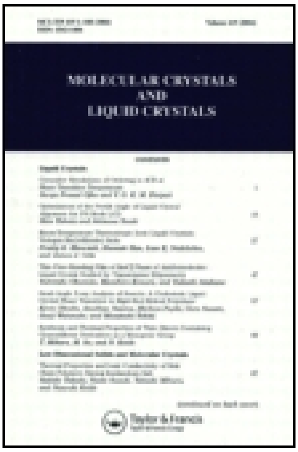

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Surface Transitions, Critical Adsorption, and Spontaneous Polarization Inversion in Freely Suspended Liquid-Crystal Films

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Surface Transitions, Critical Adsorption, and Spontaneous Polarization Inversion in Freely Suspended Liquid-Crystal Films[†]

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A summary is given of recent results of ellipsometric measurements on freely suspended films, between two and several hundred molecular layers thick, of 2-methylbutyl 4-alkanoyloxybiphenyl-4′-carboxylate liquid-crystal compounds showing smectic-A and ferroelectric smectic-C phases. The results concern in particular: the sign inversion of the spontaneous polarization in thin films, the thickness divergence of the surface-induced smectic-C order on approaching the bulk smectic-A – smectic-C transition in very thick films, and the behavior of the smectic-A – smectic-C surface transition in thin and thick films. Special attention is paid to new observations the origins of which are still to clarify.

1. INTRODUCTION

Freely suspended films of smectic liquid-crystal compounds are valuable tools for experimental studies concerning dimensionality effects, surface phenomena, and structural investigations (some recent reviews are [1] [2] [3]). Freely suspended films consist of an integral number (between some thousands and only two) of molecular smectic layers, the layer planes being parallel to the two free surfaces. Especially when phenomena are studied, which involve a tilting of the molecules (e.g., smectic-A – smectic-C transitions or transitions to ferrielectric and antiferroelectric smectic-C phases which are assumed to possess special tilt direction alternation patterns), ellipsometry has turned out to be a useful method for the study of freely suspended films [4] [5] [6] [7] [8]. In ellipsometry, one determines two quantities, Δ and Ψ, which describe the state of polarization of light which is reflected by or transmitted through the sample [9]. In the present study, we use a null-ellipsometer and analyze the polarization of light which transmitts the film under an angle of incidence of $\frac{\pi}{4}$; details of our set-up are given in [6].

If the molecules are chiral the smectic-C phase shows a spontaneous electric polarization $\vec{P}_s$, the direction of $\vec{P}_s$ being definitely coupled to the direction of the molecular tilt [10]. By applying a d.c. electric field which aligns the direction of $\vec{P}_s$,

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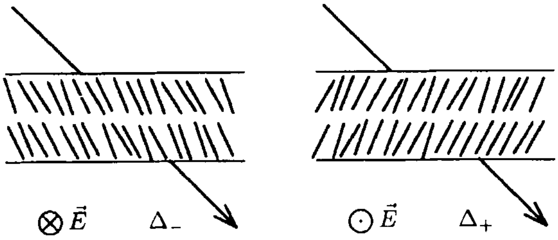
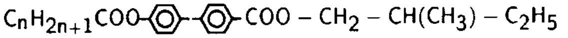


FIGURE 1: Experimental geometry for measuring Δ_+ (tilt direction away from incident laser beam) and Δ_- (tilt direction towards incident laser beam) in ferroelectric smectic-*C* films.

TABLE 1: Compounds under investigation

			
		transition temperatures	$\vec{P}_s$ inversion temperature
MBOOBC	(n = 8)	Sm-*C* 41°C Sm-*A* 60°C iso	18°C
MBNOBC	(n = 9)	Sm-*C* 48°C Sm-*A* 62°C iso	29°C
MBDOBC	(n = 10)	Sm-*C* 48°C Sm-*A* 63°C iso	27°C
MBNOBC/MBDOBC (3:2)		Sm-*C* 48°C Sm-*A* 62°C iso	28°C

one can thus fix the tilt direction in the smectic-*C* phase which would be otherwise free to take any azimuthal orientation between 0 and 2π. Since one of the ellipsometric quantities, namely Δ (the phase difference between the *s*- and *p*-polarized components of the transmitted light), depends strongly on the position of the optical axis, we can obtain in ferroelectric smectic-*C* films two different values Δ_+ and Δ_- corresponding to two opposite tilt directions (one for each polarity of the applied d.c. field, cf. fig. 1). The difference $\Delta_+ - \Delta_-$ is a measure of the mean tilt angle $\langle\theta\rangle$ of the optical axis of the film[1]; if $\langle\theta\rangle$ is zero (e.g. in a smectic-*A* phase or in an antiferroelectric smectic-C_A phase), Δ_+ is equal to Δ_-.

