A study of the surface anchoring at a polymer/liquid crystal interface in the neighbourhood of the glass transition

Yimin Ji[a]; Jack R. Kelly[a]; John L. West[a]

[a] Department of Physics, Liquid Crystal Institute, Kent State University, Kent, Ohio, U.S.A.

PLEASE SCROLL DOWN FOR ARTICLE

A study of the surface anchoring at a polymer/liquid crystal interface in the neighbourhood of the glass transition

by YIMIN JI, JACK R. KELLY* and JOHN L. WEST

Liquid Crystal Institute and Department of Physics, Kent State University, Kent, Ohio 44242, U.S.A.

Recently, we have observed dramatic changes in the electro-optic properties of PDLC films composed of droplets of the liquid crystal E7 in a matrix of polyvinylformal (PVFM) in the vicinity of the glass transition temperature of the matrix. One plausible explanation for these changes is a decrease in the surface anchoring strength on passing through the glass transition. For this reason, we undertook a study of the surface anchoring strength between E7 and a thin film of PVFM using the technique of Yokoyama and van Sprang. To mimic the properties of the matrix more closely, we dissolved 20 per cent E7 liquid crystal into the PVFM film. The surface anchoring for this film was compared with that of a pure PVFM film. From these data, we observed no obvious changes in the surface anchoring on passing through the glass transition of the matrix. However, the incorporation of liquid crystal into the matrix did cause a decrease in the surface anchoring strength. We discuss the impact of these results on the interpretation of the PDLC electro-optic properties.

1. Introduction

The electro-optic properties of polymer dispersed liquid crystal (PDLC) films depend on a variety of parameters: the types of liquid crystal and polymer material; the solubility of the liquid crystal in the polymer; droplet size, shape and density; the PDLC film thickness; the working temperature and so on [1,2]. In a recent investigation we studied the response of the liquid crystal E7 in a polyvinylformal (PVFM) matrix and found that the drive voltage and turn-off time of these films change abruptly as the temperature is raised above the glass transition temperature (T_g) of the PVFM matrix. Also, we observed essentially no hysteresis below, but significant hysteresis above T_g [3]. Studies of the dielectric response of PDLC films have demonstrated that the driving voltage can be dramatically increased by conductive shielding of the applied field [4, 5]. However, for this system, no electrical or mechanical process was observed that could explain these results. We hypothesized that these changes result from a decrease in the (homogeneous) surface anchoring strength on passing through the glass transition temperature. To test this hypothesis, we studied the surface anchoring strength between E7 and a thin film of PVFM.

2. The experiment

We performed our experiments using two samples, each consisting of two $1 \times 1\frac{1}{4}$ in by $\frac{1}{4}$ in thick glass plates with transparent, patterned ITO electrodes joined to form a sandwich-type cell with a nominal gap of 60 μm. The gap was maintained with mylar strips. We prepared these two samples as follows: one was coated with a

* Author for correspondence.

solution of PVFM (1 per cent by weight) and $CHCl_3$ (99 per cent as solvent), and the other was coated with a solution of E7 (0·2 per cent), PVFM (0·8 per cent) and $CHCl_3$ (99 per cent) which we used to mimic the properties of the PVFM matrix of PDLC films more closely. The amount of liquid crystal remaining in the polymer matrix after phase separation was estimated by differential scanning calorimetry; the shift of the PVFM glass transition in the phase separated PDLC films (33°C) corresponded to that observed in an 80/20 mixture of PVFM and E7. At 20 per cent E7, no phase separation occurs and the liquid crystal acts as a plasticizer of the polymer. Each solution was coated onto two pieces of glass plate by spin coating at 2000 rpm for 30 s, then heated in an oven at 95°C for 90 min to drive out any remaining solvent. The coated films were about 0·2 μm thick as measured by a mechanical profilometer. The direction of planar homogeneous alignment of the liquid crystal was set by rubbing the coated films by hand with a velvet cloth. The cells were then capillary filled, with flow along the rubbing direction. Good homogeneous alignment was verified with a polarizing microscope. The thickness of the liquid crystal layers of the two cells was determined to be 63·5 μm (PVFM/E7) and 67·6 μm (PVFM) at the centres of the overlapping ITO areas by an optical interference method [6] prior to filling the cell with the liquid crystal. The overlap area of the ITO was about 1·327 cm² for both cells.

