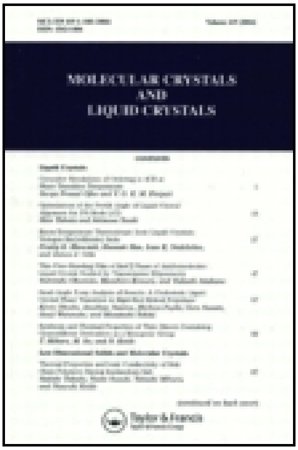

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The Pre-Transitional Effect in Antiferroelectric Liquid Crystals: a Comparison between Theory and Experiment

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The Pre-Transitional Effect in Antiferroelectric Liquid Crystals: a Comparison between Theory and Experiment

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We have investigated, experimentally and theoretically, the low field (pre-transitional) behaviour of an AFLC material. By measuring the light transmission through a device between crossed polarizers, as a function of both orientation and applied voltage, we determine the variation of both the effective optic axis tilt angle ϕ and the optical anisotropy Δn as a function of voltage. In order to model this behaviour we use an order parameter theory based on changes to the distribution of molecules within the AFLC layers rather than the *soft* mode description. With this model we have been able to describe the observed tilt and anisotropy behaviour.

Keywords: antiferroelectric; pre-transitional effect; optical anisotropy; order parameter theory

INTRODUCTION

Antiferroelectric liquid crystals AFLCs[1] are very promising materials for display applications. Their intrinsic non-linearity allows for a large number of rows to be passively multiplexed while a symmetrical driving scheme[2] ensures good resistance to ionic memory effects and makes grey scale feasible. One of the main factors limiting the exploitation of AFLCs is the so-called electroclinic-like, pre-transitional regime, observed for low fields which affects the achievable contrast and hence prevents the reproduction of a large number of grey levels. This effect, characterised by a fast response[3], reduces the immunity to crosstalk data in passively addressed displays. The nature of this regime is still not understood fully, although there is strong evidence that this is not a pure soft mode electroclinic behaviour[4].

In this paper we extend previous experimental and theoretical investigations [5,6] of this regime to consider both the static and dynamic electro-optic response. Experimentally we investigate this regime by means of accurate measurements of optical transmission of a device placed between crossed polarisers. Changes in optical anisotropy and of optic axis orientation have been separated as a function of applied voltage, together with their mutual relationship.

Subsequently we use an order parameter theory which may explain the behaviour in this regime. Instead of the usual description of smectic materials solely in terms of an average direction within a layer we include the *spread around the smectic cone* of molecules about this direction. This spread is then a measure of the order within the layer. The interaction of an applied electric field with the permanent molecular dipoles will tend to move molecules towards the preferred side of the smectic cone. The electric field will therefore cause an increase in the spread (a decrease in order) if the layer director is *not* on the preferred side of the smectic cone and cause a decrease in the spread (an increase in order) if the layer director *is* on the preferred side of the smectic cone thus altering the optic axis and optical anisotropy. Using this model we can calculate the free energy in terms of the spread in the odd layers and the even layers of the AFLC material. The energy is assumed to consist of contributions from the thermodynamic potential in each layer, the interaction between the molecular dipoles *within* each layer and *between* each layer, and the interaction between dipoles and the applied electric field parallel to the layers.

A comparison of the experimental results to the theory of previous work[5,6] and the present dynamic extension is then carried out and good qualitative agreement is found.

EXPERIMENT

We use simple low pre-tilt antiparallel rubbed polyimide aligned cells of thickness $\simeq 3\mu$m, filled with the AFLC mixture Chisso CS4000. Observation of such cells under a polarising microscope shows that a general feature is their strong tendency to form poor quality alignment with domains of two distinct orientations, being observed (Fig. 1).

Inside the domains a distribution in alignment orientation also exists, indicating that the structure in the cell is quite complex. It should also be noted that the relative density of the two types of domains varies considerably over the area of the cell.

An appropriate analytical description of the optic transmission should

Figure 1: The structure of our AFLC cell which comprises of two sets of domains oriented at an angle of approximately 17° relative to each other.

therefore take into account the domain structure of the cell. This can be done by splitting the contribution to the overall transmitted light intensity into that for the two domains, giving:

$$I = I_0 \left(A_1 \sin^2(2\psi) + A_2 \sin^2\left(2(\psi - \Delta\psi)\right)\right) \sin^2\left(\frac{\pi d \Delta n}{\lambda}\right) \qquad (1)$$

where I_0 is the incident intensity on the slab, Δn is the optical anisotropy, d is the cell thickness and ψ is the angle between the optic axis (ϕ) and the direction of incoming polarised light (Ψ) of wavelength λ. The constants A_1 and A_2 describe the relative areas of the two parts of the domain structure, and $\Delta\psi$ the difference in their average orientation. In this expression ψ is therefore the angle which the optic axis of the domains weighted with area A_1 makes with the polariser axis and $\psi - \Delta\psi$ is the angle of the optic axis for the domains weighted with area A_2. A direct evaluation of $\Delta\psi$ can be made by independently measuring under the microscope the average orientation difference of the extinction positions of the two sets of domains. For our devices it is found to be $\simeq 17°$.

