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Pulsed voltage studies of electric field effects on the optical permittivity of a nematic liquid crystal

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Prism coupling to resonant optical modes in a thin layer of homeotropically aligned nematic liquid crystal has been used to characterize the change in refractive indices which occurs when an electric field is applied. Reflectivity data, recorded over a range of angles of incidence for both TE and TM radiation show sharp minima corresponding to the excitation of optical modes in the liquid crystal layer. Application of a pulsed AC voltage, pulsed to avoid heating, while synchronously monitoring reflectivity changes allows detailed characterization of the shift in the position of these minima due to the influence of the electric field on both the ordinary and extraordinary refractive indices. By fitting theoretical predictions of Fresnel theory a complete characterization of change in both these parameters up to an applied field of some $5 \times 10^6\,\mathrm{V\,m^{-1}}$ is achieved. The refractive index changes recorded are compared with the director fluctuation order parameter theory with which good agreement is found.

1. Introduction

Liquid crystals are mesophases between the crystalline and isotropic liquid states. A nematic liquid crystal exhibits long range orientational ordering and translational disordering of the molecules. The orientational order may be described, microscopically, by the Maier–Saupe [1] order parameter S and macroscopically it may be described by the director $\mathbf{n}$. For a uniaxial nematic the director direction coincides with the symmetry axis of the dielectric tensor spheroid (and, of course, the optic axis). The optical properties of this liquid crystal are then described by $\varepsilon_{\parallel}(\omega)$ and $\varepsilon_{\perp}(\omega)$ which are respectively the relative optical permittivities (here ω is the frequency), for polarization parallel to the director and orthogonal to it. These parameters are not only functions of frequency, but through changes in the order parameter, they are also temperature dependent. However it is also well known that most properties of a nematic, including $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, are influenced by an applied electric field. This may be through two possible effects. First, on a microscopic level the electric field interacts with the molecules through both permanent and induced moments to change the order parameter. Secondly, director fluctuations may be progressively quenched. Microscopic and macroscopic theories for these voltage dependent changes have been produced [2] and experiments have been reported [2, 3] which agree to an extent with the theory. These experiments involve measuring the change of a combination of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ using an elegant experimental technique involving the transmission birefringence changes in relatively thick cells of homeotropically aligned liquid crystal.

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In the current study we use the excitation of optical modes in a thin homeotropically aligned liquid crystal layer to determine accurately and independently the changes in $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ as a function of voltage. A homeotropically aligned layer of liquid crystal in the nematic phase corresponds to a uniaxial slab of material. If this is probed with an optical beam polarized so that its electric vector is perpendicular to the plane of incidence (a TE beam) then it senses only $\varepsilon_{\perp}$. When the plane of polarization of the incident beam is rotated by 90° (a TM beam) then the electric field vector is neither parallel nor perpendicular to the uniaxial director direction and so the reflectivity from a thin cell is sensitive to both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$. By carefully fitting angular dependent reflectivity data for both polarizations to theoretically modelled reflectivities, using Fresnel theory, we obtain $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and the cell thickness, d.

In the process of conducting these experiments we found, not surprisingly, that the changes in $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ caused by the voltage are easily masked by changes caused through heating. Furthermore it is very difficult to measure accurately the change in temperature of the liquid crystal layer in a 6 μm thick cell, in the region where it is being probed by the laser beam. Because of this we have developed a technique which easily allows us to distinguish between heating and direct voltage induced effects. An AC voltage pulse is applied to the cell, and then the cell is left to recover over a sufficient time before applying the pulse again. By synchronously measuring the reflectivity with the voltage cycling we are then able to determine changes resulting from the voltage alone.