The results presented here concern some members of the 2-methylbutyl 4-alkanoyloxybiphenyl-4′-carboxylate homologous series [11] and a binary mixture of these compounds. The phase sequence is always (with decreasing temperature) isotropic - smectic-*A* - smectic-*C*; the transition temperatures, molecular stuctures, and abbreviations used here are given in table 1.

Fig. 2 shows the temperature dependence of Δ_+ and Δ_- for a 26-layer film of MBNOBC. With decreasing temperature we note three "interesting" regions: At 56°C, several degrees above the bulk smectic-*A* - smectic-*C* transition, Δ_+ and Δ_- start to deviate from their common value above 56°C; this is the surface transition where the first non-zero tilt appears in the layers at the free surfaces (cf. section 2). Around 48°C (the bulk smectic-*A* - smectic-*C* transition temperature), the contribution of the interior layers to the overall amount of tilt becomes obvious; in very thick films (quasi semi-infinite samples) we observe here a divergence-like

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[1] For the actual calculation of $\langle\theta\rangle$ it is more convenient to use the difference $\Delta_+ - \Delta_A$ (Δ_A being the value determined in the smectic-*A* temperature range where $\Delta_+ = \Delta_-$) because Δ_+ is almost linearly related to $\langle\theta\rangle$ whereas for Δ_- this is the case only for small $\langle\theta\rangle$ [6].

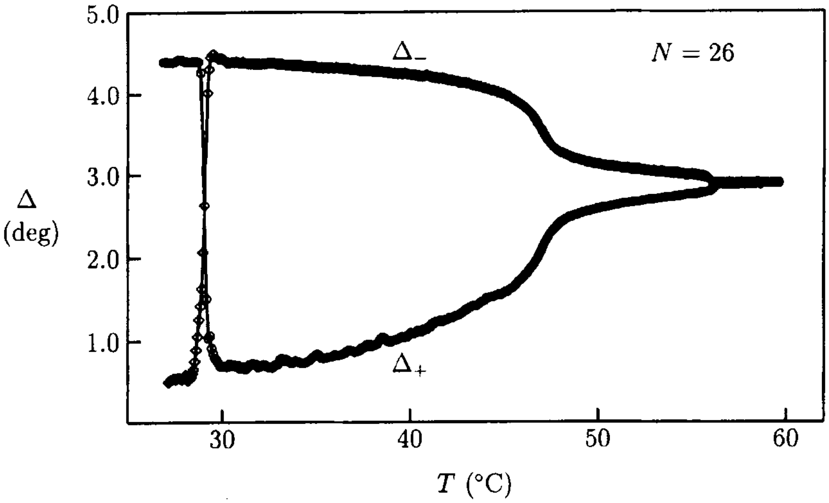

FIGURE 2: Temperature dependence of Δ_+ and Δ_- in a 26-layer film of the compound MBNOBC. One can distinguish between regions where the tilt is zero in all layers ($T >$ 56°C), where mainly the surface layers are tilted (50°C $< T <$ 56°C), and where all layers are tilted ($T <$ 48°C). At 29°C, a spontaneous inversion of the tilt direction with respect to the direction of the applied constant d.c. field occurs.

phenomenon which should be describable by the Fisher-de Gennes-model of critical adsorption [12] (cf. section 3). At 29°C, deep within the smectic-C phase, there is a sudden interchange of the Δ_+ and Δ_- values, i.e., there is a spontaneous inversion of the tilt direction with respect to the applied field direction; the origin of this observation rests in the so-called sign inversion of $\vec{P}_s$ which occurs also in bulk samples of the compounds studied here (cf. section 4).

