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Droplet shape and reorientation fields in nematic droplet/polymer films

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Polymer films containing droplets of nematic liquid crystal form an important class of new electro-optic light valves and displays. While previous work has shown that the nematic droplet size is an important factor in the electro-optic properties of these films, here we report that the droplet shape is equally important in determing the electro-optics of the film. Electron micrographs show that for films using polyvinyl alcohol as the polymeric binder the cavities formed by the polymer matrix are oblate in nature, and aligned with the minor axis perpendicular to the film plane. In oblate cavities the elastic-deformation free energy is minimized when the director field in the droplet is aligned along a major axis of the spheroid; the electric field performs work on the nematic in reorienting the nematic into a higher-energy state, equal to the elastic-free-energy difference between the two configurations. Calculations and experiment are used to estimate the elastic and electric field free-energy-density changes that occur upon reorientation of the nematic droplet. The general agreement between these two values is used to indicate that droplet shape anisotropy is a major factor in determining the electro-optic properties of these films.

1. Introduction

Nematic droplet/polymer films (known as NCAP or PDLC films) are a new class of liquid-crystal devices suitable for both large-area light valves and displays [1–4]. These films consist of nematic droplets of the order of micrometres in diameter, dispersed in a film of the order of tens of micrometres thick. Macroscopically, the films scatter light strongly in the unpowered state, but become transparent when an electric field is applied. If a pleochroic dye is present in the nematic, the films possess a controllable absorbance in addition to the scattering effect. These films can be constructed on flexible substrates and made quite large, with single-piece light valves 1 m wide and nearly 3 m long having been constructed. The basic operation of these devices can be understood in terms of the rotation of bipolar nematic droplets by the electric field, changing the effective refractive index of the droplets. (This bipolar orientation has the nematic director field lying parallel to the cavity walls, with two point dislocations at opposite ends of the cavity—see figure 2 for a schematic representation.) If the ordinary refractive index of the nematic is chosen to closely match the refractive index of the polymer then reorientation of the droplets by an electric field turns a highly scattering film into a transparent one.

The electric field performs work by orienting the nematic, increasing the elastic-deformation free energy in moving from the rest orientation to the high-field orientation of the nematic droplet. Elastic forces return the droplet to its rest configuration once the field is removed. Previously, the source of these elastic free energy forces has been ascribed [3, 4] to surface interactions, meaning that the rest (lowest-energy) configuration of the nematic is defined by an alignment direction imposed by the polymer wall. Recently, however, one of us [5] has suggested that this energy is determined by the difference in free energy obtained from reorienting nematic contained in *non-spherical* cavities. In a non-spherical cavity the elastic free energy will depend on the orientation of the nematic in the cavity. This results in a unique rest alignment for the nematic droplet, an observation which has been made experimentally. (It has been observed using polarized microscopy that in PVA binder films each droplet possesses a unique rest orientation direction [1]. The droplet returns to this configuration after the electric field is removed, and also after heating the nematic to the isotropic state and then cooling back to the nematic.) Here we present some estimates of the elastic and electric free-energy densities for nematic in an oblate cavity in the zero and high-field limits. Conservation-of-energy arguments show that these data are consistent with the view that droplet shape is a critical factor in the behaviour of these films.

2. Elastic-deformation free-energy density

The films for this study were made by emulsifying a nematic into a polyvinyl alcohol (PVA) solution, coating this dispersion onto a conductive substrate, and allowing the film to dry [1, 2, 5]. The resulting film then has a second conductive substrate laminated to it to form a device. An electron micrograph of a typical film (with nematic removed) shows that in general the nematic cavities in these films are oblate, with their minor axes aligned perpendicular to the film plane (see figure 1). The nematic droplets in these films adopt a bipolar configuration, and minimize their elastic deformation energy when the bipolar symmetry axis is aligned along a major