To control the temperature, the samples were placed in a specially designed brass oven that is capable of holding the temperature within ±5 mK over 24 h.

To determine the anchoring strength, we followed Yokoyama and van Sprang's method [7]. This method requires simultaneous measurement of the birefringence and capacitance of a homogeneously aligned NLC cell as a function of applied voltage. A sinusoidal AC voltage (1 kHz) was applied in small increments from 0 V to 165 V. At each voltage the capacitance was measured with an HP4284A precision LCR meter, and the birefringence was determined by monitoring the phase retardation of linearly polarized light from an HeNe laser [8]. The phase retardation of the light exiting the cell was monitored electronically using a polarizer, controlled by a stepping motor, in series with a photo-diode and amplifier whose output was fed to a Keithley 199 System DMM Scanner. All equipment was interfaced to a computer via either an IEEE-488 parallel interface or an RS-232 serial interface. Figure 1 shows a schematic diagram of the measurement system. With this system, we could determine the retardation to within 0·1°, and the capacitance to within 0·1 pf.

3. Results

The addition of liquid crystal into a thermoplastic has the principal effect of acting as a plasticizer, lowering the polymer's glass transition temperature. We confirmed the shifting of the glass transition temperature of PVFM by differential scanning calorimetry. According to DSC scans, a film composed of PVFM/E7 in a weight ratio of 4 : 1 has a T_g at 33°C; a pure PVFM film has $T_g = 78$°C, which is above the clearing temperature of E7 liquid crystal ($T_{NI} \sim 60$°C).

According to the analysis of Yokoyama and van Sprang [7], when the applied voltage, V, becomes much larger than the Fréedericksz threshold ($V > 6 V_{threshold}$ is sufficient), the following relation between the retardation, R, the applied voltage, V, and the capacitance, C, holds for a cell of thickness d
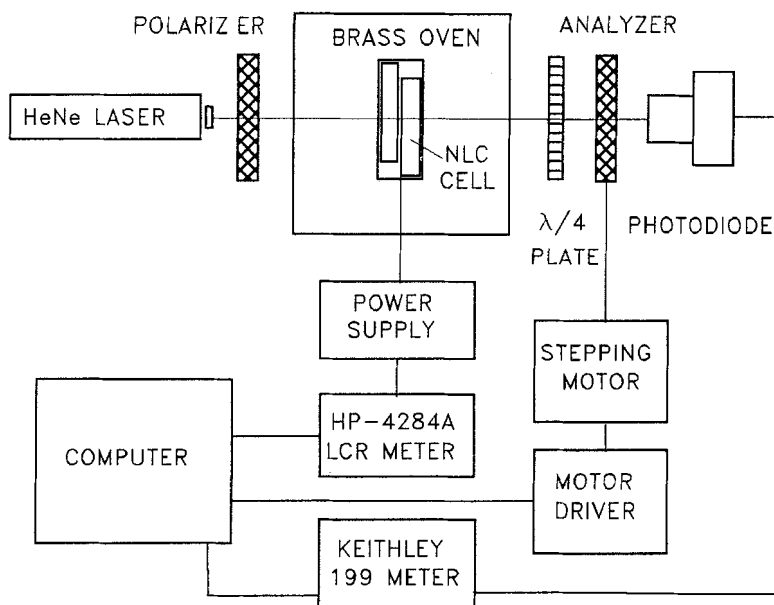
Figure 1. Schematic diagram of the measurement system.

$$\frac{R}{R_0} = \frac{I_0}{CV} - \frac{2d_e}{d}.$$ (1)

I_0 is a constant independent of voltage—but depending on material properties and cell geometry—and R_0 is the retardation at $V=0$. R_0 is known in terms of the birefringence of the liquid crystal, Δn, and the wavelength of the incident light, λ.