2. THE SMECTIC-A - SMECTIC-C SURFACE TRANSITION

It is generally observed that the free surface of a liquid-crystalline material has a strong ordering effect: if a phase transition is approached from the high-temperature side, the surface layers of freely suspended films transform into the low-temperature phase several degrees above the bulk transition temperature. On further approaching the bulk transition, the thickness of the ordered surface domain grows in most cases (i.e., for most smectic – smectic transitions) via a series of individual layer-by-layer transitions [13] [14] [15] even if the bulk transition is continuous [16].

In the case of the smectic-A – smectic-C transition, however, only one well-defined transition, namely a transition in the surface layers, characterized by a steep increase of $\langle\theta\rangle$ within a few tenth of one degree centigrade, is observed. Below this surface transition the overall amount of tilt grows continuously without reflecting the layered structure of the smectic phases [4] [5]. This is also the case for the compounds of the present study: Fig. 3 shows the temperature dependence of $\Delta_+ - \Delta_A$ (cf. footnote 1) in the temperature region of the smectic-A – smectic-C surface

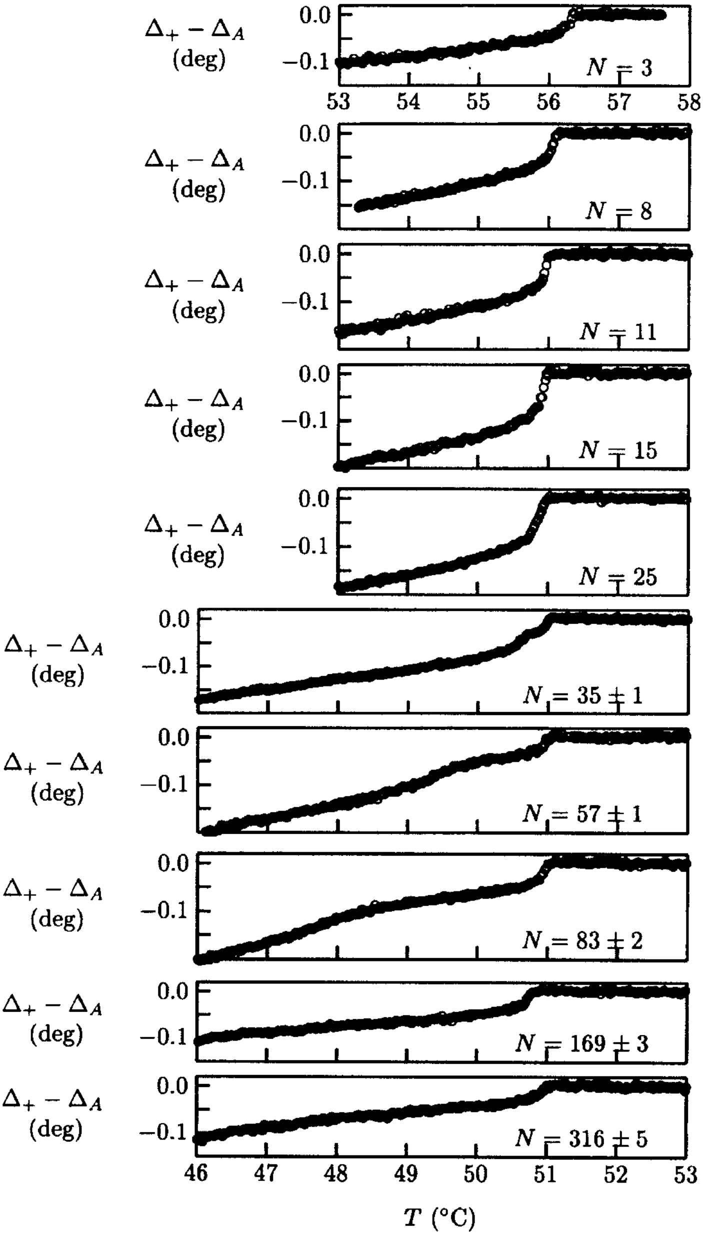

FIGURE 3: Temperature depedence of the difference $\Delta_+ - \Delta_A$ (Δ_A being the Δ-value in the Sm-A phase, cf. footnote 1) in films with thicknesses between three and ≈ 300 layers (given by N) of MBOOBC. The amount of $|\Delta_+ - \Delta_A|$ is almost linearly related to the mean tilt angle $\langle\theta\rangle$ of the optical axis of the film [6]. (Note that the temperature scale of the 3-layer film is shifted by 5 K with respect to the other films.)