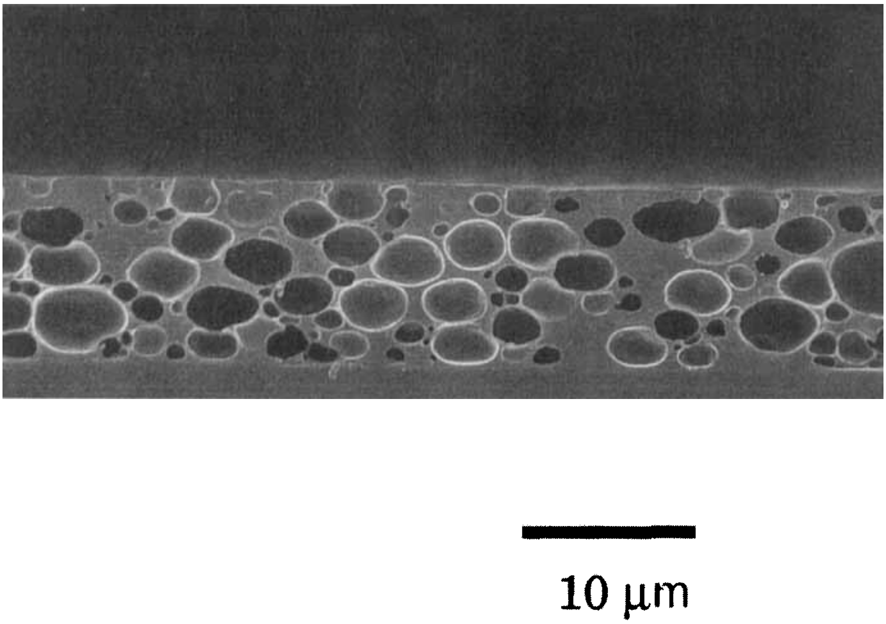

Figure 1. Electron micrograph of PVA-based NCAP film (nematic removed).

axis of the spheroid. (Experiments on stretched NCAP show that in a spheroidal cavity the bipolar axis aligns along the long axis of the cavity [2, 4]). In the PVA films shown here, the nematic director field within a droplet is aligned parallel to the film plane, although there is a random distribution of each droplet's symmetry axis within the plane. Application of an electric field rotates this symmetry axis to lie parallel to the electric field, where qualitatively it is apparent that there is an increase in the curvature of the director field within the droplet. These configurations are shown schematically in figure 2.

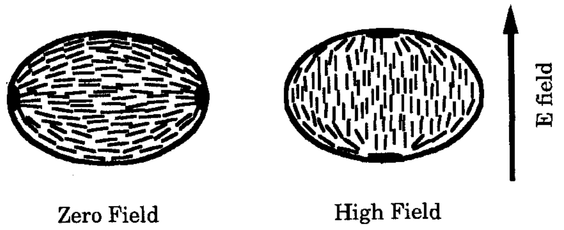

Figure 2. Schematic representation of a bipolar nematic droplet in its zero-field and high-field configurations.

Examination of electron micrographs of a number of PVA films containing different liquid crystals but similar nematic droplet sizes and nematic weight fractions shows that there is a broad but fairly reproducible distribution of the ratio of the minor/major axis lengths of the film cavities [6]. For PVA films in which the nematic-droplet mean volume diameter was near 3 μm and the film was 62 per cent by weight nematic, the peak of the distribution for the minor/major axis ratio was 0·6, with 90% of the droplets possessing ratios between 0·5 and 0·9. The distribution of these ratios was fairly uniform for droplets in the 1–5 μm range, with a tendency for smaller droplets to be rounder.

Recently, one of us has developed a numerical method based on finite-element analysis, which correctly predicts the appearance of bipolar, axial and radial nematic droplet configurations, based on variations in the nematic surface alignment and elastic constants [7]. We have applied this formalism to examine the free-energy dependence of a bipolar nematic droplet in an oblate cavity as a function of orientation. For these initial calculations, the three nematic elastic constants were set equal ($K_{11} = K_{22} = K_{33} = 1{\cdot}5 \times 10^{-11}$ N), with a droplet volume equal to that of a sphere of radius 0·5 μm. The resulting calculations show that the droplet is at its lowest energy when the bipolar axis is aligned along a major axis of the spheroid, with other orientations of the droplet symmetry axis increasing the deformation energy within the droplet. We have carried out these calculations as a function of the ratio of the minor to major axes of an oblate spheroid in order to estimate an averaged free-energy density difference between the two configurations shown in figure 2. Figure 3 shows the results of these calculations. For a droplet of radius 0·5 μm with a minor/major axis ratio of 0·6 these calculations estimate that the energy-density difference between the two configurations is 220 J m^{-3}. For a ratio of 0·8 the energy-density difference drops to 90 J m^{-3}, and for a ratio of 0·5 the energy density difference is 300 J m^{-3}. We show in the following sections that the change in electric-field free-energy upon reorienting a 1 μm diameter droplet in a PVA film is of the same order of magnitude as these elastic free-energy values.