2. Experimental

An equilateral high index glass prism ($n = 1{\cdot}80$ at $\lambda = 632{\cdot}8\,\text{nm}$) is coated on one face with a thin layer ($\sim 50\,\text{nm}$) of 99·999 per cent pure silver using conventional vacuum evaporation procedures. The optical parameters and thickness of this film were determined by using the attenuated total reflection technique [4] to excite the surface plasmon and subsequently fitting the resultant reflectivity versus angle data using Fresnel theory. In the present case this gave for the silver layer, at 632·8 nm, $\varepsilon = -18{\cdot}0 + 0{\cdot}74\,i$ with a thickness of 54 nm. An optical flat was also coated with a thicker layer of silver to give a high quality mirror. This was used as the back plate in the liquid crystal cell structure. These two silver coated surfaces are then covered with a thin lecithin layer by dipping into a dilute solution of lecithin in diethylether. This provides a surface aligning layer to give homeotropic orientation of the nematic liquid

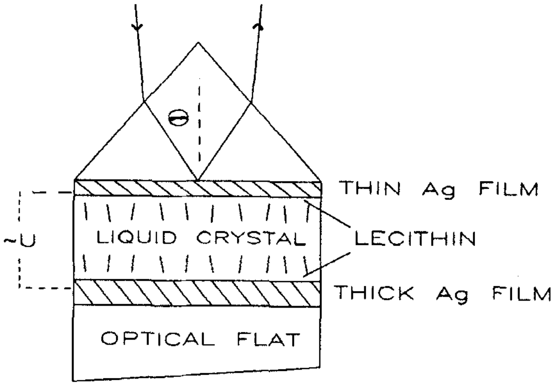

Figure 1. Schematic diagram of the sample assembly.

crystal. Finally the complete cell of coupling prism, 6 μm thick mylar spacers and optical flat back plate were assembled together in a clean room. The cell was then capillary filled with E7 (a eutectic liquid crystal mixture supplied by Merck, Poole, Dorset, England). The complete sample arrangement is illustrated schematically in figure 1.

This sample was then mounted, in an isothermal environment, on an optical system for monitoring accurately the reflectivity from the prism–silver–lecithin–nematic boundary as a function of the angle of incidence using either TE or TM polarized radiation. The reflectivity data so recorded displayed a series of sharp resonance dips corresponding to the excitation of guided modes in the nematic layer. From our knowledge of the silver parameters and ignoring the optical influence of the lecithin layer ($\sim$1 monolayer) it is then possible to determine accurately the relevant ε and the cell thickness by comparing the predictions of Fresnel reflectivity theory with the acquired data. Note that in order to give a very high signal to noise ratio the incident laser beam was modulated and the signal was detected at that frequency.

A pulsed AC (20 kHz) voltage was applied to the cell, the liquid crystal responding to the rms value, U, of the applied voltage. To avoid accumulated heating the ON time of the pulse, 20 ms, was much shorter than the OFF time, 1000 ms. The sample was rotated on a stepper motor controlled stage, and at every step in angle the pulsed voltage was applied and the reflectivity data recorded, see figure 2. The incident beam was chopped using an acousto-optic modulator operating at 100 kHz and the reflected signal detected using phase sensitive detection. Data was taken every 1 ms for each voltage pulse, beginning 5 ms before the application of the pulse and finishing after 200 ms or more. By repeatedly cycling the pulse and adding the data a very clean response could readily be recorded such as that shown in figure 3. Once this data was acquired at a given angle the sample was moved to a new angle of incidence and the

