Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

A pulsed voltage study of the influence of an electric field on the optical permittivity of both smectic A and nematic phases of a liquid crystal

Lizhen Ruan[a]; G. W. Bradberry[a]; J. R. Sambles[a]
[a] Thin Film and Interface Group, Department of Physics, University of Exeter, Exeter, Devon, England

To cite this Article Ruan, Lizhen , Bradberry, G. W. and Sambles, J. R.(1992) 'A pulsed voltage study of the influence of an electric field on the optical permittivity of both smectic A and nematic phases of a liquid crystal', Liquid Crystals, 12: 5, 799 — 814
To link to this Article: DOI: 10.1080/02678299208029123
URL: http://dx.doi.org/10.1080/02678299208029123

LIQUID CRYSTALS, 1992, VOL. 12, NO. 5, 799–814

A pulsed voltage study of the influence of an electric field on the optical permittivity of both smectic A and nematic phases of a liquid crystal

by LIZHEN RUAN, G. W. BRADBERRY* and J. R. SAMBLES
Thin Film and Interface Group, Department of Physics,
University of Exeter, Stocker Road, Exeter, Devon EX4 4QL, England

(*Received 16 March 1992; accepted 22 May 1992*)

Guided optical wave techniques have been used to measure the changes in the optical permittivity of a thin, well aligned layer of a liquid crystal, 4-*n*-octyl-4′-cyanobiphenyl, as a function of applied voltage. The behaviour of both TE and TM guided modes has been studied, in the nematic and smectic A phases, using a pulsed voltage technique to avoid heating effects. Small changes of both $\epsilon_\perp$ and $\epsilon_\parallel$ have been detected, of the order of 10^{-5}, and these changes can be interpreted, for both smectic A and nematic phases, in terms of the suppression of director fluctuations. Close to the smectic A–nematic transition the observed change in $(\epsilon_\parallel - \epsilon_\perp)$ in the smectic A phase reverses in sign. This unexpected behaviour is discussed in terms of dipole–dipole interactions.

1. Introduction

It has long been established that the optical permittivity of liquid crystals are influenced by an applied electric field. For a liquid crystal in either a nematic or smectic A phase it is generally appropriate to characterize the optical permittivity by a uniaxial tensor with the optic axis along the director. (This also appears to be closely true for the smectic C and C* phases.) Then the liquid crystal is simply characterized by two relative optical permittivities, $\epsilon_\parallel$ for the applied field along the optic axis and $\epsilon_\perp$ for the applied field perpendicular to the optic axis. These two parameters are functions of excitation frequency, temperature and order parameter. Since the order parameter is influenced by an electric field then, even in the absence of gross voltage-induced realignment, these parameters may be altered via the influence upon the local order parameter.

Both microscopic and macroscopic theories for voltage dependent changes of $\epsilon_\parallel$ and $\epsilon_\perp$ through changes in the order parameter have been produced [1] and experiments have been conducted which agree to a certain extent with the theories [1, 2]. It is suggested that the changes brought about by the applied field may be through two effects. First, on a microscopic level, there will be an interaction between the applied field and the molecules both through permanent and induced dipole moments. Secondly, and possibly more importantly, fluctuations in the director, the collective descriptor of the liquid crystal, may be progressively quenched with increased applied field. For a well aligned nematic phase, it is typically the director fluctuation quenching which manifests itself. On the other hand in the smectic A phase with the

* Author for correspondence.

0267–8292/92 $3·00

extra density wave constraint it is conceivable that fluctuations of the director are reduced and it is the influence of changes of the microscopic order that is dominant.

In this study we are interested in determining the changes in optical permittivity in both nematic and smectic A phases brought about by an applied electric field. A thin homeotropically aligned liquid crystal cell was fabricated and probed optically using guided wave techniques. By use of a pulsed voltage technique to avoid what would otherwise be the dominating influence of temperature changes we were able to measure independently changes in both $\epsilon_{\parallel}$ and $\epsilon_{\perp}$. From these measurements we were then able to establish the most appropriate theoretical model for such systems.

2. Experimental

An equilateral high index glass prism ($n = 1{\cdot}80$ at $\lambda = 632{\cdot}8$ nm) was coated on one face with a thin layer (~ 40 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 with p-polarized (TM) radiation to excite the surface plasmon and subsequently fitting the resultant reflectivity versus angle data using Fresnel theory. (Typically we find for the silver films $\epsilon = -17{\cdot}8 + 0{\cdot}6i$ for a thickness close to 40 nm.) An optical flat was also coated with a much thicker layer of silver (~ 200 nm) to give a high quality mirror. These two silver coated surfaces were next covered with a thin layer of lecithin which acts as a homeotropic aligning agent. This coating was achieved by dipping both silver coated surfaces into a dilute solution of lecithin in diethylether. Excess lecithin was removed, the solvent evaporated and the prism and optical flat sandwiched together, with the silver faces spaced by 12 μm mylar spacers. This cell was now capillary filled with the appropriate liquid crystal, in this case 4-*n*-octyl-4′-cyanobiphenyl (8CB). The final, homeotropically aligned sample geometry is illustrated schematically in figure 1.

This complete sample was then mounted in an isothermal environment, on an optical system designed for the accurate determination of the angular dependent

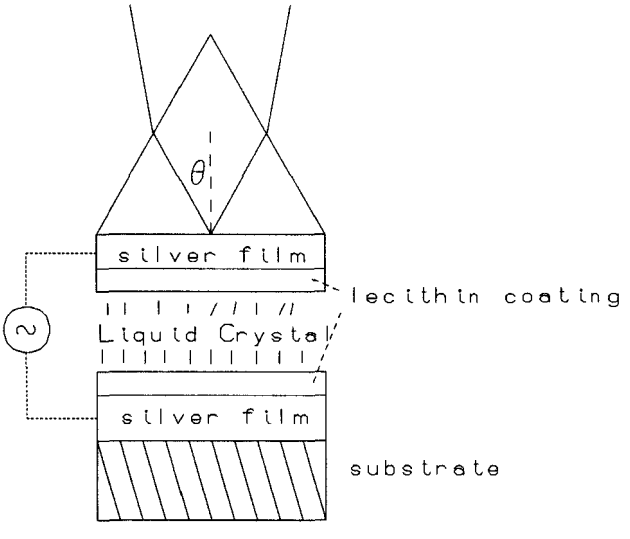


Figure 1. Schematic diagram of the sample assembly.

