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Behaviour of the anchoring strength coefficient near a structural transition at a nematic–substrate interface

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A nearly symmetric alkoxyphenylbenzoate monomer is found to exhibit a transition from perpendicular to tilted alignment at a lecithin-treated glass substrate several degrees below the nematic-isotropic phase transition. By means of the Freedericksz transition the coefficient B of the anchoring energy has been obtained. It is found that B rapidly decreases, and the tilt susceptibility increases on approaching this transition.

During the past two decades there has been tremendous activity concerning interactions at liquid crystal–non-liquid crystal interfaces [1]. Perhaps one of the more unusual discoveries was by Bouchiat and Langevin–Cruchon, who found a strong temperature dependence of the director orientation at the free surfaces of MBBA and PAA [2]. This finite alignment angle, which has become known as the 'pretilt angle,' has since become the subject of much activity, both experimental and theoretical. Using capacitance techniques, Kahn [3] and Toda, Mada, and Kobayashi [4] determined the pretilt angles vs. temperature at a solid substrate for various materials. Theoretically, two approaches have been used to account for the temperature dependent pretilt angle. Mada has introduced [5, 6] the concept of an 'easy axis' in conjunction with a field energy associated with a misalignment of the director from this axis. The equilibrium orientation arises from a competition between the easy axis term and the bulk deformation energy. Recently, however, several of Mada's predictions have shown to be faulty [7]. By contrast, Parsons treats the tilt angle as a competition between dipolar and quadrupolar interactions [8]. For sufficiently strong quadrupolar interactions, the director will be at some non-zero angle θ relative to the interface normal. As the temperature changes the relative strengths of the two interactions will vary, thereby causing θ to have a temperature dependence.

One of the interesting consequences of the Parsons theory is the prediction of a structural phase transition at a nematic–non-liquid crystal interface. Carefully repeating the Bouchiat–Langevin–Cruchon experiment, Chiarelli, Faetti, and Fronzoni found just such a phase transition at the free surfaces of MBBA and EBBA. Below this surface transition temperature T_s they measured the polar tilt angle at the interface, biasing the azimuthal orientation of the director with a magnetic field [9]. Fitting their data to an algebraic form, they obtained a mean field exponent $\beta = 0{\cdot}5 \pm 0{\cdot}04$ for the tilt angle θ vs. reduced temperature. Above T_s (but still within the nematic phase) the director is normal to the interface. Again using a differential reflectivity scheme in conjunction with a ramped magnetic field, they were able to

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deduce the surface anchoring energy coefficient B [10], which is defined by the surface free energy $F_s = \frac{1}{2}B\theta^2$. B was also fitted to an algebraic form; the resulting critical exponent $\gamma = 1{\cdot}0 \pm 0{\cdot}15$ is consistent with the classical mean field susceptibility exponent, as expected in light of the result for β.

Despite these fascinating results, however, it is still *treated substrates* which provide the most technologically useful and scientifically rich interfaces available. Along these lines Ryschenkow and Kleman have observed [11] a tilt transition for MBBA at a solid substrate, and obtained an approximate value for B in the tilted phase. Hiltrop and Stegemeyer performed both Freedericksz and contact angle measurements to elucidate the nature of liquid crystal anchoring [12], and also observed a tilt transition in the nematic phase. Von Känel *et al.* used surface relief gratings to study a homeotropic to homogeneous alignment transition [13]. Very recently, in fact, Köhler has characterized [14] eight varieties of surface transitions depending upon substrate, surface treatment, and mesogen. Thus there has clearly been a significant degree of activity commensurate with the importance of liquid crystal–substrate interactions.

