpha}{2} \langle \sin 2\phi \sin^2 \theta \rangle & -\frac{\alpha}{2} \langle \cos \phi \sin 2\theta \rangle \\ -\frac{\alpha}{2} \langle \sin 2\phi \sin^2 \theta \rangle & \epsilon_{\perp} + 2\epsilon_p + \alpha \langle \cos^2 \theta + \cos^2 \phi \sin^2 \theta \rangle & -\frac{\alpha}{2} \langle \sin \phi \sin 2\theta \rangle \\ -\frac{\alpha}{2} \langle \cos \phi \sin 2\theta \rangle & -\frac{\alpha}{2} \langle \sin \phi \sin 2\theta \rangle & \frac{\epsilon_{\perp} + \epsilon_{\parallel} + 4\epsilon_p - \alpha \langle \cos 2\theta \rangle}{2} \end{pmatrix}.$$

The angular brackets denote averaging over θ and ϕ of all the inclusions in the mixture. This result is greatly simplified in cases where the averages over θ and ϕ can be calculated exactly. Two such examples are the following.

(1) For very large fields, the dielectric axes of all the inclusions are aligned with the applied field ($\theta=0$). The MG effective dielectric tensor is

$$\tilde{\epsilon}_e = \begin{pmatrix} \epsilon_x & 0 & 0 \\ 0 & \epsilon_x & 0 \\ 0 & 0 & \epsilon_z \end{pmatrix} \quad (17)$$

where

$$\epsilon_x = \epsilon_p + \frac{3f\epsilon_p(\epsilon_{\perp} - \epsilon_p)}{(\epsilon_{\perp} - \epsilon_p)(1-f) + 3\epsilon_p} \quad (18)$$

and

$$\epsilon_z = \epsilon_p + \frac{3f\epsilon_p(\epsilon_{\parallel} - \epsilon_p)}{(\epsilon_{\parallel} - \epsilon_p)(1-f) + 3\epsilon_p}. \quad (19)$$

As expected, this tensor is uniaxial and its diagonal elements are given by the scalar MG results for inclusions with dielectric coefficients ϵ_{\perp} and ϵ_{\parallel} , respectively. Similar results are obtained when all the inclusions are oriented in the x direction ($\theta=\pi/2, \phi=0$), by exchanging the x -axis and z -axis terms, or when all the inclusions are oriented in the y direction ($\theta=\pi/2, \phi=\pi/2$) by exchanging the y -axis and z -axis terms.

(2) Uniform orientation distribution over $\theta \in [0, \pi]$ and $\phi \in [0, 2\pi]$. It is clear that in this case the material should be isotropic, with a scalar dielectric coefficient. Carrying out the averaging in Eq. (16) we indeed obtain

$$\epsilon_e = \epsilon_p + 3f\epsilon_p \frac{(\epsilon_{\perp} + 2\epsilon_p)(\epsilon_{\parallel} - \epsilon_p) - 2\epsilon_p(\epsilon_{\parallel} - \epsilon_{\perp})}{(1-f)(\epsilon_{\perp} + 2\epsilon_p)(\epsilon_{\parallel} + 2\epsilon_p) + f\epsilon_p(\epsilon_{\perp} + 2\epsilon_{\parallel} + 6\epsilon_p)}. \quad (20)$$

III. FIELD-DEPENDENT TUNING OF THE DIELECTRIC RESPONSE

In Sec. II we presented a simple method for calculating the dielectric behavior of PDLC films, based on the Maxwell Garnett approximation. The results obtained depend explicitly on the orientation distribution of the droplet directors. Various averages of this distribution must be evaluated for the different elements of the bulk effective dielectric tensor. To determine the field-dependent distribution it is necessary to consider the two opposing torques acting on each of the LC droplets. One is the electrostatic torque that seeks to orient the droplet in the direction of the applied field. This torque is derived from the electrostatic energy

$$\mathcal{E}_{elec} = -\frac{1}{2} p_s \cdot E, \quad (21)$$

where p_s is the dipole moment of the droplet and E is the electric field in its vicinity. In the MG approximation p_s is given by (10) and $E = E_{ex}$ is given by (9). The second torque is an elastic torque that seeks to hold the droplet in its original direction. It is derived from an elastic energy of the general form [11]

$$\mathcal{E}_{elas} = -WV_s(M \cdot N)^2, \quad (22)$$

where $M = (\cos \phi_0 \sin \theta_0, \sin \phi_0 \sin \theta_0, \cos \theta_0)$ is the original director vector, in the absence of the field, and $N = (\cos \phi \sin \theta, \sin \phi \sin \theta, \cos \theta)$ is the director in the presence of an applied field. As in previous studies of this problem [11,14], we consider the bipolar configuration of each of the droplets to be stable in the presence of an applied field, i.e., the effect of the field on a droplet is to change the orientation of the bipolar director while just slightly affecting the internal arrangement of the LC molecules. This assumption is supported by most of the experimental studies mentioned in the Introduction. In this approximation the droplet is assumed to rotate as a rigid body with an anisotropic dielectric tensor given by Eq. (14). The prefactor W represents the elastic distortion required to align a bipolar droplet by an electric field to preserve the tangential anchoring of the liq-

uid crystal at the droplet interface. It depends on the droplet shape and temperature, which affect the strength of the elastic surface anchoring [4,11]. In the following, we will assume for simplicity that W is similar for all droplets in the system, either because the PDLC is monodispersed or because W depends weakly enough on droplet shape and size. In perfectly spherical droplets the various orientations of the bipolar configuration are degenerate in zero field. In this case alignment is achieved at relatively low fields where the anisotropic component of the electrostatic energy is larger than the thermal rotation energy. However, in practice the droplets are usually slightly elongated and therefore have preferred orientations to which they tend to reorient when the applied field is removed. In such slightly ellipsoidal droplets the elastic energy density may be approximated as

$$W \approx \frac{K}{R^2}, \quad (23)$$

where K is the Frank elastic constant and R is the droplet radius [4,11].

The calculation of the effective dielectric properties may be generally divided into two steps. In the first step, the droplet orientation distribution function is evaluated as a function of the applied field, given the initial conditions appropriate for the specific case of interest. In the second step, this distribution function is used to calculate the different elements of the dielectric tensor, under the same initial conditions. In this section we present three simple examples of this procedure to demonstrate the usefulness of the method derived in Sec. II.

A. Perfectly aligned droplets

One of the simplest distribution functions is the δ function. In this case all droplets are aligned in parallel in a given initial direction with orientation angles θ_0 and ϕ_0 . Such an initial δ -function distribution may be obtained by using a small orienting field or by slightly shearing the PDLC film during its formation. In this case it is easy to derive the θ -dependent part of the electrostatic energy density from Eqs. (9) and (10),

$$\mathcal{E}_{elec} = -\frac{9\epsilon_p^2 E_0^2 (\epsilon_{\parallel} - \epsilon_{\perp}) \{(\epsilon_{\perp} + 2\epsilon_p)(\epsilon_{\parallel} + 2\epsilon_p) - f^2[\epsilon_p^2 - \epsilon_p(\epsilon_{\parallel} + \epsilon_{\perp}) + \epsilon_{\parallel}\epsilon_{\perp}]\} \cos 2\theta}{8\pi [\epsilon_{\perp} + 2\epsilon_p - f(\epsilon_{\perp} - \epsilon_p)]^2 [\epsilon_{\parallel} + 2\epsilon_p - f(\epsilon_{\parallel} - \epsilon_p)]^2}. \quad (24)$$