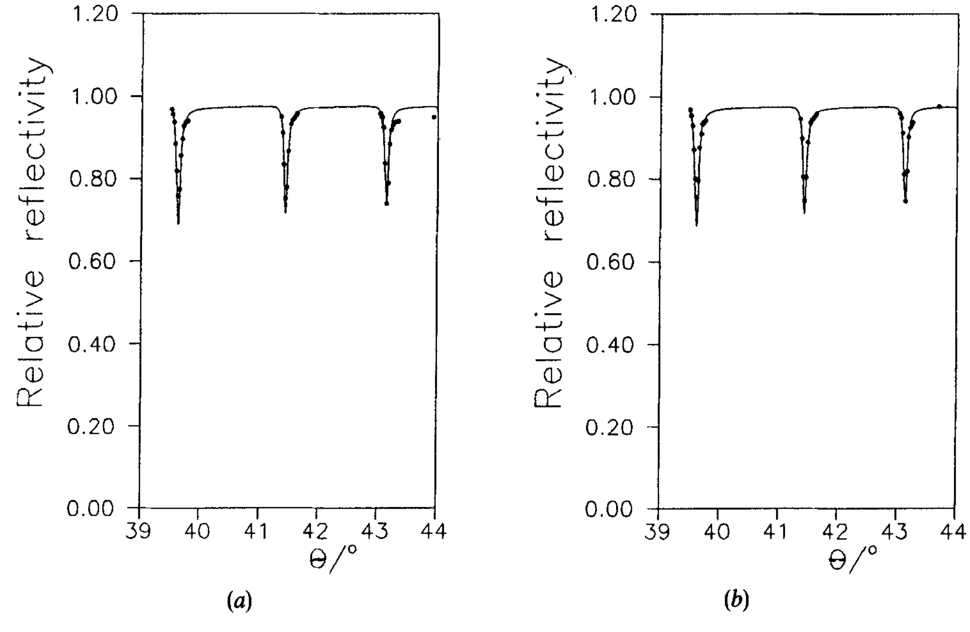

Figure 2. Reflectivity data for TE modes as a function of the incident angle, θ, showing several guided modes in a cell with a thickness of 5·99 μm, for the applied potential (*a*) $U=0$ V and (*b*) $U=25$ V.

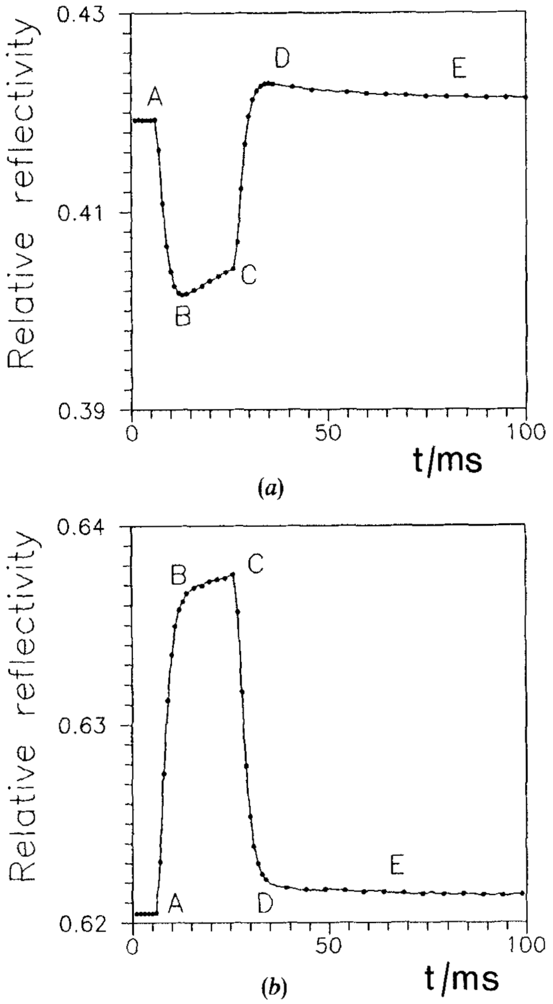

Figure 3. Reflectivity data with a pulsed voltage of 25 V obtained for a fixed angle (*a*) of 41·41°, the leading edge and (*b*) of 41·48°, the trailing edge of a TE guided mode.

process was repeated. When finally all appropriate angles have been characterized in this manner for the chosen AC voltage the procedure was repeated over the same angle scan for different voltages. The angle dependent data taken with the pulsed voltage applied, that is during the ON state of the cycle, for each angle may be compared directly with that taken at zero volts. Detailed comparison of figures 2 (*a*) and (*b*), for example in the region of the second minimum, shows that data points taken to the right of the dip move up when the voltage is ON while data points to the left move down. This corresponds to a very small shift in the position of the mode to lower angles for this polarization. The experiment was then repeated for the other polarization of the incident beam. To limit the time taken to perform the experiment only a few high order guided modes were examined because such modes are sensitive to both changes in ε and *d*. Voltages of up to 34 V were applied at which point the strong, but transient, thermal effects distort the results beyond acceptable levels.

