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A simple and reliable method for measuring the liquid crystal anchoring strength coefficient

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By measuring the electric Fréedericksz transition threshold in a wedged capacitance cell, we have developed a simple method for determining the anchoring strength coefficient for tilt of the director relative to the substrate normal. This technique requires neither a knowledge of the absolute cell thickness nor a knowledge of the optical birefringence. Moreover, it applies to both the homeotropic orientation for $\Delta\chi < 0$, and to the planar orientation for $\Delta\chi > 0$, where $\Delta\chi$ is the dielectric susceptibility anisotropy.

1. Introduction

The anchoring strength coefficient W is an important quantity in liquid crystal physics and technology. Here W is defined as the coefficient of the quadratic term in the free energy which is associated with deviations of the director orientation from its 'easy axis' [1]. From the standpoint of interfacial phenomena, W represents an agglomeration of much of the physics associated with a liquid crystal at a surface. Perhaps more important, though, is its role in devices, as the anchoring strength plays a crucial part not only in the performance of a device (for example, its gray scale), but even in the utility of an entire technology (for example, ferroelectric liquid crystal devices). Unfortunately, an easy and reliable method of determining W has long eluded the liquid crystal community. A variety of techniques currently exists, including (but not limited to) electric and magnetic field Fréedericksz transitions, tilt saturation methods at high fields, attenuated total internal reflection (ATIR) in magnetic or electric fields, direct measurement of mechanical torque, and light scattering. An excellent review has been given by Blinov *et al.* [1], and a very nice description of anchoring measurements can also be found in a more general review article on surfaces by Jerome [2]. What becomes painfully clear from the literature, however, is the wide discrepancy among the many results for W , sometimes by two orders of magnitude. For virtually all methods an important problem is the extreme sensitivity of the anchoring

strength coefficient to small changes in the detected signal. This is understandable, as the bulk liquid crystal generally dominates the measured electrical or optical response. Even for optical techniques such as ATIR which examine only the 'surface', the optically probed region—typically of order a wavelength of light—is still generally larger than the 'extrapolation length' associated with non-rigid anchoring. For many methods one additionally needs to know the cell thickness or birefringence *very* accurately, perhaps far more so than is realistically possible. For example, a measurement of the Fréedericksz transition in wide and narrow cells has been a favoured method of determining the anchoring strength for at least a dozen years [3]. For accuracy of ± 10 per cent, this method requires a knowledge and reproducibility of the cell thickness to about one part in one hundred, even as the temperature may be changing over tens of degrees. This is an extraordinarily difficult challenge, to say the least.

2. Results and discussion

With this in mind we have developed a new technique—actually a variation on the narrow/wide two cell method [3]—to measure W . Consider an 'easy axis' of the liquid crystal director which is oriented at an angle θ_0 with respect to a substrate normal. For small polar deviations from θ_0 , the free energy F associated with the director oriented at an angle θ is given by $F = \frac{1}{2}W(\theta - \theta_0)^2$, where W is the anchoring strength coefficient [4]. We now assume a capacitance cell with homeotropic orientation, i.e. the easy axis is normal to the cell ($\theta_0 = 0$). Moreover, we assume that the dielectric susceptibility anisotropy $\Delta\chi$ is negative, such that a bend distortion is induced above the Fréedericksz threshold field E_{th} . The principle of our

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measurement is based upon the Rapini–Papoular equation [4], namely

$$\cot \left[\frac{\pi E_{\text{th}}}{2 U_3} \right] = \frac{\pi K_3 E_{\text{th}}}{tW U_3}, \quad (1)$$

where t is the sample thickness, K_3 the bend elastic constant, and U_3 the threshold field for rigid anchoring, i.e.

$$U_3 = \frac{\pi}{t} \left(\frac{K_3}{|\Delta\chi|} \right)^{1/2}. \quad (2)$$

An analogous pair of equations can be written for a magnetically-induced Fréedericksz transition.