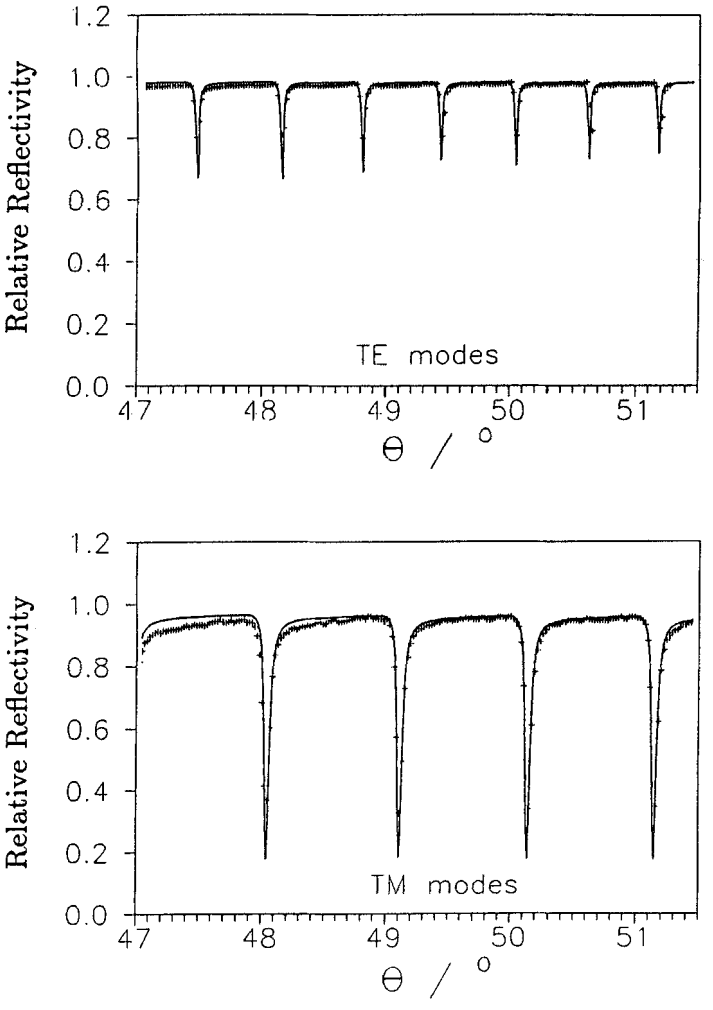
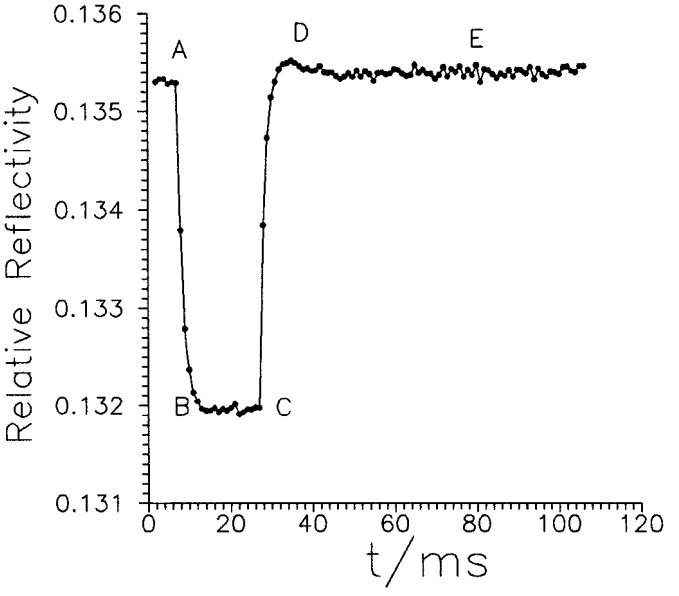
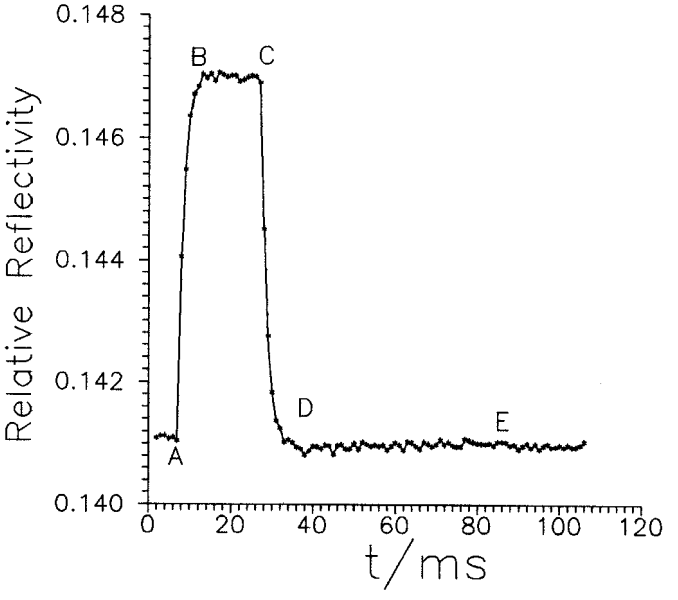


Figure 2. Reflectivity data at 30·1°C for TE and TM modes as a function of the incident angle with no voltage applied.