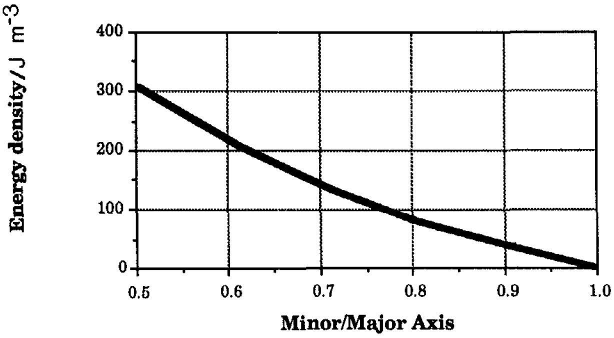

Figure 3. Calculated difference in elastic free-energy density between the zero-field and high-field orientations of a 1 μm diameter nematic spheroidal droplet, as a function of the spheroid shape. The zero-field and high-field configurations are shown schematically in figure 2. The free-energy-density values are averages over the droplet volume.

3. Nematic alignment in PVA-based NCAP films

In order to estimate the free-energy difference for a nematic droplet film in its low-field and high-field states, we need to know the orientation of the nematic in these states. The orientation of the nematic droplets in the zero-field and high-field states can be probed by measuring the capacitance of the film, so that an effective dielectric constant for the film can be determined for both cases. This dielectric constant may then be compared with a theoretical estimate based on mixture rules for heterogeneously mixed dielectrics. These calculations can be performed for a nematic aligned parallel, perpendicular or randomly with respect to the film plane. Comparison of the measured dielectric constant values to the calculated values will indicate the state of alignment of the nematic droplets. A similar study [8] has already been reported using NCAP/PDLC films made by the phase separation of nematic droplets in a polymerized matrix (see [2–4] for experimental details regarding the nucleation method for forming NCAP films). In that study (employing only unpowered films) the data suggested that the nematic droplets in those zero-field films were randomly oriented. This is consistent with electron micrographs of those films, which show droplets that were slightly non-spherical and randomly shaped, implying a random distribution of the nematic [4].

From the dielectric-mixture literature [9] Boettcher's formula (equation (1)) and Bruggerman's formula (equation (2)) appear to be the most appropriate equations for films with a high concentration of dispersed spherical particles:

$$\varepsilon_m = \varepsilon_1 + \frac{3v_2\varepsilon_m(\varepsilon_2 - \varepsilon_1)}{2\varepsilon_m + \varepsilon_2}, \tag{1}$$

$$1 - v_2 = \frac{\varepsilon_2 - \varepsilon_m}{\varepsilon_2 - \varepsilon_1}\left(\frac{\varepsilon_1}{\varepsilon_m}\right)^{1/3}. \tag{2}$$

In these equations v_2 is the volume fraction of spheres, ε_1 is the matrix dielectric constant (equal to 8·0 for PVA here), ε_2 is the dielectric constant of the spheres, and ε_m is the mean dielectric constant of the mixture. To test our alignment model, we have used equations (1) and (2) for three cases: ε_2 set equal to either $\varepsilon_\perp$, $\varepsilon_\parallel$, or the weighted average dielectric constant of the nematic ($\varepsilon_{\text{random}}$). Table 1 shows the measured

Table 1. Measured and calculated dielectric constants for NCAP films.†

Nematic	Nematic dielectric constants‡		Calculated film dielectric constants		Measured film dielectric constants
			Boettcher	Bruggerman	
ZLI 1840	$\varepsilon_\perp$	4·3	5·5	5·6	5·7 low field
	$\varepsilon_\parallel$	16·2	12·6	12·5	12·6 high field
	$\varepsilon_{\text{random}}$	8·3	8·2	8·6	
ZLI 1957/5	$\varepsilon_\perp$	3·5	4·9	5·0	5·0 low field
	$\varepsilon_\parallel$	8·0	8·0	8·3	8·0 high field
	$\varepsilon_{\text{random}}$	5·0	6·0	6·1	
ZLI 2452	$\varepsilon_\perp$	3·6	5·0	5·1	5·7 low field
	$\varepsilon_\parallel$	9·7	9·0	9·0	9·8 high field
	$\varepsilon_{\text{random}}$	5·6	6·5	6·5	
ZLI 3096	$\varepsilon_\perp$	6·6	7·1	7·2	8·1 low field
	$\varepsilon_\parallel$	28·0	18·5	17·9	19·4 high field
	$\varepsilon_{\text{random}}$	13·7	11·3	11·3	
ZLI 3281	$\varepsilon_\perp$	6·1	6·8	6·8	8·0 low field
	$\varepsilon_\parallel$	25·5	17·3	16·9	18·4 high field
	$\varepsilon_{\text{random}}$	12·6	10·7	10·6	
ZLI 3201-000	$\varepsilon_\perp$	5·8	6·6	6·6	7·4 low field
	$\varepsilon_\parallel$	22·2	15·7	15·4	16·8 high field
	$\varepsilon_{\text{random}}$	11·3	9·9	9·9	
E7	$\varepsilon_\perp$	5·2	6·2	6·2	6·7 low field
	$\varepsilon_\parallel$	19·0	14·1	13·9	14·5 high field
	$\varepsilon_{\text{random}}$	9·8	9·1	9·1	