An approach based upon equations (1) and (2) has already been utilized [3, 5], wherein Fréedericksz measurements were performed in both a narrow and a wide cell. A determination of the threshold field for both cells, along with a *very* accurate knowledge of cell thickness, in principle resulted in an absolute determination of both the bend elastic constant and the anchoring strength potential. As pointed out above, however, such measurements are very difficult to make in a reliable manner. Moreover, Barbero and Durand have since pointed out an additional potential difficulty [6, 7]. They noted that ionic impurities tend to adsorb at the surfaces of the cell, giving rise to a classical electrical double layer extending over a distance comparable to the Debye–Hückel length κ^{-1} . The resulting surface-localized electric field tends to decrease the Fréedericksz threshold field E_{th} . The main source of trouble comes about because the ionic adsorption depends upon sample thickness, as the ions attempt to maintain a uniform chemical potential throughout the cell. Thus, the adsorbed ion concentration is different for the wide cell and the narrow cell, resulting in a different value of W for the two cells. Thus, an analysis of the data based upon only equations (1) and (2) would actually be underdetermined, involving n equations in $n + 1$ unknowns.

These problems may be obviated by utilizing a wedged cell having an angle φ of order a few milliradians. In a cell in equilibrium the ion concentration is spatially uniform, having a value c_{bulk} throughout the bulk and a surface value c_{surface} over the entire surface. In consequence the anchoring strength coefficient—which certainly includes a component from ionic impurities—is uniform across the surface of the cell. Moreover, equations (1) and (2) can be combined and rewritten in terms of voltages instead of fields:

$$\frac{V_{\text{th}}(K_3|\Delta\chi|)^{1/2}}{\cot \left[\frac{V_{\text{th}}}{2} \left(\frac{|\Delta\chi|}{K_3} \right)^{1/2} \right]} = tW, \quad (3)$$

where $V_{\text{th}} [= tE_{\text{th}}]$ is the threshold voltage for the Fréedericksz transition. Note that for rigid anchoring ($W \rightarrow \infty$) the threshold voltage is independent of sample thickness. Moreover, in a cell with a small and uniform wedge angle, the local thickness $t = \varphi x + t_0$, where x is the

lateral distance across the surface of the sample and t_0 is the (constant) offset thickness at $x = 0$. Thus, differentiating equation (3) with respect to x we find that

$$d \left\{ \frac{V_{\text{th}}(K_3|\Delta\chi|)^{1/2}}{\cot \left[\frac{V_{\text{th}}}{2} \left(\frac{|\Delta\chi|}{K_3} \right)^{1/2} \right]} \right\} / dx = \varphi W. \quad (4)$$

The anchoring strength coefficient W can thus be extracted as follows: at a given temperature the threshold voltage V_{th} is measured as a function of position x along the cell. Additionally, the susceptibility anisotropy $\Delta\chi$ and the wedge angle φ can be determined separately. φ , which is relatively temperature insensitive, can easily be obtained by measuring the distance between two laser spots reflected from an empty cell. One then *chooses* a value for K_3 and plots the function

$$V_{\text{th}}(K_3|\Delta\chi|)^{1/2} / \cot \left[(V_{\text{th}}/2)(|\Delta\chi|/K_3)^{1/2} \right]$$

versus x , adjusting K_3 to achieve optimum linearity of this function with x . The slope then corresponds to the product of the anchoring strength coefficient W times the wedge angle φ . An absolute determination of the sample thickness is not necessary, and W is less sensitive to uncertainties in φ than it is to uncertainties in sample thickness when using the narrow/wide two cell technique. From this description it should be clear that an identical experiment can be performed for a planar-aligned, positive dielectric anisotropy liquid crystal, the sort used in, for example, a twisted nematic cell. In this case one obtains the splay (rather than the bend) elastic constant, and W corresponds to the anchoring strength coefficient associated with a tilt of the director away from the plane of the surface.