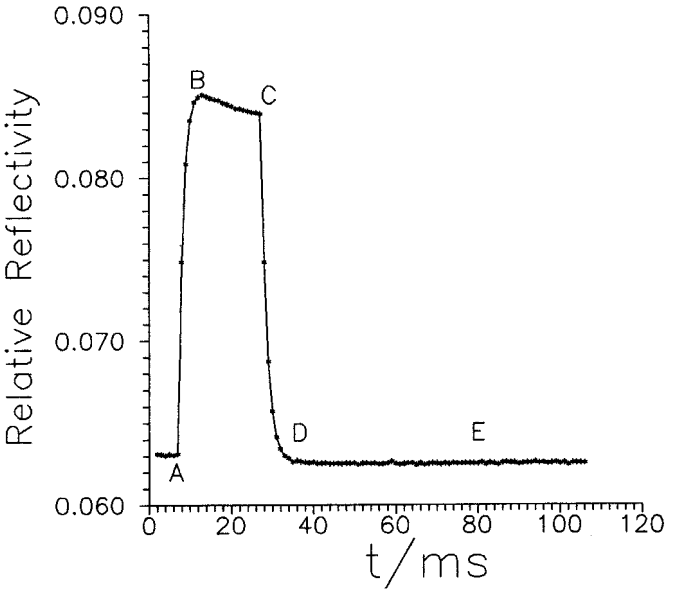
reflectivity from the prism/silver/lecithin/liquid crystal boundary. Using either pure p-polarized or s-polarized (TE) light the angle dependent reflectivity shows a series of sharp resonance dips corresponding to the excitation of guided optical modes in the liquid crystal layer. With our foreknowledge of the optical parameters of the silver it is then possible to determine accurately the relevant ϵs and thickness of the liquid crystal layer by comparing the predictions of Fresnel theory with the data. In this fitting the lecithin layers are assumed to be so thin (~ 1 monolayer) that they may be ignored. Also the liquid crystal is assumed to be a homogeneous medium since the ϵ changes we observe are small and any spatial variation of ϵ in the cell will produce a much smaller second order effect. Typical fitted data for both TM and TE angular dependent reflectivities are illustrated in figure 2. The TE modes are much shallower than the TM purely because of the strong reflectivity of the 40 nm silver layer on the entrance face. (At higher angles of incidence for the TM data there also exists a strong surface plasmon resonance.) High signal to noise was achieved here by modulating the input beam,



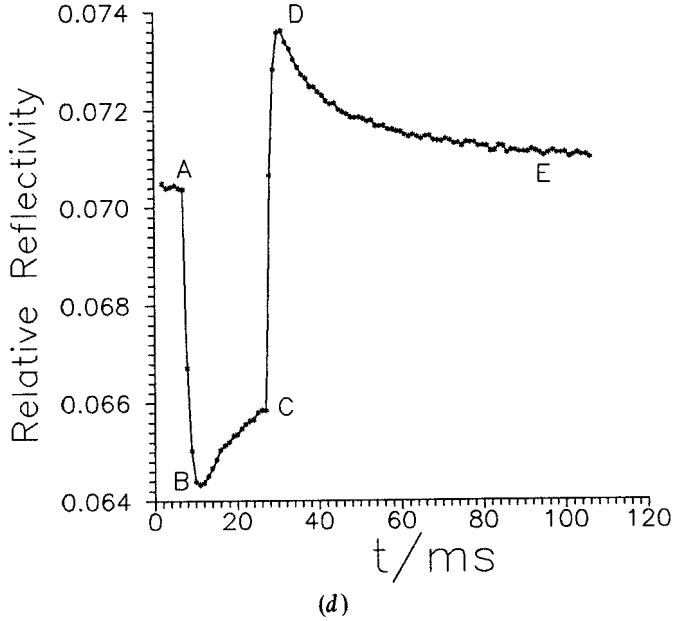
(*a*)



(*b*)

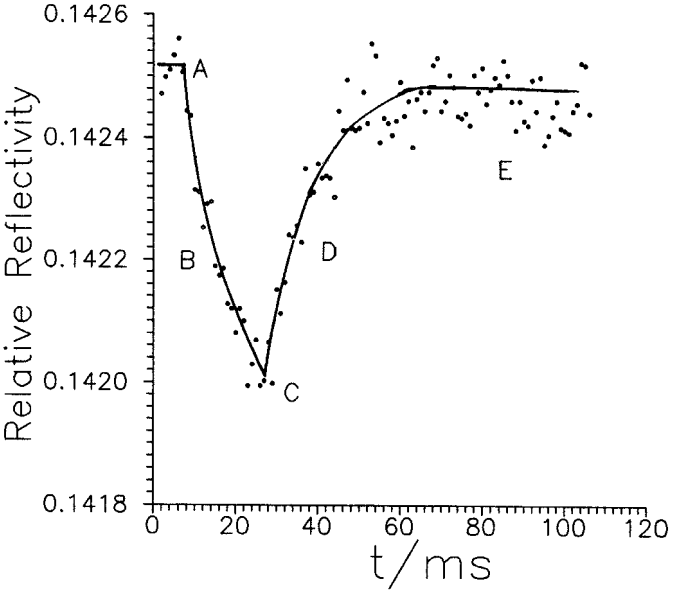


(*c*)

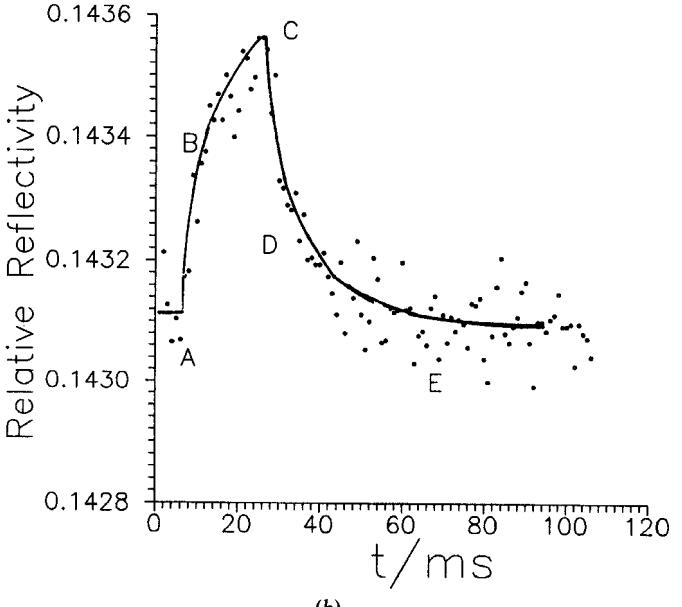


(*d*)