The acquired data now have to be reduced to an appropriate form. At all angles the data taken before the application of the voltage correspond to the reflectivity data of the system for no voltage applied—the reference set. All voltage-changed reflectivities for each angle were then determined from curves such as that shown in figure 3 (*a*). Notice in this curve a turn-on time constant of ~2 ms, which is that of the signal PSD operating at 100 kHz and the slow decrease in reflectivity to point C due to a small amount of heating before the pulse is removed. Not all angles showed signals like this, for regions of figure 2 between reflectivity minima virtually no change in reflectivity was recorded during the voltage cycling. This latter behaviour is to be expected unless the application of the voltage shifts the momentum and hence the angle of excitation for one of the resonances into this region.

3. Results and discussion

E7 has a positive dielectric anisotropy and hence for the homeotropic alignment studied here no Freedericksz transition or gross director realignment will occur. Thus changes in the reflectivity data must correspond to changes in d and/or the relevant ε. For the TE reflectivity, the angle of coupling to the sharp resonant modes will depend only on d and $\varepsilon_\perp$ and hence any changes are associated only with d and/or $\varepsilon_\perp$ while for the TM reflectivity the changes are associated with d and/or largely $\varepsilon_\parallel$. Of course in this latter case since the electric field vector of the incident radiation is not along the director then the angle of excitation, corresponding to the momentum of the TM guided modes, depends also on $\varepsilon_\perp$ but to a much lesser extent than on $\varepsilon_\parallel$.

In modelling the cell we assume that both $\varepsilon_\perp$ and $\varepsilon_\parallel$ are the same throughout the cell although it is probable that in the middle of the cell there is more disorder than at the lecithin surfaces. Most data were recorded in the vicinity of the guided mode resonances. In figures 3 (*a*) and (*b*) we show the response to a 25 V pulse for reflectivities in the vicinity of a TE guided mode. The first set of data (see figure 3 (*a*)) is recorded at an internal angle of incidence of 41·41°, the low momentum side of the mode, while the second set (see figure 3 (*b*)) was recorded at an angle of 41·48°, the high momentum side. Figures 4 (*a*) and (*b*) show the reflectivity dependence, again with a 25 V pulse, for a TM guided mode. For all of these curves note that from A to B there is a voltage induced effect, from B to C we see a heating effect, from C to D there is the influence of turning the voltage off and from D to E a slow cooling process is evident. Notice for all of these traces and particularly the TM data (see figure 4) the heating effect, even over 20 ms may be substantial. It is clear that for both TE sets of data (see figure 3), heating adds to the change in reflectivity caused by the voltage, while for both TM sets (see figure 4) heating reduces the effect caused by the voltage. Now it is well-known that heating causes a decrease in $\varepsilon_\parallel$. This will tend to move the TM resonant modes to lower angles and hence the voltage induced changes in $\varepsilon_\parallel$ must represent the opposite effect, that is an increase in $\varepsilon_\parallel$. In the data of figure 2 the shifts in resonant angle are very difficult to see directly. However we are effectively detecting the differential signal by the pulsed technique which therefore easily allows a resolution of the small shifts. The reflectivity corresponding to the beginning of the voltage pulse is obtained by an extrapolation of the region BC of the curve back to a reflectivity for the ON voltage at point A. This extrapolation is straightforward since the curvature at the beginning of the signal is an exponential associated with the time constant of the detecting circuit and the thermal effect is readily modelled as a linear influence over the duration of the pulse. From such extrapolations the change in reflectivity due to the voltage alone is determined and

