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Electric field studies of liquid crystal droplet suspensions

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The responses of freely-suspended micron-sized liquid crystal droplets subjected to an alternating electric field are presented. By examining droplets of isotropic, nematic bipolar, and nematic radial configurations, we test the effect of anchoring on the droplet response. Specifically, using birefringence and scattering dichroism we measure the relaxation of electric field-induced orientation following a field pulse. Results indicate that bipolar and radial droplets in suspension orient in the field through very different mechanisms. Bipolar droplets are observed to rotate their defect axes in the field while radial droplets orient through a nematic distortion. By varying the field pulse, we observe that droplets also respond differently to the field depending on their relative sizes. In radial droplet suspensions we quantitatively measure time scales associated with the reorientation and restructuring of the defect region.

1. Introduction

Much of the work that has been done involving liquid crystal droplets has been focused on their use in polymer dispersed liquid crystal droplet (PDLC) films. Research in this area has covered many of the important issues that affect the performance of these films. Of principal concern is an understanding of the director configuration within the droplets and the change in that configuration upon application of an electric field.

When an electric field is applied to a PDLC film, the director configuration changes substantially. The electric field orients the liquid crystal in the direction of the field due to the rather large anisotropy in the dielectric tensor of most conventional liquid crystals. Because surface anchoring is maintained in the operation of the PDLC films, bipolar and radial droplets will orient in an electric field differently. In the bipolar case, the defect axis must rotate in the direction of the field; however for radial drops, a simple distortion of the nematic achieves field alignment. The mechanism by which this reorientation occurs has been the subject of many investigations [1–17].

Doane and coworkers have pioneered the research, both experimental as well as theoretical, regarding PDLC films. In a series of papers [1–3], these researchers derived simple expressions for both the voltages required to drive PDLC films as well as the response times to turn the films on and off. Their theory captured the effects of three important parameters in contributing to the response of the film: (1) droplet size (2) relative resistivities/conductivities of the polymer and liquid crystal and (3) droplet shape, particularly in the case of bipolar droplet films. Kelly and Palffy-Muhoray have more recently proposed an extension of the original theory by Doane *et al.*, based on a hierarchy of order parameters [4].

During an applied field, the bulk of the liquid crystal nematic aligns in the direction of the field while still maintaining the anchoring at the polymer interface. In spherical bipolar drops, there is actually little or no distortion of the nematic necessary to align in the field direction. A simple rotation of the optical axis formed by the defects allows the desired alignment. For spherical bipolar drops this also means that there is little if any difference in the energy state of an unaligned and an aligned droplet, and therefore no mechanism other than very slight anisotropies in the shape for the droplets of the film to return to the original scattering state. Thus the reorientation process of spherical droplets is rather slow. In order to increase the speed of the response, bipolar drop films are usually prepared with elongated or oblate droplets.

When the field is removed, the reorientation dynamics are controlled by the elastic forces of the liquid crystal and the viscous forces which oppose the reorientation to the original free energy minimum state. A balance of the elastic and viscous torques yields an expression for the time scale for the film to turn off:

$$\tau_{\text{off}} = \frac{\gamma R^2}{K \varepsilon^2 S S_{\text{d}}} \qquad (1)$$

where the eccentricity ε is related to the lengths of the

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semi-major ($2a$) and semi-minor ($2b$) axes through $\varepsilon^2 = 1-(b/a)^2$, γ is the rotational viscosity coefficient, R is the radius of curvature of the director field, the scalars S and S_d are the nematic orientational order parameter and droplet order parameters, respectively, and K is the elastic constant [4]. Equation (1) captures the most profound effect which has been observed in aspherical drop films, that of drastically reduced relaxation times from spherical drop films. Smaller drop films also show decreased relaxation times. Preparing films with higher aspect ratio droplets has both advantages and disadvantages in performance. An increased aspect ratio also increases the voltage required to drive the film. The enhanced response time (by a factor of 100) of shaped droplets of aspect ratios a/b as low as 1·1, however, makes the elongation of droplets a desired characteristic in many applications. Equation (1) also illustrates the effects of the nematic and droplet order parameters on the response. A faster response time is observed for droplets with stronger order.

In radial drops, the mechanism by which the nematic aligns in the field is somewhat different than in the bipolar case. In this case, the nematic is distorted in the direction of the field, but does not require a reorientation of the defects. Hence the response time should have a similar form balancing elastic distortional and viscous effects but without a shape effect [2, 5],

$$\tau_{\text{off}} = \frac{\gamma a^2}{K}. \qquad (2)$$

We will use this expression in the discussion of our experimental results in the upcoming sections.

Several researchers have experimentally measured response times of PDLC films of bipolar droplets. Drzaic [5] monitored the change of absorbance in pleochroic dye-doped nematic droplet films and reported the observation of two decay times, one approximately 1–10 ms followed by a longer 10–100 ms response. The short time-scale was attributed to the relaxation of the interior nematic which disorients on the time scale of a distortional relaxation. The longer response, which incidentally was the larger optical effect, was found to be due to the rotation of the bipolar defect axis. In the absence of an electric field this axis lies in the plane of the film, however, upon application of an electric field, the defect axis must rotate normal to this preferred direction. Thus, the longer 10–100 ms response must be due to the rotation of the defect axis to its original state.

Jain and Rout [6] later published a similar experimental study where white light transmission was used to quantify the relaxation of micron-sized PDLC films. In spherical bipolar droplet films, a slow response time (2–10 s) was observed at low voltages while fast (20 ms) and slow responses were seen at higher voltages. The slow relaxation was attributed to the rotation of the defect axis which has little driving force to return to its original state in near-spherical droplets. The fast relaxation present at the higher voltages was said to be due to an additional distortion of the nematic in the direction of the field which relaxed quickly on the time-scale of an elastic distortion as in equation (1). In ellipsoidal droplet films, the authors verified the model proposed by Drzaic by examining the voltage dependence of the relaxation process. At very low voltages only the faster relaxation (10–20 ms) observed by Drzaic was seen and was therefore attributed only to a progression to state (*b*) of the model. A full reorientation of the defect axis in the field direction (with time-scales of relaxation 10 seconds–minutes) was only achieved at high voltages, therefore the dual relaxation process was only observed for large electric fields. Similar research was performed by Mucha [7].

Radial droplet PDLC films have been investigated in detail by Bondar and coworkers using microscopy [12]. The authors described and photographed a hedgehog to ring transition of radial droplets aligning in an alternating field. They were able to do this by visualizing nematic restructuring along two axes: one normal to the applied field and the other parallel to it. When observed normal to the applied field, they see for voltages above a certain threshold a movement and splitting of the centre defect from the droplet core to the surface, resulting in an axial configuration. Viewing the drop along the field direction, a very different restructuring is observed. As the directors align in the field direction while maintaining their normal anchoring, a twist of the nematic is seen. This is followed by growth of a ring defect at the droplet surface at voltages above the threshold voltage. If the voltage is then dropped below the threshold but is maintained above zero, the ring is observed to collapse inward indicating that the central liquid crystal molecules are still aligned in the field while the surface molecules have returned to their original radial state. This research provided a detailed picture of the nature of radial droplet restructuring (for droplets 3–30 μm) in an electric field.

Reamey and coworkers investigated how electro-optical properties of bipolar PDLC films were influenced by the liquid crystal/polymer interface [13]. In a manner similar to Bondar *et al*., the authors slowly increased/decreased the magnitude of an applied alternating field to investigate the mechanism by which the director in bipolar drops eventually becomes fully aligned in the field direction. Interesting features were observed particularly as the voltage was applied (slowly increased). At intermediate voltages, a small central region of the nematic stretching from pole to pole (in the film plane) was found to be highly oriented along the polar axis and normal to the electric field. Molecules along the outer edge of the droplet do not lose their tangential anchoring when orienting in the field and therefore were observed to orient quickly. The central core of the droplet along the polar axis orients more slowly due to the energy barrier to the reorientation of the defects. The authors suggest that these liquid crystals must pull away from the droplet wall before reorienting and thus require higher voltages for movement. This is in keeping with the work of Drzaic and Jain and Rout described earlier, but adds an additional picture of the detailed restructuring involved by the defects. The effect was not seen when the field was lowered, indicating a different transition mechanism.

