The effect of an electric field on a homeotropically aligned smectic C liquid crystal

Lizhen Ruan[a]; J. R. Sambles[a]; M. J. Towler[a]

[a] Thin Film and Interface Group, Department of Physics, University of Exeter, Exeter, England

PLEASE SCROLL DOWN FOR ARTICLE

The effect of an electric field on a homeotropically aligned smectic C liquid crystal

by LIZHEN RUAN*, J. R. SAMBLES and M. J. TOWLER

Thin Film and Interface Group, Department of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, England

A homeotropically aligned layer of smectic C liquid crystal has been studied using optical excitation of half leaky guided modes. Under the application of an AC voltage, the director configuration changes over a time-scale of the order of seconds. Fitting model results to the recorded angle dependent reflectivity data indicates firstly a change of tilt angle of the primary director, suggesting perhaps a layer tilt, and secondly a reduction of the imaginary part of the optical permittivity, implying a suppression of fluctuations. There is no evidence for a Helfrich-like deformation in the liquid crystal layer. Detailed analysis finally shows that the results are correctly interpreted as an increase in cone angle, not layer tilt, with field. Then from the fitted data, the change of tilt angle with field is obtained and hence information on the mean-field theory parameters.

1. Introduction

Recently there has been much interest in the physics of smectic liquid crystals due both to interests in fundamental science and also device application potential. Early work by Saupe and co-workers [1–3] on the theory of the smectic C phase has lately been superseded by a general non-linear theory [4], although the full implications of this theory have yet to be evaluated. One view arising from the theory is that if a homeotropically aligned cell is produced, then the density wave, assumed to have a wavevector normal to the cell surface, will, for a negative uniaxial material, distort under the application of a field. This is readily visualized if one considers the influence of the voltage on the low frequency dielectric tensor. The molecules, lying initially on average at the cone angle to the cell surface normal, will be driven to a higher tilt. Unless layer flow occurs this must result in some sort of 'puckering' of the layers in the middle of the cell, the magnitude of the distortion shrinking to zero at the cell walls. This is a Helfrich distortion [5] and the simplest mathematical solution is a sine wave distortion of the layers in the centre of the cell, with the amplitude of the wave falling to zero at the cell walls.

As far as we are aware no one has attempted to study this effect; indeed very few quantitative studies of the influence of a voltage on the homeotropic S_C alignment have been undertaken [6]. Unlike the nematic case, the smectic C case has layer constraints (the density wave), as well as orientational constraints upon the director.

In this present work we have used the half leaky guided mode technique [7, 8] to study the director configuration of a homeotropically aligned smectic C liquid crystal both with and without an applied voltage.

2. Experimental

The sample geometry used in this work is illustrated in figure 1; an approximately $5\,\mu m$ thick layer of racemic liquid crystal (SCE13R) is sandwiched between a high index ($n_1 = 1\cdot733$ at $632\cdot8\,nm$) glass plate and a low index ($n_2 = 1\cdot459$ at $632\cdot8\,nm$) glass substrate. These two different index plates, which provide the required half leaky geometry, both have a coating of a thin layer of transparent conductor (indium tin oxide, ITO). On top of these transparent electrodes is deposited a thin layer of lecithin by dipping the plates into a dilute solution of lecithin in diethyl ether. Excess of lecithin is removed by gently wiping the coated surface with lens tissue soaked in diethyl ether. By being careful to wipe the tissues in only one direction, the symmetry of the aligning surface is broken sufficiently to encourage the formation of a monodomain in the S_C phase.

The two coated glass plates are then assembled together with $6\cdot5\,\mu m$ mylar spacers in a clean room and the high index plate is placed in optical contact with a glass pyramid using a matching fluid. The glass pyramid and the matching fluid have the same index as the high index plate. This complete assembly is then placed into a temperature controlled environment and capillary filled with the
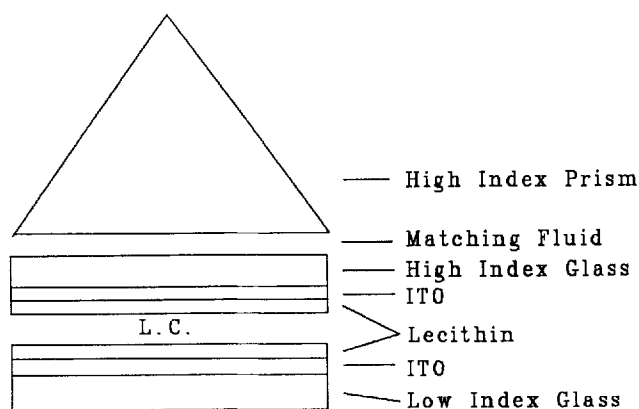
* Author for correspondence.