The existence of a range of orientations within the domains visible in Fig. 1 is neglected, and the distribution of the orientation in each domain is approximated with the mean value. This is acceptable because the range within each domain is of the order of a few degrees and thus much smaller then $\Delta\psi$ and can be kept low if the cell is prepared carefully. No reconfiguration of the overall domain structure is observed for any field; the domains have been somehow frozen in after the phase transition and are not disturbed even during full switching. This indicates clearly that the domain structure observed is due to the smectic layer structure in the cell, and not (for example) to surface switched states of the molecular director. Thus the above description of the domain structure (eq. 1) can be used.

Data are taken for a typical device as absolute transmission between crossed polarisers (i.e. normalised to unity for parallel polarisers) at a fixed wavelength of $\lambda = 632.8$ nm.

We are interested in determining the independent variations of the optic axis orientation ϕ and the optical anisotropy Δn with voltage, so when a voltage is applied contributions to transmission variations from changes of optical anisotropy and of optic axis direction must be separated. This can be done by mapping the intensity of the light transmitted by the cell as a function of device orientation between crossed polarisers for different applied voltages. These voltages are applied as quasi-DC signals of 0 V, ± 2 V, ± 5 V, ± 10 V, ± 15 V. Now the data are fitted for each voltage to (eq. 1) with the substitution $\psi = \Psi - \phi$. The fitting parameters are A_1, $A_2, \Delta n$ and ϕ (We are measuring *relative* transmission and therefore $I_0 = 1$). Finding ϕ and Δn for each voltage enables us to find the functions $\phi(V)$, $\Delta n(V)$ and $\Delta n(\phi)$ as shown in Fig. 2. It is clear from Fig. 2a, which is a plot of $\phi(V) - \phi(0)$, that the behaviour of the director orientation with voltage is super-linear. This is in contrast with the common smectic A electroclinic effect where the re-orientation angle saturates at higher voltages for temperatures near the phase transition, and is always sub-linear (or at most linear)[7]. Such direct evidence that the AFLC electroclinic like, pre-transitional, behaviour is not a soft mode response is important in developing theoretical understanding of the effect.

The behaviour of $\Delta n(V)$ is shown in Fig. 2b. It is clear that the behaviour of the optical anisotropy as a function of voltage is approximately quadratic. The optical anisotropy versus the optic axis re-orientation is shown in Fig. 2c. It is worth noting that this is subtly different from the behaviour of Δn with voltage, being sharper around the zero re-orientation region, and being almost linear for an optic axis $\phi > 0.01$ radians. This is interesting because it leads to information about the nature of the re-orientation under an applied field, and how this is coupled to changes in the effective optical anisotropy. The dynamic response to the application of a triangular AC field of varying frequency is shown in Fig. 3. A hysteresis loop is formed as the response *lags behind* the applied field. As the frequency increases the hysteresis loop widens which causes a decrease in the maximum achievable transmission. It should also be noted that there is a

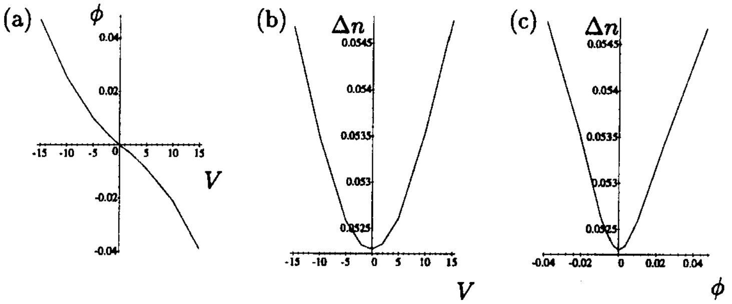

Figure 2: Experimental results: (a) Optic axis ϕ (in radians) versus voltage (in volts), (b) Optical anisotropy Δn versus voltage, (c) Δn versus ϕ.

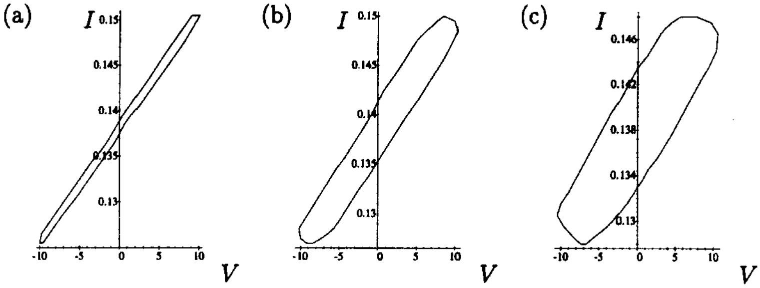

Figure 3: Transmission versus voltage for a triangular AC field of frequencies 2kHz, 10KHz and 20KHz

slight asymmetry in the response due to changes in the optical anisotropy.