Adamczyk [17] studied 5CB bipolar droplets in glycerol, the system which we also used in our experiments. He examined the Cotton–Mouton effect which describes the quadratic dependence of the induced birefringence on the magnetic field strength. Of particular interest to this author was an investigation of the magnitude of the proportionality constant associated with that relationship. Although few details are given, the author does mention that he measured relaxation times following the removal of the applied field which are associated with the Brownian rotational diffusion of the spherical droplets. We will also see this relaxation in our experimental results.

An understanding of the response and nature of restructuring of nematic droplets subjected to orienting fields is clearly of interest. Several studies have indicated that the response is quite complicated and is still not fully understood. In this project we hope to shed further light on the effect of an electric field on confined liquid crystals. We have investigated induced orientation in both bipolar and radial nematic droplets as well as in isotropic droplets of each anchoring condition. By examining these droplets in dilute suspension rather than in a film, we hope to better explain the nature of the relaxation processes which occur upon removal of an applied electric field.

We have observed very different behaviour between bipolar and radial droplets when subjected to an electric field. In the bipolar case, the entire droplet appears to rotate and align its defect axis in the field direction, while in the radial droplets a nematic distortion occurs. These two effects have very different relaxation times associated with them. Upon removal of an electric field, bipolar droplets disorient with respect to one another through a Brownian rotational diffusion. In the radial case we observe two relaxation mechanisms: one which is attributed to a molecular distortion and the second which is thought to be due to a healing of the defect structure.

2. Experimental

We have examined nematic restructuring in bipolar, radial, and isotropic micron-sized liquid crystal droplets. These droplets were studied in dilute suspension. This medium has several advantages over hardened films. First of all, the nature of the film preparation can drastically alter the shape of the droplet. The elongation of the droplet shape has been found to significantly affect the response and threshold voltages of liquid crystal films. By eliminating the shape variable from our study, we can simplify the analysis of our results. Studying freely suspended droplets does allow the possibility of changes in shape, but we saw no evidence of this effect in either our polarimetry experiments or with microscopy. A second major advantage of studying the electro-optical properties of the droplets in suspension rather than a film is the elimination of multiple scattering effects present in most film studies performed to date. Jain and Rout [6] obtained experimental relaxation times from transmission experiments of films as discussed in the last section. A measurement of turbidity does allow one to study small submicrometer droplets and obtain quantitative dynamics, but multiple scattering effects inherent in experiments performed with concentrated drop dispersions certainly will contaminate the measured results, thereby affecting time scales attributed to certain relaxation mechanisms.

Microscopy has been previously used to examine nematic restructuring in both radial and bipolar droplets in films as well as, in a few studies, suspensions. These investigations however, limit the researchers to an observation of rather large droplets, several microns in diameter. Several experimental and theoretical studies indicate a substantial dependence of droplet size on the restructuring. It is therefore useful to understand the restructuring in submicrometer droplets as well. Microscopy is also limiting in that only one droplet can be examined in detail at a time. The dynamics of individual droplets obviously may not be representative of the entire sample. In addition, the studies using microscopy generally describe qualitative dynamics and are not quantitative in terms of response times which are of principal importance.

To overcome these limitations of multiple scattering, qualitative dynamics, and restrictions to large droplet sizes, we have chosen to employ the optical polarimetry techniques of time-dependent birefringence and scattering (form) dichroism to this problem. These nonintrusive methods allow one to obtain quantitative dynamics of the induced orientation in our droplet samples. Because these are extremely sensitive techniques, we can observe very small levels of induced anisotropy and measure the dynamics of that orientation quantitatively. Hence we can probe very dilute suspensions, eliminating multiple scattering effects. Orientation of submicrometre length scales, as in the droplets of interest, is also easily obtained. By using these techniques in a complementary fashion, we can obtain information of anisotropy at the nematic length scale as well as at larger domain scales which may have, as we shall see, different responses. We have also found that these two techniques give us information about orientation of the different droplet sizes of our polydisperse samples; thus we can learn about the droplet size dependence of the field-induced orientation. Liquid crystals have a rather large molecular birefringence, $\Delta n \sim 0{\cdot}2$ for cyanobiphenyl molecules. A measurement of birefringence is therefore a clear choice for probing the orientation of the molecules within the droplets and small droplet orientation. Because form dichroism is a scattering technique, it weights large droplets more strongly and is also particularly sensitive to defect movement/orientation in the liquid crystal droplets.

We examined suspensions of droplets in a nonbirefringent, nondichroic medium, that of glycerol. Cyanobiphenyl droplets in glycerol are spherical in shape, thus our study eliminates orientation effects associated with elongation of the droplet. By changing the surface anchoring of the nematic, we can make interesting comparisons between droplets of different internal configurations.

In this section we will describe our experimental approach and give details regarding the measurement of induced orientation due to an electric field in liquid crystal droplet suspensions.

2.1. *Sample description*

The liquid crystal used in this study is a cyanobiphenyl molecule, 4-*n*-pentyl-4′-cyanobiphenyl (5CB) from BDH Ltd. which has a nematic phase between 24 and 35·3°C. The 5CB at room temperature was crystalline, so in order to prepare emulsions, the liquid crystal was first heated to a temperature in the nematic regime. Following this, the emulsion was prepared by vortex mixing the liquid crystal and 99 per cent pure glycerol (Baker) with a liquid crystal concentration of 0·5 per cent by weight. The emulsion was prepared using a stirring motor (LFE Corp., Model 5VB) in series with a variac at a setting of 105 V and shearing for 2 min, 15 s. After degassing, part of this suspension was further diluted with glycerol to a final liquid crystal concentration of 0·013 wt %.

This sample, approximately 250 ml in volume, was stirred over the course of several days using a stir plate and magnetic bar to prepare samples of the desired droplet size range. Size was roughly monitored using microscopy, but samples were very polydisperse. The extent of polydispersity was characterized using dynamic light scattering. These measurements indicate that the degree of polydispersity P is at least 40 per cent, where this value is related to the standard deviation of the size distribution with diameter D:

$$\frac{P}{100} = \left[\frac{D^2 - D^2}{D^2}\right]^{1/2}. \qquad (3)$$

The dynamic light scattering measurement was made for only one bipolar drop sample, but we believe that the results are fairly representative of the rather broad size distribution of the droplets present in all samples. Final measured samples for which results will be reported had droplet diameters below 2 μm with a large percentage of the droplets in the submicrometer range, as determined with microscopy. Unfortunately, a slow coagulation of the liquid crystal droplets of the samples occurred over time, so upon approximate size measurement, an attempt was made to do the optical measurements quickly after preparation (within at least 1 week, usually within 1 day).

Glycerol was chosen as the suspension matrix for several reasons. Several previous research studies which were mentioned in the introduction used this matrix since it is immiscible with the cyanobiphenyl liquid crystal and thereby forms a well phase-separated droplet system. Because glycerol is fairly viscous, droplet dynamics controlled by the solvent are slowed down and are therefore more easily measured. It is an ideal matrix for our studies because it is neither birefringent nor dichroic at the wavelength studied. However, as mentioned, suspensions with cyanobiphenyl liquid crystals are not very stable over time. In addition, glycerol easily absorbs water from the atmosphere and therefore must be kept under tight seal to prevent this effect. Room temperature viscosity coefficients are found in the CRC Handbook of Chemistry and Physics [18], but this parameter rapidly drops off as water is absorbed by the liquid. For this reason we have made only approximate estimates of the suspension viscosity as will be discussed later. We have attempted to keep the glycerol samples sealed, but some water absorption is unavoidable.