Here we took into account the fact that $\phi = \phi_0$, since ϕ does not change when the field is applied in parallel to the z axis. In this case we can choose, without loss of generality, $\phi_0 = 0$. The elastic energy density is

$$\mathcal{E}_{elas} = -W \cos^2(\theta - \theta_0). \quad (25)$$

The orientation θ obtained by a droplet depends on its initial orientation θ_0 and on the applied field E_0 . It can be calcu-

lated by finding the minimum of $\mathcal{E}_{tot} = \mathcal{E}_{elec} + \mathcal{E}_{elas}$. A simple minimization over θ leads to

$$\tan 2\theta = \frac{\sin 2\theta_0}{\cos 2\theta_0 + (E_0/E_{cr})^2}, \quad (26)$$

with a volume fraction dependent critical field

$$E_{cr}^2 = \frac{8\pi W[\epsilon_{\perp} + 2\epsilon_p - f(\epsilon_{\perp} - \epsilon_p)]^2[\epsilon_{\parallel} + 2\epsilon_p - f(\epsilon_{\parallel} - \epsilon_p)]^2}{g\epsilon_p^2(\epsilon_{\parallel} - \epsilon_{\perp})\{(\epsilon_{\perp} + 2\epsilon_p)(\epsilon_{\parallel} + 2\epsilon_p) - f^2[\epsilon_p^2 - \epsilon_p(\epsilon_{\parallel} + \epsilon_{\perp}) + \epsilon_{\parallel}\epsilon_{\perp}]\}}. \quad (27)$$

In dilute systems, which are simply the $f=0$ limit of this case, this result reduces to

$$E_{cr}^2 = \frac{8\pi W(\epsilon_{\perp} + 2\epsilon_p)(\epsilon_{\parallel} + 2\epsilon_p)}{g\epsilon_p^2(\epsilon_{\parallel} - \epsilon_{\perp})}. \quad (28)$$

The effect of the electrostatic interaction between the inclusions is simply to decrease the critical field (assuming that $\epsilon_{\parallel}, \epsilon_{\perp} > \epsilon_p$) as the volume fraction of the inclusions increases. The switching voltage of a PDLC film can be easily estimated using Eq. (28). Let us consider a 100- μm PDLC film made of a polymethylmethacrylate (PMMA) polymer matrix and E7 LC droplets with typical radius of 1 μm . Typical values for dielectric coefficients of these materials are $\epsilon_p=5$, $\epsilon_{\parallel}=18$, and $\epsilon_{\perp}=6$. A typical value of Frank constant $K=10^{-6}$ dyn leads to an elastic energy density $W=100$ erg/cm³. Substituting these values in (28), we get a threshold voltage $V_{th} \approx 43$ V. This value is in good agreement with the experimental results of Amundson [4] for PDLCs at low temperatures where the anchoring at the droplet interface is strong.

Similar equations have been previously obtained for the critical field in the dilute case (the independent droplet limit) by different methods by Wu *et al.* [11] and Reshetnyak *et al.* [14]. The above derivation shows that for nondilute systems of aligned inclusions the angle θ follows exactly the same behavior as in the dilute limit but with a lower critical field. It is also apparent that the dependence of this critical field on the droplets volume fraction is usually quite weak. Figure 1 shows θ as a function of θ_0 for different values of applied field. As expected, θ decreases as E_0 increases. However, the form of the transition strongly depends on the initial orientation. For small θ_0 , θ decreases smoothly to zero. The behavior at large θ_0 is less intuitive. For $\theta_0 = \pi/2$, $\theta = \theta_0$ for small fields and $\theta = 0$ for higher fields. At the critical field $E_0 = E_{cr}$ the energy is independent of θ and the droplet orientation is unstable. This causes a very sharp transition between the low field state $\theta_0 = \pi/2$ and the high field state $\theta = 0$. Similar, but slightly smoother, transitions occur at all large θ_0 . This leads to a nonmonotonic dependence of θ on θ_0 for fields larger than the critical one.

The sharp transition at the critical field for $\theta_0 = \pi/2$ had already been noticed by Reshetnyak *et al.* [14]. They attributed it to a droplet cooperative effect in which the transition in one droplet induces a transition in the others. However, the results shown above demonstrate that this effect appears also in the dilute limit, where the droplets are considered as independent. The effect of the interaction between the droplets is simply to reduce the critical field at which this sudden transition occurs. The origin of this behavior is the special dependence of the total energy density on θ , for $\theta_0 = \pi/2$. The first derivative of the total energy density is then

$$\left[\left(\frac{E_0}{E_{cr}} \right)^2 - 1 \right] W \sin 2\theta. \quad (29)$$

This derivative is zero either at $\theta = \pi/2$, which is a minimum for $E_0 < E_{cr}$, $\theta = 0$, which is a minimum when $E_0 > E_{cr}$, or at $E_0 = E_{cr}$. At the latter situation, the energy is independent of θ and the droplet may be oriented in any direction. This is an unstable state, in which the energy is degenerate.

The effects of an externally applied field on $\tilde{\epsilon}_e$ are easily deduced from the above results. The effective dielectric tensor of Eq. (16) is

$$\tilde{\epsilon}_e = \epsilon_p + \frac{3f\epsilon_p(\epsilon_{\parallel} - \epsilon_p)}{\epsilon_{\parallel} + 2\epsilon_p - f(\epsilon_{\parallel} - \epsilon_p)} \begin{pmatrix} \sin^2\theta & 0 & \frac{1}{2}\sin 2\theta \\ 0 & 0 & 0 \\ \frac{1}{2}\sin 2\theta & 0 & \cos^2\theta \end{pmatrix}. \quad (30)$$

Here we used for simplification the fact that PDLC films are ideally fabricated such that the dielectric coefficient of the polymer ϵ_p is closely matched to the dielectric component ϵ_{\perp} of the liquid crystal. The field dependent dielectric behavior described below does not depend on this assumption. Equation (26) can now be used to evaluate the different elements of $\tilde{\epsilon}_e$ as a function of applied field for different values of initial orientation θ_0 . Results for the diagonal element $\epsilon_{zz} = \cos^2\theta$ are shown in Fig. 2. The second diagonal element $\epsilon_{xx} = 1 - \epsilon_{zz}$ clearly follows a similar behavior. It is evident that the sharpness of the transition at the critical field and the contrast between the two extremal states, at zero field and very large fields, can be controlled by determining the initial orientation angle θ_0 . Applications that require a sharp transition and a large contrast between the ‘‘on’’ and ‘‘off’’ states should use PDLCs with large θ_0 . Smaller values of θ_0 will be appropriate for applications that require a more gradual transition.

B. Planar orientation distribution

Let us now consider the case in which in the initial state all the bipolar droplet axes are in the x - y plane, $\theta_0 = \pi/2$, with ϕ distributed uniformly over $[0, 2\pi]$. Such a distribution is an approximate description of PDLC films formed by encapsulation methods, which typically have their major axes distributed near the film plane [12]. The application of an external field in the z direction does not change the distribution of the azimuthal angle ϕ . The effective dielectric tensor will therefore remain uniaxial throughout the switching process. The angle θ , on the other hand, will decrease as the field is increased. The electrostatic energy density can again be derived from Eqs. (9) and (10)

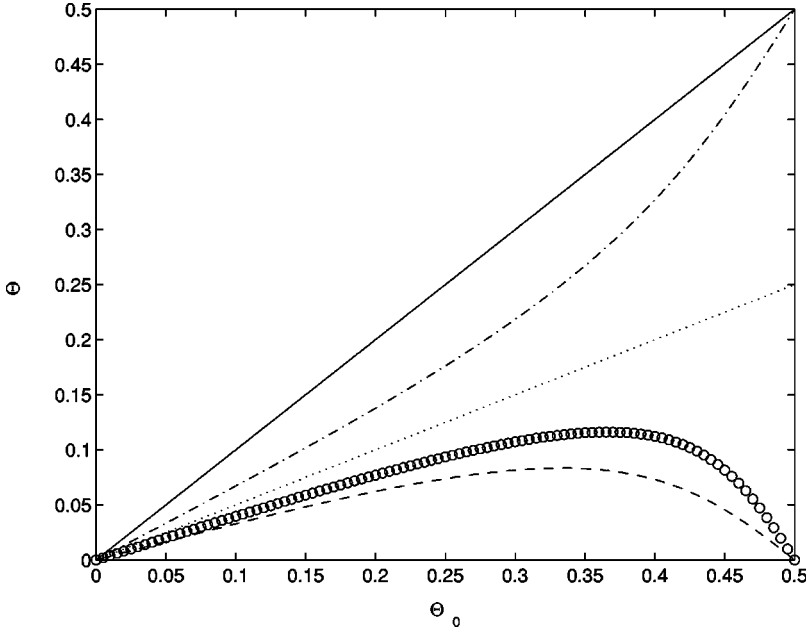


FIG. 1. θ as a function of θ_0 (in units of π) for different values of applied field intensity $C = (E_0/E_{cr})^2$. Results are shown for $C=0$ (solid line), $C=0.5$ (dash-dot line), $C=1$ (dotted line), $C=1.5$ (circles), and $C=2$ (dashed line).