In the next section we model the observed behaviour in terms of an order parameter theory.

THEORY

As in our previous, static, model[6] we assume that the average molecular direction within each layer remains the same as in the zero field AFLC state. Therefore the molecules in the odd layers are distributed on the opposite side of the smectic cone to the molecules in the even layers (Fig. 4). The mean of the distribution of molecules will remain constant whilst the extent of the spread changes with applied field. Assuming a uniform distribution of molecules between the angles $\pi - d\phi_o$ and $\pi + d\phi_o$ in the odd layers and between $-d\phi_e$ and $+d\phi_e$ in the even layers we assume that the free energy depends on $d\phi_o$ and $d\phi_e$ and may be written as

$$\begin{aligned} F &= A\left((d\phi_o - d\phi)^2 + (d\phi_e - d\phi)^2\right) + \frac{B}{2}\left(\frac{\sin(d\phi_o)}{d\phi_o} - \frac{\sin(d\phi_e)}{d\phi_e}\right)^2 \\ &\quad + E\,C\left(\frac{\sin(d\phi_o)}{d\phi_o} - \frac{\sin(d\phi_e)}{d\phi_e}\right) \end{aligned} \tag{2}$$

where the first term is the thermodynamic potential, the second term is the interaction energy between molecular dipoles and the third term is the interaction between the applied electric field and the molecular dipoles. The thermodynamic potential models the excluded volume effect in each layer and exhibits a minimum at the equilibrium values, $d\phi_o = d\phi = d\phi_e$. This term is essentially the first term in the Taylor expansion of the actual thermodynamic potential function and as such is only an approximation. By estimating the amount of spread in a nematic liquid crystal close to the smectic phase transition we set $d\phi = 0.4$ radians. The dipole-dipole interaction energy term is the sum of the self interaction of the polarization of each layer (the intralayer interaction) and the interaction between the polarizations of one layer with its adjacent layer (the interlayer interaction). If the local molecular polarization is P and the polarization vector for each molecule is $\mathbf{P}_m = P(\cos\Phi, \ ,0, \ \sin\Phi)$ where Φ is the angle between the

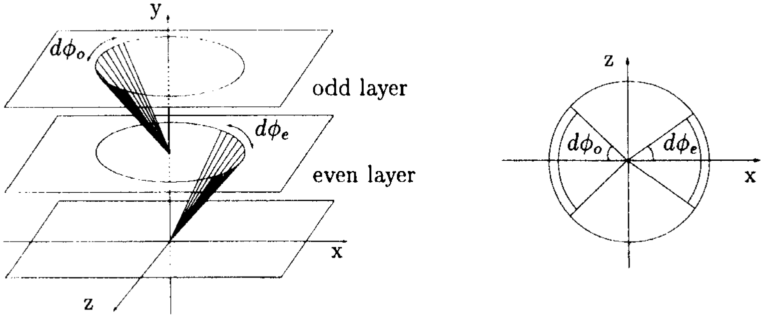

Figure 4: Molecular distributions in the odd and even layers described by the spreads $d\phi_o$ and $d\phi_e$ around the smectic cone.

dipole and the x-axis, due to the reflective symmetry of the spread about the x-axis (see Figure 4) the only contribution to the net polarization in a layer comes from the x component of $\mathbf{P}_m$. Thus integrating $P\cos\Phi$ over all molecules within the spread gives the net polarization within the even and odd layers as $P_e = P\sin(d\phi_e)/d\phi_e$ and $P_o = P\sin(d\phi_o)/d\phi_o$ respectively. The *intra*layer energy derives from the self-energy (density) of a polarization P_1 within a material of susceptibility χ which is $P_1^2/(2\chi)$ [8] and the *inter*layer energy derives from the interaction energy (density) of two polarizations P_1 and P_2 in a material of dielectric permittivity ϵ which is $-P_1P_2/(\epsilon\epsilon_0)$. Since χ and $\epsilon\epsilon_0$ are of the same order we will assume they are equal. We are able to numerically solve the system for $\chi \neq \epsilon\epsilon_0$ but since the qualitative behaviour remains unchanged we will use the constraint $\chi = \epsilon\epsilon_0$ and the sum of the intra and interlayer interactions becomes the second term in (eq. 2) with $B = P^2/\chi$. The electric field term in (eq. 2) is due to the interaction between the polarization in the AFLC layers and an applied electric field along the z-axis which may be written as $\mathbf{P}.\mathbf{E}/2$ and leads to the third term in (eq. 2) with $C = P/2$.