With this in mind we have been studying a variety of systems at a liquid crystal–surfactant treated solid interface [15, 16, 17]. One such system, which consists of the liquid crystal '5OO5' ($C_5H_{11}OC_6H_4COOC_6H_4OC_5H_{11}$) [18] sandwiched between two glass slides coated with the diacetylenic phospholipid surfactant $DC_{8,9}PC$ (1,2-bis(10,12,tricosadiynoyl)-*sn*-glycero-3-phosphocholine), is found to exhibit a surface structural transition several degrees below the nematic-isotropic (NI) transition temperature T_{NI}. Using polarized optical microscopy, the sample is found to be uniformly aligned in the homeotropic (perpendicular) orientation above T_s, where $T_s \approx T_{NI} - 7°C$. Just below T_s a Schlieren type texture becomes visible, increasing in brightness as the temperature is further reduced. By exerting a slight pressure on the sample and optically observing the texture, we verified that the liquid crystal is indeed nematic (and not some other phase) below T_s; further confirmation was obtained by differential scanning calorimetry. It should be noted that using the same surfactant we are unable to obtain homeotropic orientation of the dimer version of this mesogen ('5-10-5'), which consists of a pair of 5OO5 monomers (minus two hydrogens) attached end-to-end. Moreover, neither the ionic surfactant hexadecyltrimethylammonium bromide (HTAB) nor the silane compound 3-(trimethoxysilyl) propyldimethyloctadecyl ammonium chloride results in homeotropic orientation of the monomer 5OO5 at any temperature. [We speculate that the alignment capabilities of $DC_{8,9}PC$ arise from the polymerizable nature of the end-chain, which would form a rigid comb-like network when the monolayer is irradiated with ambient U.V. light. This surfactant has also been found to form unusual morphologies (tubules) in water [19], which can be rigidfied by exposure to either a UV or beta source]. In light of these qualitative results we have measured the anchoring strength coefficient B vs temperature above T_s. This quantity has also been measured in other systems, and was found to increase with decreasing temperature in the nematic phase [15, 20]. The central result of our measurement is that, sufficiently far below T_{NI}, B tends to *decrease* with decreasing temperature. In fact B apparently vanishes at T_s, below which the director exhibits a temperature dependent pretilt angle. This result for B is the first such reported for a solid substrate.

In order to obtain B vs T we performed Freedericksz measurements in the bend geometry for both very narrow (thickness $\ell_n \sim$ few microns) and wide samples (thickness $l_w \sim$ many tens of microns). For the case of rigid anchoring ($B = \infty$), the

Freedericksz threshold field $U(\ell)$ is given by [21]

$$U(\ell) \equiv \pi/\ell(K_3/\Delta\chi)^{1/2}, \tag{1}$$

where ℓ is the sample thickness, K_3 is the bend elastic constant, and $\Delta\chi$ is the magnetic susceptibility anisotropy. If, however, B is finite, then Rapini and Papoular have shown that the threshold field $H_{th}(\ell, B) < U(\ell)$ and is given by the implicit equation [22]

$$\cot(\pi H_{th}/2U) = (\pi K_3/\ell B)H_{th}/U \tag{2}$$

In the limit that $B \to \infty$, of course, $H_{th}(\ell) \to U(\ell)$ in equation (2). If we assume that B is sufficiently large that H_{th}/U is nearly equal to 1 [i.e. $1 - (H_{th}/U) \ll 1$], equation (2) can be expanded in the variable H_{th}/U around $H_{th}/U = 1$. The resulting expression can then be inverted to show [16]

$$H_{th}/U = 1 - 2K_3/\ell B + \mathcal{O}(K_3/\ell B)^2 \tag{3}$$

From equation (3) we see that the decrease in $H_{th}(\ell)$ from the rigid anchoring case scales as the ratio of the bulk energy to the surface energy. Moreover, it's clear from equation (3) that large reductions in H_{th} occur for narrow sample cells; for wide sample cells H_{th} is nearly identical to U. We thus performed our measurements of H_{th} vs T on two samples of very different thickness: one in which H_{th} deviates significantly from U, and the other in which H_{th} nearly coincides with U. Since K_3 vs temperature can be approximated quite well (see below), at a given temperature the threshold field $H_{th}(\ell)$ and thickness were separately inserted for each sample into equation (2). (We note that the structural transition temperature T_s was found to be identical in both samples.) Noting that $U(\ell_n) = (\ell_w/\ell_n)U(\ell_w)$, the two resulting equations were then solved simultaneously to obtain both B and $U(\ell_w)$ (and, of course, $U(\ell_n)$) as functions of temperature.