To prepare the radial droplets, 1-α-phosphatidylcholine didecanoyl (Sigma Chemical Co.), commonly called lecithin, was added to the samples at very dilute concentrations. This molecule acts as a surfactant in the system and induces normal anchoring of the liquid crystal droplet by lowering the surface tension at the interface, thereby transforming bipolar droplets to radial ones. Lecithin was chosen over other surfactants which would have similar effects because of its use in prior works [19, 20]. It is miscible in glycerol due to similarities in the two structures. In the sample preparation, lecithin in a powder form was added at a weight concentration of 29 ppm to glycerol and stirred for 24 h. The 0·5 per cent liquid crystal/glycerol emulsion was then added to this system to obtain a concentration of liquid crystal of 0·013 wt % as before. The sample was then stirred as before for several days. Prior to the addition of liquid crystal, the lecithin/glycerol sample was tested for possible electro-optical orientation. These results will be discussed in an upcoming section, but it was found that there was very little measurable orientation of the lecithin.

2.2. *Optical technique*

Induced orientation in the liquid crystal droplet suspensions was measured using optical polarimetry methods. This experimental technique has been shown in many previous studies to be an important and effective way of measuring the orientation of liquid crystalline as well as polymeric materials. Details of the technique can be found in reference [21]. Measured birefringence and dichroism may each arise from form and/or intrinsic effects. Intrinsic contributions arise from anisotropic polarizabilities of the oriented 8CB molecules whereas form effects arise due to scattering by the suspended droplets and disclinations in the director. In this system, the intrinsic contribution of the birefringence is much larger than the form contribution. Furthermore, the liquid crystal used does not absorb light of the wavelength used in this study (633 nm), so we do not expect intrinsic dichroism in the experiments. Measured dichroism is therefore a form or scattering effect.

The optical train is shown in figure 1. In these experiments, the He–Ne laser beam passes sequentially through a polarizer at 0°, a photoelastic modulator at 45°, a quarter wave plate at 0°, and the sample. It then enters the polarization state analyser (PSA) which consists of a quarter wave plate at 0° followed by a polarizer at −45°. Using Mueller calculus, one can calculate the resulting intensity to be of the form

$$I = I_{\mathrm{DC}} + I_{\omega}\sin(\omega t) + I_{2\omega}\cos(2\omega t) + \ldots \qquad (4)$$

where ω is the frequency of the photoelastic modulator, t is time, and '...' denotes harmonics of higher frequencies that are not measured. The use of lock-in amplifiers set at reference frequencies corresponding to ω and 2ω allows one to determine the Fourier coefficients, I_{ω} and $I_{2\omega}$, which are functions of the birefringence, dichroism, and the corresponding orientation angles of the optical anisotropies.

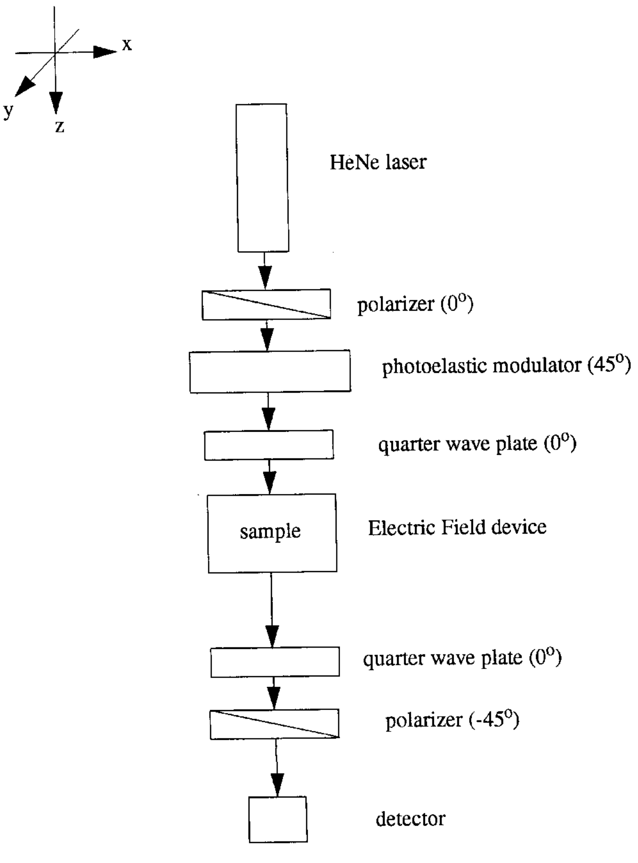

Figure 1. Schematic of the optical train used to measure birefringence and dichroism. The circular polarizer is only used in birefringence experiments.

The electric field in the experiments is applied at 90° relative to the initial polarization of the He–Ne beam. We only expect two possible orientations of the liquid crystals relative to the field: either in the direction of the field or normal to it. Very little if any anisotropy will be induced in any other direction. Furthermore, because we are working with very dilute suspensions in which the measured anisotropies are very small, trigonometric functions of the retardation/birefringence and extinction/dichroism are also greatly simplified. The expressions for $R_1 = I_{\omega}/I_{\mathrm{DC}}$ and $R_2 = I_{2\omega}/I_{\mathrm{DC}}$ become

$$R_1 = \pm\delta' J_1 \qquad (5)$$

and

$$R_2 = \pm\delta\, J_2 \qquad (6)$$

where δ' and δ are the retardation and extinction respectively, and J_1 and J_2 are calibration constants. Recall that the retardation and the extinction are directly proportional to the birefringence $\Delta n'$ and dichroism Δn, respectively through $\delta' = (2\pi d\Delta n'/\lambda)$ and $\delta = (2\pi d\Delta n/\lambda)$ where d is the path length and λ is the wavelength of the probing light. By calibrating the train with samples of known orientation we have determined that negative values of R_1 and R_2 indicate induced alignment in the direction of the electric field and positive values indicate alignment normal to it. The values of J_1 and J_2 were determined by calibrating the optical train with a quarter wave plate. We have checked the simplifications made in this analysis and have determined that they are perfectly reasonable for the magnitudes of the signals measured. We have therefore used these simple equations in our calculations of birefringence and dichroism which follow. Clearly this optical train has advantages in that we can simultaneously determine the magnitudes as well as the orientation angles (parallel or perpendicular to the electric field) of the birefringence and the dichroism. We can therefore obtain information regarding both the molecular orientation as well as larger domain orientation and defect restructuring in one simple measurement.

2.3. *Electric field cell*

The electric field cell used in these experiments was constructed by Wirtz and Berend and is described by Wirtz [22]. It is pictured in figure 2. Briefly, the cell consists of two stainless steel electrodes placed 1·65 mm apart. The cell is made of black Delrin plastic and fits into a stainless steel block which can be heated/cooled with a temperature-controlled water bath. The electrodes are sandwiched by two quartz windows which allow passage of the probing laser beam normal to the direction of the electric field. The beam is positioned in the approximate centre of the electrode gap and passes through 9 mm of the sample. The temperature of the cell can be measured at the insulating block. The sample is well sealed from the air with O-rings placed between the electrodes and optical windows. The field is applied at 2 stainless steel screws which contact either electrode.