L. Ruan *et al.*

Figure 1. The sample cell construction used in the experiments.

liquid crystal in the isotropic phase at 120°C. Rapid cooling into the nematic phase, at about 100°C, then occurs, at which point slow cooling is initiated. In particular, very slow cooling, of the order 0·5°C per hour, through the S_A to S_C phase transition (60·8°C) is conducted so that large (> 3 mm^2) monodomains form in the S_C phase. The lowest working temperature was chosen to be 28·2°C.

In order fully to characterize the optics of the cell, data are recorded in the form of reflectivity verses angle of incidence. This is facilitated by placing the cell assembly plus thermal enclosure on to a computer controlled rotating table. Then, following the experimental procedure described in detail by Yang and Sambles [8], angle-dependent reflectivity data are recorded for a laser beam of wavelength 632·8 nm from a helium–neon laser. In these particular measurements only R_{ss} (s-polarized, transverse electric, input and output) and R_{sp} (s-polarized input and p-polarized output) were recorded and compared with theoretical models. With the gentle rubbing direction aligned to be out of the plane of incidence of the radiation, then, in the tilted S_C phase, the director lies tilted out of the plane of incidence. This means that the polarization conversion signal, R_{sp}, which is sensitive to director tilt, is quite strong.

On applying a voltage to the cell, at a frequency of 5 kHz, changes in the angle-dependent reflectivity are recorded. In figure 2 we show two sets of data, both taken at 28·2°C. One set is at zero applied volts, and the other with a rms voltage of 52·2 volts. Note the strengthening of the R_{sp} signal at the mode maxima on application of the field. This implies, without fitting in detail, an increased overall tilt of the director.

The sample is then warmed to 43·0°C and this same procedure repeated, taking data at zero and 52·2 volts rms (see figure 3). Now the changes are even more dramatic, particularly striking is the sharp mode at about 58°.

Because these changes are monitored using an angle scanning technique which takes several minutes, then a different type of experiment was conducted to examine the speed of response. Setting the sample at a fixed angle corresponding to one of the strong polarization conversion peaks (at 58·9°), a long pulse of AC voltage of frequency 5 kHz was applied and the fixed angle reflectivity recorded

Figure 2. R_{sp} reflectivity data at 28·2°C as a function of the incident angle with no voltage applied (crosses) and with an applied voltage of 52 V at 5 kHz (continuous line).
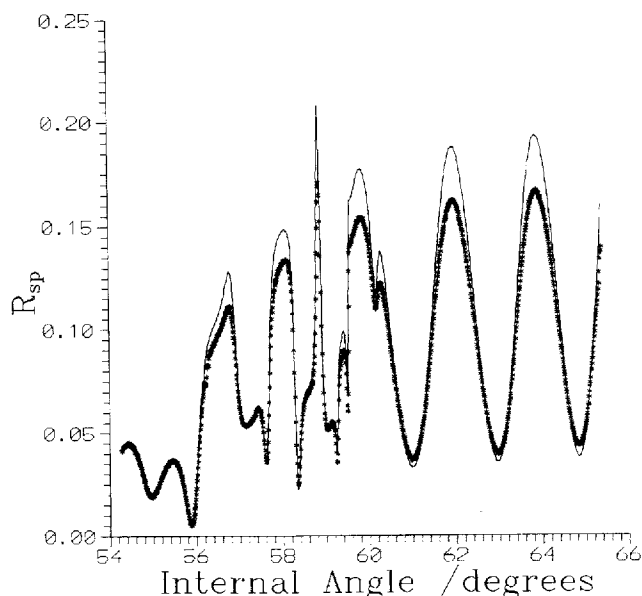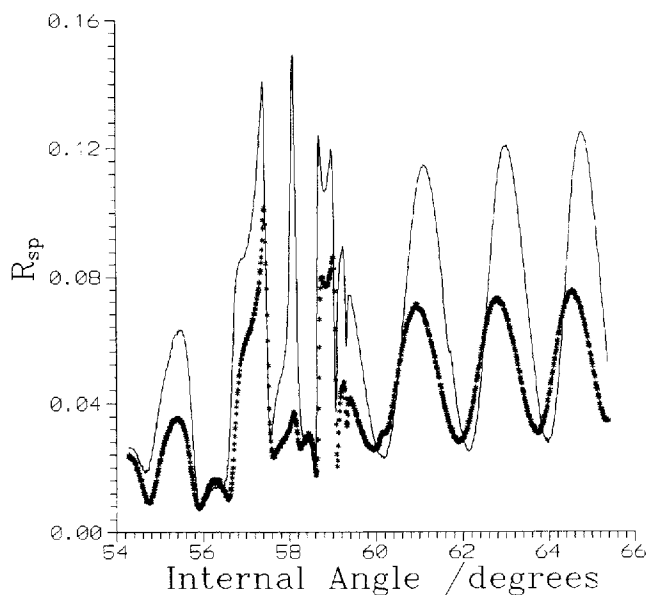