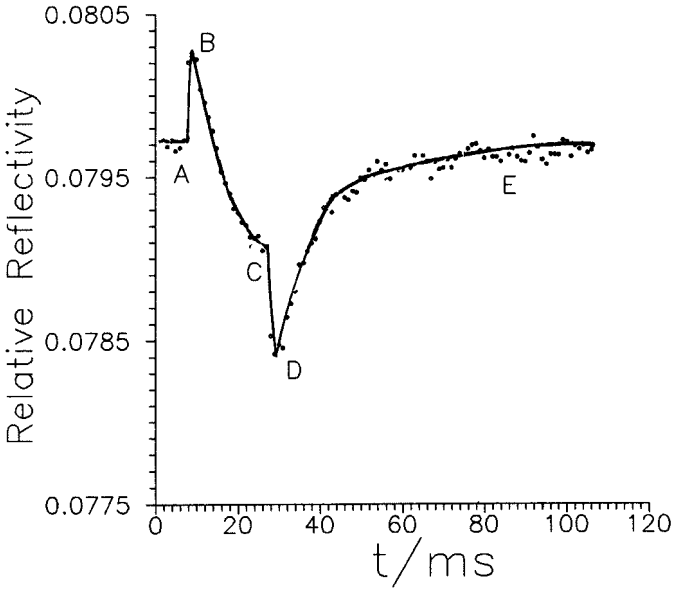
Figure 3. Reflectivity data for the nematic phase at 36·0°C with a pulsed voltage of 50 V rms and a fixed angle of (*a*) 49·19°, the leading edge of a TE mode (*b*) 49·23°, the trailing edge of a TE mode (*c*) 48·58°, the leading edge of a TM mode and (*d*) 48·62°, the trailing edge of a TM mode.



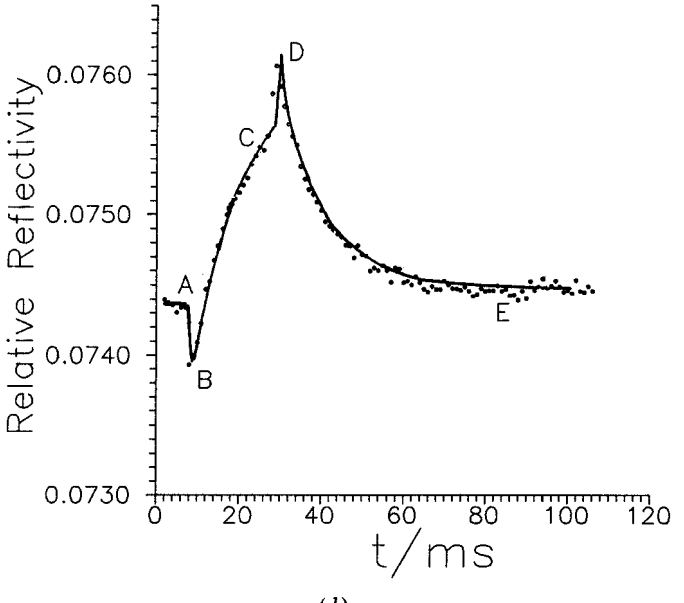
(*a*)



(*b*)



(*c*)



(*d*)

Figure 4. Reflectivity data for the smectic A phase at 30·1°C with a pulsed voltage of 54 V rms for a fixed angle of (*a*) 48·14°, the leading edge of a TE mode (*b*) 48·19°, the trailing edge of a TE mode (*c*) 48·16°, the leading edge of a TM mode and (*d*) 48·20° the trailing edge of a TM mode. The solid lines through the data have been drawn to indicate its general trend.

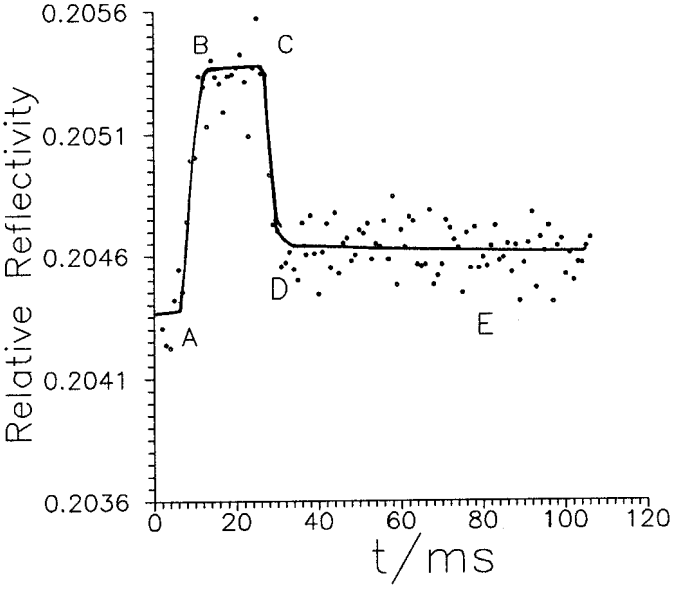
through the use of an acousto-optic modulator operating at 100 kHz, and detecting the signal using a phase sensitive detector. By fitting a series of such curves of this kind we have established values for cell thickness, d, and both $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ over the temperature range encompassing the smectic A to nematic transition.

However our primary interest here is the influence of voltage upon the parameters. If an AC signal is applied to the cell we expect the ϵ values to change and thus mode shifts to be observed in the data such as shown in figure 2. Unfortunately the expected shifts correspond to changes in ϵ of only 10^{-5} or less which is easily masked by any changes due to heating. To avoid just this effect we have used a pulsed voltage procedure. The sample was set at a given angle and a 20 kHz AC signal was applied in a cycle having a 20 ms ON time and a 1000 ms OFF time. The reflectivity was recorded every 1 ms using the phase sensitive detector operating at 100 kHz, beginning 5 ms before the application of the pulse and finishing after 100 ms or more. By repeatedly cycling the pulse and accumulating data relatively noise free responses such as shown in figure 3 were recorded. The data shown here was taken at angles within the range of one of the resonances, so shifts in intensity at fixed angle simply correspond to shifts in the angle of the resonance which is equivalent to changes in ϵ, or cell thickness, or both. This procedure was repeated for a range of applied voltages. Then, further angles were chosen and the experiment repeated. Data was also taken in a similar fashion for the other polarization before changing the cell temperature and repeating the whole procedure. Thereby we end up with a large amount of data in the form of that shown in figure 3, for the nematic phase, and figure 4, for the smectic A phase. We now have to interpret these reflectivity changes in terms of changes in $\epsilon_{\parallel}$, $\epsilon_{\perp}$ and possibly cell thickness. Of course we can very easily see, without any detailed analysis, that there is a very large difference in the response of the nematic phase to that of the smectic phase. Figure 3 (*a*) shows a reflectivity change of perhaps 5 per cent while figure 4 (*a*) (at about the same voltage) shows a change of only 0·3 per cent, an order of magnitude different. We now turn to a full interpretation of these results.