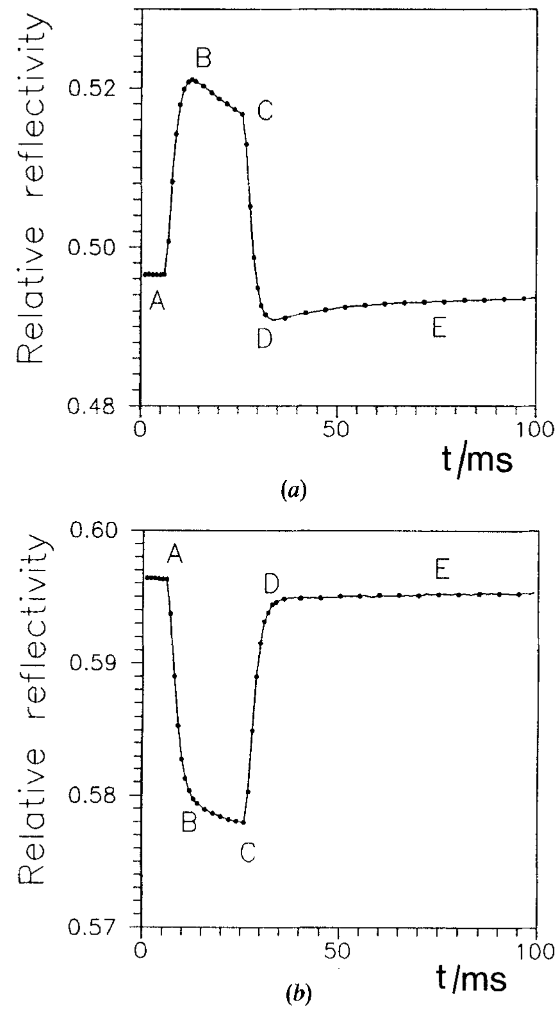

Figure 4. Reflectivity data with a pulsed voltage of 25 V obtained for a fixed angle (*a*) of 46·85°, the leading edge and (*b*) of 46·90°, the trailing edge of a TM guided mode.

hence the reflectivity data obtained as a function of voltage for the three modes studied. The shift in these modes, just visible in figure 2, can be accounted for by shifts in $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ alone, with no detectable change in cell thickness. (Any change in cell thickness shifts the lower momentum, lower angle modes more than the higher ones and thus this is easily discriminated from a change in ε which shifts all nearly equally.) After this analysis is complete, bearing in mind that the extrapolation of the pulsed reflectivity data to the voltage-on point is progressively more difficult as the voltage is increased and the temperature change becomes larger, the voltage dependent $\varepsilon_{\perp}$ and $\varepsilon_{\parallel}$ values are found as shown in figures 5 and 6. As expected, with increasing voltage, $\varepsilon_{\perp}$ decreases while $\varepsilon_{\parallel}$ increases. These results represent pure electric field effects, as the effects of thermal and possible cell dimension changes have been eliminated by the pulsing technique and carefully fitting the shifts of all three modes to Fresnel theory. Inspection of figures 5 and 6 shows that both $\varepsilon_{\perp}$ and $\varepsilon_{\parallel}$ vary approximately linearly with voltage, particularly at higher fields.

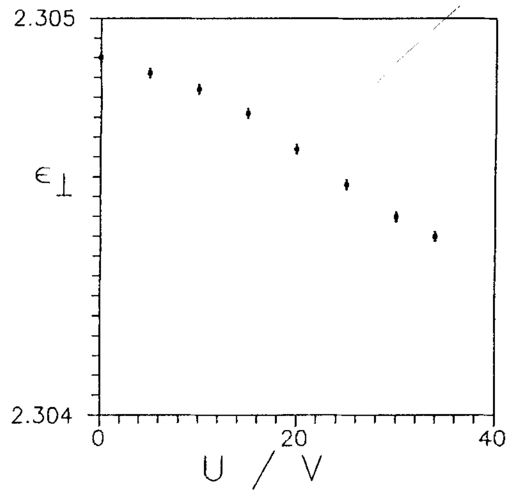

Figure 5. The voltage dependence of $\varepsilon_\perp$.