Figure 3. R_{sp} reflectivity data at 43·0°C as a function of the incident angle with no voltage applied (crosses) and with an applied voltage of 52 V at 5 kHz (continuous line).
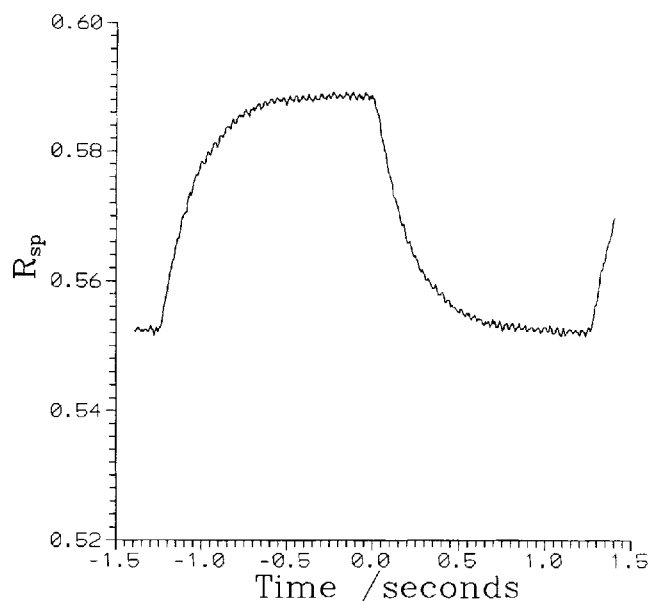
Figure 4. R_{sp} reflectivity data with a pulsed AC voltage of 13 V obtained for a fixed angle of 58·9°C at 28·2°C.

using a storage oscilloscope. The response is shown in figure 4, for a rms voltage of 13·0 volts with the cell at 28·2°C. From this trace, the very slow reorientation time (of the order of seconds) of the S_C phase is apparent.

3 Results and discussion

The first objective is to determine in detail the liquid crystal director profile in the cell at zero applied volts. From the lecithin surface treatment it is expected that the director will be primarily homeotropic with a possible small tilt reflecting the weak rubbing of the two surfaces. Cooling into the S_C phase should then result in a director tilt of the order of the cone angle in most of the cell, with the possible exception of a region near the cell surfaces. In figure 5 (a) we show our final fit that multilayer optics modelling of the director profile produces. As far as it is possible to determine, the primary director is everywhere tilted in the rubbing direction to an angle of 21° with respect to the surface normal, and has optical permittivities at 28·2°C of

$$\varepsilon_\| = 2\cdot7870 + i0\cdot0005$$

and

$$\varepsilon_\perp = 2\cdot2350 + i0\cdot0005$$

with a layer thickness of $d = 5\cdot435\,\mu m$.

Notice that biaxiality effects are insignificant for this geometry with the optical tensor configured as it is relative to the cell surfaces and the plane of incidence. Also note that the mode at about 60·2° (marked in figure 5 (a)) is very sensitive to the inclusion of any thin surface layer. Even imposing a thin layer of normally oriented liquid crystal

at the surfaces of thickness 0·01 μm destroys this mode in the modelling. Therefore it appears that for this particular mixture of racemic smectic C material the homeotropic alignment is rather weak.