$$\mathcal{E}_{elec} = -\frac{3\epsilon_p E_0^2}{8\pi} \frac{X}{(1-fX)^2}, \quad (31)$$

where

$$X = a - b \sin^2 \theta, \quad a = \frac{\epsilon_{\parallel} - \epsilon_{\perp}}{\epsilon_{\parallel} + 2\epsilon_p}, \quad b = \frac{3\epsilon_p(\epsilon_{\parallel} - \epsilon_{\perp})}{(\epsilon_{\perp} + 2\epsilon_p)(\epsilon_{\parallel} + 2\epsilon_p)}. \quad (32)$$

The elastic energy density is

$$\mathcal{E}_{elas} = -W \sin^2 \theta. \quad (33)$$

The first derivative of the total energy density is

$$\left(\frac{3\epsilon_p b E_0^2}{8\pi W} \frac{1+fX}{(1-fX)^3} - 1 \right) W \sin 2\theta. \quad (34)$$

As in the case $\theta_0 = \pi/2$ discussed in Sec. III A, this derivative is zero either at $\theta = \pi/2$, which is a minimum when the term in the parentheses is negative, $\theta=0$, which is a minimum when this term is positive, or when this term itself is zero. At the latter situation, the energy is again independent of θ and the droplet may be directed in any orientation. However, in contrast to the previous example, this term itself depends on θ through the variable X . This means that it will vanish at different values of applied field depending on the initial orientation. If we start with $\theta = \pi/2$ at zero field, then increasing the field gradually will have no effect on θ until we reach the point

$$E_0^2 = \frac{8\pi W}{3\epsilon_p b} \frac{[1-f(a-b)]^3}{1+f(a-b)} \quad (35)$$

at which the term in the parentheses of (34) vanishes. At this

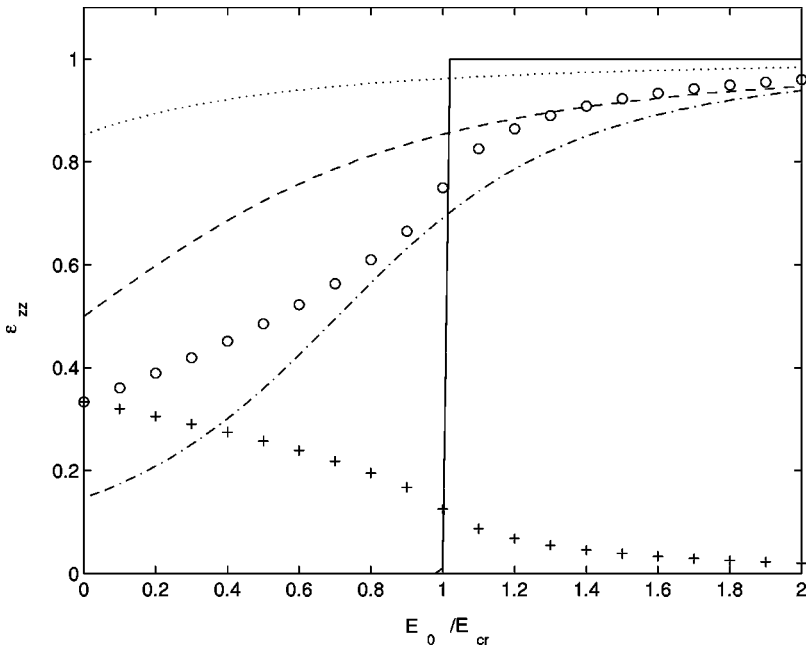


FIG. 2. The diagonal elements of (30) and (44) as a function of applied field. Results are shown for ϵ_{zz} of (30) with $\theta_0 = \pi/2$ (solid line), $\theta_0 = 3\pi/8$ (dash-dot line), $\theta_0 = \pi/4$ (dashed line), and $\theta_0 = \pi/8$ (dotted line), and for ϵ_{zz} (circles) and ϵ_{xx} (crosses) of (44) in the dilute limit.

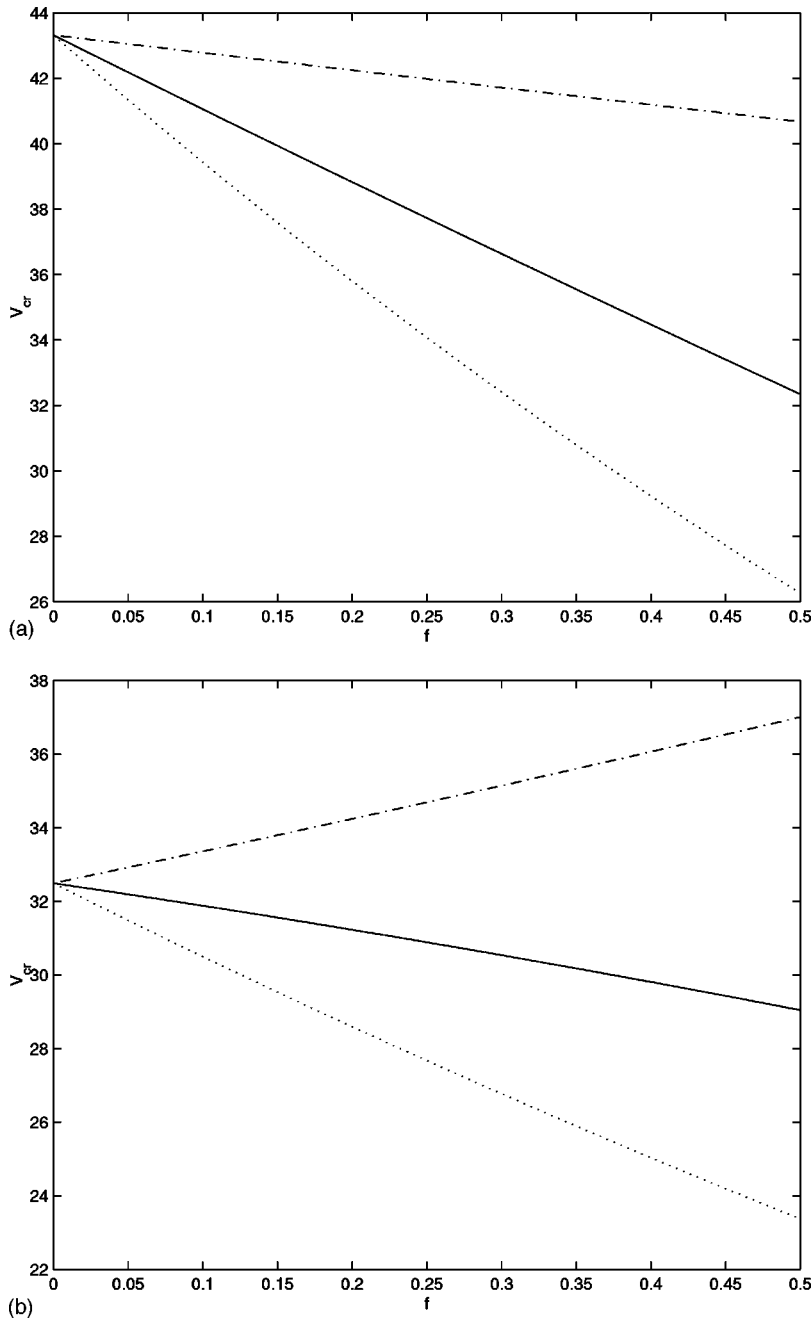


FIG. 3. The threshold voltages (in volts) corresponding to the three critical fields of (27) (solid line), (35) (upper curve), and (36) (lower curve) as a function of droplet concentration for a $100\mu\text{m}$ PDLC film. (a) $\epsilon_p=5$, $\epsilon_{\parallel}=18$, and $\epsilon_{\perp}=6$. (b) $\epsilon_p=8$, $\epsilon_{\parallel}=19$, and $\epsilon_{\perp}=5.2$.