To demonstrate this approach we use equation (3) to generate a series of model ‘threshold voltages’ V_{th} versus cell thickness t by choosing the typical values $W = 5 \times 10^{-2}$ erg cm², $K_3 = 4 \times 10^{-7}$ dyne, and $\Delta\chi = -0.03$. Figure 1 shows the calculated values of V_{th} versus t . We now demonstrate the sensitivity of equation (3) to variations in K_3 . Using the above values for W , $\Delta\chi$, $V_{\text{th}}(t)$, and t , we vary the elastic constant K_3 and, in figure 2, plot the left hand side of equation (3) versus t for three different values of the bend elastic modulus: the ‘correct value’ $K_3 = 4.00 \times 10^{-7}$ dyne, as well as a slightly high and low value, namely, $K_3 = 3.95 \times 10^{-7}$ dyne and 4.05×10^{-7} dyne. Note the curvature for the ‘incorrect’ values of K_3 . Clearly the curve is very sensitive to K_3 , although when dealing with real data for the threshold voltages, experimental noise makes it more difficult to find a value of K_3 which optimizes the linearity.

Before measuring the Fréedericksz thresholds, we first determined the electric susceptibility anisotropy for methoxybenzylidene butylaniline (MBBA). Two indium–

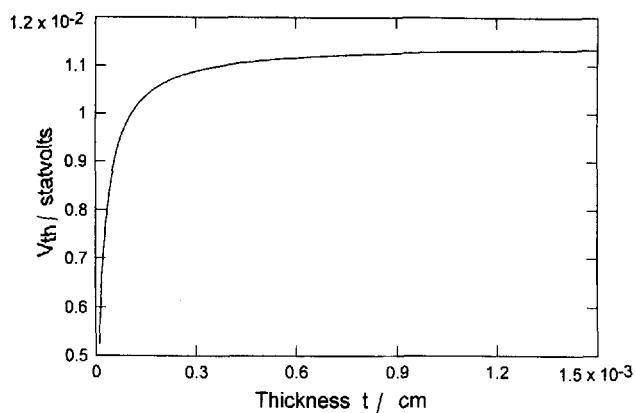


Figure 1. Model calculation for threshold voltage V_{th} versus cell thickness, based upon equation (3). Values of W , K_3 , and $\Delta\chi$ are given in the text.

tin oxide (ITO) coated glass slides were etched to leave a well defined rectangular pattern, and then dipped into a 0.05 per cent solution of dodecyltrimethyl ammonium chloride (DTAC) in ethanol to promote homeotropic alignment. The slides were allowed to air dry. They were then spaced apart with $10\ \mu\text{m}$ nylon beads and epoxied together; the overlap area of the electrodes was approximately $1.5\ \text{cm}^2$. A variable amplitude low frequency (50 Hz) sinusoidal voltage was added to a fixed high frequency sinusoid (1 kHz, $10\ \text{mV}_{\text{rms}}$) and applied through a shunt resistor ($R = 1850\ \Omega$) to the empty cell [8]. A phase-locked measurement (referenced to the 1 kHz voltage) of the voltage across the shunt resistor yielded the empty cell capacitance. The result was checked for consistency with an Andeen–Hagerling Model 2500A high precision capacitance bridge. The cell was then filled with the liquid crystal which was oriented homeo-

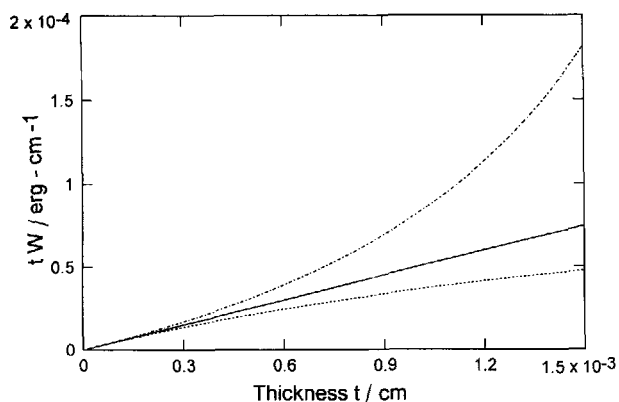


Figure 2. Model calculations of the left-hand side of equation (3) (having units of thickness times anchoring energy) versus cell thickness. Solid line corresponds to the 'correct value' of $K_3 = 4.00 \times 10^{-7}$ dynes. Dash-dot line corresponds to 'incorrect value' $K_3 = 3.95 \times 10^{-7}$ dynes, and dotted line to 'incorrect value' $K_3 = 4.05 \times 10^{-7}$ dynes.