$$R_0 = \frac{2\pi d \Delta n}{\lambda}.$$ (2)

The surface extrapolation length, d_e, can be obtained from the intercept on a plot of R/R_0 versus $1/CV$. The surface anchoring strength, W_0, is directly related to d_e; in particular, for the Rapini–Papoular surface potential, $W_0 \sin^2 \theta$, we have

$$W_0 = \frac{K_1}{d_e},$$ (3)

where K_1 is the splay elastic constant. We note two limiting cases: $W_0 \rightarrow \infty$; as $d_e \rightarrow 0$ and $W_0 \rightarrow 0$ as $d_e \rightarrow \infty$.

Above, θ is the angle that the director makes with the easy direction at the Gibbs surface [9]. This need not coincide with the interface, and likely will not, since there generally exists a surface layer of finite thickness, ξ, inside of which the behaviour of the liquid crystal differs from the bulk. For comparison with experiments, we need a microscopic model, i.e. one that describes the structure in the surface layer. To this end, the usual approach is to take the true interface as the Gibbs surface. Some care is required when interpreting results obtained in this way. It is obvious that the microscopic picture has broken down when logically inconsistent results are

obtained, such as a negative extrapolation length; but even when the results are not logically inconsistent, they may be wrong. As noted by Yokoyama, the surface anchoring strength is a good thermodynamic quantity, but it may not give a realistic microscopic description of the interfacial energy [9].

Figure 2 shows the experimental results of relative retardation R/R_0 versus $1/CV$ at 20°C, 50°C and 57°C for the 80 per cent PVFM/20 per cent E7 film. We obtain straight lines, as predicted, with both negative intercepts $(T > 52°C)$ and positive intercepts $(T < 52°C)$. The more negative the intercept, the weaker the anchoring strength.

The temperature dependence of the extrapolation length is shown in figure 3. Below 52°C the extrapolation length becomes negative. From a microscopic point of view, the largest value of the intercept should be zero, corresponding to infinite anchoring strength $(W_0 \rightarrow \infty, d_e \rightarrow 0)$. Although we have used the Rapini–Papoular potential to define W_0, this is true for any surface interaction that has a delta function dependence at the interface. To account for the negative d_e, there must be a surface layer of finite extent which properties differ from the bulk.