point θ will abruptly jump from $\pi/2$ to zero and will stay there at all higher fields. On the other hand, if we start at very high fields with $\theta=0$, then decreasing the field gradually will have no effect on θ until we reach the point

$$E_0^2 = \frac{8\pi W}{3\epsilon_p b} \frac{(1-fa)^3}{1+fa} \quad (36)$$

at which the term in the parentheses of (34) again vanishes. For $f=0$ both transition points are reduced to the dilute limit critical field (28). In the nondilute case, the interaction between the different droplets causes splitting in the transition point with two critical fields instead of one. The width of the resulting hysteresis loop depends on the volume fraction of

the droplets and on the dielectric coefficients of the components. This is demonstrated in Fig. 3, where we consider a $100\text{-}\mu\text{m}$ PDLC film with two different compositions. In Fig. 3(a), we repeat the example of a PMMA/E7 mixture with $\epsilon_p=5$, $\epsilon_{\parallel}=18$, and $\epsilon_{\perp}=6$ and $W=100\text{ erg/cm}^3$. In Fig. 3(b), we consider the example used in Ref. [14] with $\epsilon_p=8$, $\epsilon_{\parallel}=19$, and $\epsilon_{\perp}=5.2$ and the same elastic energy density. The switching voltages corresponding to the critical fields (35), (36), and (27) are plotted as a function of f . As expected, the three voltages converge to the same value at $f=0$. In the first example all threshold voltages decrease with increasing f , the strongest dependence shown by the smallest one. In the second example, the variation of the two lower voltages is much weaker and the higher threshold voltage increases with increasing f . A discussion of the hysteresis in PDLC with a planar initial orientation distribution was previously presented by Reshetnyak *et al.* [14]. However, us-

ing their effective medium approach the existence of this behavior could only be deduced from a numerical calculation and not from an explicit analytical argument as in this paper. They obtained a dependence of the critical fields on LC concentration that is similar to that shown in Fig. 3(b).

The effects of an externally applied field on $\tilde{\epsilon}_e$ may again be easily deduced from the above results. The effective

dielectric tensor of Eq. (16) is

$$\tilde{\epsilon}_e = \epsilon_p + 3f\epsilon_p(\epsilon_{\parallel} - \epsilon_p) \begin{pmatrix} \epsilon_{xx} & 0 & 0 \\ 0 & \epsilon_{xx} & 0 \\ 0 & 0 & \epsilon_{zz} \end{pmatrix}, \quad (37)$$

where

$$\epsilon_{xx} = \frac{(1/2)\sin^2\theta}{(1-f)(\epsilon_{\parallel} + 2\epsilon_p) + f\{3\epsilon_p + (\epsilon_{\parallel} - \epsilon_p)[\cos^2\theta + (1/2)\sin^2\theta]\}} \quad (38)$$

and

$$\epsilon_{zz} = \frac{\cos^2\theta}{(1-f)(\epsilon_{\parallel} + 2\epsilon_p) + f[3\epsilon_p + (\epsilon_{\parallel} - \epsilon_p)\sin^2\theta]}. \quad (39)$$

Here, again, we used for simplicity the assumption of perfect dielectric matching between the polymer matrix and the perpendicular element of the LC droplets, $\epsilon_{\perp} = \epsilon_p$ [in this case the upper critical field of (35) is independent of the LC concentration f]. As explained above, starting from a planar distribution, θ has only two states. The low field state $\theta = \pi/2$ and the high field state $\theta = 0$. Therefore, the effective

dielectric tensor also has only two possible values corresponding to these states, the transition between which is determined by the critical fields of (35) and (36).

C. Random initial distribution

Let us now consider the case in which in the initial state the bipolar droplet axes are uniformly distributed over all possible orientations $\theta_0 \in [0, \pi/2]$ and $\phi_0 \in [0, 2\pi]$. As in the previous example, the effective dielectric tensor remains uniaxial throughout the switching process. The electrostatic energy of each droplet now depends in a complicated way on the orientations of all the other droplets

$$\mathcal{E}_{elec} = -\frac{3\epsilon_p E_0^2}{8\pi} \frac{(\epsilon_{\perp} + 2\epsilon_p)(\epsilon_{\parallel} + 2\epsilon_p)[(\epsilon_{\perp} + 2\epsilon_p)(\epsilon_{\parallel} - \epsilon_p) - 3\epsilon_p(\epsilon_{\parallel} - \epsilon_{\perp})\sin^2\theta]}{\{(1-f)(\epsilon_{\perp} + 2\epsilon_p)(\epsilon_{\parallel} + 2\epsilon_p) + 3f\epsilon_p[\epsilon_{\perp} + 2\epsilon_p + (\epsilon_{\parallel} - \epsilon_{\perp})\langle\sin^2\theta\rangle]\}^2}. \quad (40)$$

This should be minimized together with the elastic energy density (25) to find θ as a function of θ_0 and E_0 . In most cases this minimization problem, although easy in principle, does not have an analytic solution but can only be solved numerically.

The exception to this rule is the dilute limit in which the orientation dependent part of the electrostatic energy (40) is reduced to that of Eq. (24) with $f=0$,

$$\mathcal{E}_{elec} = -\frac{9\epsilon_p^2 E_0^2}{8\pi} \frac{(\epsilon_{\parallel} - \epsilon_{\perp})\cos 2\theta}{(\epsilon_{\perp} + 2\epsilon_p)(\epsilon_{\parallel} + 2\epsilon_p)}. \quad (41)$$

The minimization of the energy of a single droplet then leads to the same result as in Sec. III A,

$$\tan 2\theta = \frac{\sin 2\theta_0}{\cos 2\theta_0 + (E_0/E_{cr})^2} \quad (42)$$

for θ as a function of θ_0 and E_0 , with the dilute limit critical field

$$E_{cr}^2 = \frac{8\pi W(\epsilon_{\perp} + 2\epsilon_p)(\epsilon_{\parallel} + 2\epsilon_p)}{9\epsilon_p^2(\epsilon_{\parallel} - \epsilon_{\perp})}. \quad (43)$$

Starting with a uniform distribution function P_{θ} of $\theta_0 \in [0, \pi/2]$, an externally applied field will change P_{θ} , concentrating it at smaller angles, while preserving its symmetry around $\theta=0$. This effect is demonstrated in Fig. 4. At low fields $E_0 < E_{cr}$, P_{θ} is no longer uniform but still spans the entire range of possible θ values $[0, \pi/2]$. At the critical field $E_0 = E_{cr}$ the distribution is again uniform, but over the narrower range of angles $[0, \pi/4]$. Above the critical field (see inset of Fig. 4), P_{θ} no longer spans the entire range $[0, \pi/2]$ but is concentrated at small angles, with a strong divergence at the maximum of the corresponding curve in Fig. 1. The sharp change of P_{θ} at the critical field leads to a significant change in the value of the effective dielectric coefficient. The uniform orientation distribution over $\theta_0 \in [0, \pi/2]$ and $\phi_0 \in [0, 2\pi]$ leads to a uniaxial effective dielectric tensor similar to that of Sec. III B (again choosing perfect dielectric matching $\epsilon_{\perp} = \epsilon_p$)