On application of 52·2 volts rms at 5 kHz there is, as indicated in figure 2, a significant change in the angle dependent reflectivity. Because the material has a smaller
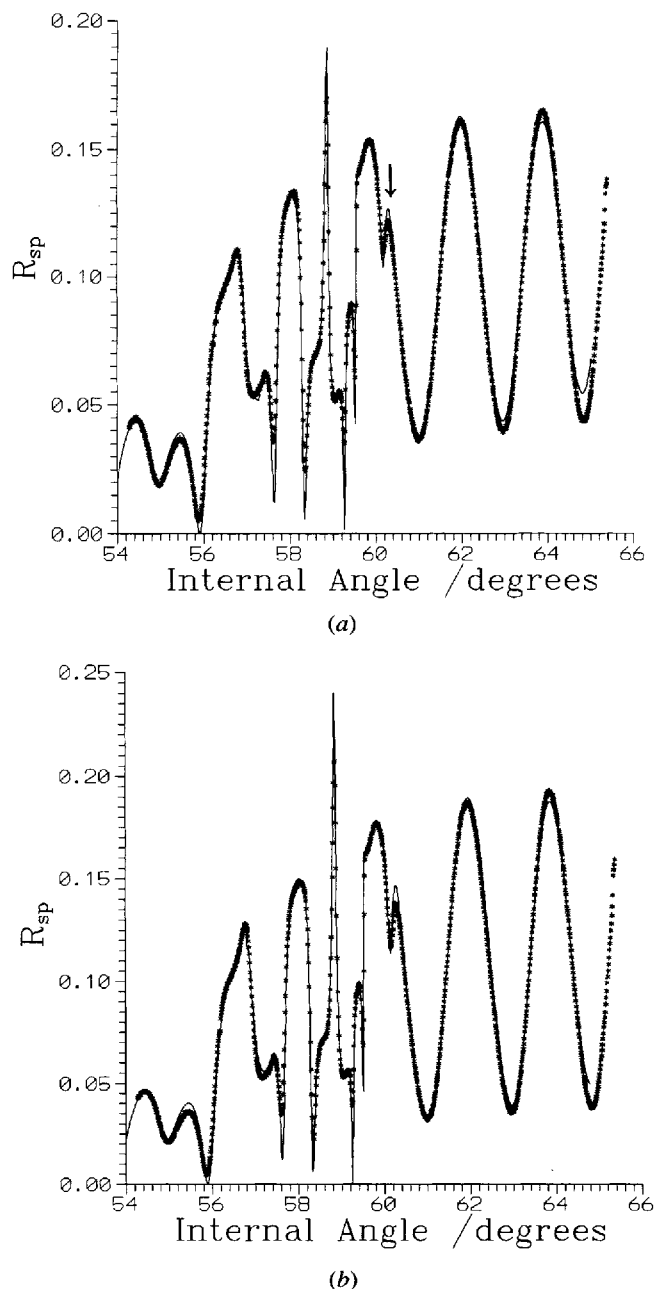

(a)

(b)

Figure 5. R_{sp} reflectivity data (crosses) and theoretically fitted results (solid line) (a) for no voltage at 28·2°C and (b) for an applied voltage of 52 V at 5 kHz at 28·2°C. Here the permittivity of ITO is 3·27 + i0·025 with a thickness of 5·30 × 10⁻⁸ m.

low frequency dielectric constant along the primary director than orthogonal to it, then under the application of a field we expect an increase in tilt. However, unlike the nematic phase, the smectic C phase has also the density wave constraint; thus it is not clear what type of dielectric distortion results on application of an electric field.

Fitting, again, model multilayer optics theory predictions to the data shows the result found in figure 5. The primary director tilt angle has now increased up to 21·7° and the imaginary parts of the optical permittivity have been reduced to 0·0003, indicating a decrease in director fluctuations. Note there are two possible interpretations of the increase in tilt angle, either we have some increase in cone angle associated with the change in free energy of the liquid crystal on application of the voltage or there is a layer (density wave) tilt. As we shall see, the first explanation satisfactorily fits all the data. There is certainly no sign of layer puckering (a sine wave) which would be the expected Helfrich type distortion, since this would cause mode broadening.