For infinite anchoring, according to equation (1), RCV = constant at higher voltages; deviations only occur when the effects of finite anchoring become important $(d_e \neq 0)$. To study this, we plotted RCV/R_0 versus V at several temperatures; representative results are plotted in figure 4. For temperatures very near the clearing temperature, deviation from a constant value has negative slope and occurs at relatively low fields. As the temperature is reduced, the extrapolation length decreases and a continuously higher voltage is required to see deviations from infinite anchoring. This is the behaviour one typically imagines: the anchoring goes from weak to strong as we move to lower temperatures. However, when the
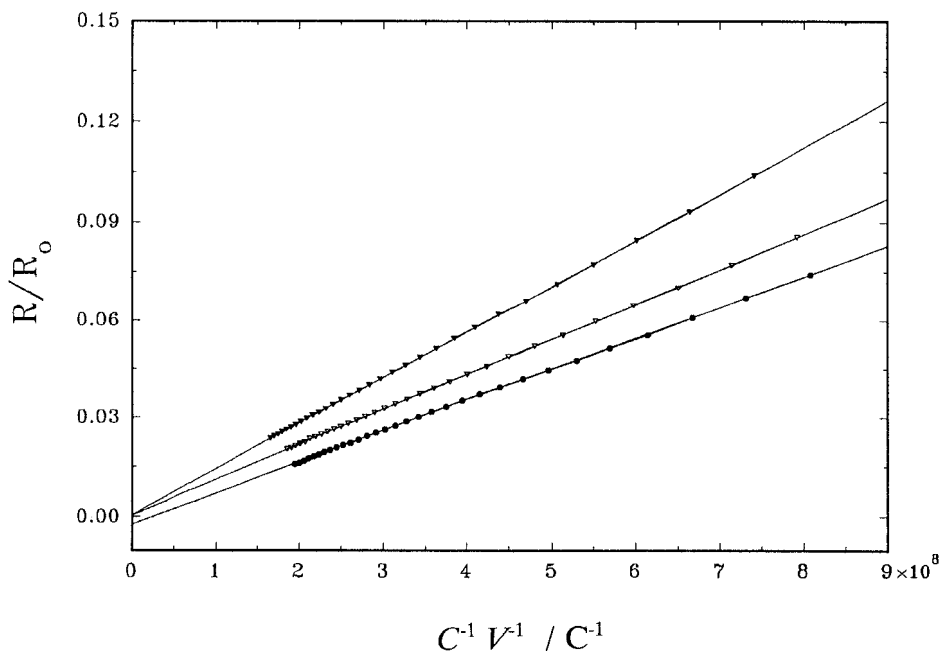
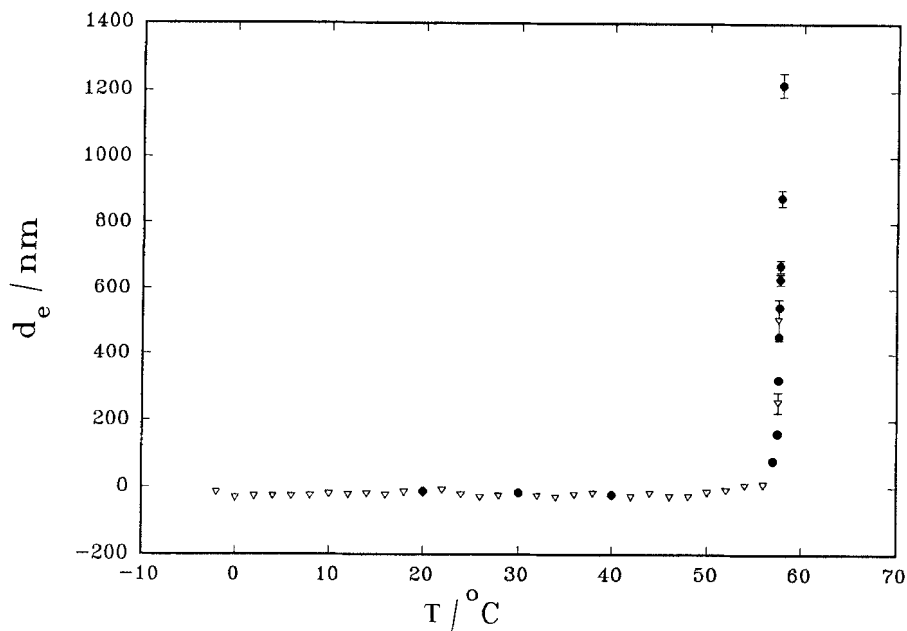Figure 2.   Relative phase retardation R/R_0 versus $1/CV$ at 20°C (▼), 50°C (▽) and 57°C (●).