transition for several films of MBOOBC. Similar as found for the well-known compound DOBAMBC [4] [5], the tilt angle grows below the surface transition smoothly with decreasing temperature. However, we have found [17] for the MBnOBC compounds some new features which were not observed in the earlier studies [4] [5] of DOBAMBC:

First, the surface transition clearly involves more layers than just the first smectic layer adjacent to the surface. This becomes obvious when regarding films of different thicknesses and comparing the amount of $\Delta_+ - \Delta_A$, determined 0.3 degrees below the surface transition (i.e., at a temperature just below the steep increase of $\langle\theta\rangle$). In the thickness range up to 30 layers, $|\Delta_+ - \Delta_A|$ first increases with increasing film thickness and then tends to saturate. Since the amount of $\Delta_+ - \Delta_A$ corresponds directly to the "total amount" of tilt in a given film, i.e., the average tilt angle per layer multiplied by the number of layers, $\langle\theta\rangle N$, we can conclude that more layers than just the first surface layer participate in the surface transition (otherwise the interior layers would not contribute to the overall tilt and $\Delta_+ - \Delta_A$ would not depend on the film thickness): our data are consistent with an exponentially decaying tilt profile with a correlation length of four layers just below the surface transition [17].

Secondly, we observe a splitting of the surface transition into two "steps", which appears for film thicknesses above 25 layers and vanishes again for thicknesses above 100 layers, because the second "step" at lower temperatures becomes more and more smeared out with increasing thickness (cf. fig. 3). This two-step transition is not consistent [17] with the layer-by-layer behavior observed for most smectic phase transitions. We propose here, that our observation might result from the neighbourhood of a prewetting critical point: systems, which show in bulk a first-order phase transition, can show at an interface a wetting transition where one of the two coexisting phases forms a macroscopically, in principle infinitely thick layer at the interface (see e.g. [18]). If this wetting transition is first-order, a line of first-order prewetting transitions, terminating at a prewetting critical point, should be present in the phase diagram [19]. Only few experimental observations of prewetting transitions, where the thickness of the wetting layer alters abruptly from thin to thick (but still finite), have been reported so far [20] [21] [22]. In our experiment, of course, we do not approach a first-order bulk transition. Thus, the behavior of the smectic-C phase interposing the smectic-A/air interface is to be described by critical adsorption (cf. section 3) rather than by wetting. Nevertheless, it is not impossible that a prewetting critical point is situated close to our experimental path in the temperature-order parameter-diagram and just as the closeness of a liquid-gas critical point leads in a supercritical fluid to a steep temperature dependence of the density in a certain temperature range, the closeness of a prewetting critical point may lead to a steep temperature dependence of the thickness of the surface layer in a certain temperature range, i.e., the second "step" which we observe in the $\Delta_+ - \Delta_A$ curves at lower temperatures would then correspond to a sudden increase of the thickness of the tilted surface domain. According to theoretical studies [23], the coordinates of a prewetting critical point depend on several quantities such as surface fields and surface enhancements of the molecular interactions. If we assume that a variation of the film thickness leads to a variation of these quantities, it might be possible to explain why the second "step" vanishes again in films thicker than

100 layers. However, the above discussion is strongly speculative and further experiments are needed.

3. APPROACHING THE BULK TRANSITION IN THICK FILMS: DIVERGENCE OF THE SURFACE-INDUCED EXCESS ORDER

Since the smectic-A – smectic-C transition is second-order in the compounds studied here, there is no coexistence of a tilted smectic layer and an adjacent untilted layer. Thus, when the first finite tilt appears at the surface transition there will be a tilt profile across the whole film (far away from the surface, however, the tilt may be unobservably small). In a semi-infinite system, in which a critical point or second-order transition is approached, the profile $m(z)$ (z being the distance from the surface and m the difference of the local value of the order parameter to its bulk value) of such a surface-induced excess order is expected to show a universal behavior known as critical adsorption [12] [24]. The behavior is governed by the divergence of the bulk correlation length ξ: for temperatures far above the bulk critical temperature T_c (or for large values of z/ξ), an exponential decay $m(z) \propto e^{-z/\xi}$ is predicted, whereas close to the critical point (or for small values of z/ξ), $m(z)$ should decay algebraically as $(z/\xi)^{-\beta/\nu}$ (β and ν being the order parameter and correlation length critical exponents); as T_c is approached, the integral $\int_0^\infty m(z)dz$, corresponding to the overall amount of the excess surface order, is expected to diverge as [12] [24]:

$$\int_0^\infty m(z)dz \propto t^{-(\nu-\beta)} \qquad \text{with } t = (T - T_c)/T_c. \tag{1}$$