At the higher temperature of 43·0°C the experiment was repeated, now of course with a lower cone angle. Again fitting the data, figure 6 (*a*), gives a uniform tilted director of 15·3° with

$$\varepsilon_\| = 2·7530 + i0·0005,$$

$$\varepsilon_\perp = 2·2260 + i0·0005$$

and

$$d = 5·424 \, \mu m.$$

Now on application of the AC field, the reflectivity shows substantial changes. Fitting the data, figure 6 (*b*), was extremely difficult. Firstly, for most of the cell, the director had to have an increased tilt angle of 18·5°, while the imaginary parts of the optical permittivity had to be reduced to 0·00014—an even greater reduction than at lower temperature. Secondly, surface layers have to be introduced in which the director at the surface starts at 15·5° (close to the zero volt case) and increases to 18·5° over a thickness of the order 0·17 μm. The best fits were obtained using a thickness of 0·18 μm at the top of the cell and 0·16 μm at the bottom, with the assumption of a linear change in these thin layers. It appears that this surface layer is directly related to the rather large voltage induced change of tilt at this temperature. Again note that there is no evidence for layer puckering, and only for an increase in director tilt in the majority of the cell.

Now consider the final results of change of reflectivity R_{sp} at fixed angle of incidence (see figure 4). Studying this response at different temperatures in the S_C phase, at different voltages, response times of the order of seconds have been repeatedly found. Why is this? An increase in cone angle should be very fast; indeed any local molecular reorientation should be sub-millisecond. This implies
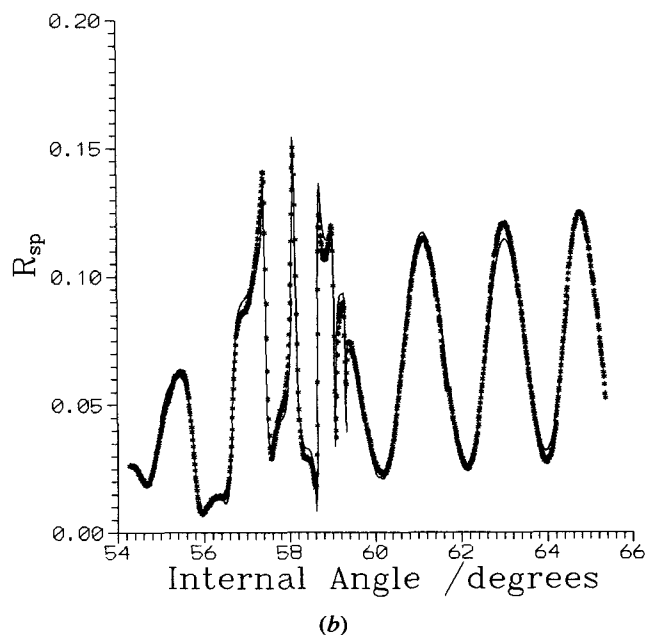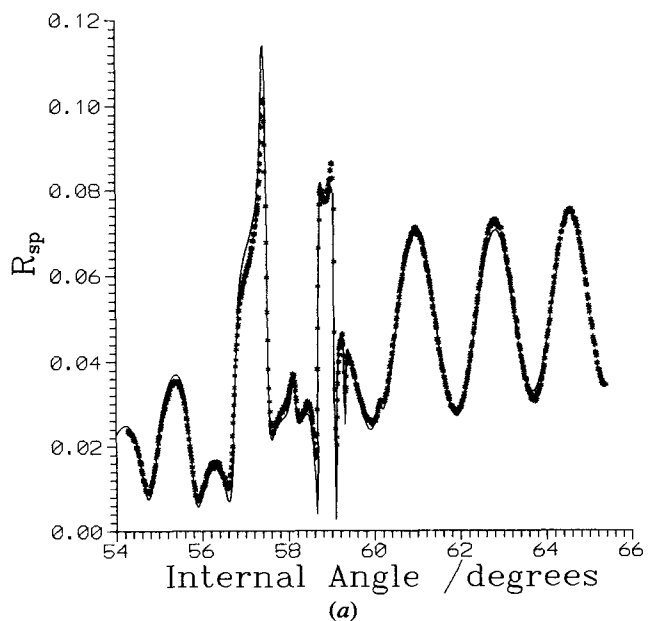

(a)

(b)

Figure 6. R_{sp} reflectivity data (crosses) and theoretically fitted results (solid line) (*a*) for no voltage at 43·0°C, and (*b*) for an applied voltage of 52·2 V at 5 kHz at 43·0°C.

