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Smectic tilt susceptibility: Anharmonic behavior in surface-induced smectic layers above the nematic–smectic-*A* transition temperature

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Fréedericksz transition measurements were performed on the Merck liquid crystal SCE12R. The results were used to determine the quartic contribution to the free energy associated with molecular tilt relative to the layer normal in the surface-induced smectic layers above the nematic–smectic-*A* transition temperature T_{NA}. Both the quadratic and quartic coefficients are consistent with the scaling relation $(T-T_{NA})^{-3\nu}$, where ν is the correlation length critical exponent, and their ratio was approximately constant with T. The dielectric constants, the refractive indices, and the bend elastic constant for SCE12R also are reported.

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The smectic-*A* (Sm-*A*) phase is characterized by a periodic density wave of amplitude ψ and wave vector q_0 perpendicular to the average molecular orientation (i.e., the "director" $\hat{n}$), which we define as being parallel to the z axis [1]. Two types of elastic distortions are associated with smectic layering: Compression of the layers involves an energy per unit volume that, to lowest order, is given by $f_{compr}=\frac{1}{2}B(\partial u/\partial z)^2$, where B is the compression elastic constant and u is the deviation of the smectic layer from its undisturbed position. Additionally, there is an energy cost per unit volume when the molecules tilt by an angle θ with respect to the layer normal; to lowest order this is given by $f_{tilt}=\frac{1}{2}D_2\theta^2$, where D_2 is the tilt elastic constant. Both B and D_2 scale as $\langle\psi^2\rangle$ [1], and increase with decreasing temperature below the nematic–Sm-*A* phase transition temperature T_{NA}, which we found to be 79.5 °C. For $T>T_{NA}$ smectic fluctuations occur in the bulk nematic phase. Moreover, for a sufficiently smooth substrate treated for homeotropic orientation, surface-induced smectic layers appear, such that the order parameter ψ is largest at the substrate and decays into the bulk over a temperature-dependent correlation length ξ [2–8]. In a recent paper we examined the effect of surface-induced smectic layering in the nematic phase for a substrate treated to produce *tilted* alignment well above T_{NA} [9]. In this system there are two nematic easy axes, one approximately perpendicular and one approximately parallel to the surface, causing the liquid crystal to adopt a temperature-dependent equilibrium surface tilt angle θ_s determined by the strengths of the two easy axes [9,10]. We found that at temperatures far above T_{NA} the molecules tilt by a nonzero angle $\theta_s(T)$ [11]. On cooling, however, the energy term f_{tilt}, which promotes a director orientation perpendicular to the surface-induced smectic layers, becomes dominant and results in $\theta_s(T)\to 0$ at a temperature $T_a(>T_{NA})$; for $T_{NA}<T<T_a$ we found that $\theta_s=0$.

Let us now consider the anchoring properties at the liquid crystal–substrate interface in the purely homeotropic temperature region, viz., $T_{NA}<T<T_a$. In the absence of smectic order, the anchoring energy per unit area is given by $F_{anch}=\frac{1}{2}W_2\theta_s^2+\frac{1}{4}W_4\theta_s^4+\cdots$, where W_2 and W_4 are the quadratic (Rapini-Papoular) [12] and quartic anchoring strength coefficients [13], respectively. Note that $W_2<0$ for a surface treated so as to induce a nonzero polar pretilt angle θ_s [9,11]. To this we now must add the areal contribution $F_{tilt}=\frac{1}{2}\int_0^d dz\, D_2^0 e^{-2z/\xi}\theta_s^2\approx\frac{1}{4}\xi D_2^0\theta_s^2$ due to surface-induced smectic layering [9], which effectively stiffens the homeotropic anchoring and reduces the molecules' ability to tilt. Here it is assumed that θ_s is approximately constant over the length scale ξ and that $D_2(z)=D_2^0 e^{-2z/\xi}$ reflects the rapid decay of the surface-induced smectic order from the interface into the bulk, where $\xi\ll$ the cell thickness d. Thus, the effective surface free energy per unit area becomes

$$F_{surf}^{eff}=\frac{1}{2}\left(W_2+\frac{1}{2}\xi D_2^0\right)\theta_s^2+\frac{1}{4}W_4\theta_s^4\equiv\frac{1}{2}W_2^{eff}\theta_s^2+\frac{1}{4}W_4\theta_s^4.$$