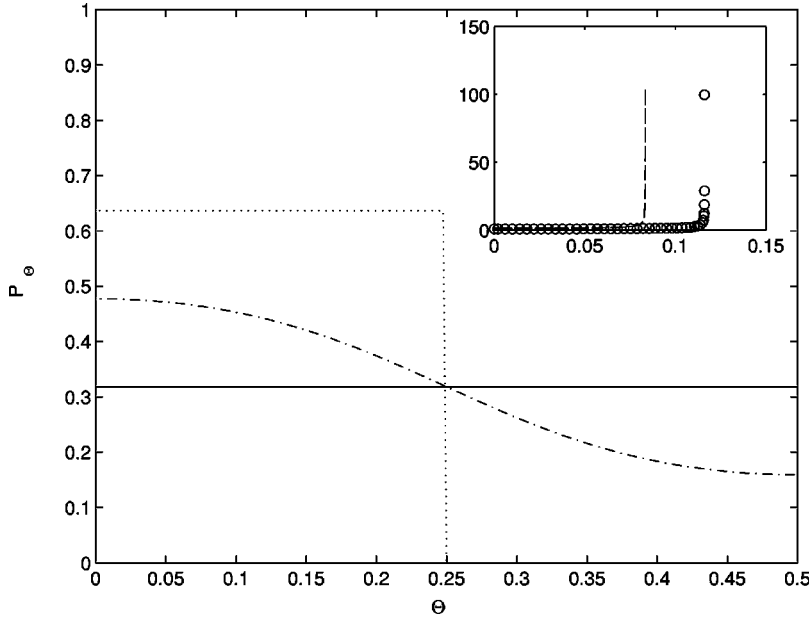


FIG. 4. The distribution function P_θ of θ (in units of π) for applied field intensities below and above (inset) the critical field. The different curves are for field values as in Fig. 1.

$$\tilde{\epsilon}_e = \epsilon_p + 3f\epsilon_p(\epsilon_{\parallel} - \epsilon_p) \begin{pmatrix} \epsilon_{xx} & 0 & 0 \\ 0 & \epsilon_{xx} & 0 \\ 0 & 0 & \epsilon_{zz} \end{pmatrix}, \quad (44)$$

where

$$\epsilon_{xx} = \frac{(1/2)\langle \sin^2 \theta \rangle}{(1-f)(\epsilon_{\parallel} + 2\epsilon_p) + f[3\epsilon_p + (\epsilon_{\parallel} - \epsilon_p)\langle \cos^2 \theta + (1/2)\sin^2 \theta \rangle]} \quad (45)$$

and

$$\epsilon_{zz} = \frac{\langle \cos^2 \theta \rangle}{(1-f)(\epsilon_{\parallel} + 2\epsilon_p) + f[3\epsilon_p + (\epsilon_{\parallel} - \epsilon_p)\langle \sin^2 \theta \rangle]}. \quad (46)$$

In the dilute limit we simply set $f=0$ in the denominators of (45) and (46). The results for this case, with P_θ of Fig. 4, are also shown in Fig. 1. The result for nondilute materials is considerably more complicated because of the additional dependence of the denominators on weighted averages of P_θ . The diagonal elements of (44) are shown, for different values of f , in Fig. 5. They were calculated choosing $\epsilon_{\parallel}=19$ and $\epsilon_p=8$. The variation of the dielectric tensor elements is much smoother than in the examples of the previous sections and increases, as expected, with increasing f .

IV. THE DIELECTRIC RESPONSE NEAR THE NEMATIC-ISOTROPIC TRANSITION

As mentioned in the Introduction, a recent experimental study by Amundson [4] demonstrated that near the nematic-isotropic transition inside the LC droplets the droplets undergo an internal structural transition. The transition starts by creating a shell of isotropic liquid at the droplet walls such that each droplet contains a nematic spherical core sur-

rounded by liquid. The volume fraction of the nematic component appears roughly the same inside all droplets and is decreasing continuously with temperature from unity, a few degrees below the transition, to zero at the transition, where the entire droplet becomes isotropic. From these observations Amundson identified the source of the change in the electro-optical properties of the PDLC near the transition as a dramatic drop in the anchoring energy, since the nematic component is no longer in contact with the polymer matrix but instead with its own isotropic liquid phase. He also observed Brownian reorientation of the droplets at zero field, which suggests that the balance between thermal energy and electrostatic energy is the dominant factor that determines the droplet orientation distribution in this temperature range. In this section we use an adaptation of the MG approximation of [15] to coated inclusions to calculate the field-dependent dielectric tensor of a PDLC film near the transition, which is considered as a random dispersion of coated spheres, with an anisotropic core and an isotropic shell, embedded in an isotropic host.

A. Dielectric response of mixtures of coated spheres

Consider a parallel plate condenser whose plates are large enough so that edge effects can be neglected. The condenser is filled by a homogeneous polymer with a scalar dielectric constant ϵ_p in which nonoverlapping spheres of liquid crys-

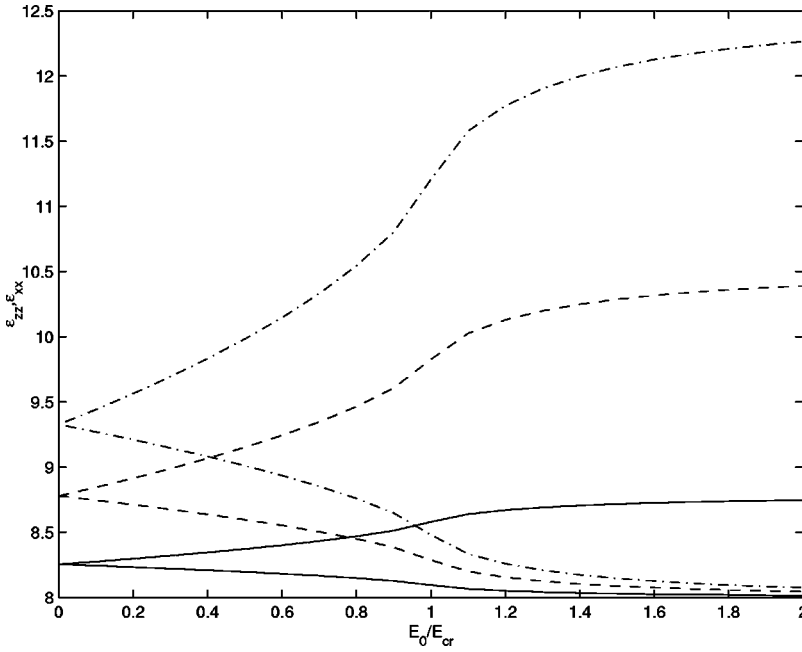


FIG. 5. The diagonal elements of (44) as a function of applied field for $\epsilon_p=8$, $\epsilon_{\parallel}=19$ and $f=0.1$ (solid lines), $f=0.3$ (dashed lines), and $f=0.5$ (dash-dot lines). The upper curve in each couple is ϵ_{zz} and the lower curve is ϵ_{xx} .

tal are distributed randomly but uniformly. Each of the spheres is made of a nematic core with dielectric tensor $\tilde{\epsilon}_s$ of (1) and (14) and an isotropic coating with dielectric constant ϵ_c that depends on ϵ_{\parallel} and ϵ_{\perp} . A common method to evaluate ϵ_c is to view the coating material as a polycrystalline collection of anisotropic, randomly oriented, compact domains much smaller than the coating itself. Its dielectric properties can then be calculated from the elements of the local dielectric tensor ϵ_{\parallel} and ϵ_{\perp} using the well known effective medium approximation (EMA) [16]. For a locally uniaxial material, this approximation leads to the relation

$$\frac{\epsilon_{\parallel} - \epsilon_c}{\epsilon_{\parallel} + 2\epsilon_c} + 2\frac{\epsilon_{\perp} - \epsilon_c}{\epsilon_{\perp} + 2\epsilon_c} = 0. \quad (47)$$

Solved for ϵ_c , this gives

$$\epsilon_c = \frac{\epsilon_{\perp} + \sqrt{\epsilon_{\perp}^2 + 8\epsilon_{\parallel}\epsilon_{\perp}}}{4}. \quad (48)$$

Our aim in this section is to derive an expression for the bulk effective dielectric tensor of this mixture of coated spheres.