The liquid crystal 5OO5 (and its dimer) were synthesized according to procedures described elsewhere [18, 23]. The lipid DC$_{8,9}$PC was obtained from Avanti Polar Lipids (Birmingham, Alabama) and used as received. A small quantity of DC$_{8,9}$PC was dissolved in absolute ethanol, a drop of which was placed on each of two 12·7 mm diameter glass windows. After drying, the residue was gently removed with a Kimwipe. (This procedure caused no apparent problems, given the good reproducibility of the results.) The two windows were separated by narrow Mylar spacers and optically adjusted for optimum parallelism. Using an interferometric scheme [16] the spacing of the empty narrow cell was determined to be $\ell_n = 3{\cdot}55 \pm 0{\cdot}03\,\mu$m, and that of the empty wide cell to be $\ell_w = 85{\cdot}33 \pm 0{\cdot}04\,\mu$m. The sample holder was then filled with liquid crystal, inserted into a brass oven which was temperature controlled to 0·01°C, and placed in the bore of a superconducting magnet with transverse optical ports. The orientation of the magnetic field **H** was parallel to the plane of the sample and thus perpendicular to the director. Using the normal Freedericksz bend geometry, light from a He-Ne laser passed consecutively through a light chopper at frequency ν = 319 Hz, a lens of focal length 483 mm, a polarizer oriented at 45° with respect to the field, the sample, an analyzer, and into a detector. The diameter of the beam at the sample was measured to be approximately 300 μm. The output from the detector was fed into a lock-in amplifier referenced to the light chopper, and the lock-in output (proportional to the intensity at the detector) was fed into a computer based data acquisition system. For the narrow sample the field was ramped upward at 10·8 G/s, and the detector intensity was recorded vs. H. Owing to the very small thickness of

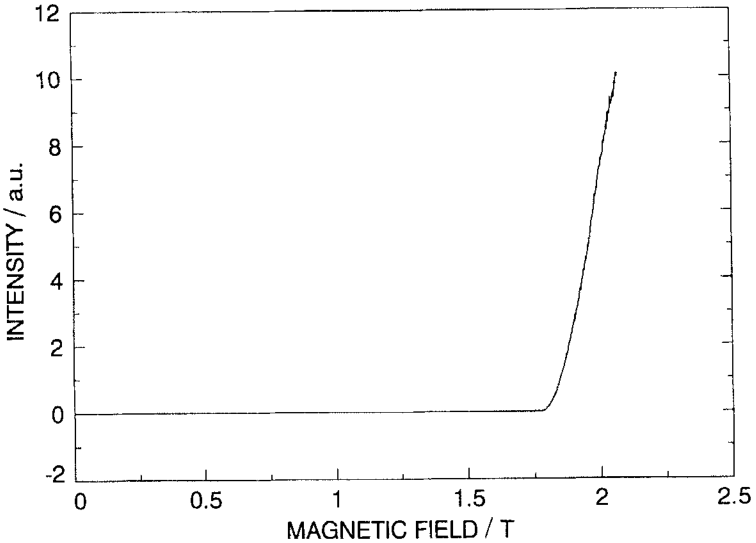

Figure 1. Detector intensity (arbitrary units) vs magnetic field (Tesla) for narrow sample at $T = 76{\cdot}58°C$.

the sample this ramp rate was sufficiently slow to maintain quasiequilibrium. For the wide sample, on the other hand, the rate had to be much slower. In this case the field was increased step-wise in 5 G intervals every 10 s. This rate was found to produce reasonable equilibrium conditions, and is consistent with ramp rates reported in the literature for samples of comparable thickness [24].

Intensity vs. field traces were obtained at a number of temperatures; a typical trace is shown in figure 1. Determination of the threshold fields H_{th} (figures 2 and 3) was