Close to T_{NA}, where both D_2^0 and ξ become large, the coefficient W_2^{eff} is large and positive, and the director is oriented homeotropically. This is consistent with the large quadratic anchoring strength observed within the Sm-*A* phase by Li and Lavrentovich [14]. With increasing temperature and a concomitant decrease in surface-induced smectic order, W_2^{eff} decreases and eventually vanishes at T_a for a substrate treated for nonzero pretilt, resulting in the previously observed tilt transition from $\theta_s=0$ to $\theta_s>0$ for $T>T_a$ [9]. The interfacial behavior in the region $T_{NA}<T<T_a$, which reflects both the inherent nematic easy axes as well as surface-induced smectic layering, may be examined by means of a Fréedericksz transition technique [1]. In this experiment an applied electric field competes with surface anchoring and bulk elasticity, such that the director undergoes a nonzero tilt above a threshold field E_{LC}^{th}. It easily can be shown that

$$\cot(\pi E_{LC}^{th}/2U)=\pi K_{33}E_{LC}^{th}/(dW_2^{eff}U) \tag{1}$$

[13], where K_{33} is the bend elastic constant, $\Delta\chi$ is the (negative) electric susceptibility anisotropy, and $U=(\pi/d)(K_{33}/\Delta\chi)^{1/2}$. Here U corresponds to the Fréedericksz threshold field in the limit that the quadratic

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anchoring strength coefficient $W_2^{eff}\to\infty$ and/or $d\to\infty$. Note that E_{LC}^{th} does not depend on beyond-quadratic terms in F_{surf}. In this paper we report on optical transmission measurements around the Fréedericksz transition threshold for temperatures below the tilt transition temperature T_a. In addition to finding an expected small threshold field E_{th} on heating toward T_a due to the vanishing of W_2^{eff}, we also observe a *very* slow initial increase in transmitted optical intensity I with increasing field for $E>E_{LC}^{th}$, behavior that permits us to observe and measure the quartic coefficient in F_{surf}^{eff}. Although the quartic—and higher order—terms play an important role at the bulk smectic-*A*–smectic-*C* phase transition where D_2 vanishes, until now it has been inconsequential at temperatures far above that transition. Our central result is that the quartic coefficient of the tilt energy in the surface-induced smectic layers increases rapidly in the nematic phase as the temperature is decreased toward T_{NA}. This result indicates that the molecules' resistance to tilt in the surface-induced layers involves not only the quadratic coefficient D_2, but depends critically on beyond-quadratic terms as well.

