

Substrate-induced order in the isotropic phase of a smectogenic liquid crystal: A deuteron NMR study

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Using deuteron nuclear magnetic resonance, we study the pretransitional wetting behavior of the smectogenic and nematogenic liquid crystal 8CB in the isotropic phase confined to 200 nm diameter channels of Anopore membranes. The channels were treated with aliphatic acid to impose homeotropic alignment. Just above the nematic-isotropic transition we observe an enhanced line splitting compared to non-smectogenic homologs such as 5CB; moreover, the line splitting is characterized by a discontinuity of its slope at approximately 5 K above the transition temperature. This deviation from a purely nematic wetting scenario is attributed to the substrate-stabilized smectic order within the wetting film, which appears to be stimulated by the proximity of the smectic-A phase: in 8CB, the smectic-A-nematic transition occurs approximately 7 K below the nematic-isotropic transition. We interpret the data in terms of a semimicroscopic Landau–de Gennes type model, which allows us to estimate the thickness of the presmectic film—which consists of 2 bilayers—as well as the parameters of the surface interaction and the effective smectic-nematic coupling.

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I. INTRODUCTION

Among the main reasons for the undisputed technological importance of liquid crystals are their orientability and orderability by solid substrates, which propagate over macroscopic distances, and the coupling between the liquid-crystalline molecules and the confining walls is undoubtedly one of the most thoroughly studied topics of the physics of mesophases [1,2]. In particular, this coupling can give rise to various types of substrate-stabilized order, which modifies the pretransitional behavior of liquid crystals significantly.

An intriguing and widespread feature of the substrate-stabilized order in liquid crystals is the smecticity of the boundary layer, which has basically a purely steric background—the impenetrability of the wall—although it can also be induced by chemical as well as mechanical treatment. The evolution of the positional order of the molecules can be studied very effectively by x-ray scattering [3,4] but it can also be detected either directly or indirectly by other experimental techniques [5–7]. For example, nuclear magnetic resonance (NMR) methods—sensitive to the degree of orientational order and indispensable for the identification of liquid-crystalline structures in confined geometries—offer an insight into the presmectic order through the coupling between the positional and the orientational degrees of freedom.

In this study, we focus on the pretransitional substrate-induced order in the isotropic phase of α -deuterated 4'-n-4-octyl-cyanobiphenyl (8CB) confined to treated Anopore membranes.

By measuring the splitting of the deuteron NMR spectrum at temperatures above the nematic-isotropic phase transition temperature T_{NI} , we monitor the evolution of the wetting layer. We find that in 8CB, which has the phase sequence crystal \leftrightarrow smectic-A \leftrightarrow nematic \leftrightarrow isotropic, the pretransitional orientational order in the isotropic phase is much more pronounced than in its alkylcyano-biphenyl homolog 5CB, which does not form a smectic phase. We interpret the 8CB spectra in terms of a phenomenological Landau–de Gennes-type model of wetting. The analysis indicates that the enhanced line splitting is related to pretransitional smectic order within the boundary layer.

The disposition of the paper is as follows. In the next section we describe the experiment, and then the theoretical model of the wetting behavior is presented. In Sec. IV we analyze the data and propose a plausible scenario of the development of the substrate-induced order in 8CB. Section V concludes the paper and summarizes some of the open questions raised by the study.

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II. EXPERIMENT

A. Sample

The wetting behavior of liquid-crystalline systems can be studied in a variety of confined geometries, such as spherical cavities of PDLC's, porous glasses, aerogels, polymer networks, filter membranes, and so on [2]. Among these, the inorganic Anopore membranes (Al_2O_3) are most suitable for NMR experiments for a number of reasons. First, the cylindrical geometry of the pores is well defined and the distribution of their diameters is strongly peaked around the nominal value (Fig. 1), which simplifies the data analysis significantly.

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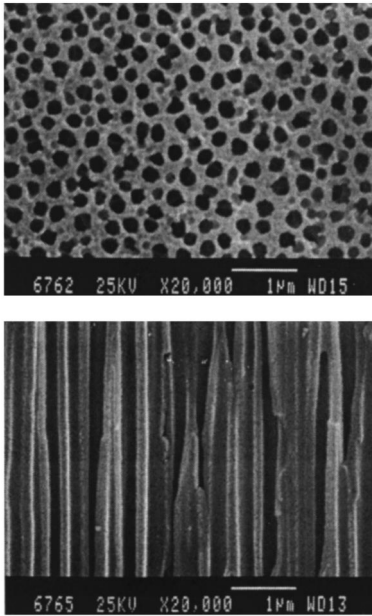


FIG. 1. Scanning electron micrograph of Anopore membranes: top surface (top) and cross-section (bottom). Micrograph provided by Ceramics Department, J. Stefan Institute, Slovenia.

cantly. Secondly, the membranes are highly porous and are easily permeated by chemical agents that control the anchoring and wetting parameters. Anopore membranes are commercially available in several pore sizes ranging from 20 to 200 nm; we used 60- μm -thick membranes with 200-nm-diameter channels.

Our samples were prepared by immersing the membranes in a 2% methanol solution of $\text{C}_{15}\text{H}_{31}\text{-COOH}$ for 1 min and baking them in a vacuum oven for about 1 h at 140 °C. After that they were cut into strips and filled with the isotropic phase of α -deuterated 8CB. To attain the desired signal-to-noise ratio, 40 strips were stacked on top of each other and sealed in a thin-walled NMR tube.