Figure 3. Temperature dependence of the surface extrapolation length for the (●) PVFM and (▽) PVFM/E7 20 per cent sample.
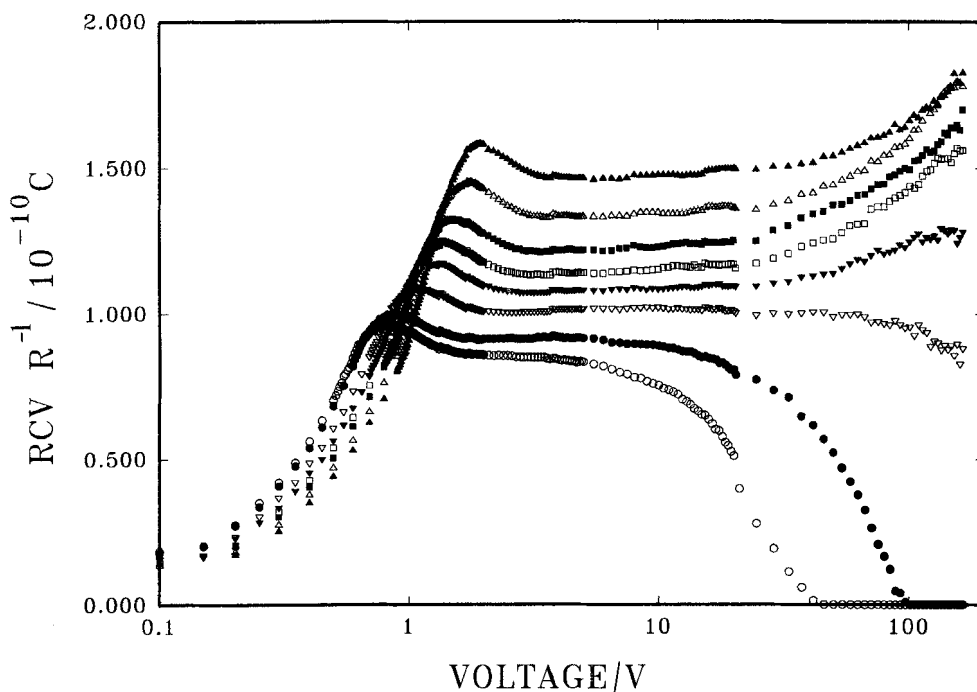

Figure 4. RCV/R_0 versus applied voltage at 57·5°C (○), 57°C (●), 54°C (▽), 50°C (▼), 46°C (□), 40°C (■), 28°C (△) and 12°C (▲).

extrapolation length crosses over to negative values, the finite surface effects again are seen at lower voltages. Deviations in this regime have positive slope and occur at voltages as low as 20 V. Apparently, the surface layer is playing a major role in the response even at relatively low fields (as low as ~ 0.3 V μm^{-1}).

The extrapolation length remains constant at approximately -20 nm for temperatures below 50°C. This temperature independent behaviour has been observed previously for a liquid crystal–SiO interface [10] and a liquid crystal–polyimide interface [11]. However, in those cases, the extrapolation length remained positive at lower temperatures.

Figures 5 and 6 are two typical examples of relative phase retardation change with applied voltage at 50°C and 57°C. The gross behaviours of the two response curves are very similar. However, we can clearly see a marked difference in the high field behaviour. Under weaker anchoring at 57°C, the saturation voltage is below 100 V, but under stronger anchoring at 50°C, the saturation voltage is an order of magnitude higher. If we define the electrical coherence length in the usual way by $d = [\sqrt{(K_1/\varepsilon_0 \Delta\varepsilon)}/V]$, we find that the electrical coherence lengths at saturation for these two temperatures are ~ 200 nm and ~ 20 nm, respectively ($K_1 \approx 10^{-11}$ N, $d \approx 60$ μm, and the dielectric anisotropy $\Delta\varepsilon \approx 9$).