Electrically conducting indium tin oxide–coated glass slides were cleaned with detergent, acetone, and ethanol, and then spin coated with the polyamic acid SE-1211, for which there exists a pair of easy axes that result in a nonzero tilt of the director far above T_{NA} [7,11]. The slides were prebaked for 30 min at 80 °C and baked for 50 min at 200 °C, and then rubbed uniformly with a single pass under a rayon cloth (Yoshikawa Chemical Co., YA-20-R, average fiber density was $\sigma_f=1411$ threads cm^{-2}) using an Optron rubbing machine. The "rubbing strength" n_f, which is defined in Ref. [15], was $n_f\approx 1.27\times 10^6$ cm^{-1}. Two slides, separated by Mylar spacers of nominal thickness 2 μm, were placed together in an antiparallel configuration, cemented, and placed into a temperature controlled oven. The thickness d of the cell gap, defined as the empty region between the polyimide alignment layers, was measured by an interferometric technique and found to be 4.28 ± 0.05 μm. The negative dielectric anisotropy racemic liquid crystal mixture SCE12R (Merck) was introduced into the cell in the isotropic phase and cooled into the nematic phase. Light from a He-Ne laser at wavelength $\lambda=633$ nm passed through a polarizer, the sample whose rubbing direction was oriented at 45° with respect to the polarizer, an analyzer crossed with respect to the polarizer, and into a photodiode detector, whose output was fed into a digital voltmeter. An ac voltage at frequency $\nu=1000$ Hz was applied across the liquid crystal cell. The amplitude of the applied voltage was increased in steps of $V_{cell}=0.075$ V, each voltage having a dwell time of 6 s before the next increase. We remark that the actual voltage difference V_{LC} applied across the liquid crystal layer was less than the voltage V_{cell} applied to the cell, viz., $V_{LC}=V_{cell}/[1+d_P/(\varepsilon_P\int_0^d\varepsilon^{-1}dz)]$, where ε is the temperature- and θ-dependent dielectric constant of the liquid crystal. The reduced voltage is due to the capacitive voltage drop across the two polyimide layers, having a combined thickness $d_P=1.90$ μm (as measured using a Dektak II profilometer) and dielectric constant $\varepsilon_P=2.9$ (as specified by the manufacturer). Note that data will be plotted as a function of V_{cell}, although modeling will be performed with V_{LC}. Measurements of intensity I vs applied voltage were made first at 87 °C, and subsequent measurements were made at decreasing temperatures toward T_{NA}. Figure 1 shows typical data over part of this temperature range.

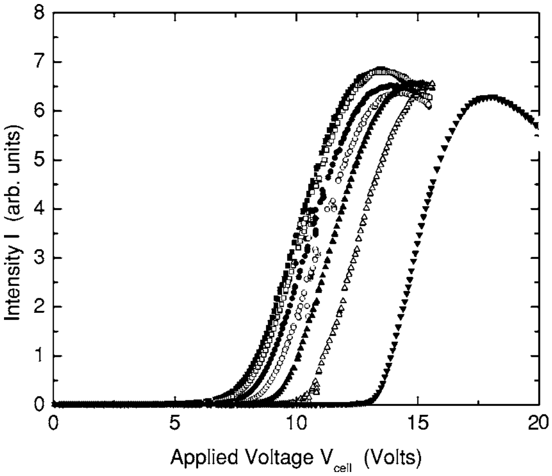

FIG. 1. Intensity vs voltage V_{cell} applied to the cell at selected temperatures of ■ 87, □ 86, ● 85, ○ 84, ▲ 83, △ 82, and ▼ 81 °C.

There are two features of note for the intensity scale used in Fig. 1: (i) there *appears* to be a Fréedericksz transition at moderately high threshold voltages V_{cell}^{th} for all temperatures $T<T_a\approx 85.5$ °C—this will turn out *not* to be the case—and (ii) the intensities at $V_{cell}=0$ for $T>T_a$ are significantly larger than the intensities measured at $T<T_a$. Figure 2(a) shows the intensity scale magnified by a factor of 200, and Fig. 2(b)