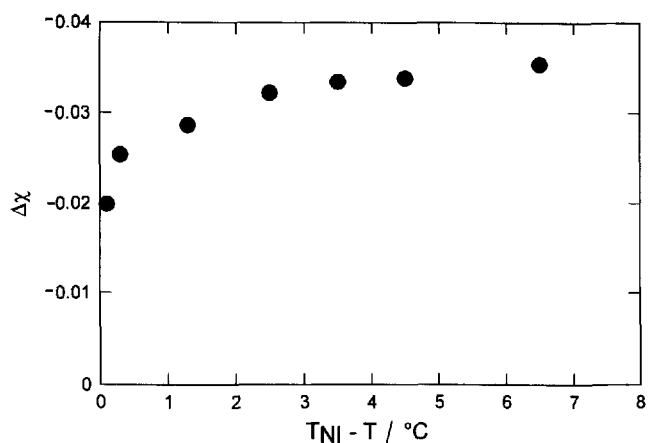


Figure 3. Measured susceptibility anisotropy versus temperature relative to T_{NI} .

tropically, and the capacitance was again measured. The ratio of the filled cell capacitance to the empty cell capacitance was taken to be ϵ_{\parallel} . The 50 Hz voltage was then ramped up to approximately 7 V, well above V_{th} for a Fréedericksz transition. By 7 V the shunt resistor voltage detected at 1 kHz had saturated, from which we extracted ϵ_{\perp} for the filled cell. The (negative) electric susceptibility anisotropy $\Delta\chi = (\epsilon_{\parallel} - \epsilon_{\perp})/4\pi$ is plotted in figure 3. These results compare quite well with those in the literature [9].

The Fréedericksz measurements were performed with a cell constructed using ITO coated glass slides, where the ITO was chemically removed along one edge of the slide. The slides were treated with DTAC as before for homeotropic alignment. They were then placed together, with a Mylar spacer of nominal thickness $12.5\ \mu\text{m}$ along one edge, and adjusted for a uniform wedge angle across the surface by observing the reflection from a monochromatic light source. The cell was cemented with a high temperature epoxy and cured according to the manufacturer's curing schedule. After curing, the cell was placed in an oven (temperature controlled to better than 20 mK), which in turn was mounted on a micrometer translation stage. Light from a He–Ne laser was nearly normally incident at the surface. Two reflected spots were observed at a distant point about 12 m away, from which we obtained the wedge angle $\phi = (1.70 \pm 0.05) \times 10^{-3}$ rad. This angle was found to be constant as the cell was translated in front of the fixed laser beam, and was also found to be independent of temperature up to approximately 50°C . At higher temperatures—approximately 80°C — ϕ was found to increase by about 5 per cent, an effect for which we can easily compensate if we needed to perform the experiment at these elevated temperatures.

The cell was filled with MBBA, obtained from 3M and used without further purification. Two hours after filling, the nematic–isotropic transition temperature T_{NI} was found

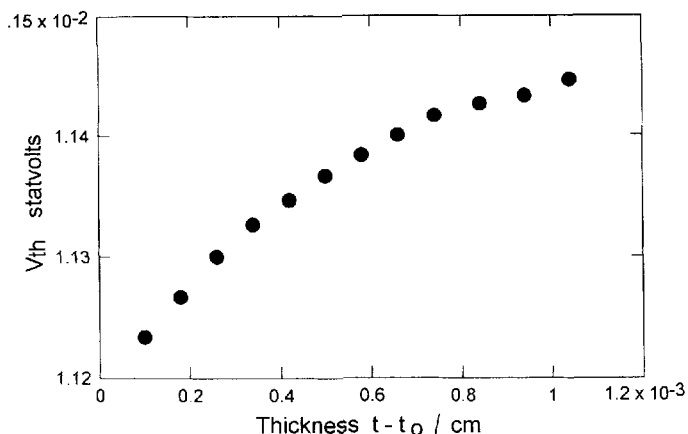


Figure 4. Measured threshold voltage V_{th} versus relative thickness.