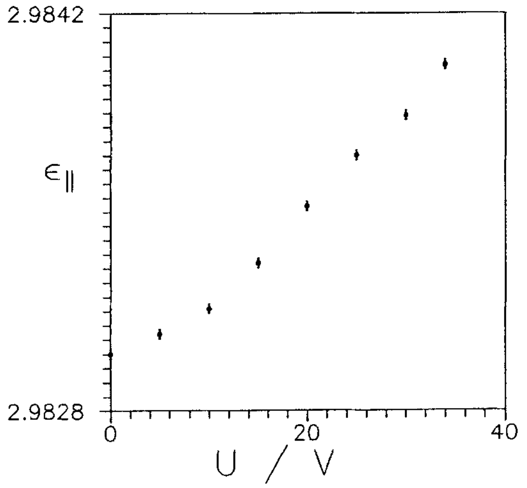

Figure 6. The voltage dependence of $\varepsilon_\parallel$.

Another combination of these parameters which has been of interest in previous studies is the refractive index anisotropy $\Delta n = n_\parallel - n_\perp$. The change in this anisotropy, $\delta\Delta n$, with voltage from its value for zero applied voltage is shown in figure 7. The magnitude of the measured anisotropy of a liquid crystal depends on its orientational order so changes in the anisotropy reflect changes to this order. As mentioned earlier, generally the Maier–Saupe order parameter, S, is used to quantify the orientational order of the liquid crystal, and it might be argued that changes in S brought about by the applied voltage are the cause of the changes we record. However, in view of the nearly linear dependence on voltage of the changes we observe it is unlikely that the changes in S can be used as an explanation since the molecular field theories give a quadratic dependence of this parameter with electric field [4]. Further, the induced order, predicted by the molecular statistical theory is likely to be much smaller than that recorded. Hence we turn to the idea developed by Faber [5] of suppression of director fluctuations, as a consequence of the applied field.

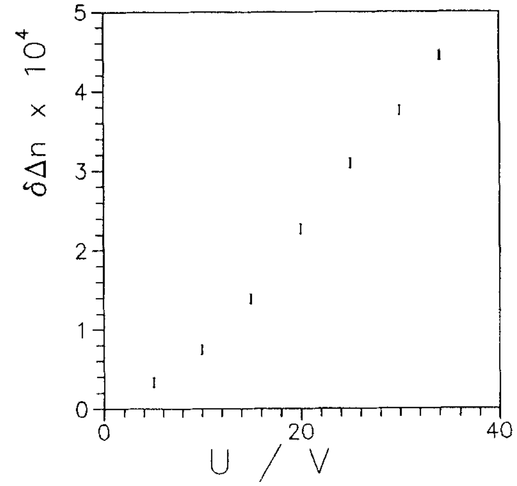

Figure 7. The variation in the refractive index anisotropy, $\delta\Delta n$ with the applied voltage, U, where $\delta\Delta n = (n_\parallel - n_\perp)_U - (n_\parallel - n_\perp)_0$.

The spatial variation of the director $\mathbf{n}(r)$ can be expressed in terms of a series of Fourier components $\mathbf{n}(q)$, having wavevector $q = 2\pi/\lambda$. Then for a uniaxial nematic, using a one elastic constant approximation, the order parameter defined through the macroscopic director fluctuations may be expressed [2] as

$$\langle S_{zz} \rangle = S_0 \left[1 - \frac{3kT}{2\pi^2} \int_{q_{\max}}^{q_{\max}} (Kq^2 + \Delta\chi E^2)^{-1} q^2 dq \right] \tag{1}$$

giving

$$\langle S_{zz} \rangle = S_0 \left[1 - \frac{3kT}{2\pi^2 K} (q_{\max} - q_{\min} - \xi^{-1}(\tan^{-1} \xi q_{\max} - \tan^{-1} \xi q_{\min})) \right], \tag{2}$$

where

$$\xi = \left(\frac{K}{\Delta\chi E^2} \right)^{1/2}$$

is a field dependent coherence length; S_0 is the average local order parameter, which is not influenced by E; K is the elastic constant and $\Delta\chi = \varepsilon_0 \Delta\varepsilon$ is the permittivity anisotropy. The final two variables $q_{\max}$ and $q_{\min}$ are defined respectively by the molecular length, l, $q_{\max} = 2\pi/l$ and the cell thickness, d, $q_{\min} = 2\pi/d$. In the present case $q_{\min} \approx 10^6\,\mathrm{m}^{-1}$ and if we let $l = 2\,\mathrm{nm}$, then $q_{\max} \approx 3 \times 10^9\,\mathrm{m}^{-1}$. We now require a value for ξ. For E7 $K \sim 15 \times 10^{-12}\,\mathrm{N}$, $\Delta\chi \approx 1{\cdot}2 \times 10^{-10}\,\mathrm{Fm}^{-1}$, so