† Capacitance data for these films measured at 1 kHz with 1·0 V excitation. The powered film values were obtained using a 130 V low-frequency square-wave signal summed with the A.C. signal to align the nematic.

‡ Data from E. Merck and BDH catalogues.

dielectric constants for a number of nematic droplet/PVA films in both their rest and field-aligned states, as well as the calculated dielectric constants for the films using both mixture formulae and the three different values for ε_2. It can be seen that there is generally good agreement between the zero-field film dielectric constant and the calculations using the ordinary dielectric constant of the nematic. Likewise, the high-field film values agree best with the calculation when the extraordinary dielectric constant is used. Neither set of experimental data agrees particularly well with the calculations using a random alignment of the nematic for most of the films. Thus the capacitance data supports the model of the nematic aligned along the film plane in the zero-field state, and perpendicular to the film plane in the high-field state. Given this good alignment and symmetry considerations, it is not a bad approximation for the purpose of these calculations to treat the nematic in the zero-field case as an isotropic material with dielectric constant $\varepsilon_\perp$, and the nematic in the high-field case as an isotropic material with dielectric constant $\varepsilon_\parallel$.

4. Electric-field free-energy density

We have established that the alignment of the nematic in these PVA-based NCAP films is consistent with the orientations shown in figure 2. Knowing this alignment, we can use energy-balance arguments to determine whether the experimental electric fields required to operate these films are consistent with our calculations of the elastic free-energy density difference between the two droplet orientations described earlier. A large discrepancy between these calculated elastic energy values and experimental electric field energies would argue that some factor other than droplet shape is dominant in controlling the operating fields of these films. Here, we show that the experimental electric free-energy densities are of the same order as the calculated elastic free-energy densities for this droplet alignment.

A ubiquitous problem in estimating electric free energies (or electric torques) in these films is the assignment of a critical electric field for the nematic reorientation. In these PVA-based films we must estimate the critical field E_c required to reorient a single size of droplet in a film possessing a distribution of droplet sizes. To do this, we recognize that previous work [2] has shown that there is an approximate inverse relationship between the field required to orient a nematic droplet and the droplet diameter. This is as expected, since in a coherence-length model [10] the elastic deformation energy density scales as K/ξ^2, where K is an elastic constant and ξ is a deformation length. Since the electric field energy density scales as εE^2, the approximate relationship $E \approx \xi^{-1}$ holds. Given that the distribution of droplet sizes can be measured prior to forming a PVA film, we can use this relationship between E and ξ to estimate the field required to reorient a droplet of a given size in a polydisperse NCAP film. It has been shown [2] that modelling experimental curves of per cent haze versus voltage for different films allows for the estimation of the field required to orient a 1 μm droplet in each film. (Per cent haze is defined as the light from a collimated source that is scattered out of a 4° angle by a translucent material, and correlates well with the perceived level of scattering in plastics; see ASTM standard D-1003, American Society for Testing and Materials. For these experiments a Hunterlab D25-9 colorimeter was used for per cent haze measurements.) Measurements of this sort were carried out for six different NCAP films, and estimates made of the field required to orient a 1 μm diameter droplet in each of the films (see table 2).

The equations

$$V\,\Delta Q = \tfrac{1}{2}V^2\,\Delta C + \Delta U_K + U_{\text{loss}} \tag{3}$$

and

$$\Delta F_K = \tfrac{1}{2}\varepsilon_0 \Delta\varepsilon E_c^2/f \tag{4}$$

describe the energy balance for this reorientation. In equation (3) $\frac{1}{2}V^2\,\Delta C$ is the change in electric free energy stored in the film, as the reorientation of the nematic changes the effective capacitance of the film (see above). $V\,\Delta Q$ is the work done by the external power supply in bringing additional charge ΔQ to the cell at a potential V, ΔU_K is the increase in elastic free energy within the nematic, and U_{loss} represents the dissipative energy losses due to viscous drag and dielectric losses. Experimentally, we have performed our measurements of the film orientation so that we can neglect the dissipative U_{loss} term in this energy-balance analysis. In the determination of the electro-optic response as a function of voltage, the voltage was ramped up very slowly, in order to minimize viscous dissipation. Additionally, it was found that at a 60 Hz excitation frequency the voltage : current phase angle was near 90°, indicating low dielectric losses.