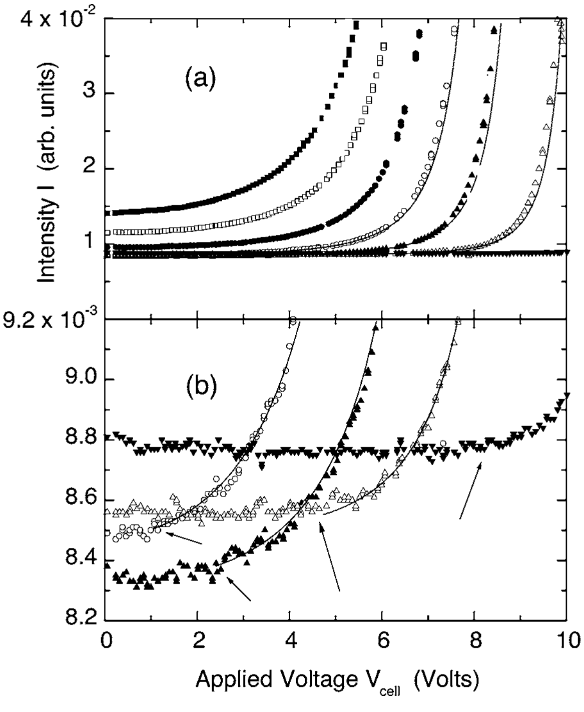

FIG. 2. Intensity vs V_{cell}. Scale enlarged by a factor of (a) 200 and (b) 8000 relative to Fig. 1. Solid lines show examples of calculated intensity, and arrows show the threshold voltage at several temperatures. Note that V_{LC} was calculated from the applied voltage V_{cell}. Symbols correspond to ○ 84, ▲ 83, △ 82, and ▼ 81 °C.

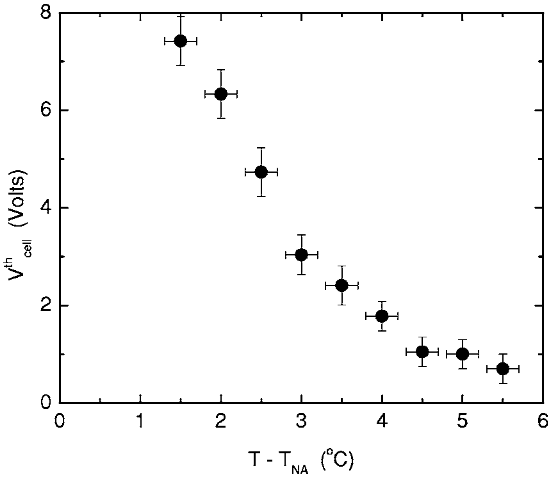

FIG. 3. V_{cell}^{th} vs $T-T_{NA}$. Note that the threshold vanishes above $T=T_a$, corresponding to approximately 85.5 °C.

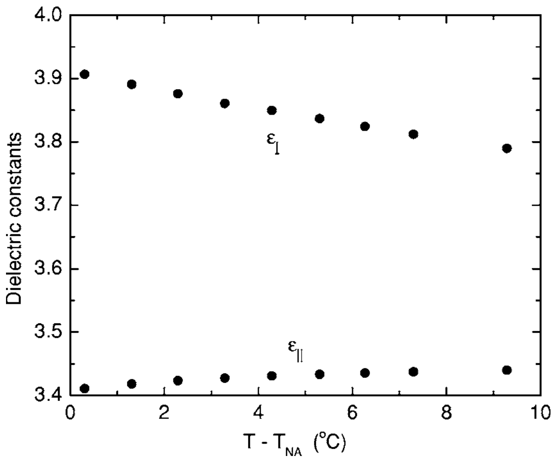

FIG. 4. Dielectric constants $\varepsilon_\perp$ and $\varepsilon_\parallel$ vs reduced temperature $T-T_{NA}$.