Figure 7 shows the experimental results for the anchoring strength versus temperature in the vicinity of the clearing point. Here there are easily observable differences between the two types of film. For both films, the anchoring strength decreases rapidly with increasing temperature, but the anchoring strength for the coating with 80 per cent PVFM/20 per cent E7 is weaker than that with pure PVFM
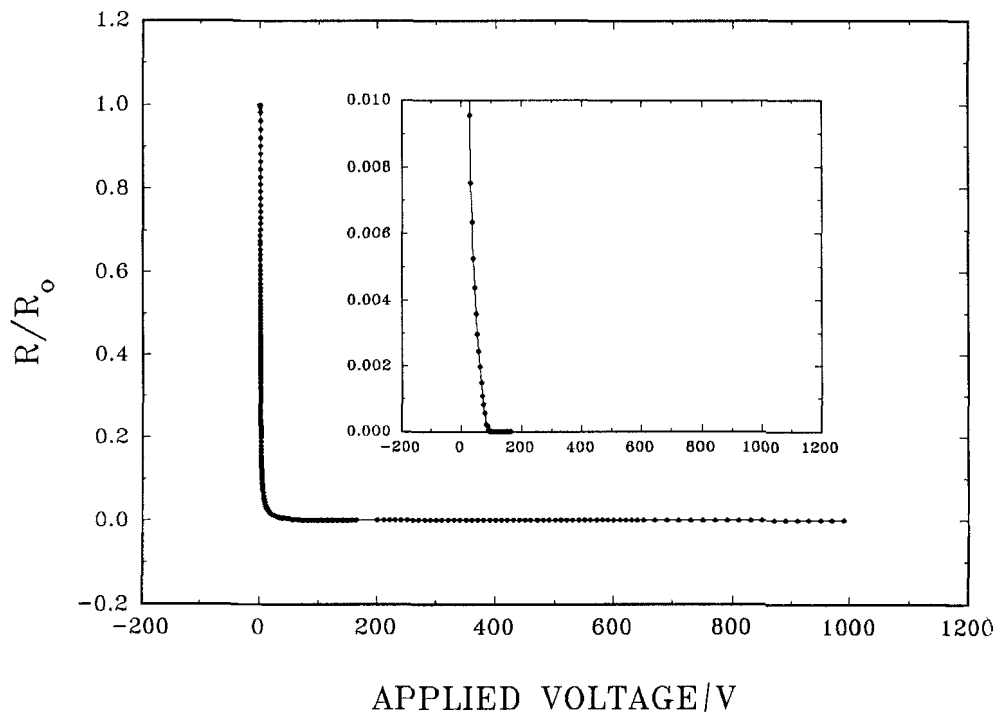

Figure 5.   Relative phase retardation R/R_0 versus applied voltage at 57°C.

films. The decrease of anchoring strength depends not only on the elastic constant K_1, but also on the extrapolation length. It is the fast increase of extrapolation length with increasing temperature that causes the fast decrease of the anchoring strength. This temperature induced weakening of the anchoring strength can be interpreted as a decrease in order (increase in entropy) near the interface which is more easily effected when subjected to an external field than when the ordered structure in the bulk nematic is under consideration.

4. Discussion

We were unable to detect any differences in the surface anchoring characteristics between a PVFM/E7 alignment layer and a pure PVFM layer in the vicinity of the glass transition of the former. However, based on the results presented here, we cannot definitively rule out surface effects as a possible source of the changes in electro-optic properties.

There are a number of reasons for this. Possibly, the pure PVFM film absorbs liquid crystal through diffusion after the cell is filled, so that the films in fact have the same composition of liquid crystal. Still, we do see a difference in their behaviour close to the clearing point. Alternatively, the mechanism for controlling the surface free energy away from the clearing point may be insensitive to the details of the surface structure. Finally, to what extent does a rubbed planar cell mimic the key
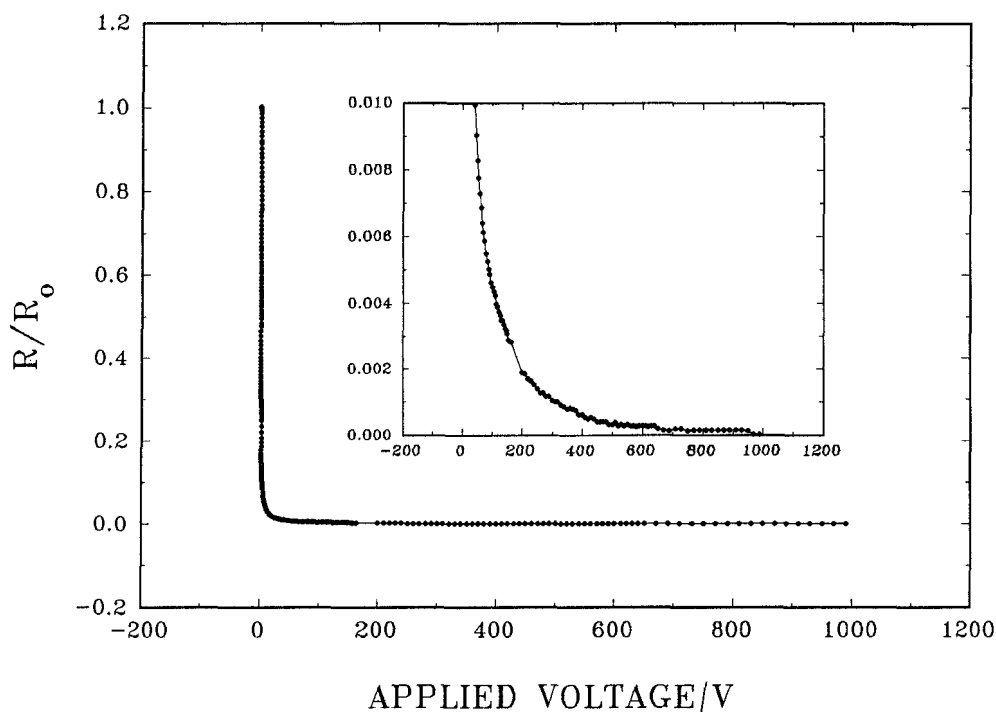