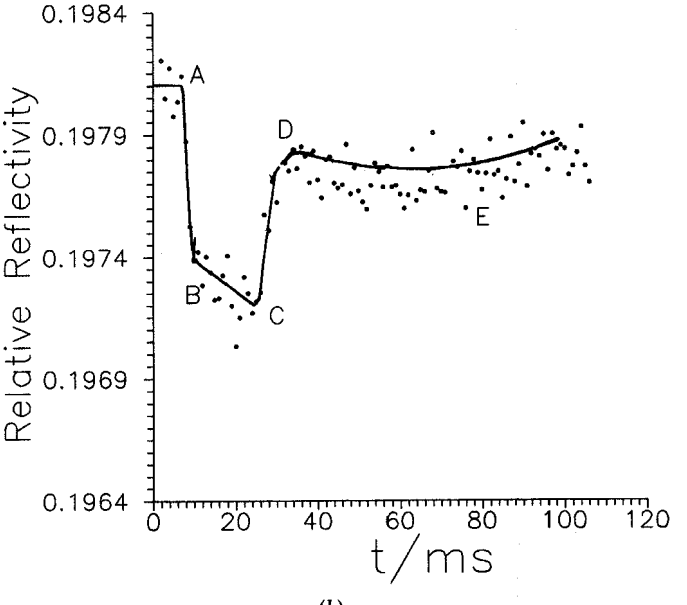
3. Results and discussion

8CB was chosen for this study since it has both smectic A and nematic phases in an easily accessible range of temperatures. From 21·5°C to 33·5°C it is in the smectic A phase while from 33·5°C up to 40·5°C it is in a nematic phase. This material was also chosen because it has a positive dielectric anisotropy, hence in the homeotropic alignment studied here no Freedericksz transition or gross director reorientation will occur under an applied field. Thus changes in the reflectivity data must correspond to changes in the relevant ϵ and/or d. For the TE reflectivity the changes are associated with $\epsilon_{\perp}$ and/or d while for the TM mode the changes are associated primarily with $\epsilon_{\parallel}$ and/or d.

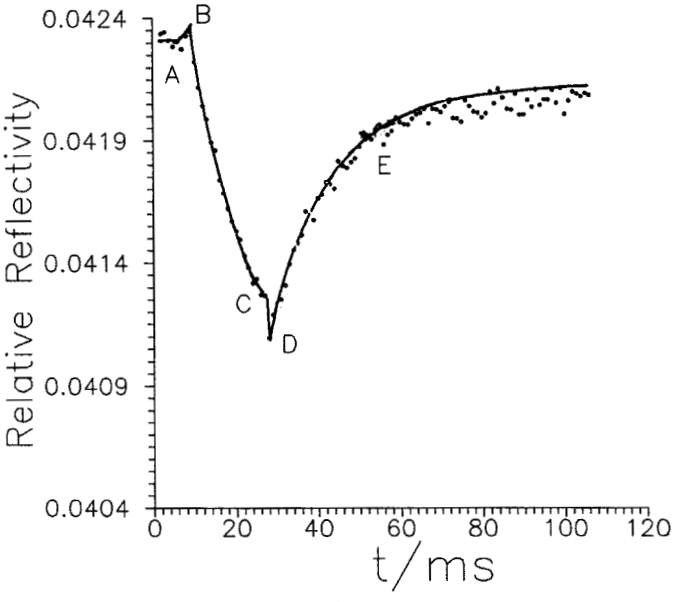
In figure 3 we show the responses of the reflectivities near TE and TM guided modes, respectively for an applied voltage of 50 V rms for the nematic phase at 36·0°C. Figure 4 shows comparative responses for the smectic A phase at 30·1°C and figure 5 shows that for the smectic A phase at 33·3°C, very close to the phase transition temperature. In all of these curves, there are fast voltage induced effects from A to B and C to D, with the time constant of the order 2 ms being dictated by the signal phase sensitive detector operating at 100 kHz. From B to C there is a heating effect and from D to E a slow cooling effect. In all cases the influence of heating is much stronger for the TM modes (c curves) than for the TE modes (a curves), simply because $\delta\epsilon_{\parallel}/\delta T$ is



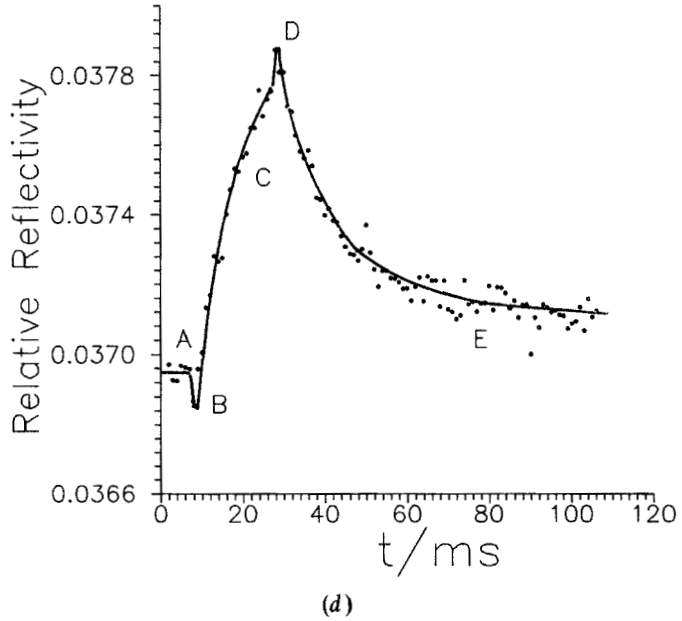
(*a*)



(*b*)



(*c*)



(*d*)

Figure 5. Reflectivity data for the smectic A phase (pulsed voltage of 53 V) very near the transition to the nematic (33·3°C) for a fixed angle of (*a*) 48·21°, the leading edge of a TE mode (*b*) 48·23°, the trailing edge of a TE mode (*c*) 44·7°, the leading edge of a TM mode and (*d*) 47·94°, the trailing edge of a TM mode. The solid lines through the data have been drawn to indicate its general trend.