2.4. *Experimental protocol*

In the electro-optical experiments, an alternating current field (sine wave pulse) was applied to the sample with peak-to-peak voltage values in the range of 100–1000 V. The values of the peak voltages will be quoted as the applied voltage across the 1·65 mm gap in the upcoming results section. The a.c. field wave was generated using a Hewlett–Packard model 3325B function generator and amplified one thousand times with a Trek model 609-6 voltage amplifier. The frequency of the applied field was typically 1 kHz but frequencies in the range of 1–30 kHz were examined. In this range of frequencies, the dominant cause of induced orientation is due to the anisotropy in the dielectric tensor of the liquid crystal and not the anisotropy in the electrical conductivity. Electrical conductivity becomes increasingly important at field frequencies below the range employed [12]. Fields were typically pulsed between 1 and 5 s in order to capture the initial dynamics of orientation prior to more complicated orientation effects. The field duration was computer-controlled through the use of a RS-232 interface. Dynamics were measured using the polarimetry techniques during and following this applied pulse in order to capture the full dynamics of the induced orientation.

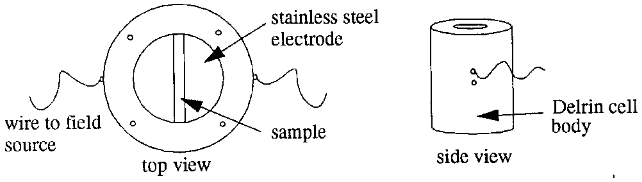

Figure 2. Electric field cell. The field was applied across the sample sandwiched between the stainless steel electrodes shown in the top view. Wires connected to the electrodes with stainless steel screws link the cell to the fields.

2.5. *Expected droplet dynamics*

The possibility of at least two relaxation time scales can be examined prior to any experimentation. As in the work of Adamczyk [17] and in light of our previous experiments regarding the dynamics a biconcave disc-shaped droplet [23], we might expect a Brownian rotational diffusion to be important, particularly in the relaxation of aligned bipolar droplets as shown in figure 3. Once the field is removed, the aligned optical axes of the bipolar droplets disorient with respect to one another through rotational diffusion and the magnitude of the optical anisotropy will therefore decrease. The time-scale over which this will occur is

$$\tau = \frac{4\pi \eta_{\mathrm{p}} R^3}{3 k_{\mathrm{B}} T} \tag{7}$$

where η_{p} represents the viscosity of the surrounding matrix. We will use this expression to later determine if such a relaxation is indeed observed.

A second important relaxation process is one associated with nematic distortion. As elastic forces quickly relax following an applied electric field, an opposing force due to viscous forces slows the effect. A time-scale can be estimated as

$$\tau = \frac{\eta R^2}{K} \tag{8}$$

where η now represents the viscosity of the liquid crystal. As discussed in the introduction, this effect is particularly important in the relaxation of elongated bipolar droplets.

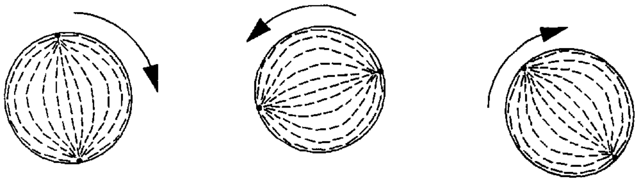

Figure 3. Brownian rotational diffusion of bipolar spherical droplets. This relaxation can be observed as the optical axes of the droplets disorient with respect to one another.

In our experiments bipolar droplets are instead spherical in shape, but radial droplets may show this relaxation process as shown in figure 4. These two time scales of equations 7 and 8 are separated in magnitude by several orders of magnitude and should therefore be easily discernible in our experiments.

3. Results and discussion

We have measured orientational behaviour during and following an applied alternating electric field for three basic cases. First we will examine drops that are at elevated temperatures so that they are in their isotropic orientational state in the absence of an electric field. An applied field weakly orients the nematic within these drops in the direction of the field. In these experiments we see only the presence of a birefringence; no dichroism is seen due to the very small length scales over which the orientation propagates and due to the absence of large defect structures in these droplets.

We will then examine the two nematic cases of bipolar and radial droplets. Nematic droplets show an induced dichroism in addition to the birefringence, and the magnitudes of the signals are greatly increased. We see very different relaxation behaviour between radial and bipolar droplets. These results as well as the voltage, frequency, and field duration dependence of the signals will be discussed.

3.1. *Isotropic drop suspensions*

Samples of both nematic bipolar and radial-type droplets were raised into their isotropic regime by changing the temperature of the water bath which heated/cooled the field cell. In these experiments, the temperature was first allowed to equilibrate for 4 h at a bath temperature of 50°C. This translated to a sample temperature of approximately 42°C as measured near the electric field cell wall. This temperature is well above the nematic/isotropic transition temperature of 35°C, so we are assured that the droplets are in the isotropic state. Presumably in these experiments, orientation at the droplet/glycerol interface is preserved; therefore it is interesting to compare orientation effects between samples with normal and tangential anchoring. We see the results of such a comparison in figure 5. The plot shows induced retardation/birefringence for both tangential anchoring (*a*) as well as normal anchoring (*b*). In the experiments, the field is applied from approximately time = 2 to 7 s, after which we measure the decay of the anisotropy to the original isotropic state. The first thing to note is the very small magnitude of the induced retardation following the 5 s pulse. In fact, a 1 s pulse does not induce any measurable anisotropy, unlike results in the nematic state as we shall see later. The data are quite noisy due to the very small magnitude of this effect. We see in these plots the voltage dependence of the orientation and can see that, clearly, with increased voltage, there is an increased orientation. The negative sign of the signal indicates orientation in the field direction as one would expect.

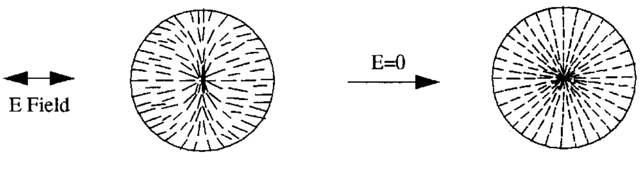

Figure 4. Nematic distortional relaxation of a radial droplet. In the droplet on the left, the nematic of the bulk of the interior aligns in the field direction while maintaining the normal anchoring. This results in a stretching of the defect region in a direction normal to the applied field and an eventual splitting of the defect as it migrates to the surface. When the field is turned off, the nematic quickly relaxes to the original radial configuration as seen on the right.

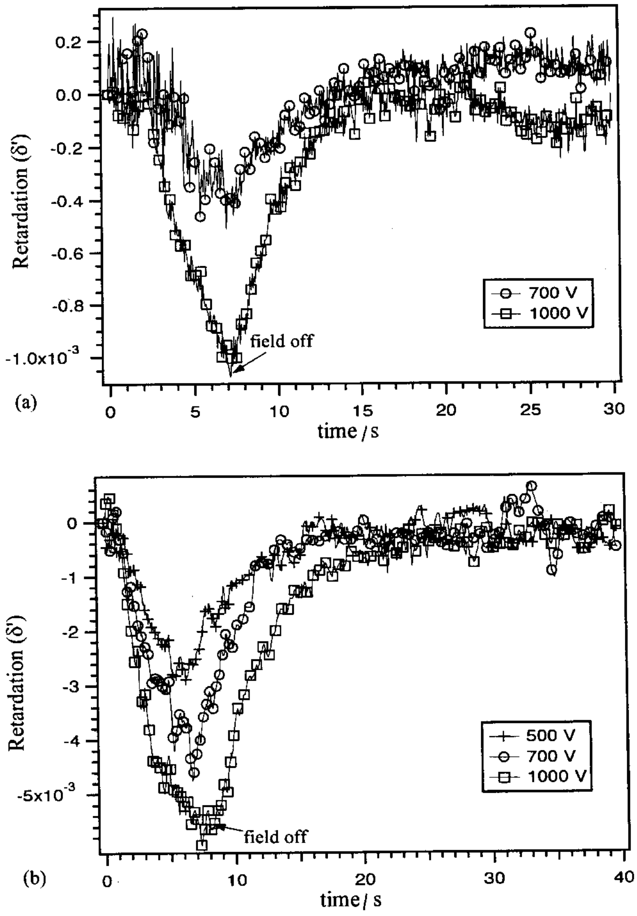

Figure 5. Response of isotropic ($T=42$°C) droplets to an applied electric field. (*a*) Tangential anchoring. (*b*) Normal anchoring. The field of 1 kHz frequency is applied from approximately time = 2 to 7 s. An exponential relaxation follows.