With our present ellipsometric setup it is difficult to obtain direct informations about the tilt profile, but relation (1) should be easily to check by our experiment: in a thick film at $T > T_c$, the quantity $\langle\theta\rangle N$ (i.e., the mean tilt angle multiplied by the number of layers) corresponds directly to the integral $\int_0^\infty m(z)dz$ of relation (1). We have thus recently determined [25] the temperature dependence of $\langle\theta\rangle$ in films consisting of hundreds of layers. Figure 4 shows the temperature dependence of Δ_+ and Δ_- for a 316-layer film of MBOOBC. Close to the bulk smectic-A smectic-C transition temperature (41°C), the difference $|\Delta_+ - \Delta_-|$ becomes large showing the expected divergence-like behavior.

The corresponding temperature dependence of $\langle\theta\rangle N$ is shown in figure 5. We find that a simple power law as

$$\langle\theta\rangle N \propto t^{-a} \tag{2}$$

can describe our data only in a certain temperature range from 0.1 degree to 1 degree above T_c. In this temperature region, we find for the exponent a a value of about 0.5. A second measurement on a 690-layer film yielded practically the same result.

In the Fisher-de Gennes-model, a equals the difference between the order parameter and correlation length exponents, i.e., $a = \nu - \beta$. For the $3d$-XY universality class one obtains $\nu - \beta = 0.32$; clearly, our result is not consistent with this prediction. A possible reason for this may be that the transition is to be placed in an

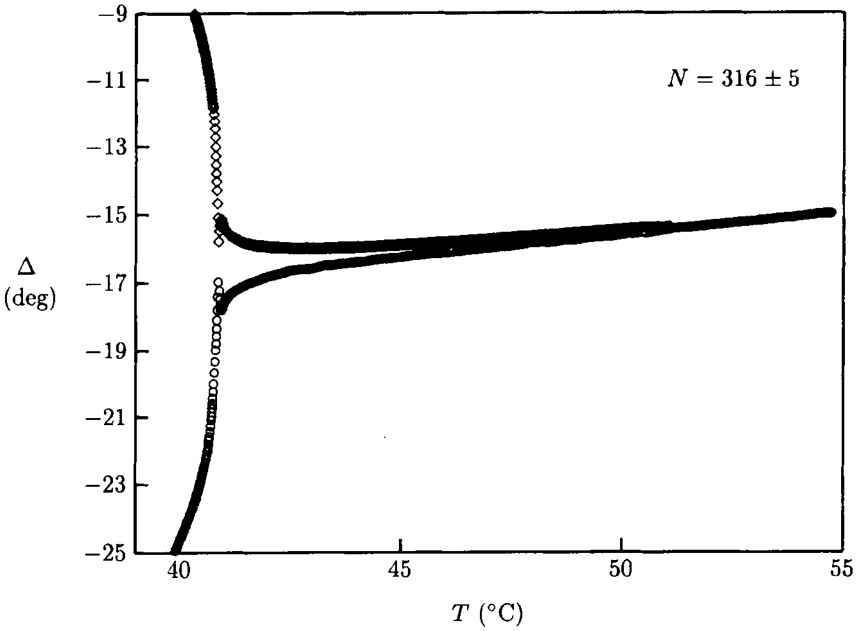

FIGURE 4: Temperature depedence of Δ_+ (○ symbols) and Δ_- (◇ symbols) for a 316-layer film of the compound MBOOBC.