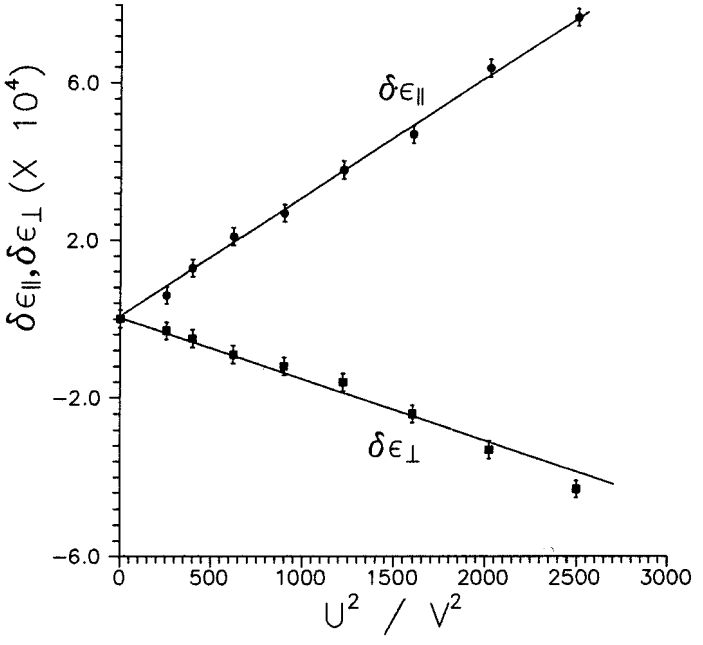


Figure 6. Variation of $\delta\epsilon_{\parallel}$ and $\delta\epsilon_{\perp}$ with U^2 for the nematic phase.

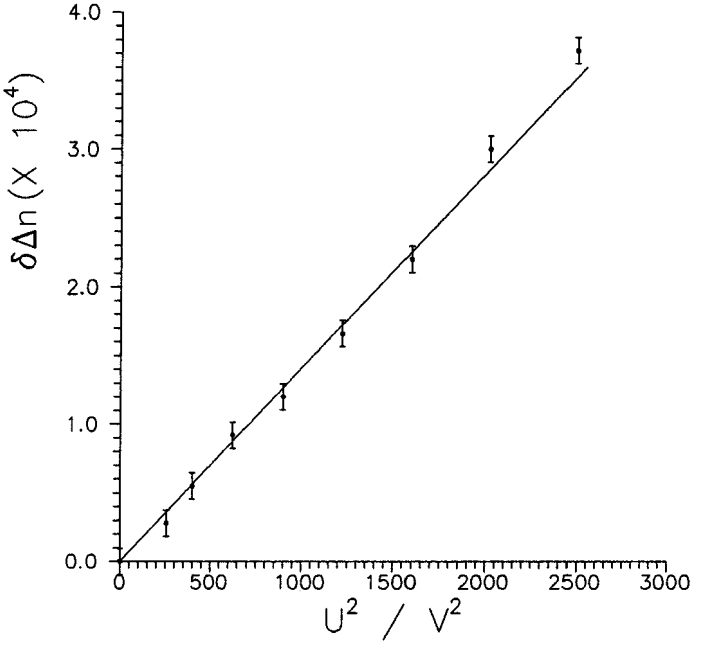


Figure 7. Variation in the refractive index anisotropy, $\delta\Delta n$, with U^2 in the nematic phase.

much stronger than $\delta\epsilon_\perp/\delta T$. Notice also the enormously increased sensitivity of figures 4(*a*) and (*b*) and 5(*c*) and (*d*) over the other data and the consequential apparent increase in noise.

For the nematic phase (see figure 3) the pulsed voltage shifts the TE modes to lower wavevectors, while the TM modes shift to increased wavevectors. Provided that d is unaffected by the applied field then the wavevector shifts observed here result from changes in $\epsilon_\parallel$ and $\epsilon_\perp$ alone. This suggests immediately that for the nematic phase $\epsilon_\perp$ decreases with increasing voltage while $\epsilon_\parallel$ increases. If there were a change in the cell thickness due to the applied field then an increase in d would move the guided modes to higher wavevectors whilst a decrease has the opposite effect. However the TE and TM modes are observed to move in opposite directions. Further, as seen later close to the smectic A–nematic transition the shifts are very small so any contribution from thickness changes has to be even smaller. Thus in the nematic phase any contribution from changes in the cell thickness is negligible. So these results for changes in ϵ, shown against U^2 in figure 6, represent pure electric field effects. It is a simple matter to obtain the change in optical anisotropy, $\delta\Delta n=\delta(n_\parallel-n_\perp)$ from changes in $\epsilon_\parallel(=n_\parallel^2)$ and $\epsilon_\perp(=n_\perp^2)$ with voltage. This is shown in figure 7 for the nematic phase. These results are very similar in magnitude to those obtained for E7 in our earlier study [3] although the linear dependence found in that case at high fields now seems to be dominated by the lower field quadratic dependence. For E7 in the nematic phase the change in order parameter induced by the electric field was interpreted as being due mainly to the suppression of director fluctuations as suggested by Faber [4]. From the continuum theory for liquid crystals the order parameter defined through the macroscopic director fluctuations may be expressed [1] as

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

where S_0 is the average local order parameter, which is not influenced by E, K is an assumed isotropic elastic constant and $\Delta\chi=\epsilon_0\Delta\epsilon$ is the permittivity anisotropy. The director fluctuations, described by the wavevector q, extend from q_{min} ($\sim 2\pi/d$, where d is the cell thickness) to q_{max} ($\sim 2\pi/d_{mol}$, where d_{mol} is of the order of a molecular length). For fields E such that $(K/\Delta\chi E^2)q_{min}\gg 1$ this equation takes the form

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

which gives the quadratic dependence observed in this case for $\delta(\Delta n)$, since $\Delta n\propto\langle S_{zz}\rangle$. It is, however, not these results for the nematic phase which concern us so much here, rather it is those for the smectic A phase (see figures 4 and 5).