shows the scale magnified by a factor of 8000. (Note that, although the intensity is expressed in arbitrary units, these units are the same in both Figs. 1 and 2. Thus, the intensity scales shown in the figures may be compared directly.) From Fig. 2(a) we see that the intensities for $T>T_a$ at $V_{cell}=0$ vary considerably with temperature and that the slopes $dI/dV_{cell}>0$ at $V_{cell}=0$. These features are a clear indication that the director has a nonzero pretilt angle θ_s in the absence of an applied field. On the other hand, for $T<T_a$ it is obvious from Fig. 2(b) that the remnant intensity at $V_{cell}=0$ is much less temperature sensitive and that the slopes $dI/dV_{cell}=0$ at $V_{cell}=0$. (The small differences in intensity at $V_{cell}=0$ can be ascribed to temperature-dependent variations in the strain birefringence in the glass, as well as to variations of the laser intensity over time.) It is obvious that the initial intensity is very small and remains constant with increasing voltage until a temperature-dependent threshold voltage is reached (shown approximately by the arrows), above which I begins to increase very slowly with voltage [cf. Figs. 1 and 2(a)]. Thus the actual threshold voltages are considerably smaller than the apparent threshold voltages noted in Fig. 1 and item (i) above, with the discrepancy being largest at T_a (where W_2^{eff} is expected to vanish) and decreasing on lowering the temperature toward T_{NA} (where W_2^{eff} is expected to become large due to surface-induced smectic ordering). Thus the *apparent* Fréedericksz transition threshold voltages in Fig. 1 are artifacts of the extremely weak rise of the intensity for voltages just above the real Fréedericksz threshold, which actually occurs at lower voltages. It turns out that the intensity vs voltage behavior for very small W_2^{eff} depends strongly on the magnitude of the effective quartic coefficient W_4^{eff}, as we shall see below.

We analyzed the data first by estimating a value for T_{NA} and obtaining $W_2^{eff}(T)$ directly from the Fréedericksz threshold voltages V_{LC}^{th} applied across the liquid crystal—V_{LC}^{th} may be calculated from V_{cell}^{th} across the cell, as noted above—and from Eq. (1). V_{cell}^{th} vs $T-T_{NA}$ is shown in Fig. 3. We then considered the total volumetric free energy density $f_{tot}=f_{elastic}+f_{electric}+f_{surf}$, where $f_{elastic}=\frac{1}{2}K(d\theta/dz)^2$, $f_{electric}=D^2/[2\varepsilon_\perp(1-R\cos^2\theta)]$, and $f_{surf}=F_{surf}^{eff}[\delta(z)+\delta(z-d)]$. Because fittings are performed from $V_{LC}=V_{cell}=0$ to a voltage only slightly above V_{LC}^{th}, bend deformation dominates and therefore we used the single elastic constant approximation with $K=K_{33}$. Additionally, $R\equiv(\varepsilon_\perp-\varepsilon_\parallel)/\varepsilon_\perp$, where $\varepsilon_\perp$ and $\varepsilon_\parallel$ are the liquid crystal dielectric constants perpendicular and parallel to $\hat{n}$, respectively, and D is the magnitude of the electric displacement vector given by $D=-\varepsilon_\perp V_{LC}/\int_0^d(1-R\cos^2\theta)^{-1}dz$. The dielectric constants $\varepsilon_\perp$ and $\varepsilon_\parallel$ were measured using an Andeen-Hagerling 2500 capacitance bridge operating at 1000 Hz; results are shown in Fig. 4. The bend elastic constant K_{33} was obtained by measuring the Fréedericksz transition threshold for a thick cell (58.6 μm)—this threshold voltage corresponds approximately to U in the thick cell regime—and by taking $\Delta\chi=(\varepsilon_\parallel-\varepsilon_\perp)/4\pi$; results for K_{33} are shown in Fig. 5. Using the measured material parameters, exploiting the symmetry of θ about $z=d/2$, and temporarily estimating a value for the adjustable parameter W_4^{eff}, these equations were solved in a manner similar to that in Ref. [11] to obtain $\theta(z,V_{LC},T)$. The optical phase retardation $\alpha_{calc}(V_{LC},T)$ then was calculated as a function of temperature using $\theta(z,V_{LC},T)$, viz.,