A single exponential fits the relaxation data of these samples quite well. In such a fit, the time scale of relaxation is approximately 3–6 s in both cases. Interestingly there is little difference between the orientational behaviour of the normal and tangential anchoring cases. The magnitudes of induced anisotropy are of the same order of magnitude; differences are due principally to differences in polydispersity of the two samples, which is very difficult to control, particularly at the elevated temperatures where polydispersity was found, using dynamic light scattering, to increase by at least 20 per cent from the original room temperature value.

A simple description for the orientational and relaxation behaviour observed can be offered. Upon application of the field, the liquid crystal within the droplet begins to align in the field direction, but because the droplets are in the isotropic regime, the orientation of liquid crystal molecules have little effect on one another. The resultant alignment is, therefore, rather small. Upon removal of the field, the induced orientation relaxes, but because there is no elastic distortional mechanism for this to occur, the time-scale is rather slow.

We have observed electric field-induced orientation in isotropic drops of two different anchoring conditions and have observed similar results. A small retardation/birefringence is seen with a time-scale of relaxation of approximately 3–5 s following a 5 s pulse.

3.2. *Bipolar drop suspensions*

Figure 6 shows polarimetry results for bipolar droplets at 25°C where 5CB is in the nematic regime. This particular sample is measured subsequent to being in the isotropic state as described in the last section. The act of sweeping the temperature was found to change the polydispersity in the samples but was also found to have the beneficial effect of healing any droplets which had structures that were not perfectly bipolar. Data are therefore easier to understand for samples that have undergone a prior temperature sweep. In the experiments shown, an a.c. field is applied for 1 s at the beginning of the experiment and the relaxation of the induced orientation is monitored until it is complete, after approximately 140 s in this case. In the figure we show induced retardation (*a*) as well as induced extinction (*b*). The appearance of an extinction now, unlike the isotropic droplets, is due to the scattering by the defects of the bipolar droplets which have an optical direction identical to that of the nematic orientation. The extinction signal is also more sensitive to larger length scale orientation than the retardation and, thus, its occurrence is expected due to the enhanced orientation of the liquid crystal molecules in the nematic state.

In comparing figures 5 and 6, we see a much larger orientation induced in 1 s in the nematic bipolar droplets compared to the isotropic ones. If in fact we continue to apply the electric field for 5 s as in the isotropic drop experiments, the induced orientation continues to increase. Orientation is also induced at lower voltages compared to the isotropic droplets. Here we see an induced orientation at voltages as low as 200 V across the gap. As before, the sign of the signal indicates orientation is induced parallel to the direction of the electric field as one might expect.

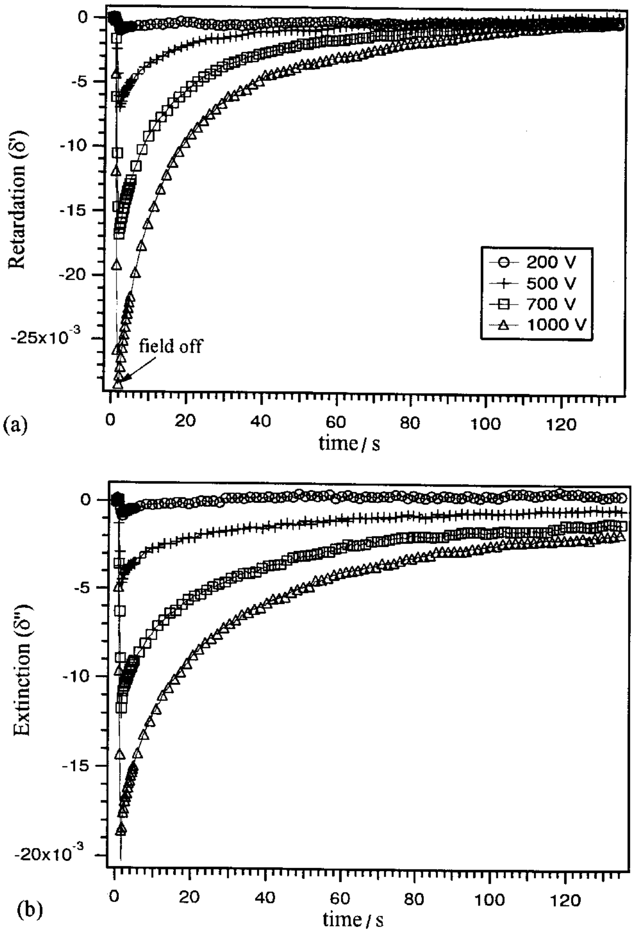

Figure 6. Optical response of bipolar drop suspension to an applied alternating electric field of $\omega = 1$ kHz. The field is applied for 1 s at the start of the experiment. (*a*) Retardation, and (*b*) extinction.

The extinction signal is of the same order of magnitude as the retardation and has a similar orientational response with alignment in the direction of the electric field. The agreement indicates that the optical axis of the defect as well as large domain orientation within the droplet have a similar orientation to the liquid crystal molecules as measured in the birefringence signal. This is of course in keeping with the bipolar droplet geometry where the orientation of the optical axis of the defect prescribing large domain orientation is parallel to the orientation of the nematic molecules. The similarity of the signals is also a result of similar orientation effects in small and large droplets to which the birefringence and dichroism, respectively, are particularly sensitive.

We see in figures 6 and 7 that orientation is increased as both the applied field is increased as well as the applied frequency of the field is increased. As one would expect, induced orientation is increased as the strength of the field is elevated. The frequency dependence of the response could be due to a number of effects. Perhaps higher frequencies couple with the orientation of smaller droplets, thus contributing to a greater orientation of the sample population of droplets. In addition, the frequency dependence may also be due to differences in the magnitude of the local field within the drops which would therefore affect alignment [12]. Previous work [24] indicates that as the frequency of the field is increased, one moves away from a regime where the electric field couples with the anisotropy in the electrical conductivity of the liquid crystal and into a regime where the important aligning effect is in the anisotropy of the dielectric constant. The relative magnitudes of the dielectric constants of the suspension matrix to liquid crystal tends to be much larger than that of the electrical conductivities thereby contributing to a larger local field in the high frequency regime. This would in turn explain the observed increase in nematic alignment with frequency. In these experiments we do not achieve perfect alignment of the droplets in the field, indicated by the fact that we do not reach a steady state in the signals but rather observe only a continuous increase in induced orientation. We are concerned only with initial response to the field and its relaxation, thus avoiding more complicated signals which are observed if the field is held for longer durations.