Figure 6. Relative phase retardation R/R_0 versus applied voltage at 50°C.

features of a nematic droplet in a polymer matrix? A planar cell is not topologically equivalent to a liquid crystal droplet; the latter has defect structures [12]. The defects may be much more sensitive to the surface interactions and respond quite differently to an applied field.

Although no definitive differences were observed, we were able to see some interesting behaviour common to both surface layers. The notion of a simple surface term (for example, $W_0 \sin^2 \theta$) for describing the anisotropic part of the interfacial energy between PVFM and E7 breaks down at temperatures far from the clearing point. Some spatial variation in the liquid crystal properties must be included to achieve a consistent picture. This could be simple in form, such as a change in the scalar order parameter S [10], or more complex, with biaxiality appearing in the order parameter tensor [13] or coupling of nematic and smectic order parameters, as examples [14]. Using a van der Waals interaction, Yokoyama has demonstrated that it is possible to write the surface contribution to the free energy in terms of two extrapolation lengths, one associated with the spatial variations in nematic properties and another corresponding to the ubiquitous Rapini–Papoular term (see equation (3))

$$d_e = d_e(1) + d_e(2). \tag{4}$$

It is the first term that drives d_e to be negative. To be more concrete, Yokoyama found $d_e(1)$ for an exponential surface deviation in S to be

$$d_e(1) = \xi \left(\frac{S_b - S_0}{S_0} + \ln \frac{S_b}{S_0} \right), \tag{5}$$
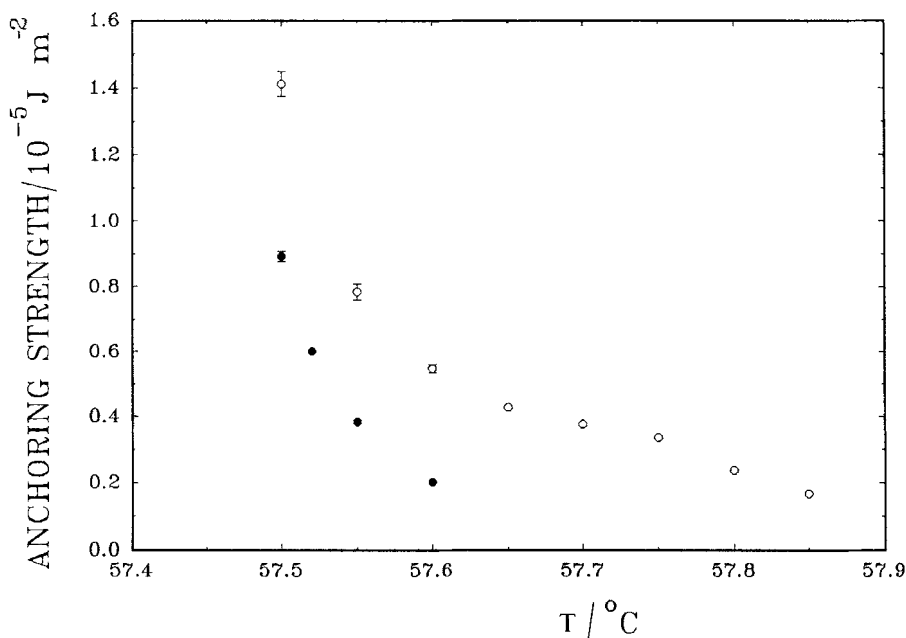