to be 45.1°C . The cell was allowed to equilibrate in the nematic phase for at least 24 h before the experiment was performed. Light from a He-Ne laser passed consecutively through a polarizer, then a lens to focus the beam to a measured spot size of $70\ \mu\text{m}$, the cell, an analyser, a light chopper, and into a photodiode detector. The signal from the detector was input to a lock-in amplifier, which was referenced to the light chopper's frequency of 317 Hz. A 1 kHz voltage was applied to the cell, and ramped from approximately 0.5 V below V_{th} to several hundred millivolts above V_{th} over approximately 200 s. This slow ramping facilitated near-equilibrium conditions of the director. (Note that even slower ramp rates were used for the wider parts of the cell.) The output from the lock-in amplifier, proportional to the detector signal, was computer recorded, and V_{th} was obtained as a function of position of the cell relative to the incident laser. The experiment was performed at several temperatures in the nematic phase. Because of the well-known chemical instability and concomitant drift of transition temperatures in Schiff's base compounds, the nematic-isotropic transition temperature was measured immediately after each 2 h run.

Figure 4 shows V_{th} versus relative thickness $t - t_0$ along the face of the cell for one experimental run at temperature $T_{NI} - T = 2.5^\circ\text{C}$. (As the data analysis does not depend upon the absolute thickness [cf. equation (4)], the local cell thickness need only be determined to within the constant offset t_0 .) Clearly, in narrower regions the threshold voltage is reduced, as expected from equation (3). In wider regions V_{th} approaches a maximum, where the effects of finite anchoring are less important. We note that in very wide regions of the cell (much larger x) the threshold voltage was found to decrease *slightly* from its maximum value. We feel that this effect may be due to incomplete equilibration of ionic impurities, such that a small excess

of ions exists at the surfaces in these regions. This effect was strongest when the experiment was performed immediately after filling the cell, and was our motivation for waiting at least 24 h before taking reliable data. After this period we found that this artifact was nearly non-existent, and that the results were stable and independent of time. Nevertheless, when analysing the data, we chose to include only those data points obtained at the first dozen or so positions at the narrow end of the cell, as shown in figure 4.

In figure 5 we plot the left-hand side of equation (3) versus $t - t_0$ at $T_{NI} - T = 2.5^\circ\text{C}$, finding that a bend modulus $K_3 = (4.39 \pm 0.02) \times 10^{-7}$ dyne results in the best linearity. To determine K_3 we plotted the left-hand side of equation (3) versus $t - t_0$ for various values of K_3 , fitting each curve to a second order polynomial in $t - t_0$. The value of K_3 which minimizes the coefficient of the quadratic term was considered the correct value, and was obtained to an accuracy of much better than ± 1 per cent. According to equation (4) we can obtain W from the slope of figure 5, i.e. from the coefficient of the linear term in the fit. For this example $W = (5.2 \pm 1.2) \times 10^{-2}$ ergs. In figure 6 we show K_3 versus temperature relative to the nematic-isotropic transition temperature T_{NI} , and in figure 7 we show W versus $T_{NI} - T$. The bend elastic modulus is consistent with accepted values and, in fact, accounts for the effects of a finite anchoring strength coefficient on the Fréedericksz transition. Our values for W are larger by approximately a factor of two when compared to results that one of us (CR) had taken about ten years ago using a magnetic Fréedericksz transition in a wide/narrow two cell experiment [5]. The earlier results could have been complicated by ion adsorption as described above. Additionally, the earlier results were based on DTAC deposited on glass, whereas the results described herein are based on DTAC on ITO. Relative