Table 2. Electric field free-energy densities for a 1 μm droplet.

Nematic	Reorientation field† E_{appl}/V m^{-1}	Estimated energy density‡/J m^{-3}	Nematic elastic constants		
			$K_{11}/10^{-11}$ N	$K_{22}/10^{-11}$ N	$K_{33}/10^{-11}$ N
ZLI 1840	$4{\cdot}1 \times 10^6$	855	13·3	7·4	23·7
ZLI 2452	$5{\cdot}3 \times 10^6$	849	15·0	8·4	20·1
E7	$3{\cdot}7 \times 10^6$	788	11·1	6	17·1
ZLI 3096	$2{\cdot}5 \times 10^6$	521	8·9	5·0	13·1
ZLI 1957/5	$4{\cdot}7 \times 10^6$	489	11·2	5·5	12·8
ZLI 3201-000	$2{\cdot}2 \times 10^6$	336	10·7	6·1	19·3
ZLI 3281	$2{\cdot}0 \times 10^6$	307	9·8	5·4	13·0

† Estimated error ±20 per cent.
‡ Estimated error ±40 per cent.
§ Data from E. Merck and BDH catalogues.

Recognizing that $V\,\Delta Q = V^2\,\Delta C$, we find that in the absence of any other losses the change in electric field free energy equals the change in elastic free energy for these films. Including free-energy density terms, we arrive at equation (4), where ΔF_K is the change in elastic free-energy density upon reorienting the nematic droplets in these films, $\Delta\varepsilon$ is the change in film dielectric constant and E_c is a critical reorientation field. The nematic volume-fraction term $f(=0{\cdot}6$ here) is necessary since the experimental free-energy density is derived from the film volume, while the elastic free-energy density is derived from the total droplet volume. In order to apply equation (4), the term $\Delta\varepsilon$ is taken from the measured changes in dielectric constant of the NCAP films. The term E_c is taken from the modelling of the electro-optic curve using the nematic droplet-size distribution. Strictly speaking, this equation describes the electric free-energy change in a film of uniform 1 μm droplets, rather than the polydisperse droplet distribution actually studied. However, we find that the measured change in the capacitance of these PVA-based NCAP films depends only weakly on the size and distribution of the nematic droplets within the film. Thus the measured film dielectric constants are a very likely a good estimate of the dielectric constant of a film of uniform 1 μm droplets.

Table 2 shows the results of these calculations. For the films studied, we estimate an electric field free-energy density of about 300–900 J m^{-3}. This can be compared with our earlier theoretical estimates of an elastic free-energy density of 100–300 J m^{-3} for oblate droplets with a major/minor axis ratio in the range 0·5–0·9. It can also be seen qualitatively that for most of the films there is a positive correlation between the estimated energy density and the nematic elastic constants, even though much more work needs to be done to put these differences on a quantitative basis. Given the large number of approximations that went into this derivation, as well as the uncertainty in the proper value for the critical field E_c, the proximity of these two values indicates that, at the very least, droplet shape anisotropy contributes significantly to the energy required to orient a nematic droplet in an NCAP film, and provides a strong driving force for droplet relaxation once the electric field is removed. These results are in agreement with a previous report [5], which shows that rounder droplets require smaller fields for reorientation in NCAP films, at the cost of a slower relaxation time. Rounder droplets will possess a smaller energy difference between the rest and field-oriented alignment directions.

It should be noted that some NCAP/PDLC films using different polymer matrices show electro-optic effects indicative of strong directional alignment of the nematic by the polymer; in these cases it is expected that surface alignment effects will be in competition with droplet-shape anisotropy effects, and especially in round droplets the surface effects may dominate [11] (see also (5) for a listing and discussion of some of these surface alignment effects). Still, the present results show that droplet-shape anisotropy effects must be considered in explaining the electro-optic behaviour of NCAP films. (Recent work by Doane *et al.* [12] reaches similar conclusions regard the importance of droplets shape for the reorientation fields for these films.) Work is in progress refining these calculations and measurements, and a fuller account will appear at a later date.

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