B. The dilute limit

First we consider a single sphere with core $\tilde{\epsilon}_s$ and coating ϵ_c immersed in the host ϵ_p . A voltage is applied between the

condenser plates such that the volume averaged field in the system is E_0 . Solving the Laplace equation for this system we find that the electrical potential is

$$\phi_s(r, \theta) = -E_s r \cos \theta \quad (49)$$

inside the core,

$$\phi_c(r, \theta) = \left(E_c r + \frac{E'_c}{r} \right) \cos \theta \quad (50)$$

in the coating, and

$$\phi_h(r, \theta) = \left(-E_0 r + \frac{P_s}{r} \right) \cos \theta \quad (51)$$

in the host. Applying the continuity conditions on the potential and the parallel component of the field at the surfaces of the core ($r=r_s$) and the coating ($r=r_c$) we find the uniform field in the core

$$E_s = \frac{9\epsilon_c\epsilon_p E_0}{(\tilde{\epsilon}_s + 2\epsilon_c)(\epsilon_c + 2\epsilon_p) + 2f(\tilde{\epsilon}_s - \epsilon_c)(\epsilon_c - \epsilon_p)} \quad (52)$$

and the induced dipole moment of the coated sphere P_s . The average dipole moment density inside the sphere is

$$P_s = \frac{P_s}{V_s} = \frac{(\tilde{\epsilon}_s + 2\epsilon_c)(\epsilon_c - \epsilon_p) + f(\tilde{\epsilon}_s - \epsilon_c)(2\epsilon_c + \epsilon_p)}{(\tilde{\epsilon}_s + 2\epsilon_c)(\epsilon_c + 2\epsilon_p) + 2f(\tilde{\epsilon}_s - \epsilon_c)(\epsilon_c - \epsilon_p)} \frac{3}{4\pi} E_0, \quad (53)$$

where $V_s = 4\pi r_c^3/3$ is its volume and $f \equiv (r_s/r_c)^3$. From this it follows that if the medium contains a few such spheres, sufficiently far apart for their mutual interactions to be negligible, then the volume average of their polarization in the medium is

$$\langle P \rangle \equiv \frac{1}{V} \sum_s P_s = f_s \frac{3}{4\pi} \Psi E_0, \quad (54)$$

where

$$\Psi = \left\langle \frac{(\tilde{\epsilon}_s + 2\epsilon_c)(\epsilon_c - \epsilon_p) + f(\tilde{\epsilon}_s - \epsilon_c)(2\epsilon_c + \epsilon_p)}{(\tilde{\epsilon}_s + 2\epsilon_c)(\epsilon_c + 2\epsilon_p) + 2f(\tilde{\epsilon}_s - \epsilon_c)(\epsilon_c - \epsilon_p)} \right\rangle_{\theta\phi}, \quad (55)$$

$\langle \rangle_{\theta\phi}$ denotes an average over the dielectric tensor orientations inside the inclusion cores and $f_s = \sum_s V_s/V$ is the volume fraction of the coated spheres.

The bulk effective dielectric tensor, defined as the ratio between the volume averaged displacement field $D_0 = \langle D \rangle$ and the volume averaged electric field $E_0 = \langle E \rangle$, is therefore

$$\epsilon_e = \epsilon_p I + 3f_s \epsilon_p \Psi. \quad (56)$$

This is the dilute limit result valid to first order in the volume fraction of the inclusions.

Substituting (14) in (56) we get a result for the effective dielectric tensor that depends explicitly on the distribution of θ and ϕ . This result is particularly simple in two limiting cases.

(1) The dielectric axes of all the inclusions are oriented in the direction of the applied field ($\theta = 0$). This would be the dielectric tensor of the system when a strong electric field is applied. This tensor is uniaxial. Its x and y diagonal elements are obtained from (56) by discarding the averaging over θ and ϕ and substituting ϵ_\perp for $\tilde{\epsilon}_s$. The z element as well as the uniform field inside the core are similarly obtained by substituting ϵ_\parallel for $\tilde{\epsilon}_s$ in (56) and (52), respectively.

(2) Uniform orientation distribution over $\theta \in [0, \pi/2]$ and $\phi \in [0, 2\pi]$. In this case the composite is isotropic, with a scalar dielectric coefficient. Carrying out the averaging of Eq. (56) over ϕ we find a uniaxial tensor of the form

$$\begin{pmatrix} f_x \langle \cos 2\theta \rangle & 0 & 0 \\ 0 & f_x \langle \cos 2\theta \rangle & 0 \\ 0 & 0 & f_z \langle \cos 2\theta \rangle \end{pmatrix}. \quad (57)$$

If θ is also uniformly distributed, as is the case in the absence of applied field, then $\langle \cos 2\theta \rangle = -1/3$ and we find $f_x (-1/3) = f_z (-1/3)$, which indeed leads to a scalar dielectric coefficient. If a field is applied then θ is no longer uniformly distributed but its distribution may be obtained from a simple thermodynamic calculation. Since the experimental evidence [4] points to negligible weak elastic forces at the interface between the core and the shell, the orientation distribution is completely determined by the electrostatic forces and thermal fluctuations. The electrostatic energy of a single coated inclusion is

$$\mathcal{E} = -\frac{1}{2} P_s \cdot E_0 = -(a + b \cos 2\theta) r_c^3 E_0^2, \quad (58)$$

where a and b are functions of ϵ_\parallel , ϵ_\perp , ϵ_p , and f . $\langle \cos 2\theta \rangle$ is therefore given by

$$\langle \cos 2\theta \rangle = \frac{1}{Q} \int e^{-\mathcal{E}/k_B T} \cos 2\theta d\Omega = \frac{2\pi e^{(a/b)E}}{Q} \times \left[\frac{e^E}{E} - \frac{(1+2E)\sqrt{(\pi/2)\text{erfi}(\sqrt{2E})}}{2(E)^{3/2}e^E} \right], \quad (59)$$

where

$$Q = \int e^{-\mathcal{E}/k_B T} d\Omega = \frac{2\pi e^{(a/b)E}}{\sqrt{E}e^E} \sqrt{\frac{\pi}{2}} \text{erfi}(\sqrt{2E}),$$

$$E = \frac{br_s^3 E_0^2}{2k_B T}, \quad (60)$$

$\text{erfi}(x) = \int_0^x e^{t^2} dt$ is the modified error function, k_B is Boltzmann constant, and T is the temperature. When calculating this average for a given temperature we should bear in mind that f is itself a function of the temperature and should be adjusted appropriately to give the correct values for a and b . A plot of $\langle \cos 2\theta \rangle$ as a function of the normalized field E appears in Fig. 6. As expected, when $E=0$, θ is distributed uniformly and $\langle \cos 2\theta \rangle = -1/3$. It increases sharply at small fields and reaches saturation, $\langle \cos 2\theta \rangle = 1$, at large fields where all the droplet cores are aligned parallel to the field. The azimuthal orientation angle ϕ is unaffected by the external field and remains uniformly distributed.