As we have indicated it is clear from figure 5 that the induced changes are now much smaller than in the nematic phase. In a similar fashion to the nematic phase we plot $\delta\epsilon_\parallel$, $\delta\epsilon_\perp$ and $\delta(\Delta n)$ for the smectic A phase at 30·1°C in figures 8 and 9. The order of magnitude of the changes is only 5 per cent of that seen for the nematic phase. This is a dramatic reduction, suggesting that in the smectic phase the layering has strongly inhibited director fluctuations. It may then be more appropriate to interpret the changes as being due to the influence of the field upon the microscopic order parameter [5]. In this case we model the order induced by an external field through the Maier–

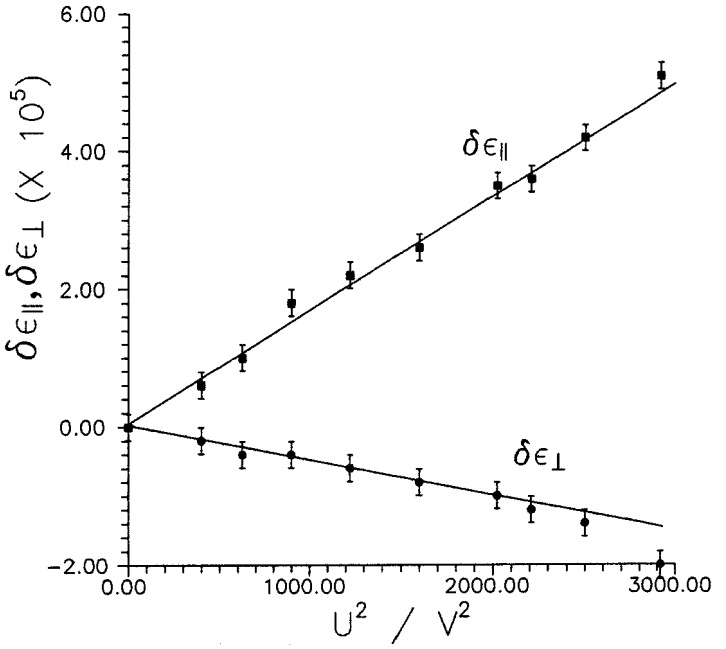


Figure 8. Variation of $\delta\epsilon_{\|}$ and $\delta\epsilon_{\perp}$ with U^2 for the smectic A phase at 30·1°C.

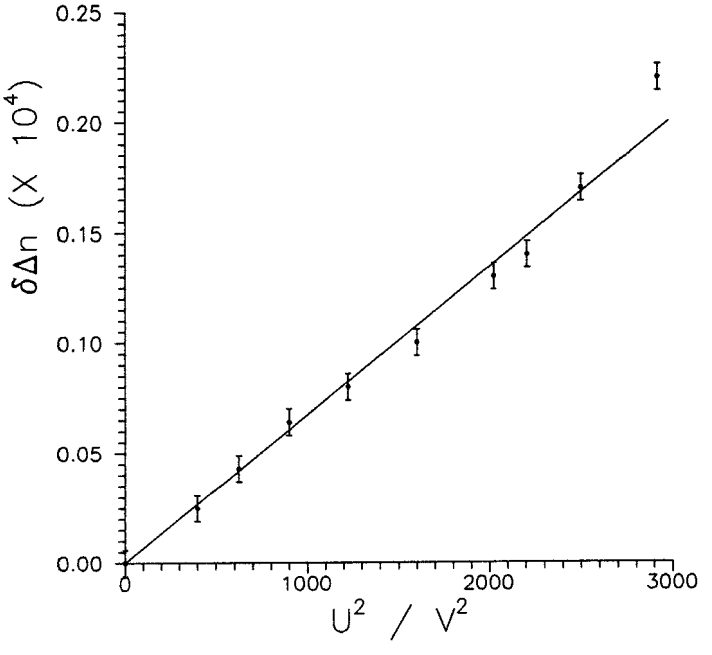


Figure 9. Variation in the refractive index anisotropy, $\delta\Delta n$, with U^2 for the smectic A phase at 30·1°C.

Saupe or Landau–de Gennes theories [6–8]. Neglecting the effects of biaxiality and internal fields the order induced by an electric field parallel to the director is given by

$$S = S_0 + \frac{\Delta\kappa E^2}{3k\pi}\left(\frac{1}{5} + \frac{2S_0}{7} + \ldots\right), \tag{3}$$

where $\Delta\kappa$ is the microscopic susceptibility anisotropy. If we now compare this with the director fluctuation suppression theory we find, for the nematic phase, that substitution of appropriate numbers makes this term less than of the director fluctuation term. Our results for the smectic A phase are however of the order of that found for the nematic phase. Hence this suggests that it is still the suppression of the now much weaker director fluctuations which cause the observed effect in the smectic A phase. Indeed since the layering can be represented by a much increased and strongly anisotropic elastic constant then we expect a much reduced quadratic dependence on the applied voltage, U, as illustrated.

So we can reasonably interpret these results in terms of suppression of director fluctuations for both phases. However we have also studied this material much closer to the smectic A–nematic transition, at 33·3°C. Now, as is apparent from figure 5(*a*) something quite extraordinary occurs. In contrast to figures 3(*a*) and 4(*a*) the data for the TE modes show an increase in $\epsilon_\perp$ with electric field, while $\epsilon_\parallel$ still appears to increase, although to a much reduced extent than at 30·1°C. On decreasing the temperature from 33·5°C to 32·5°C this reversed change in $\epsilon_\perp$ with field diminishes in magnitude and at about 32·5°C becomes immeasurable with our technique. The problem with these very small changes is that they may be confused by changes in cell thickness. However any changes in cell thickness will cause both sets of modes to move in the same direction. Thus the relative change in $\epsilon_\parallel - \epsilon_\perp$ is absolute. In figure 10 we plot $\delta\epsilon_\parallel - \delta\epsilon_\perp$ at 54 V for