The dynamic equations are found by assuming that the rate of change of the variables $d\phi_o$ and $d\phi_e$ is proportional to the gradient of the free energy at that point,

$$\eta\frac{\mathrm{d}(d\phi_o)}{\mathrm{d}t} = -\frac{\mathrm{d}F}{\mathrm{d}(d\phi_o)} \tag{3}$$

$$\eta\frac{\mathrm{d}(d\phi_e)}{\mathrm{d}t} = -\frac{\mathrm{d}F}{\mathrm{d}(d\phi_e)} \tag{4}$$

where η is the viscosity of the spreading motion.

The optic axis for a single molecule is taken as the projection of that molecule on the cell plane (the xy-plane). The macroscopic optic axis in the odd and even layers, Φ_o and Φ_e, is then the average molecular optic axis of all molecules in the distributions described by $d\phi_o$ and $d\phi_e$ respectively. The overall optic axis is the average of the two layer optic axes, $\phi = (\Phi_o + \Phi_e)/2$. The optical anisotropy $\Delta n = n_1 - n_2$ is approximated using

$$n_1 = \frac{n_e n_o}{\sqrt{n_o^2\cos^2((\Phi_o - \Phi_e)/2) + n_e^2\sin^2((\Phi_o - \Phi_e)/2)}} \tag{5}$$

$$n_2 = \frac{n_e n_o}{\sqrt{n_e^2\cos^2((\Phi_o - \Phi_e)/2) + n_o^2\sin^2((\Phi_o - \Phi_e)/2)}} \tag{6}$$

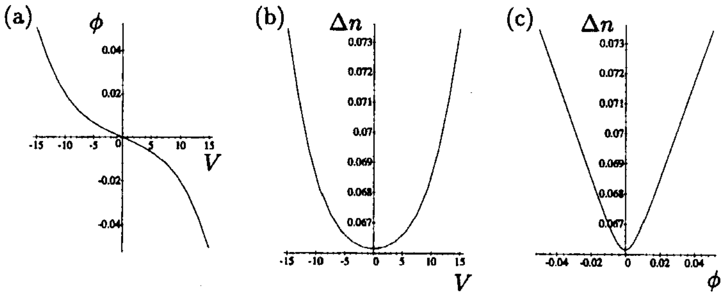

Figure 5: Theoretical results: (a) Optic axis ϕ versus voltage, (b) Optical anisotropy Δn versus voltage, (c) Δn versus ϕ.

where n_o and n_e are the refractive indices of the FLC field-induced state and θ_c is the smectic cone angle. Fig. 5 shows the optic axis versus field, Δn versus field and Δn versus optic axis plots for the parameter values $B/A = 1$, $C/A = 3$, $d\phi = 0.4$ which may be compared to Fig. 2. Figure 6 shows the dynamic response upon application of a triangular AC electric field of frequencies $f = 0.1,\ 0.5,\ 1.0$ (where frequency is measured in multiples of the parameter A/η) which is to be compared to Fig. 3. There is clearly good qualitative agreement.

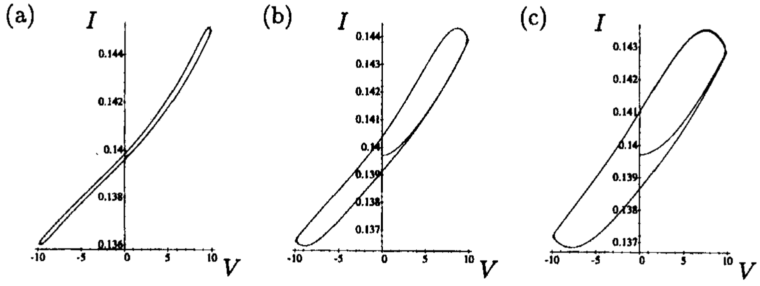

Figure 6: Transmission versus voltage for the nondimensionalised frequencies f =0.1, 0.5, 1.0 (in units of A/η).

CONCLUSIONS

We have experimentally found the optic axis and optical anisotropy as a function of voltage in the pre-transitional regime of the AFLC material Chisso CS4000 and investigated the frequency dependence of the response to an applied triangular AC field. In order to explain the static behaviour we use an order parameter theory which considers the field induced change in order in each layer of the AFLC phase[6] and extend this theory to consider the dynamical behaviour of the system. We have thus been able to show that, statically, the effective optic axis is super-linear and the optical anisotropy is quadratic as a function of (DC) field and dynamically, increasing the frequency of an applied (AC) electric field leads to a hysteretic response. Thus good agreement with the experimental evidence is obtained. Both experiment and theory support previous experimental methods which have suggested that the pre-transitional regime is *not* due to soft mode motion of the director[4,6].

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