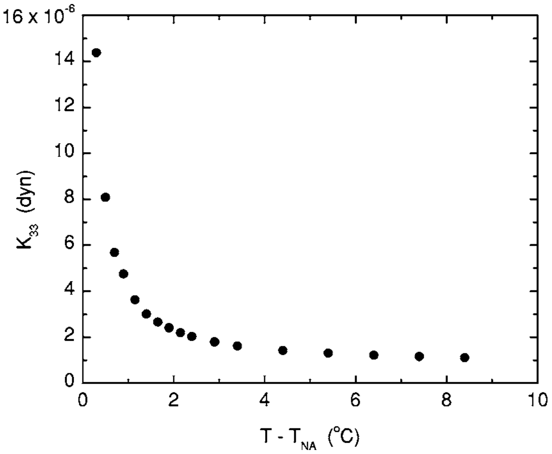

FIG. 5. Bend elastic constant K_{33} vs reduced temperature $T-T_{NA}$.

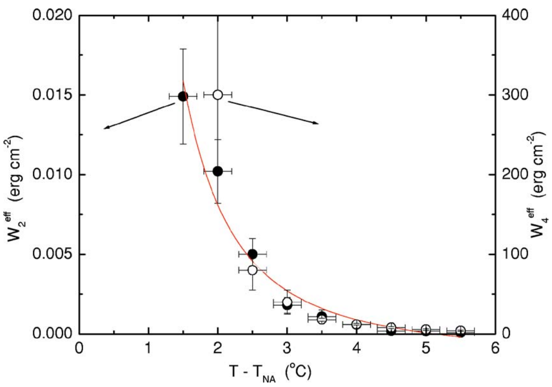

FIG. 6. (Color online) W_2^{eff} (solid circles, left-hand scale) and W_4^{eff} (open circles, right-hand scale) vs $T-T_{NA}$. Solid line is a fit of W_2^{eff} to the form $W_2+A[(T-T_{NA})/T_{NA}]^{-3\nu}$ (see text).

$$\alpha_{calc}(V_{LC},T) = n_\perp \int_0^d 2\pi\{[1-(1-n_\perp^2/n_\parallel^2)\sin^2\theta]^{-1/2}-1\}/\lambda \, dz$$

[11]. Here $n_\perp = 1.4805$ and $n_\parallel = 1.635$ are the ordinary and extraordinary refractive indices, respectively, of the liquid crystal measured at $\lambda = 633$ nm using an Abbé refractometer. Note that these values are nearly independent of temperature over the relevant temperature range. Finally, $I_{calc} = I_0 \sin^2(\alpha_{calc}/2)$ was calculated for each temperature as a function of V_{LC} (and therefore as a function of V_{cell}), where I_0 is the maximum intensity (for $\alpha=\pi$), which may be obtained experimentally from Fig. 1. A sizable region of parameter space for W_4^{eff} and T_{NA} was examined, where it was necessary to recalculate $W_2^{eff}(T)$ for each value of T_{NA}. The best agreement between the calculated and experimental intensities corresponds to a fitted value of $T_{NA} = 79.5 \pm 0.2$ °C, and is shown as a function of V_{cell} in Fig. 2(b) for several temperatures. Values for $W_2^{eff}(T)$ and $W_4^{eff}(T)$ are shown in Fig. 6. Finally, we checked the cell thickness d by applying a voltage V_{cell} up to 100 V and measuring the nearly saturated retardation. Using this technique, d was identical to the value obtained by interferometry of the empty cell.

The calculated intensities were found to be in good agreement with the experimental results, certainly up to $I \sim 0.05 I_0$, reflecting the small Fréedericksz threshold, the slow rise of intensity above the threshold, and the more rapid increase of intensity at higher voltages. However, at still higher voltages, where $I \gtrsim 0.1 I_0$, the experimental retardations rise a little more slowly than the theoretical values, requiring a larger voltage to reach I_0. Because we effectively truncated F_{surf}^{eff} at the quartic term, we believe that this slower increase of the experimental intensity with voltage is due to the presence of sixth—and possibly higher—order terms in the surface free energy density. This would imply that f_{tilt} requires not only a fourth order term, but higher order terms as well. *In other words, tilt with respect to the smectic layer normal is much stiffer than the usual harmonic approximation for f_{surf} would suggest.* The quartic and higher order terms normally are not observable in light scattering experiments due to the relatively small tilt angle (soft mode) fluctuations in the smectic layers far from the Sm-*A*–Sm-*C* transition. In this experiment, however, θ_s in the surface-induced smectic layers can become large at sufficiently large voltages, and thus the anharmonic terms in f_{tilt} become observable.