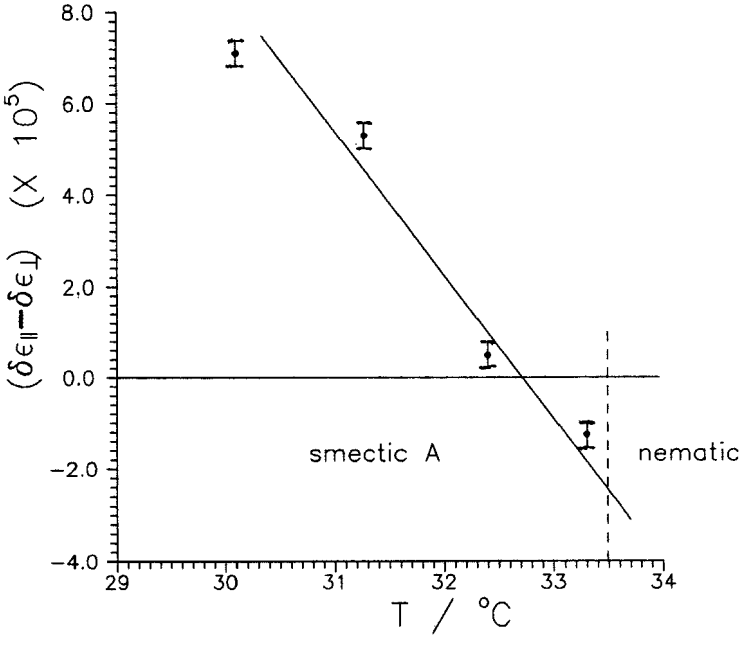


Figure 10. Variation of $(\delta\epsilon_\parallel - \delta\epsilon_\perp)$ as a function of temperature for the smectic A phase at 54 V. Note that at ~32·7°C its value goes to zero.

different temperatures, from which we see that this difference changes sign at 32·7 ±0·2°C. Hence either both $\delta\epsilon_{\parallel}$ and $\delta\epsilon_{\perp}$ become zero at this temperature or one of the two must at some stage change its sign since for lower temperatures they are opposite in sign. Either way this is a remarkable result which needs explanation.

To explain these results we need to consider physics beyond the theories so far utilised. The microscopic molecular theories do not consider dipole–dipole short range correlations. However, this dipole–dipole interaction may be expected to be rather important for dipoles situated close together in the smectic layers. Using the Kirkwood–Fröhlich theory of dielectrics [9–11] we can see that the smectic A translational ordering is likely to increase substantially the effect of dipole–dipole correlations. 8CB is a strongly polar compound [12] with overlapping head-to-tail arrangement of the molecules in the smectic phase [13]. Because of the interactions of the dipoles the longitudinal components of the molecular dipoles prefer an antiparallel mutual orientation, while the transverse ones prefer a parallel one. This effect is strongly compensated for in the nematic phase by interactions with the other dipoles. Well into the smectic phase the strong layer ordering imposes its own constraints, but close to the phase transition we have the strongly correlated dipoles but with weaker smectic layering. It is, conceivable, therefore that close to the phase transition the electric field promotes the smectic ordering, thereby increasing the dipole–dipole interactions. Then in this situation there are three factors affecting the optical permittivity. First, we have the microscopic order, which dictates S_0, and secondly the weak macroscopic director fluctuations which are partially quenched by the field. Both of these effects will act together to increase $\epsilon_{\parallel}$ and decrease $\epsilon_{\perp}$ with increasing voltage. Thirdly, there is an additional induced ordering of the dipoles, especially the antiparallel longitudinal ordering of correlated dipoles and the concurrent parallel transverse ordering which will cause a decrease in $\epsilon_{\parallel}$ and an increase in $\epsilon_{\perp}$ [11]. Very close to the phase transition it appears then that it is the influence of the electric field upon the local dipole–dipole ordering that has the strongest effect. It is of course still very small, giving for fields of $4{\cdot}4 \times 10^6\ \mathrm{Vm}^{-1}$ a negative value of $\delta(\Delta n)$ of -4×10^{-6}. On lowering the temperature a little further to 32·7 ±0·2°C the change in Δn becomes zero and on further reduction in temperature the normal behaviour returns as the layering force takes over.

4. Conclusions

Using the optical excitation of both TE and TM guided modes in homoetropically aligned nematic and smectic A phases of 8CB we have studied very small changes in the optical anisotropy induced by an applied AC field using a sensitive pulse technique. These small changes depend quadratically upon the applied voltage, with the effect in the smectic A phase being approximately an order of magnitude smaller than that observed in the nematic phase. These results are interpreted as being due to the suppression of director fluctuations, in both phases, except in the smectic A phase very close to the smectic A–nematic transition. In this region it is observed that the change in Δn passes through zero, an effect which may be related to dipole–dipole correlations in the smectic A phase.

The authors acknowledge the support and help of the University of Exeter, SERC, Dr S. J. Elston and Dr Fuzi Yang.

References

[1] DUNMUR, D. A., and PALFFY-MUHORAY, P., 1988, *J. phys. Chem.*, **92,** 1406.
[2] MACGREGOR, A. R., 1988, *J. Phys.* D, **21,** 1438.
[3] LIZHEN, RUAN, BRADBERRY, G. W., and SAMBLES, J. R., 1992, *Liq. Crystals*, **11,** 655.
[4] FABER, T. F., 1977, *Proc. R. Soc.* A, **353,** 247.
[5] DUNMUR, D. A., WATERWORTH, T. F., and PALFFY-MUHORAY, P., 1985, *Molec. Crystals liq. Crystals*, **124,** 73.
[6] HANUS, J., 1969, *Phys. Rev.*, **178,** 420.
[7] SEN, J., and WOO, C., 1981, *Phys. Rev.* A, **24,** 493.
[8] PALFFY-MUHORAY, P., and DUNMUR, D. A., 1982, *Physics Lett.* A, **91,** 121.
[9] BÖTTCHER, C. J. F., 1973, *Theory of dielectric Polarisation*, Vol. 1, 2nd ed (Elsevier).
[10] BORDEWIJK, P., 1973, *Physica*, **69,** 422.
[11] DE JEU, W. H., and GOOSSENS, W. J. A., 1974, *J. chem. Phys.*, **61,** 1985.
[12] LEADBETTER, A. J., RICHARDSON, R. M., and COLLINS, C. N., 1975, *J. Phys., Paris*, **36,** C1-37.
[13] RYDON, J. E., and COAKLEY, C. J., 1975, *J. Phys., Paris*, **36,** C1-45.