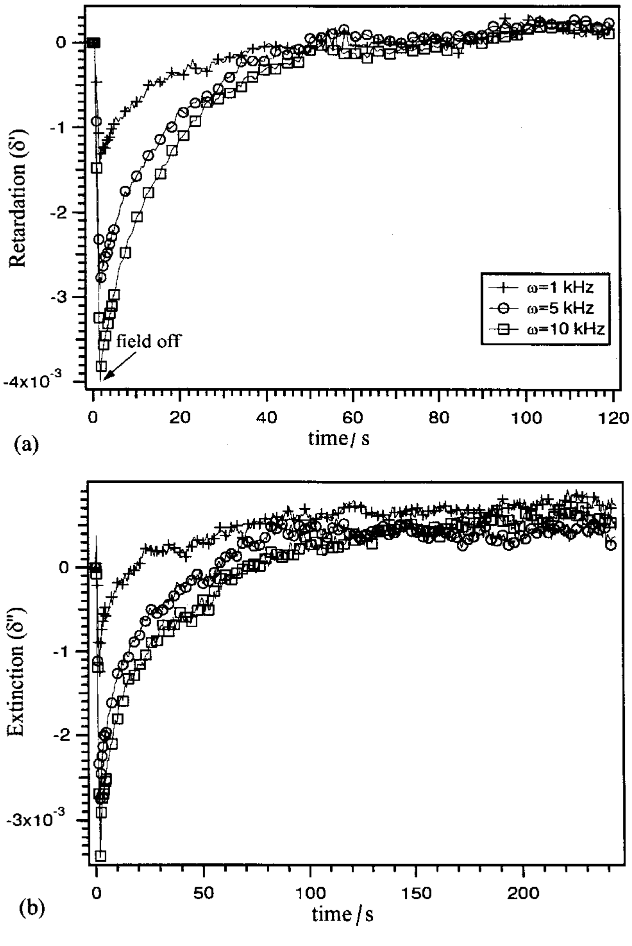

Figure 7. Frequency dependence of optical anisotropies induced in bipolar drop suspension. A sine wave pulse of 500 V was applied for 1 s at the start of the experiment. (*a*) Retardation, and (*b*) extinction.

The relaxation of both the observed retardation/birefringence and extinction/dichroism can be fitted well with double exponential curves. Time-scales of relaxation are typically 2–10 s for the faster relaxation and 40–50 s for the longer one. The magnitude of these relaxation time-scales and the known geometry of the droplets lead us to explain the relaxation process as a Brownian rotational diffusion. Using the formula of equation (7) with appropriate material constants ($\eta_{\mathrm{glyc}} \sim 10\,\mathrm{P}$), we calculate relaxation times of approximately 100 s for a 1 μm droplet, and 30 s for a 0·6 μm droplet. Given the polydispersity of the sample and possibility of variations in the viscosity of glycerol from water absorption, the time-scales are of the correct order of magnitude for this relaxation mechanism. Time-scales are much too long to be attributed to any nematic distortion which might occur in the droplets. As suggested in the magnetic field study by Adamczyk, bipolar droplets align in an orienting field with their optical axes in the field direction. In this way, the tangential anchoring at the interface can be preserved. Unlike film studies, the whole droplet can in fact rotate so that the desired alignment is achieved with no induced nematic distortion. Upon removal of the field, the droplets disorient with respect to one another through a Brownian rotational diffusion which is easily observed in the viscous glycerol matrix. The relaxation of the extinction is slightly longer than that of the retardation due to the increased sensitivity of this observable to longer length scales and thus larger droplets. We attribute the double exponential character of the relaxation to the polydispersity of the sample. As mentioned previously, samples were found to have a wide range of droplet sizes (40 per cent polydispersity in unheated samples, greater than 60 per cent polydispersity for heated samples). Following temperature sweeps, the size distribution is also found to broaden, creating in particular some very large droplets observable in dynamic light scattering measurements, and thus contributing to the two distinct time-scales. The two time-scales indicate that perhaps the sample contains a bimodal distribution of particles, but we are unable to confirm this hypothesis and only suggest, therefore, that the distribution is non-Gaussian after the performed temperature sweep.

In a separate study, we examined the effect of an increased pulse duration on the relaxation behaviour of the droplet suspensions. Results of relaxation time constants can be found in table 1. As in the aforementioned study, relaxations typically had a double exponential character, particularly at the larger voltages. Orientation produced in low fields was measurable, but rather noisy, so a single exponential was fit to these relaxations. Interestingly, the relaxation of the retardation does not appear to change significantly with increased pulse duration, but the extinction does appear to show substantially longer relaxation times following the 5 s pulse. This behaviour helps us to understand both the mechanism of orientation in the field as well as the size dependence of the induced orientation. Recall that the dichroism weights the orientational effects of larger droplets over smaller ones. We can think of the two optical measurements simply in terms of droplet size with the birefringence probing small droplet orientation and the dichroism probing large droplet orientation. The increase in the large droplet relaxation times with field duration indicates that a greater population of large droplets is being oriented in the longer pulse therefore resulting in a longer relaxation time constant. This effect is not observed in the birefringence due to the increased relative sensitivity of this technique to the smaller droplet population. These two signals also indicate that smaller droplets orient more quickly in the electric field than larger ones. This is in keeping with our picture of droplet alignment. As the field is applied the droplets rotate with their optical axes in the field direction without any measurable distortion of the nematic within the droplet. Smaller droplets rotate more quickly due to their smaller radii. The field must be held longer for larger droplets to orient in the field, and thus their response to the field to which the dichroism is sensitive is observed only with pulses of longer duration.

Thus in bipolar droplets, orientation in an electric field is principally achieved through an alignment of the droplet optical axes in the field direction. This anisotropy is observed in both birefringence as well as dichroism. Relaxation of the induced orientation occurs through a Brownian rotational diffusion.

3.3. *Radial drop suspensions*

3.3.1. *Effect of added lecithin*

As mentioned previously in the sample description, to prepare radial droplets, lecithin was added to the suspension matrix. Since lecithin is a surfactant molecule that might also self-aggregate to a certain extent in the glycerol matrix, particularly in the absence of the liquid crystal droplets, we made electro-optical measurements of lecithin in glycerol as a control study. The results of those measurements are shown in figure 8. Pictured is induced retardation in electric fields of different strengths and 1 kHz frequency during the course of experiments identical to those described before. Here the field is applied for 5 s, being turned off at approximately 7 s. We see very little induced orientation at low voltages and some measurable but still extremely small retardation at higher field strengths. An even smaller amount of dichroism is observed and is therefore not pictured. No measurable anisotropy in the lecithin sample is induced in a 1 s pulse. Although there is some induced orientation in the field in 5 s, we are assured that the effect of the lecithin (at the very low concentration used) on the radial droplet experiments is minimal. The magnitude and character of the signals change drastically once the liquid crystal droplets are added, showing the lesser role of the lecithin relative to the liquid crystal in field

Table 1. Relaxation time-scales, bipolar droplets.

Voltage/V	Long birefringence/s	Short birefringence/s	Long dichroism/s	Short dichroism/s
		1 s pulse		
300	36		7	
500	27	5	51	3
700	40	6	55	4
1000	33	6	56	5
		5 s pulse		
200	16		26	
300	17		41	3
500	33	6	100	15
700	32	6	92	15
1000	35	6	75	12

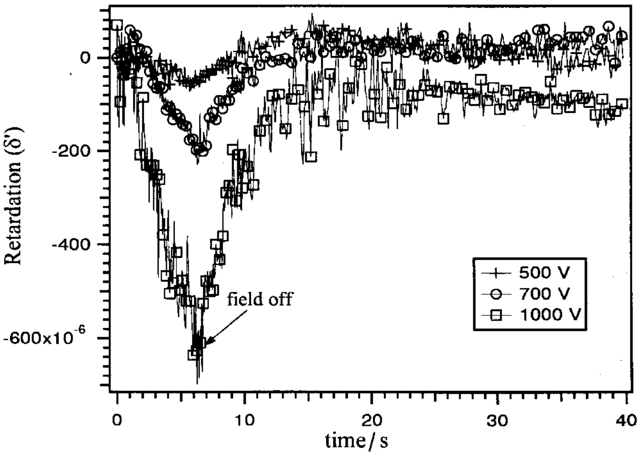

Figure 8. Induced retardation in sample of 29 ppm lecithin in glycerol. The field ($\omega = 1$ kHz) is applied for approximately 5 s. The magnitude of the retardation is very small and therefore contributes minimally to induced anisotropy observed in radial drop samples.

alignment. The same lecithin/glycerol sample shown in these experiments was used to prepare the radial droplet suspension whose electro-optical properties will be described next.