some slow global process—the obvious candidate being layer flow, the result perhaps of an increase of tilt. If we suppose the cone angle does not change with voltage, then at 28·2°C it implies a layer tilt of the order 0·8°, while at 43·0°C it corresponds to 3°. If this is true, we need to ask what force prevents further layer tilting, for example, all the way to the horizontal director? Certainly it appears from figure 4 that this slow layer flow stops and a new

equilibrium is established. In the high temperature case, the fact that the layer tilt at the surface is anchored to 15·5° gives us the answer. It would appear that at the surface the molecules try to remain at the equilibrium cone angle, presumably trying to form a density wave whose wavevector is normal to the surface, while in the bulk of the cell the density wave is tilted by 3°. But how these two sets of density waves match up at the boundary is to say the least puzzling. There has to be a high density of layer-terminating defects at the boundary of the 0·17 μm thick regions near the cell surfaces. This cannot be the case since it would cause a large increase in optical scatter and mode broadening, and instead, mode narrowing is recorded. This forces the conclusion that we have to turn to the alternative explanation of increased cone angle due to the application of the field. This is simply an AC free energy effect due to the balance between the electrostatic free energy gain of increased cone angle being balanced by entropic change due to increased order parameter. The slow response time is then simply due to the speed of layer flow, parallel to the cell surface, as a consequence of the decrease in layer thickness upon increase in cone angle.

Consider a Cartesian coordinate system in the liquid crystal cell with the primary director being in the xz-plane having a tilt θ with respect to the z axis, the density wave wavevector being parallel to the z axis. Expressing the free energy in terms of the tilt angle θ we have [9]

$$F = \tfrac{1}{2}a\theta^2 + \tfrac{1}{4}b\theta^4 - \tfrac{1}{2}\varepsilon_0\Delta\varepsilon E^2\theta^2, \qquad (1)$$

where $a = \alpha(T - T_c)$, T_c being the critical temperature: α and b are the coefficients of the mean field theory, $b > 0$, and $\Delta\varepsilon = \varepsilon_\perp - \varepsilon_\parallel$ is the low frequency dielectric anisotropy.

Minimizing this free energy with respect to θ gives

$$a + b\theta^2 - \varepsilon_0\Delta\varepsilon E^2 = 0, \qquad (2)$$

which solves for $E = 0$ to

$$\theta_0 = \left(-\frac{a}{b}\right)^{1/2}. \qquad (3)$$

On application of a field, consider a change of cone angle $\Delta\theta$; then we have

$$a + b(\theta_0 + \Delta\theta)^2 - \varepsilon_0\Delta\varepsilon E^2 = 0 \qquad (4)$$

or for small fields ($\Delta\theta \ll \theta_0$),

$$\Delta\theta \approx \frac{\varepsilon_0\Delta\varepsilon}{2b\theta_0} E^2, \qquad (5)$$

the change of tilt being proportional to the square of the field. For a larger field when $\Delta\theta$ is no longer small relative to θ_0, we have to use the full expression from equation (4), with θ^2 being proportional to E^2.

In experiments presented here, while much of the data is in the low field regime, some does extend beyond the

validity of equation (5). The fit of the data to theory using equation (5) for the low field data is superb, as seen in figure 7. However, the fit can be extended to most of the data by using instead the more general equation (4); such a fit is shown in figure 8. Further our experiments show that for the highest fields ($V > 25$ volts) there is still a small deviation of the data from this expression.
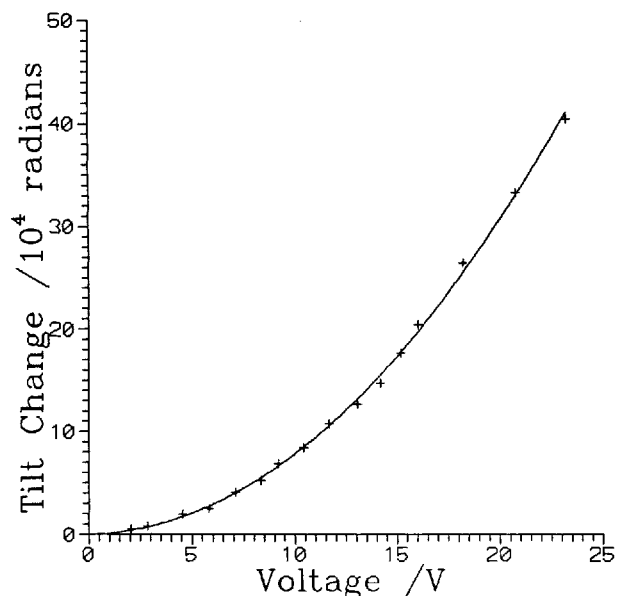