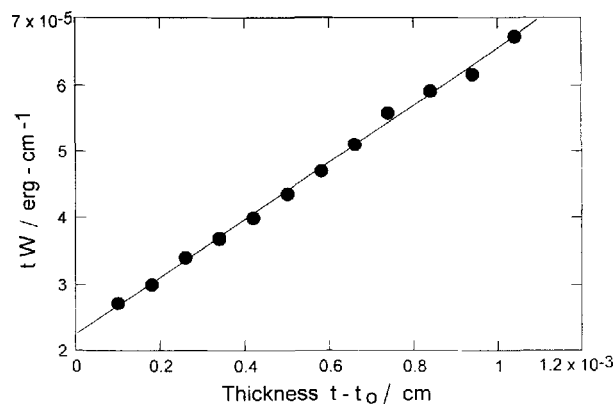
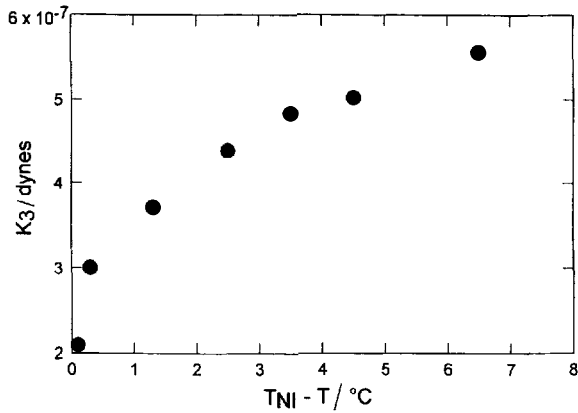
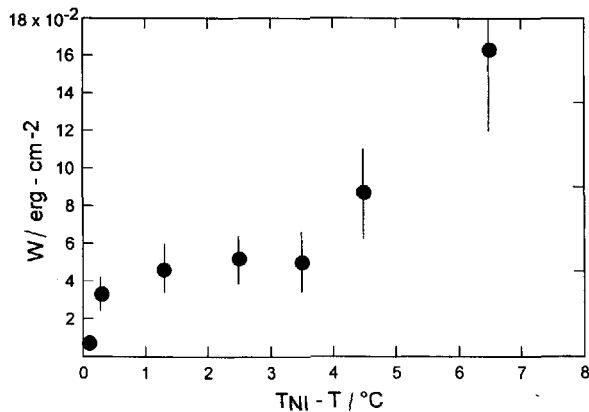


Figure 5. Left-hand side of equation (3) versus relative thickness for data shown in figure 4. To obtain the best linearity, we use $K_3 = 4.39 \times 10^{-7}$ dynes. The slope of the line corresponds to the anchoring strength coefficient W .

Figure 6. Bend elastic modulus versus $T_{NI} - T$.Figure 7. Anchoring strength coefficient W versus $T_{NI} - T$.

error bars for W are larger than for K_3 , and increase at lower temperatures. The latter effect is because W itself is increasing, so that as the anchoring becomes more rigid, V_{th} is much less sensitive to the local sample thickness.

3. Conclusions

The method described herein is a simple and reliable way of determining the polar anchoring strength coefficient for negative anisotropy, homeotropically aligned liquid crystals, as well as their positive anisotropy, planar aligned counterparts. Like other methods, it becomes less sensitive when the anchoring is strong, although it does not depend upon a knowledge of sample thickness or a knowledge of the birefringence, as do other methods. To be sure this technique has its own limitations,

not the least of which is that it is limited to an electrically conducting substrate. Additionally, one has to maintain a uniform temperature across the face of the cell, which becomes more difficult since the opening for laser light must be a slit rather than a small porthole. Near a bulk phase transition or an anchoring transition, where W is changing rapidly with temperature, temperature gradients can become problematic. Additionally, for homeotropically aligned liquid crystals, the azimuthal orientation of the director above V_{th} is completely random and could vary from point-to-point in the cell. In consequence the optical signal for $V > V_{th}$ can also vary greatly from point-to-point. This effect tends to add to the uncertainty of $V_{th}(t)$, although not greatly. One way of remedying this situation is to place both polarizers on rotation stages, yoking the two rotations stages together. One could then adjust the polarizers simultaneously to achieve a maximum signal. This improvement is planned for the future. Despite these potential problems, this is a powerful new method which adds to our already extant battery of techniques for studying liquid crystal anchoring.

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