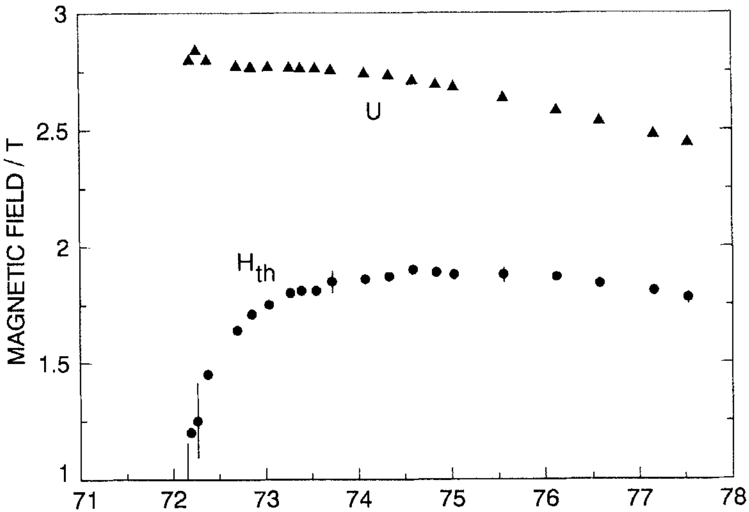

Figure 2. Threshold field H_{th} vs temperature for narrow ($\ell_n = 3{\cdot}55\,\mu m$) sample, where $T_{NI} = 78{\cdot}03°C$ and T_s is shown. Error bars represent uncertainty in H_{th} due to rounding of the intensity vs field data. U represents calculated threshold field in the limit $B \rightarrow \infty$. Note that H_{th} is considerably smaller than U at each temperature (cf. equation (3)).

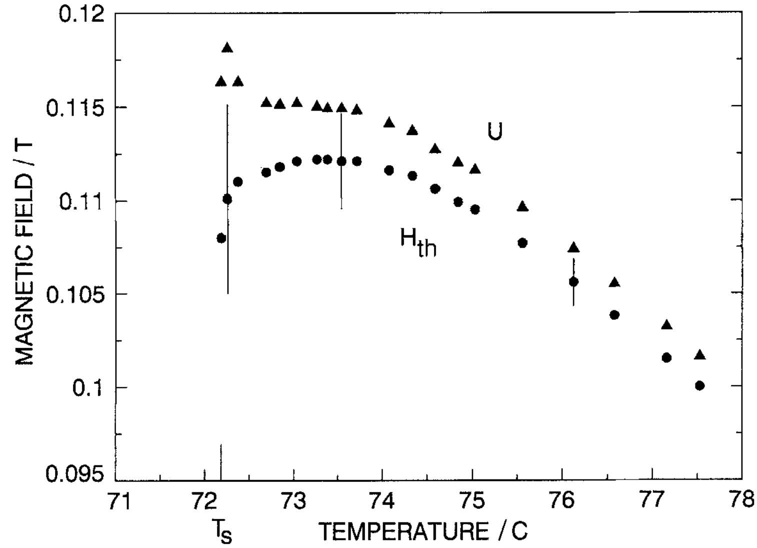

Figure 3. H_{th} vs temperature for wide (ℓ_w = 85·33 μm) sample. Since it was necessary to know the threshold fields H_{th} for both samples at the identical temperature, these data represent interpolated values based upon measurements of $H_{th}(\ell_w)$ at eight points. Note that the *fractional* error is much smaller than in figure 2. Also note that $U(\ell_w)$ is only slightly larger than H_{th} at each temperature, as expected in a wide sample (cf. equation (3)).

complicated by a rounding of the data. This rounding, which is relatively small at higher temperatures but much more severe near T_s, is largely responsible for the significant error bars in B near the tilt transition. Note that this sort of rounding near a surface structural transition has been observed previously [12]. Rounding is a common difficulty, and arises from a number of sources:

(1) Too rapid ramping of the field
(2) Thickness gradients across the face of the laser spot
(3) Tilt of the sample with respect to the magnetic field
(4) The presence of microscopic particulate matter
(5) Gradients in the anchoring coefficient B across one plate, differences in B between plates, or surface imperfections.

Item (1) was deemed unimportant for the ramping rates used. A simple calculation shows that item (2) was unimportant as well. Item (3), a sample tilt, is perhaps the most common source of rounding, and becomes more severe as the surface anchoring becomes weaker. Nevertheless, the rounding observed herein is considerably larger than found in previous measurements using the same apparatus [25], leading us to believe that sample tilt was not the dominant effect. Microscopic particulate matter could have played a role, given the larger number of defects (and corresponding larger coherence length, since the plates are much further apart) in the wide sample. At higher temperatures, moreover, the rounding was more severe in the wide than in the narrow sample, an observation consistent with the presence of small defects. Nevertheless, we feel that much of the rounding at lower temperatures arises from item 5, an inhomogeneous anchoring coefficient. Inhomogeneities would be expected to play a more significant role in the narrow sample (cf. equation 3), which they apparently do. We have tried to mitigate this effect by using a small beam diameter at the sample.