Figure 7. Voltage dependence of the director tilt change for the low field. The crosses are the data and the solid line has the functional form $\Delta\theta = 7·4 \times 10^{-6} V^2$ radian.
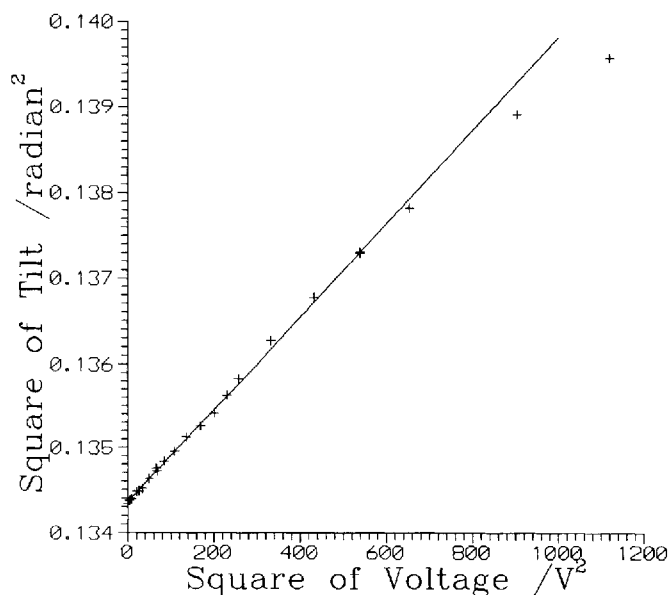

Figure 8. Square of voltage dependence of the square of director tilt for all the data. The crosses are the data and the solid line is the function $\theta^2 = 5·58 \times 10^{-6} V^2 + 0·13435$ radian^2.

From these fits we obtain the following parameter set, with $\theta_0 = 21 \cdot 0°$, $b = 5 \cdot 5(\pm 0 \cdot 2) \times 10^4 \Delta \varepsilon \mathrm{N\,m}^{-2}$ and thus with $\Delta \varepsilon = 0 \cdot 746$ [10] we find $b = 4 \cdot 1(\pm 0 \cdot 2) \times 10^4 \mathrm{N\,m}^{-2}$, and hence, from equation (3), $a = -0 \cdot 55(\pm 0 \cdot 03) \times 10^4 \mathrm{N\,m}^{-2}$. And then with $T_c = 60 \cdot 8°C$, we further find $\alpha = 0 \cdot 017$ ($\pm 0 \cdot 001) \times 10^4 \mathrm{N\,m}^{-2}/°C$.

Thus we see from this relatively simple study of homeotropically aligned liquid crystal that we have been able to obtain the fundamental coefficients of the mean field theory.

4. Conclusions

Using the half leaky guided mode technique with a homeotropically aligned liquid crystal, a racemic smectic C material, SCE13R, we have studied the director reorientation under an applied AC field. The results are interpreted as showing both an increase of cone angle with voltage and a suppression of fluctuations. In accord with the mean field theory, the cone angle change depends quadratically on the applied field. By fitting the form of the field dependence of the cone angle to the data, two of the mean field theory parameters have been determined.

References

[1] SAUPE, A., 1969, *Molec. Crystals liq. Crystals*, **7**, 59,
[2] NEHRING, J., and SAUPE, A., 1972, *J. chem. Soc. Faraday Trans.* II, **68**, 1.
[3] Orsay Liquid Crystals Group, 1971, *Solid St. Commun.*, **9**, 653.
[4] LESLIE, F. M., STEWART, I. W., and NAKAGAWA, N., 1991, *Molec. Crystals liq. Crystals*, **198**, 443.
[5] CHANDRASEKHAR, S., 1992, *Liquid Crystals*, 2nd edition (Cambridge University Press), Chap. 5, p. 313.
[6] STEPHEN, M. J., and STRALEY, J. P., 1974, *Rev. mod. Phys.*, **46**, 617.
[7] YANG FUZI, and SAMBLES, J. R., 1993, *J. opt. Soc. Am.* B, **10**, 858.
[8] YANG FUZI, and SAMBLES, J. R., 1993, *Liq. Crystals*, **13**, 1.
[9] DE GENNES, P. G., 1973, *Molec. Crystals liq. Crystals*, **21**, 49.
[10] JONES, J. C., TOWLER, M. J., and RAYNES, E. P., 1991, *Ferroelectrics*, **121**, 91.