3.3.2. *Radial drop electro-optics*

Figure 9 illustrates polarimetry measurements of radial liquid crystal droplets in the lecithin/glycerol matrix. The course of the experiments is identical to that described for the bipolar droplets: a 1 s pulse is applied at the start of the experiment. Optical anisotropies are measured during and following the pulse. One can immediately see that the relaxation occurs over a much shorter time scale than that of the bipolar study. Here relaxation is complete in approximately 15 s, compared to the 150 s of the bipolar drop suspensions.

As before, we again see the presence of a retardation/birefringence and a extinction/dichroism with the two having similar orientational and relaxation behaviours. The negative sign of the signals indicates orientation in the direction of the electric field. Orientation is induced at applied a.c. fields as low as 200 V and substantial orientation is achieved in a 1 s pulse. The magnitudes of the induced retardation and extinction are slightly smaller than those shown for the bipolar droplets in figure 6 but we attribute this more to differences in the size distributions of the sample, which has proven difficult to control, than an effect of the anchoring. We make this conclusion based on several additional experiments not shown where comparable magnitudes of orientation were observed between the two anchoring condition droplets. Figures 9 and 10 show the voltage and frequency dependences, respectively, of the optical anisotropies. We see again as we did for the bipolar case that with increased voltage an increased alignment is achieved, as one might expect. An increase in alignment is also observed with increase in frequency. We explain this as before: that the frequency effect is due to both increases in orientation within smaller droplets as well as an effect of an increased local field within the drops with higher frequency.

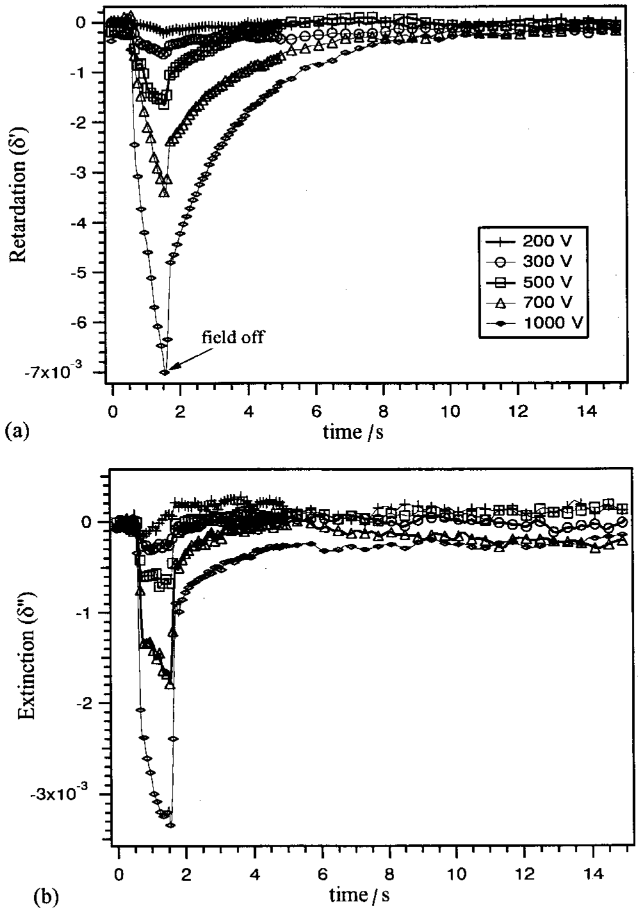

Figure 9. Voltage dependence of induced optical anisotropies in radial droplet suspensions. The alternating field ($\omega =$ 1 kHz) was applied for 1 s at the start of the experiment. (*a*) Retardation, and (*b*) extinction.

The principal difference between the responses of the radial and bipolar droplets to the electric field lies in the relaxation behaviour, and it is here where we learn about how the nematic is distorted by the field. In the radial droplet experiments we observe a very fast relaxation upon removal of the field followed by a slightly slower relaxation, but one which is still much faster than the Brownian rotational diffusion of the previous experiments. The time scales of relaxation are shown for the experiments in table 2. There are 4 time steps taken between each symbol shown in the figures, so we do quantitatively measure the fast dynamics of the

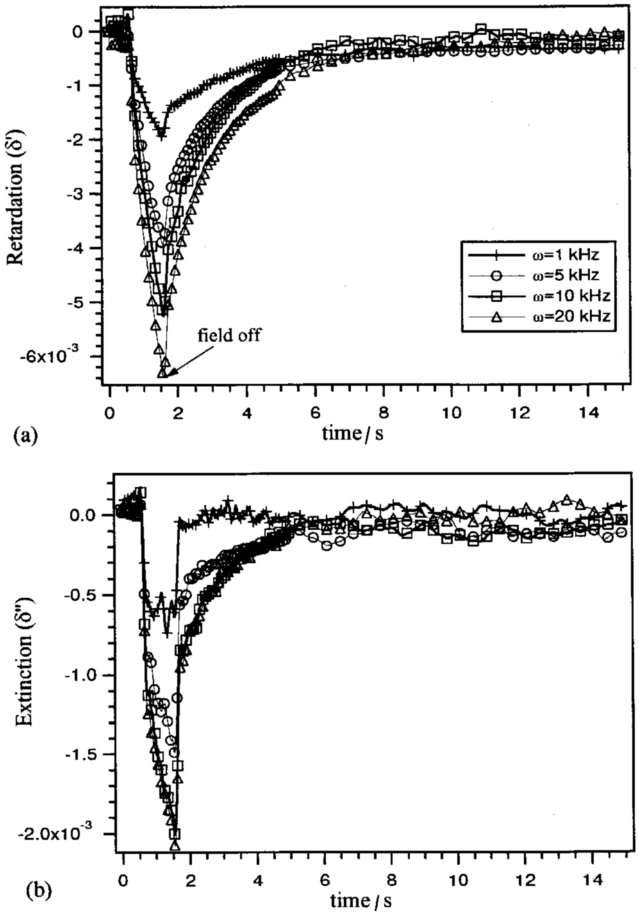

Figure 10. Frequency dependence of induced optical anisotropies in radial droplet suspensions. The alternating field ($V=500$ V) was applied for 1 s at the start of the experiment. (*a*) Retardation, and (*b*) extinction.

relaxation. We see that the fast relaxation is of order 40–80 ms for both the retardation as well as the extinction. The slower relaxation has an exponential decay constant of approximately 1 s. This double decay is most obvious at higher voltages therefore we focus our attention in this regime. The shorter decay corresponds well to what one would expect for the time scale of a nematic distortional relaxation as in equation (8). Computing this time-scale with the appropriate experimental constants (estimating $\eta \sim 1$ P from experimental values of the Leslie viscosity coefficients for 5CB [25]: $\alpha_2 = -1{\cdot}3$ P, $\alpha_3 = -0{\cdot}05$ P, and with $K = 10^{-11}$ N) does indeed indicate that this time-scale should be on the order of 10 ms.

The longer time-scale of 1–3 s has not been measured previously to our knowledge. We attribute it to the restructuring of the nematic in the vicinity of the defect. Previous microscopy work on radial droplets in films indicates that the defect is altered, sometimes drastically, when a field is applied. In order for the radial droplet to preserve its normal anchoring condition and still orient in the field, the defect must move out of the droplet centre. Bondar *et al.* [12], observed that the distorted defect illustrated in figure 4 will eventually elongate and move to the droplet surface at very high fields. As this occurs the defect splits, moving in a direction normal to the field and thereby producing a highly oriented volume of nematic in a core region which is perpendicular to the bulk alignment. We surely do not reach this condition of complete nematic alignment in our fields, but the nematic may certainly be distorted enough by the field so that the defect region is altered. Once the field is removed, much of the nematic orientation of the droplet is relaxed through the distortional relaxation described. However, in the vicinity of the defect where the orientation is already much more distorted, it will take some time for the liquid crystal molecules to return to their original states. The defect must, in a sense, diffuse to its original position. This proposed mechanism is supported by the birefringence results of figure 11. Here the field is applied for 5 s. Again two time-scales, a short and long, are present. Although the short time-scale remains on the order of 40 ms, the longer time-scale increases from approximately 2 s to 6 s.