Let us now turn to the magnitudes of $W_2^{eff}(T)$ and $W_4^{eff}(T)$. (As an aside, we first note that measurements were not made *too* close to T_{NA} because of the growing correlation length, which has the effect of squeezing down the nematic region that can undergo a Fréedericksz transition. This becomes problematical when $\xi \gtrsim 0.01d$ [6].) Both $W_2^{eff}(T)$ and $W_4^{eff}(T)$ have a "bare" contribution associated with the anchoring properties of the nematic at a substrate, as well as a contribution due to surface-induced smectic order. Previously [9] we had estimated the contribution to $W_2^{eff}(T)$ from the positive ξD_2^0 term: Approximately 1 °C above T_{NA} we had found $D_2^0 \sim 3\times 10^4$ erg cm^{-3} and $\xi \sim 4\times 10^{-6}$ cm, resulting in a value for ξD_2^0 of order 0.1 erg cm^{-2}. This contribution, which scales as $[(T-T_{NA})/T_{NA}]^{-3\nu}$ where ν is the critical exponent for ξ [9], should be considerably smaller at the higher temperatures examined in this experiment. The data in Fig. 6 (closed circles) are consistent with this estimate for ξD_2^0, although smaller by a factor of about 3. It is important to bear in mind that $\langle\psi^2\rangle$, and thus D_2^0, depends on the roughness of the particular surface, and may be expected to vary from sample to sample. Another feature is that $W_2^{eff}(T)$ vanishes at T_a, and becomes negative for $T > T_a$ where the surface has been treated so that the ordinary nematic anchoring coefficient $W_2 < 0$ [11,9]. If we fit $W_2^{eff}(T)$ to the form $W_2+A[(T-T_{NA})/T_{NA}]^{-3\nu}$, keeping $\nu=0.7$ [9] and $T_{NA}=79.5$ °C, and allowing A and W_2 to vary, we find that $W_2 = -0.0013$ erg cm^{-2}, a very reasonable value in the temperature region where surface-induced smectic order can be ignored and the director has a nonzero polar tilt θ_s at $V_{cell}=0$. The fit is shown in Fig. 6, although it must be kept in mind that precision is limited due to experimental error. Values for $W_4^{eff}(T)$ (open circles, right-hand scale, Fig. 6) are larger than $W_2^{eff}(T)$. Previously we measured the ordinary contribution W_4 for the liquid crystal pentylcyanibiphenyl (5CB), which does not have a Sm-*A* phase, finding $W_4 \sim 1$ erg cm^{-2} [11]. The presence of surface-induced smectic order increases $W_4^{eff}(T)$, although far above T_{NA} the smectic contribution to $W_4^{eff}(T)$ is small, and thus $W_4^{eff}(T)$, as expected, is comparable to our previous result for W_2 for 5CB [11]. It also is interesting to note that the ratio $W_2^{eff}(T)/W_4^{eff}(T)$ does not vary systematically with temperature, indicating that the dependence on $\langle\psi^2\rangle$ and ξ is similar for both exponents. Thus $W_2^{eff}(T)$ dominates f_{surf} for small θ_s, but for $\theta_s \gtrsim 10^{-2}$ rad the quartic term becomes larger.

To summarize, we have demonstrated the existence of and measured as a function of temperature the leading anharmonic term in the inverse tilt susceptibility for surface-induced smectic order in the nematic phase, and shown that it has a significant effect on the director profile above the Fréedericksz transition threshold voltage.

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