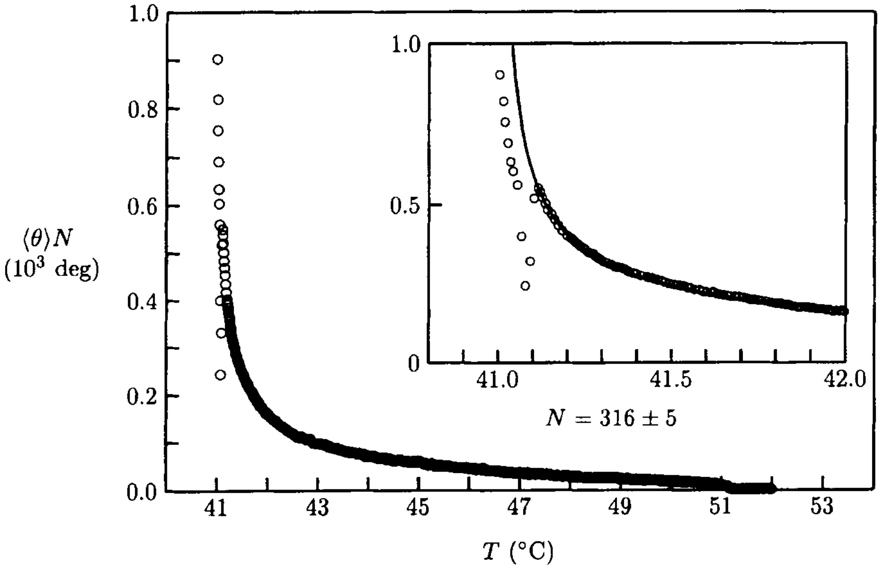

FIGURE 5: Temperature depedence of the average tilt angle $\langle\theta\rangle$, multiplied by the number of layers N, for a 316-film of MBOOBC. Inset: Temperature dependence of $\langle\theta\rangle N$ around T_c; the solid line is a fit according to equation (2) to the data in the temperature range from 41.1°C to 42.0°C with T_c and a taken as free parameters. The best fit is obtained for $T_c = 41.00$°C and $a = 0.55$.

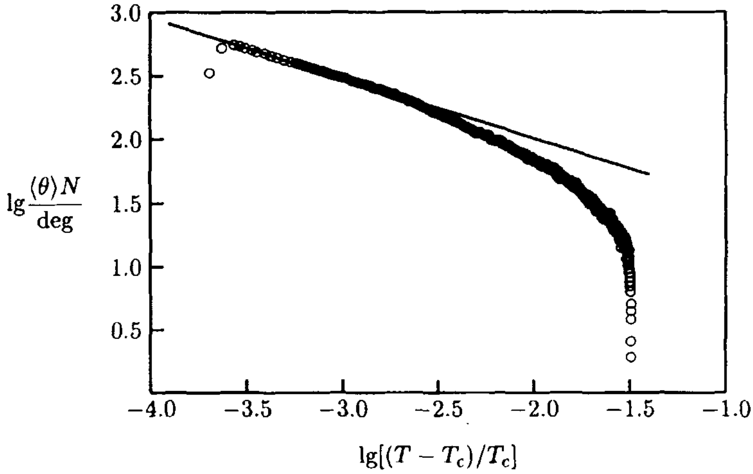

FIGURE 6: Double logarithmic plot of the temperature dependence of $\langle\theta\rangle N$ for a 316-layer film of MBOOBC. The solid line has a slope of −0.5. At $\lg t = -1.5$, the surface transition occurs where the tilt angle drops to zero.

anisotropic universality class with different exponents $\nu_{\|}$ and $\nu_{\perp}$ for the directions parallel and perpendicular to the smectic layer normal. For the nematic – Sm-A transition this seems to be indeed the case and experiments indicate $\nu_{\|} \approx 1.3\nu_{\perp}$ with $\nu_{\|}$ amounting up to 0.83 [26]. In our experiment, we also probe the correlation in the direction parallel to the smectic layer normal and a value of $\nu_{\|} \approx 0.8$ would be more consistent with our result than the "isotropic" value $\nu = 0.67$. However, although theoretical studies [27] consider the possibility of anistropic exponents for smectic phases in general, corresponding experimental studies for the Sm-A – Sm-C transition have not been reported so far. An independent determination of ν (or $\nu_{\|}$ and $\nu_{\perp}$) is thus clearly desirable in order to check the consistency of our data within the Fisher-de Gennes-model.