C. The Maxwell Garnett approximation

The electrostatic interaction between the different inclusions is taken into account within the MG approximation by considering the average field acting on each inclusion to be the Lorentz local field E_L [16]. This local field may be calculated either by the excluded volume approach used in Sec. II or by the well known relation

$$E_L = E_0 + \frac{4\pi}{3} \langle P \rangle \quad (61)$$

with $\langle P \rangle$ taken from (54), where E_L is again substituted for E_0 . Using this correction, the dipolar interaction between the inclusions is taken into account in an averaged way. Solving for E_L we find

$$E_L = \frac{E_0}{1 - f_s \Psi}. \quad (62)$$

This result can again be replaced for E_0 in Eq. (54) to calculate the volume averaged polarization and the volume averaged displacement field D_0 . This leads to the bulk effective dielectric tensor

$$\epsilon_e = \epsilon_p I + \frac{3f\epsilon_p\Psi}{1 - f_s\Psi}. \quad (63)$$

This is the MG result for mixtures of coated inclusions. In our case, it depends on the anisotropy of $\tilde{\epsilon}_s$ and on the dis-

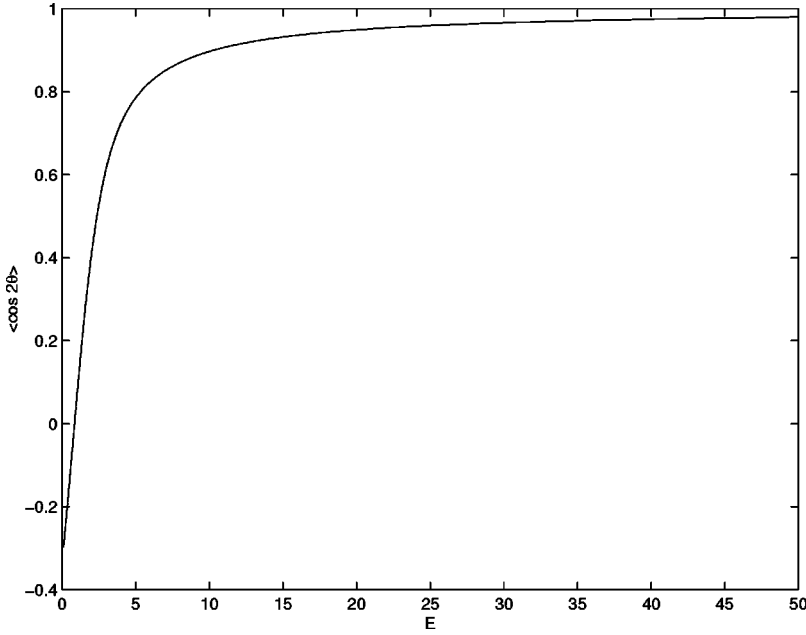


FIG. 6. $\langle \cos 2\theta \rangle$ as a function of the normalized field E for a dilute PDLC near the nematic-isotropic transition.

tribution of the droplet rotations. The field inside the inclusion cores is again uniform and is given by

$$E_s = \frac{1}{1 - f_s \Psi} \frac{9\epsilon_c \epsilon_p E_0}{(\tilde{\epsilon}_s + 2\epsilon_c)(\epsilon_c + 2\epsilon_p) + 2f(\tilde{\epsilon}_s - \epsilon_c)(\epsilon_c - \epsilon_p)}. \quad (64)$$

In the cases where $\tilde{\epsilon}_s = \epsilon_c$ or $f = 0$, (63) reduces to

$$\epsilon_e = \epsilon_p I + 3f_s \epsilon_p \frac{\epsilon_c - \epsilon_p}{(1 - f_s)(\epsilon_c - \epsilon_p) + 3\epsilon_p}, \quad (65)$$

which is the MG result for simple spherical inclusions with dielectric coefficient ϵ_c and volume fraction f_s . In the case where $\epsilon_c = \epsilon_p$, we get

$$\epsilon_e = \epsilon_p I + 3f_s f \epsilon_p \left\langle \frac{\tilde{\epsilon}_s - \epsilon_p}{(1 - f_s f)(\tilde{\epsilon}_s - \epsilon_p) + 3\epsilon_p} \right\rangle_{\theta\phi}, \quad (66)$$

which is the MG result for simple spherical inclusions with dielectric coefficient $\tilde{\epsilon}_s$ and volume fraction $f_s f$.

Let us consider again the two simple cases discussed in Sec. IV B. If the dielectric axes of all the inclusions are oriented in the direction of the applied field ($\theta = 0$), we find that the elements of the effective dielectric tensor may be obtained from (63) by discarding the averaging over θ and ϕ and substituting ϵ_\perp or ϵ_\parallel for $\tilde{\epsilon}_s$. If ϕ is uniformly distributed over $[0, 2\pi]$, (63) again reduces to a uniaxial tensor like (57) but with more complex functions of $\langle \cos 2\theta \rangle$ in the diagonal elements. These functions also obey the relation $f_x(-1/3) = f_z(-1/3)$ thus leading to a scalar dielectric coefficient in the absence of applied field, when θ is uniformly distributed. The electrostatic energy of each of the coated inclusions may again be written as

$$\mathcal{E} = -\frac{1}{2} P_s \cdot E_L = -(a + b \cos 2\theta) r_c^3 E_0^2. \quad (67)$$

In contrast to the dilute case, a and b are now also functions of $\langle \cos 2\theta \rangle$ in addition to ϵ_\parallel , ϵ_\perp , ϵ_p , and f . The distribution of θ is no longer given by an analytic solution but requires a simultaneous numerical solution of (67) and (59).

As an example, let us consider again a PDLC made of a PMMA polymer matrix and E7 liquid crystal droplets, with typical values for dielectric coefficients $\epsilon_p = 5$, $\epsilon_\parallel = 18$, and $\epsilon_\perp = 6$. Substituting ϵ_\parallel and ϵ_\perp in (47) we find $\epsilon_s = 9$. These values may now be used in (56) or (63) to find the f -dependent dielectric tensor for different distributions of the orientation angles. As discussed above, f is determined by the temperature, it is zero at the nematic-isotropic transition and 1 far below it. Its range of variation, according to the experimental results [4], is 4–5 °C. If all the inclusion cores are aligned we find, as expected, that the dielectric tensor is uniaxial with diagonal elements given by

$$\Psi_{xx} = \frac{32 - 23f}{8(19 - f)} \quad (68)$$

and

$$\Psi_{zz} = \frac{16 + 23f}{4(19 + 2f)}, \quad (69)$$

which are the results obtained for a scalar $\tilde{\epsilon}_s$ equal to ϵ_\perp or ϵ_\parallel , respectively. We can use this to estimate the electric voltage required to produce this alignment. Equating the electrostatic energy $\mathcal{E} = (1/2) P_s \cdot E_0$ for inclusions with $f = 1$ and $r_s = 0.5 \mu\text{m}$ with the thermal energy at $T = 55^\circ\text{C}$, we find $V_{th} = 1.2 \text{ V}$ for a film thickness of $20 \mu\text{m}$. This estimate is very close to the experimental results reported by Amundson [4]. For a uniform distribution of core orientations Ψ reduces to a scalar function of f