$$\xi \approx (0{\cdot}35/E) \approx (2{\cdot}1 \times 10^{-6}/U)\,\mathrm{m}.$$

Thus even at 34 V

$$\xi q_{\max} \sim 200 \gg 1$$

and therefore

$$\tan^{-1}(\xi q_{\max}) \sim \pi/2.$$

Hence

$$\langle S_{zz}\rangle \approx S_0\left\{1-\frac{3kT}{2\pi^2K}\left[q_{\max}-q_{\min}-\xi^{-1}(\pi/2-\tan^{-1}(\xi q_{\min}))\right]\right\}. \tag{3}$$

Now we have reduced the expression to only two terms containing ξ and hence U. However the term $\xi^{-1}\tan^{-1}(\xi q_{\min})$ is to within better than two per cent just $q_{\min}$ provided $\xi q_{\min} \leqslant 0{\cdot}2$, that is for voltages over about 10 V. Since this $q_{\min}$ cancels with the earlier term then for nearly all of our data the only voltage term that matters is $\xi^{-1}\pi/2$ making the final expression

$$\langle S_{zz}\rangle \approx S_0\left\{1-\frac{3kT}{2\pi^2K}q_{\max}+\frac{3kT}{4\pi K}\sqrt{\left(\frac{\Delta\chi}{K}\right)}|E|\right\}. \tag{4}$$

Thus we have a linear dependence of $\langle S_{zz}\rangle$ on E and it merely remains to relate the observed variables to $\langle S_{zz}\rangle$. We use the following relation between refractive indices and the order parameter [6]

$$\frac{n_{\parallel}^2-n_{\perp}^2}{\langle n^2\rangle-1}=\text{constant }\langle S_{zz}\rangle \tag{5}$$

or

$$\left(\frac{n_{\parallel}+n_{\perp}}{\langle n^2\rangle-1}\right)\Delta n=\text{constant }\langle S_{zz}\rangle \tag{6}$$

giving

$$\frac{\delta(\Delta n)}{\Delta n}=\frac{\langle S_{zz}\rangle-\langle S_{zz}\rangle_0}{\langle S_{zz}\rangle_0}, \tag{7}$$

where

$$\langle S_{zz}\rangle_0=S_0\left\{1-\frac{3kT}{2\pi^2k}(q_{\max}-q_{\min})\right\}$$

$$\langle S_{zz}\rangle_0\approx S_0\left\{1-\frac{3kT}{2\pi^2k}q_{\max}\right\}. \tag{8}$$

Thus at high voltages we have

$$\frac{\delta(\Delta n)}{\Delta n}\approx\left\{1-\frac{3kT}{2\pi^2k}q_{\max}\right\}^{-1}\frac{3kT}{4\pi kd}\sqrt{\left(\frac{\Delta\chi}{K}\right)}\frac{|U|}{d}. \tag{9}$$

This result is produced within a variety of assumptions, including the approximation that the director tilt induced by thermal excitations is small and so we can neglect higher order terms. It is probable that for the higher q components this is not true and Faber [7] has derived a more exact result giving

$$\frac{\delta(\Delta n)}{\Delta n}=\frac{3kT}{4\pi kd}\sqrt{\left(\frac{\Delta\chi}{K}\right)}\frac{|U|}{d} \tag{10}$$

which also gives a linear dependence of the change in birefringence with field. For this study, with E7 the liquid crystal examined, we predict from equation (10) that for $U=1$ V $[\delta(\Delta n)]/(\Delta n)\sim 3{\cdot}1\times10^{-5}$ whilst our experimental data gives $[\delta(\Delta n)]/(\Delta n)\sim 7{\cdot}2\pm0{\cdot}6\times10^{-5}$. In view of the fact that the theory is based on a model with a single K value there is quite striking agreement.