Table 2. Relaxation time-scales, radial droplets.

Voltage/V	Long birefringence/s	Short birefringence/s	Long dichroism/s	Short dichroism/s
		1 s pulse		
300	0·52		0·68	
500	1·3	$5{\cdot}3^{e-2}$–$8{\cdot}6^{e-2}$	0·68	$7{\cdot}2^{e-2}$
700	2·2	$5{\cdot}3^{e-2}$–$8{\cdot}3^{e-2}$	0·68	$7{\cdot}0^{e-2}$
1000	2·2	$4{\cdot}8^{e-2}$–$9{\cdot}4^{e-2}$	1·1	$7{\cdot}4^{e-2}$
		5 s pulse		
300	3·7			
500	3·8	1·4		
700	4·2	1·3		
1000	6·3	1·7		

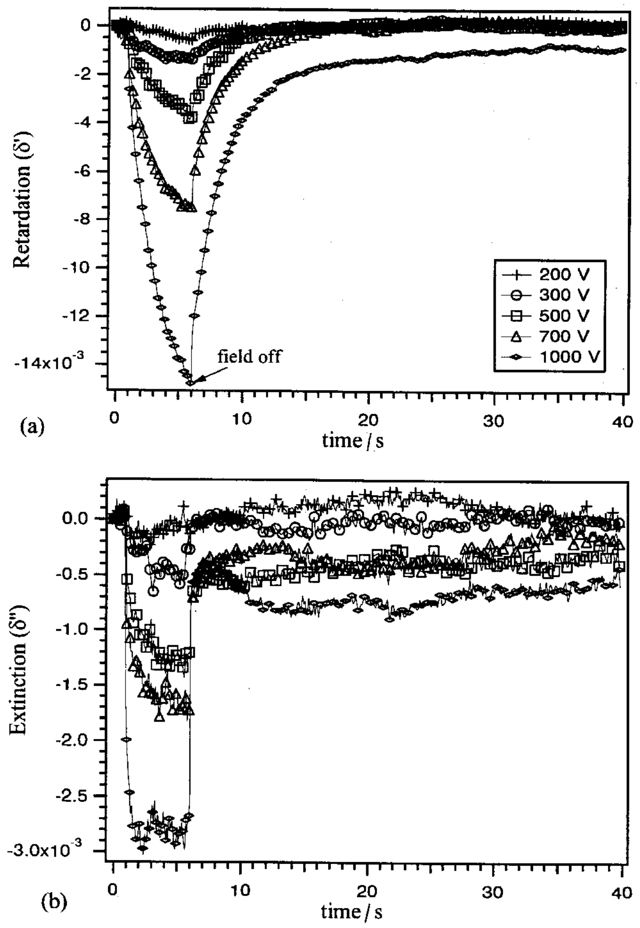

Figure 11. Voltage dependence of induced optical anisotropies in radial droplet suspensions. In this experiment, the field ($\omega = 1$ kHz) was applied for 5 s instead of the short 1 s pulse of the previous figure. (*a*) Retardation, and (*b*) extinction.

Similar behaviour is observed at higher frequencies. Thus, as the duration of field is increased, the defect region becomes more distorted and thus requires a longer time to return to its original position.

The character and dynamics of the birefringence and dichroism signals are quite similar in most of the experiments we have discussed. This is due to the fact that within small cavities the orientational dynamics of liquid crystal domains within droplets are essentially identical to those of the liquid crystal molecules which compose them. In addition, small droplet dynamics monitored more in the birefringence are essentially identical to those of larger droplets, to which the dichroism is more sensitive. We observe some deviation from that behaviour though in figure 11. There we see that for longer field duration pulses, although the extinction continues to have its fast/slow response, the fast response observed in the retardation of figure 9 has disappeared. We believe that this is due to the sensitivity of the retardation/birefringence to smaller droplets. It is clear that the defect region becomes more distorted with increased fields as a greater alignment of the liquid crystal molecules is achieved in the field direction. The distortion of the defect has a much greater influence on the orientation of the nematic as a whole for smaller droplets due to their decreased radii and the larger relative size of their defects. Thus, it is the birefringence which shows this increased distortion and the associated longer relaxation time. We have learned from previous studies, particularly those of Doane [2], that the liquid crystals within larger droplets are more easily oriented in an electric field than smaller droplets when the mechanism of orientation involves a distortion of the liquid crystal. Smaller droplets have a greater curvature and therefore a larger energy barrier towards reorientation. This is unlike the previous case of the bipolar drops where the nematic can align in the field direction by a rotation of the droplet without any restructuring of the nematic within the droplet. Thus, we see this longer relaxation effect in the retardation when the field is held for a longer duration because large and small droplets have begun to align in the field direction. The short relaxation effect is still observed in the extinction of figure 11 due to the sensitivity of this optical anisotropy to larger droplets. The larger size of these droplets decreases the influence of the defect region on the nematic orientation near the surface, so a greater volume of liquid crystal in the larger droplets can relax through the fast distortional mechanism.

We have observed electric field-induced orientation in radial droplets comparable in magnitude to orientation found in bipolar suspensions. Relaxation times differ significantly from the bipolar case. Because the defect of the droplet lies at the center rather than the surface, distortion of the nematic as well as of the defect itself must occur for the liquid crystal molecules to align in the field direction. We therefore observe two relaxation times separated by two orders in magnitude, one of which corresponds to an elastic distortional relaxation and the other which is attributed to the restructuring of the defect itself.

4. Conclusions

We have studied the effect of an electric field on dilute suspensions of liquid crystal droplets with different interfacial anchoring. We have described our measurements of optical anisotropies of electric field-induced orientation in isotropic, bipolar, and radial drops in the low viscosity matrix of glycerol. In isotropic drops, we saw only a weak induced birefringence with relatively slow relaxation times due to the very small value of the elastic constant in this temperature regime. No observable differences in the orientational or relaxation behaviours were observed between tangential and normal anchoring in isotropic drops at the droplet/glycerol interface.

In bipolar and radial droplet suspensions we observed electric field-induced birefringence and dichroism. The presence of the dichroism in these experiments is attributed to the increased scattering of the nematic droplets due to their defect structures and the increased order which therefore occurs over longer length scales in this regime. Similar magnitudes of anisotropy were induced in the two droplet configurations. Relaxation behaviours between the two samples, however, were quite different. In bipolar droplets, a Brownian rotational diffusion with time-scales on the order of 50 s was seen. The disorientation of the optical axes formed by the two defects of each droplet is the source of this relaxation. Large droplets were also observed to orient less quickly than smaller droplets, indicating that a full rotation of the droplet optical axes is necessary for field alignment. In radial droplets, two distinct time-scales were found in nematic relaxation. A fast relaxation on the order of 40–80 ms due to nematic distortion induced by the field was observed. A second longer relaxation of several seconds which was found to increase in magnitude with field duration, is attributed to the restructuring of the defect region in the droplets. Small droplets were observed to become more distorted by the field due to the comparatively larger volume affected by the defect dynamics and showed, therefore, only the long time-scale relaxation as the field duration was increased.

These experiments have increased our understanding of the field response of nematic liquid crystal droplets and the restructuring which must occur in these droplets as the electric field is applied and removed. Relaxation times were quantified in the different droplet configurations within the same suspension matrix, in some cases, for the first time. Unlike most previous studies in which droplet dynamics were measured in films, this study performed with suspensions allows an examination of the response while eliminating responses associated with constraining the droplet in a rigid film matrix. These results enhance our knowledge of how confinement and anchoring affect liquid crystal orientation in the presence of an electric field, of importance both in PDLC applications as well as in the general study of liquid crystals.

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