Figure 7.   Anchoring strength in the vicinity of the clearing temperature. Typical error bars are shown. (○) PVFM coating cell and (●) PVFM with 20 per cent E7 coating cell.

which is clearly negative when the bulk order parameter S_b is less than the surface order parameter S_0. The penetration depth, ξ, of the surface behaviour is comparable to $d_e(1)$ when there is an excess of surface order. If we take this as the primary contribution to d_e at lower temperatures, then $\xi \approx 20$ nm, which agrees with estimates of the penetration depth by others [9]. We also note that this is the electrical coherence length for saturation given earlier.

Qualitatively, then, even a simple model can explain the observed behaviour. However, one should be able to do better. The optical retardation is a very sensitive probe of the liquid-crystalline ordering. One can easily observe phase shifts as small as $0.01°$, which corresponds to an optical thickness of approximately 0.5 nm for a layer with $\Delta n = 0.2$ and HeNe laser light. Work towards this end is currently under way in our laboratory.

While a complete picture of the surface interaction requires this detailed description of the surface behaviour, one could reasonably ask if these modifications have any dramatic effect on the observed electro-optic response. For the planar cell, the answer is no. Behaviour only deviates appreciably from infinite anchoring well above the Fréedericksz threshold and consequently only after a large majority of the switching has occurred. By contrast, a PDLC droplet switches at higher fields, $1–3$ V μm^{-1} being typical. As we have seen, in this regime, the nature of the surface interaction does play a role. A better description of the surface interaction than is given by the Rapini–Papoular potential is probably required for detailed modelling of the electro-optic response of a PDLC film.

References

[1] WEST, J. L., 1990, *Liquid Crystalline Polymers* (ACS Symposium Series), edited by R. A. Weiss and C. K. Ober (American Chemical Society, Washington, DC), pp. 475–95.

[2] DOANE, J. W., 1991, *Mater. Res. Soc. Bull.*, **16**, 22.

[3] WEST, J. L., KELLY, J. R., JEWELL, K., and JI, Y., 1992, *Appl. Phys. Lett.*, **60**, 3238.

[4] KELLY, J. R., and SEEKOLA, D., 1990, *Proc. S.P.I.E.*, **1257**, 17.

[5] SEEKOLA, D., and KELLY, J. R., 1991, *Proc. S.P.I.E.*, **1455**, 19.

[6] ROSENBLATT, C., 1984, *J. Phys., Paris*, **45**, 1087.

[7] YOKOYAMA, H., and VAN SPRANG, H. A., 1985, *J. appl. Phys.*, **57**, 4520.

[8] GLEESON, J. T., 1988, M.Sc. Thesis, University of British Columbia.

[9] YOKOYAMA, H., 1988, *Molec. Crystals liq. Crystals*, **165**, 265.

[10] YOKOYAMA, H., KOBAYASHI, S., and KAMEI, H., 1987, *J. appl. Phys.*, **61**, 4501.

[11] JI, Y., and KELLY, J. R. (unpublished results).

[12] KRALI, S., ZUMER, S., and ALLENDER, D. W., 1991, *Phys. Rev.* A, **43**, 2943.

[13] PALFFY-MUHORAY, P., GARTLAND, A. C., and KELLY, J. R., 1992, *14th International Liquid Crystal Conference*, Pisa, Italy, Abstract F-P34.

[14] ANISIMOV, M. A., 1991, *Critical Phenomena in Liquids and Liquid Crystals* (Gordon & Breach).