For the lower fields when $\xi q_{\min}\gg 1$, then equation (2) becomes

$$\langle S_{zz}\rangle\approx S_0\left\{1-\frac{3kT}{2\pi^2K}\left[q_{\max}-q_{\min}+\frac{\Delta\chi}{K}\left(\frac{1}{q_{\max}}-\frac{1}{q_{\min}}\right)E^2\right]\right\} \tag{11}$$

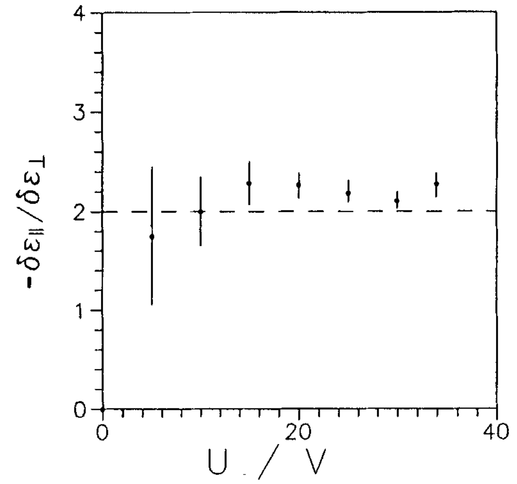

Figure 8. The ratio of the observed changes in the relative permittivities $\varepsilon_{\parallel}$ and $\varepsilon_{\parallel}$ as a function of voltage, *U*. Over a wide range of voltage this ratio is seen to be essentially constant at a value close to -2.

and a quadratic dependence on the applied voltage is anticipated. The data which, at low voltages, clearly deviate from the simple linear dependence could readily be interpreted as according well with this model. Thus it appears our data strongly support the director fluctuation suppression model for field induced changes in this system. However in establishing equation (11) it could reasonably be argued that there are problems in using $q_{\min}$ in an integral in this way. The allowed values of q may be expected to have components perpendicular to the layer which are discrete and not a continuum. In which case we should replace the integral by a sum. This is, however, probably an overcomplication, changing very little our final conclusions. Furthermore since these modes are overdamped then q should be complex and simple quantization in this fashion is probably not permissible.

One final point worthy of comment is that because we have independently determined changes in $\varepsilon_{\perp}$ and $\varepsilon_{\parallel}$ we can compare these results with the predictions for dielectric anisotropy [8] obtained from the molecular field theory. This gives $|\delta\varepsilon_{\parallel}/\delta\varepsilon_{\perp}| = 2$. We plot the data for this ratio in figure 8 where it is clear that to within better than 10 per cent this simple ratio is confirmed. It indicates that the molecular field theory expressions for $\varepsilon_{\perp}$ and $\varepsilon_{\parallel}$ may be used together with director fluctuation theory for S to give the observed ratio of permittivity changes. Although the Maier–Saupe theory gives a different dependence of S on voltage to the director fluctuation theory the ratio of the changes in $\varepsilon_{\perp}$ and $\varepsilon_{\parallel}$ are independent of this variation. Thus we have very strong supporting evidence that the changes recorded are indeed due to voltage induced changes in the order parameter.

4. Conclusion

Using optical excitation of both TE and TM guided modes in a homeotropically aligned nematic we have been able to study, using a voltage pulsing technique detailed changes in $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ as a function of voltage. The results show that applying even short, 20 ms, pulses of 25 V, 20 kHz signals causes substantial heating which normally would mask or seriously alter the deduced voltage dependent phenomenon. By careful data analysis we have measured the electric field dependent changes in both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ for fields up to $\sim 6 \times 10^6\,\mathrm{V\,m^{-1}}$ and found that for fields above $\sim 10^6\,\mathrm{V\,m^{-1}}$ these changes are linear in field. This is consistent with a description of nematics based on the concept of director fluctuations. We have also found by independently monitoring changes in $\varepsilon_{\perp}$ and $\varepsilon_{\parallel}$, that the ratio of the changes to these parameters is approximately 2 for all but the lowest voltages studied.

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