At temperatures higher than T_c+1 K, the presence of the surface transition causes significant deviations from the power law behavior as is well demonstrated by a logarithmic plot of our data (cf. fig. 6). Close to the bulk transition ($T < (T_c + 0.1$ K)), we observe an unexpected minimum of $\langle\theta\rangle N$. Instead of showing a simple cross-over from a power-law divergence above T_c to a saturation below T_c, the monotonic increase of the $\langle\theta\rangle N$ values with decreasing T is interrupted by a sudden decrease followed again by an increase. The origin of this unexpected feature is not clear. We observe it in all films thicker than about 150 layers (but not in thinner films) and in the same way in heating and cooling runs. The observed decrease of the mean tilt angle values, resulting either from a decrease of the tilt angle or the number of tilted layers or (most probably) from a combination of both, seems to indicate a sudden change of the relevant molecular interactions close to T_c. It is interesting to note that a similar behavior was observed in a study [28] of critical adsorption in a completely different system: the adsorption of fluid SF_6 on graphite also shows an unexpected decrease when the (liquid – gas) critical point is approached. Also in this case the origin of the observed behavior is still to clarify.

4. SIGN INVERSION OF THE SPONTANEOUS POLARIZATION IN THE FERROELECTRIC SMECTIC-*C* PHASE

The compounds under investigation show in their bulk ferroelectric Sm-*C* phase at a certain temperature a spontaneous inversion of the direction of the spontaneous polarization $\vec{P}_s$ with respect to the direction of the molecular tilt. Usually, the direction of $\vec{P}_s$ in a given compound is fixed, i.e., it is along either $(\vec{z} \times \vec{n})$ or $-(\vec{z} \times \vec{n})$ ($\vec{n}$ being the mean direction of the long molecular axis and $\vec{z}$ being a normal vector of the smectic layer plane). The two possible directions are distinguished by assigning a "sign" to $\vec{P}_s$, namely a positive sign if $\vec{z}\vec{n}\vec{P}_s$ form a right-handed system and a negative sign for the opposite case [29].

In 1986 a few compounds were found which showed a spontaneous sign inversion of the $\vec{P}_s$ direction at a certain temperature within the Sm-*C* phase range [30] [31] [11]; in these compounds, θ shows the usual monotonic increase with decreasing temperature whereas $|P_s|$, after an initial increase, decreases, equals zero at the inversion temperature, and increases again. Since then, this phenomenon was observed in single-component systems [32] [33], mixtures of chiral and non-chiral compounds [34], and polymer systems [35], but its actual origin is still to clarify.

The compounds under investigation are also known to show the $\vec{P}_s$ sign inversion in their bulk smectic-*C* phase [11] and we have thus looked for this phenomenom in freely suspended films [36]. As shown in fig. 2, the sign inversion occurs also in a 26-layer film as is demonstrated by the spontaneous interchange of the Δ_+ and Δ_- curves. The inversion temperature is in the 26-layer film practically the same as in the corresponding bulk sample (29°C) but shifted to lower values in thinner films. In a binary 3:2 mixture of MBNOBC with MBDOBC, in which the melting point is suppressed, the $\vec{P}_s$ sign inversion can be observed also in very thin films consisting of four and three layers where the inversion temperature amounts to 21.4°C and 18.9°C, respectively (cf. fig. 7). Comparing films of different thicknesses, we find essentially the same behavior in all films: the sign inversion of $\vec{P}_s$ occurs within a narrow temperature interval of a few tenth of one degree and thus obviously simultaneously in all layers of a given film. There is no indication of an "inversion profile" across the film, i.e., the surface layers do not show a different behaviour compared to the interior layers. Comparing films of various thicknesses, the only difference consists in the value of the inversion temperature which decreases linearly with the reciprocal film thickness (cf. fig. 8).