Nevertheless, unlike a free surface, it is quite difficult to apply an absolutely uniform and identical surfactant coating to both substrates. (Langmuir-Blodgett deposition may provide some improvement, although inhomogeneities in the substrates themselves are probably responsible for much of the rounding in the region of small *B*. We intend to investigate these issues in the future.) Thus, it is important to remember that at lower temperatures the calculated value for *B* is likely to represent some average over the two surfaces. It is therefore unreasonable to expect that a critical exponent can be extracted from this data.

In order to calculate $B(T)$ from equation (2) it is necessary to know K_3 as a function of temperature. Since this quantity is not directly known, we use equation (1) to obtain a reasonably accurate approximation. First we note that $K_3 = \Delta\chi[U(\ell_w)\ell_w/\pi]^2$. For most low molecular weight liquid crystals containing two aromatic groups, $\Delta\chi_0 \sim 7{\cdot}5 \times 10^{-8}$ cgs approximately 2°C below T_{NI} [23, 26, 27, 28], the highest temperature used in this experiment. Moreover, since $\Delta\chi$ is expected to scale linearly with S (the nematic order parameter) and K_3 with S^2, one can easily show that $\Delta\chi \sim \Delta\chi_0[U(\ell_w)/U_0(\ell_w)]^2$, where U_0 is the strong anchoring threshold at $T_{NI} - T \approx 2°C$. Finally, at these higher temperatures (well above T_s) we note that $U_0(\ell_w) \approx H_{th}(\ell_w)$, which has been measured. Thus, since $\Delta\chi_0$, $U_0(\ell_w)$, and ℓ_w are all known, K_3 becomes an implicit function of $U(\ell_w)$. This is then inserted into equation (2) and used to simultaneously calculate $U(\ell_w)$ and *B*. Owing to the uncertainty in $\Delta\chi_0$, however we have actually calculated $U(\ell_w)$ and *B* assuming three separate values: an unrealistically low value of $\Delta\chi_0 = 5 \times 10^{-8}$ (triangles), a likely value of $7{\cdot}5 \times 10^{-8}$ (circles), and an unrealistically high value of $1{\cdot}0 \times 10^{-7}$ cgs (squares). The results for *B* are shown in figure 4. Note that the absolute error, which reflects only the uncertainty in determining the values of H_{th} and not the much smaller uncertainty in determining the two cell thicknesses, is approximately constant in magnitude. Near T_s, however, the relative error becomes substantial, no doubt due to the spread in *B* across the sample.

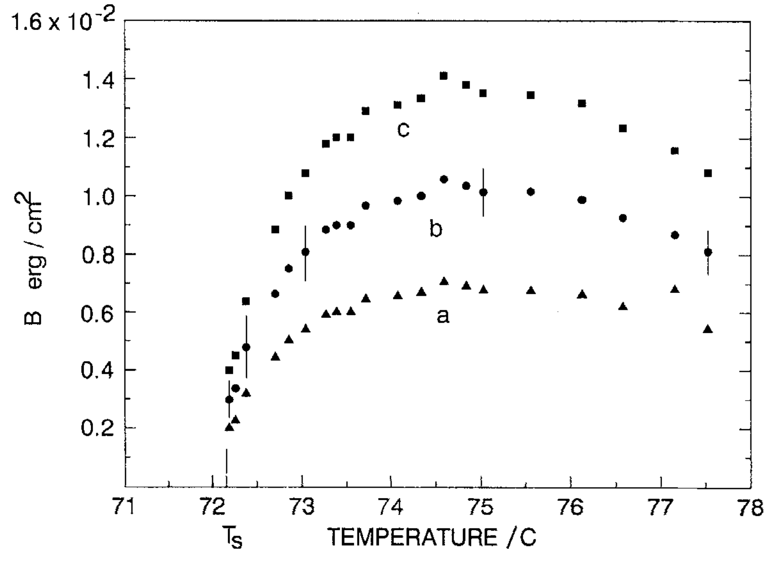

Figure 4. Calculated *B* vs temperature assuming three different values of $\Delta\chi_0$: (*a*) $\Delta\chi_0 = 5 \times 10^{-8}$ (triangles), (*b*) $7{\cdot}5 \times 10^{-8}$ (circles), and (*c*) $1{\cdot}00 \times 10^{-7}$ cgs (squares). Set (*b*) represents the most reasonable value. Note that the *relative* error increases dramatically as the temperature is reduced.