$$\Psi = \frac{(4 - f)(76 + 23f)}{4(19 - f)(19 + 2f)}. \quad (70)$$

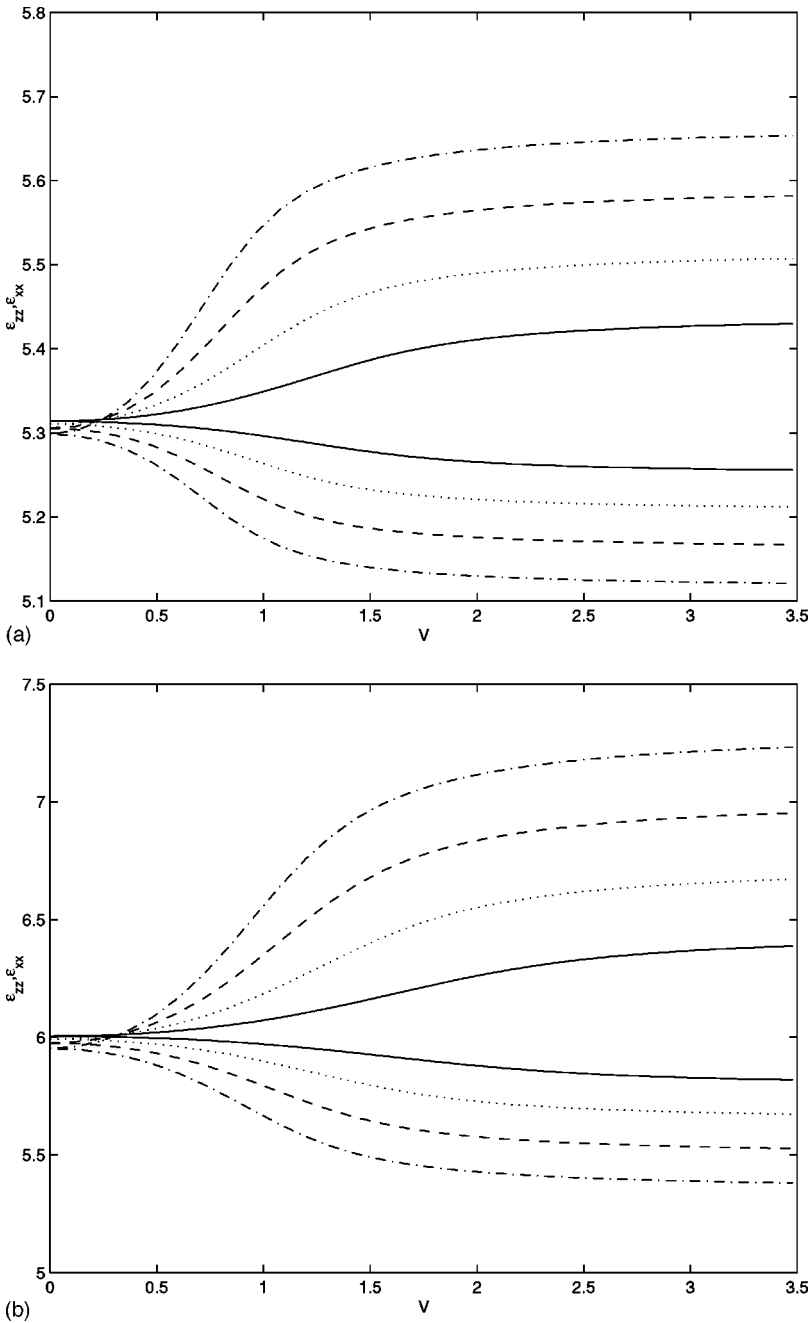


FIG. 7. The diagonal elements of the effective dielectric tensor (63) as a function of applied voltage (in volts) for core volume fractions $f = 0.3$ (solid lines), $f = 0.5$ (dotted lines), $f = 0.7$ (dashed lines), and $f = 0.9$ (dash-dotted lines). The film thickness is $20 \mu\text{m}$. (a) $f_s = 0.1$, (b) $f_s = 0.3$.

In a typical experimental setting the orientations of the inclusion cores are uniformly distributed in the absence of applied field. As the field is increased this distribution changes according to Eqs. (59) and (67) and the effective dielectric tensor becomes more anisotropic. The MGA results for a $20\text{-}\mu\text{m}$ -thick PMMA/E7 film are shown in Figs. 7 and 8, for a few different inclusion volume fractions f_s and core volume fractions f . At zero field the films are isotropic with a dielectric constant that increases as a function of f_s , since the elements of $\tilde{\epsilon}_s$ are larger than ϵ_p , but decreases slightly as a function of f . This dependence on f agrees qualitatively with the experiment where the zero field dielectric coefficient increases with temperature, since f is a monotonic decreasing function of the temperature, although the measured dependence is stronger than indicated by our calculation. As the applied field increases, the dielectric tensor

becomes more and more anisotropic and its elements vary sharply near a potential drop of ~ 1 V, above which they saturate quickly. The dielectric tensor element parallel to the field increases and the perpendicular elements decrease. Their variation is stronger and the resulting dielectric tensor more anisotropic at higher volume fractions f and f_s , since the anisotropic component of the PDLC is larger.

These results closely resemble the experimental observations of Amundson [4], which are to our knowledge the only published results for PDLC at the relevant temperature range. The main feature is the relatively low switching voltage, of the order of 1 V, and its very weak dependence on the temperature, or on the parameter f in our model. The model also provides a simple method for estimating the dependence of the electro-optical properties on the volume fraction of the LC cavities, which is still to be investigated experimentally.

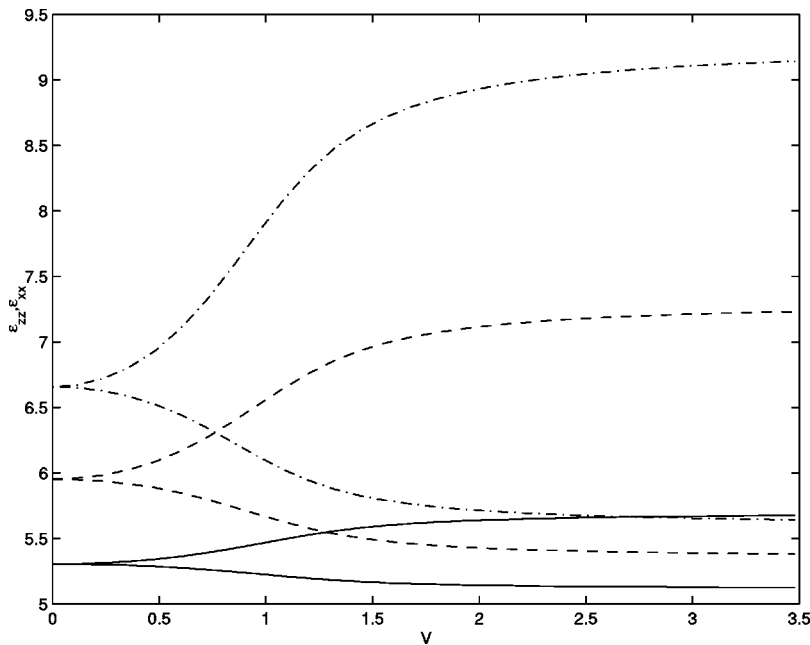


FIG. 8. The diagonal elements of (63) as a function of applied voltage (in volts) for droplet volume fractions $f_s=0.1$ (solid lines), $f_s=0.3$ (dashed lines), and $f_s=0.5$ (dash-dotted lines). The film thickness is $20 \mu\text{m}$ and $f=0.9$.

V. CONCLUSIONS

In this paper, the dielectric properties of PDLC films containing bipolar LC droplets are studied using an extension of the classical Maxwell Garnett approximation to materials with anisotropic inclusions. As in previous studies of this problem, the essential physics involves a balance between the elastic energy, which favors orientation of a droplet in a locally preferred direction, and the electrostatic energy, which favors alignment with the applied field. The MG approach provides a convenient framework for the evaluation of the electrostatic effects. On the one hand, it can handle nondilute systems and is therefore more general than most previously published studies. On the other hand, it is much simpler than the effective medium approach of [14]. It provides analytical results for nondilute systems with some initial orientation distributions and a very simple numerical scheme for all the other cases. The treatment of the elastic energy, as in all previous studies of this subject, is phenomenological. A detailed microscopic theory of this energy is still lacking.

Once an electric field is applied on a PDLC, the droplets bipolar axes start to rotate, in accordance with their initial orientations and the magnitude of the field. This reorientation process changes the macroscopic dielectric response of the material. For initially aligned droplets we found that the sharpness of the reorientation process depends on the initial orientation in a quite dramatic way. For orientations close to the film plane the process is thresholdlike with a critical field that depends on the droplet concentration. For initial orientations far from this plane it is much more gradual. This

effect may provide a simple mechanism to obtain PDLC films with various types of behavior for different types of applications. For a planar initial orientation distribution the reorientation process is again thresholdlike with some hysteresis. The width of the hysteresis depends on the LC concentration and can be calculated analytically within our model. This behavior may be used for some types of optical switching and should be quite interesting to verify experimentally. Systems with random orientation distributions exhibit reorientations that are much more gradual but are still concentration dependent. A similar gradual reorientation process occurs near the nematic-isotropic transition, where the droplets themselves become composite structures with nematic cores and liquid coatings [4]. The main qualitative difference between this relatively high temperature regime and the low temperature regime is the disappearance of the elastic anchoring energy. This leaves thermal fluctuations as the dominant force acting against complete alignment with the applied field. This physical change is accompanied by a dramatic drop in the switching voltage [4], which is well reproduced by our model.

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