The observed dependence of the inversion temperature on the film thickness reminds one to the behavior of a phase transition temperature, which is expected, according to finite-size scaling predictions [37], to decrease linearly with $1/N^{1/\nu}$ (ν being the critical exponent of the correlation length). The $\vec{P}_s$ sign inversion is of course not a phase transition; nevertheless, the downshift of the inversion temperature looks like a pure dimensionality effect, i.e., if we regard the sign inversion of $\vec{P}_s$ — according to a theoretical model [38] [39] — as the result of a shift of an equilibrium between different molecular conformers possessing opposite signs of $\vec{P}_s$, the reduced dimensionality in thin films can be expected to favour the less-ordered

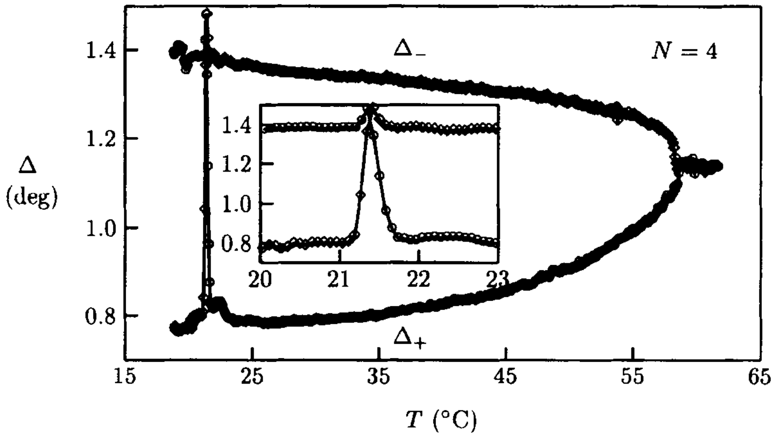

FIGURE 7: Temperature depedence of Δ_+ and Δ_- in a 4-layer film of a 3:2 MBNOBC/MBDOBC mixture. The inset shows the behaviour close the inversion temperature. (The increase of the Δ_- values immediately before and after the tilt inversion does not indicate an increase of the tilt angle but results from the change of the transmitted light polarization during the rotation of the optical axis on the tilt cone.)

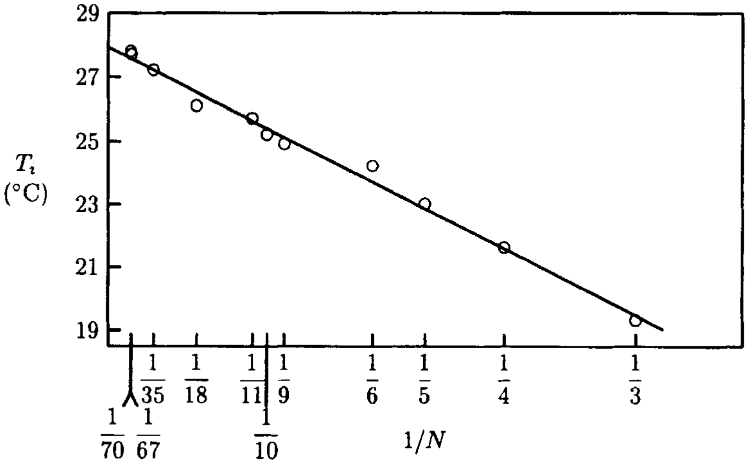

FIGURE 8: $\vec{P}_s$ sign inversion temperature T_i as a function of the reciprocal film thickness (N = number of smectic layers) for various films of a 3:2 MBNOBC/MBDOBC mixture.

molecular species (i.e., those conformers which possess the larger entropy and which prevail at higher temperature) and should thus result in a downshift of the inversion temperature.

Other theoretical models [40] [33] explaine the $\vec{P}_s$ sign inversion as the result of a competition between dipolar and quadrupolar ordering of the molecules. The potential of the molecular rotation around the long axes is expected [41] to change its form with increasing tilt angle from dipolar to quadrupolar leading to a change of the mean orientation of the molecular dipole moment and thus, for certain molecular structures, to a sign reversal of $\vec{P}_s$. Our results, however, show clearly that the value of the inversion temperature is not connected to a certain tilt angle value (in thin films the whole θ vs. T is shifted to higher temperatures whereas the inversion temperature is shifted to the opposite direction, i.e., the inversion occurs in thin films at significantly larger θ values compared to the bulk). Thus, if the competition between dipolar and quadrupolar molecular ordering is responsible for the $\vec{P}_s$ sign inversion, one has to regard other origins of the change of the rotational potential than the increasing tilt angle.

ACKNOWLEDGMENTS

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