Although this spread may be small, it nevertheless represents a large fraction of B owing to the small magnitude of B. Finally, values for $U(\ell_{\mathrm{w}})$ are shown by triangles in figure 3 and for $U(\ell_{\mathrm{n}})$ $[=(\ell_{\mathrm{w}}/\ell_{\mathrm{n}})U(\ell_{\mathrm{w}})]$ by triangles in figure 2. Note that as expected from equation (3), $U(\ell_{\mathrm{w}})$ is very close to H_{th} in the wide sample (figure 3), but that $U(\ell_{\mathrm{n}})$ is considerably larger than H_{th} in the narrow sample (figure 2). Moreover, note that both sets of U (which are in the same ratio as $\ell_{\mathrm{w}}/\ell_{\mathrm{n}}$) continue to increase with decreasing temperature. This is to be expected, of course, since U represents the threshold field in the limit that $B \to \infty$.

As is readily apparent from figure 4, the magnitude of B a few degrees below T_{NI} is consistent with values obtained previously [16]. At approximately 74·5°C, however, B no longer increases as the temperature is reduced, but rather begins to decrease. The rate of decrease becomes more rapid at lower temperatures. It appears that the transition to a tilted state is weakly discontinuous, although the resolution in the data is insufficient to be certain.

In order to understand the results of figure 4 we turn to the theory of Parsons. At an interface polar molecules are expected to orient in a perpendicular fashion so as to bury their dipoles inside or close to the higher dielectric medium. For molecules which, to lowest order, possess a quadrupole moment, Parsons has shown that the molecules prefer to lie parallel to the interface [8, 29]. He then wrote down the phenomenological surface energy

$$\gamma = \gamma_0 + \tfrac{1}{2}\gamma_Q(\mathbf{n}\cdot\mathbf{k})^2 - \gamma_{\mathrm{D}}(\mathbf{n}\cdot\mathbf{k}), \qquad (4)$$

where $\mathbf{n}$ is the director, $\mathbf{k}$ is a unit vector normal to the surface, and γ_Q and γ_D are the (temperature dependent) coefficients of the quadrupole and dipolar surface free energies, respectively. Minimizing equation (4) with respect to $\mathbf{n}\cdot\mathbf{k} = \cos\theta$, Parsons found a critical point when $\gamma_Q = \gamma_D$. For $\gamma_D > \gamma_Q$ the director is normal to the interface, but for $\gamma_D < \gamma_Q$ a tilt θ obtains. The equilibrium tilt can be obtained by expanding equation (4) for small θ near T_{s}, resulting in

$$\gamma(\theta) = \gamma_0 + \tfrac{1}{2}(\gamma_D - \gamma_Q)\theta^2 + \tfrac{5}{48}\gamma_Q\theta^4 + \dots . \qquad (5)$$

Inasmuch as there is no reason to expect γ_Q and γ_D to exhibit the same temperature dependence, one might expect a tilt transition to occur at the interface. (For example, a temperature dependent molecular conformation or orientational distribution function would give rise to such an effect.) This tilt transition was, of course, observed for the free surface in [9, 10], and is now seen at a surfactant-treated substrate. Presumably the small anisotropy arising from the ester group is sufficient to cause the molecules to remain normal to the interface just below T_{NI}. As the temperature is lowered, however, the molecules become more weakly polar; a tilt transition ensues at T_{s}. The dimer, which could not be aligned perpendicular to the surface at any temperature in the nematic phase, is a completely symmetric molecule. Although it possesses *local* dipoles, these are apparently insufficient to overcome the van der Waals interactions favouring parallel alignment. Missing from this entire discussion, of course, is the role of the surfactant. Since only $\mathrm{DC}_{8,9}\mathrm{PC}$ produced perpendicular alignment, the nature of the surfactant clearly plays an essential role in this transition. It is beyond the scope of this paper, to examine this role, which will be left to future work.

It should be noted that equation (4) predicts a second-order transition. This may be the case for the observed behaviour, although it appears from figure 4 that the transition may be weakly first order. If that is the case, equation (4) would have to be modified with addition terms.

To summarize, the coefficient B of the anchoring energy has been measured as a function of temperature above a tilt transition of the director at a nematic–substrate interface. B seems to decrease rapidly on approaching the transition temperature T_s from above, corresponding to an increasing tilt susceptibility at this temperature.

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