The NMR spectra were recorded upon cooling the sample from about $T_{\text{NI}} + 19$ K to T_{NI} in steps of 0.5 K; the temperature stability of the setup was about ± 0.1 K. In order to achieve a reasonable signal-to-noise ratio each spectrum was averaged a few thousand times. The estimated experimental error of the line splitting ranges from a few percents at $T_{\text{NI}} + 19$ K to less than one percent in the immediate vicinity of the clearing point.

The orientation of the liquid-crystalline molecules at the surface was determined by recording the spectra in the nematic phase as a function of the angle between the magnetic field and the axis of the cylindrical channels, which is normal to the membrane itself. For channels parallel to the field the splitting of the NMR spectrum turned out to be exactly half of the splitting in bulk nematic phase. This demonstrates that the anchoring is homeotropic, i.e., the molecules are aligned normal to the wall. In order to simplify the analysis of the data, our experiment was performed with channels parallel to the magnetic field.

B. Deuteron NMR spectra

Deuteron NMR represents a direct probe of the orientational order within the liquid-crystalline sample, which is

proportional to the quadrupole-splitting frequency from selectively deuterated molecules. In bulk nematic phase, the spectrum consists of two sharp lines which merge into a single narrow line above the nematic-isotropic transition temperature T_{NI} [8]. In some microconfined liquid crystals, the spectrum is split even above T_{NI} although the splitting is much smaller than in nematic phase—usually of the order of 1 kHz. This confinement-induced splitting is caused by the orientational order stabilized by the walls of the host medium.

In microconfined systems with characteristic size ~ 100 nm, the distance traversed by the molecules during the characteristic time of NMR measurement exceeds the size of the voids. As a result, the spectrum is completely motionally averaged over the volume of the void. In such a case, the line splitting in a uniaxial liquid-crystalline system is given by [9,10]

$$\Delta\nu = \Delta\nu_0 \left\langle \frac{1}{2} [3 \cos^2 \theta(\mathbf{r}) - 1] \right\rangle \langle S(\mathbf{r}) \rangle, \quad (1)$$

where $\Delta\nu_0$ is the bulk quadrupolar splitting in the perfectly ordered nematic phase, $\theta(\mathbf{r})$ is the angle between the local director and the magnetic field, $S(\mathbf{r})$ is the local degree of nematic order, and $\langle \dots \rangle$ denotes spatial average over the capillary.

It is reasonable to assume that the director structure within the boundary layer is temperature independent, which has been observed in related systems in the past [11]. This means that the only temperature-dependent factor in the line splitting [Eq. (1)] is the average degree of order, which is proportional to the so-called adsorption parameter

$$\Gamma = \int_0^\infty S(z) dz, \quad (2)$$

where z is the distance from the order-inducing wall. NMR line splitting is therefore directly related to the degree of orientational order of a liquid-crystalline system and its wetting behavior: if Γ diverges as the temperature approaches the clearing point T_{NI} , the wetting is referred to as complete, otherwise it is said to be partial [11–13].

The temperature variation of the deuteron NMR line splitting in isotropic 8CB is shown in Fig. 2; for comparison, $\Delta\nu$ in isotropic 5CB, deuterated in the same position of the aliphatic chain and confined to identical Anopore membranes [13], is also plotted in the figure. In both compounds, a considerable pretransitional increase of the line splitting is observed but in the immediate vicinity of the clearing point—from T_{NI} to $T_{\text{NI}} + 10$ K— $\Delta\nu$ is much larger in 8CB than in 5CB.

The smooth temperature variation of the line splitting in 5CB has been attributed to the continuous pretransitional growth of the orientationally ordered boundary layer [9,13]. Within the Landau–de Gennes theory [14,15], an order-inducing substrate gives rise to an exponentially decaying profile of the degree of orientational order

$$S(z) = S_N \exp(-z/\xi), \quad (3)$$

where S_N is the degree of order at the substrate (which depends on temperature) and ξ is the nematic correlation length

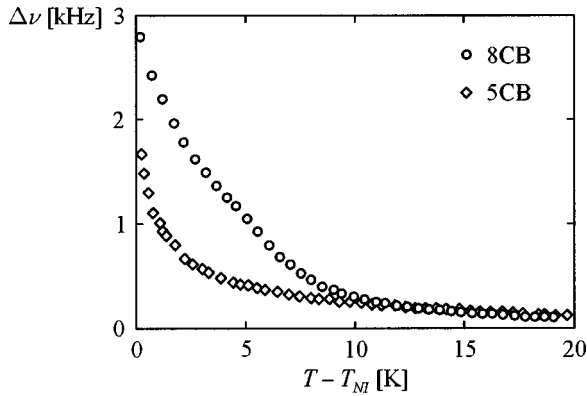


FIG. 2. Observed line splitting in the isotropic phase of α -deuterated 8CB confined to chemically treated Anopore membranes versus temperature relative to the clearing point (circles). For comparison, $\Delta\nu$ in the isotropic 5CB deuterated in the same position of the aliphatic chain is also plotted (diamonds). In 8CB, $T_{NI}=40.5^\circ\text{C}$, whereas in 5CB $T_{NI}=35.3^\circ\text{C}$.

proportional to $(T-T^*)^{-1/2}$; T^* is the supercooling limit typically 1 K below the clearing point. Given that $\xi \lesssim 10$ nm is much smaller than the radius of the channels $R = 100$ nm, the line splitting for perpendicular orientation of the director at the wall reduces to

$$\Delta\nu = \Delta\nu_0 S_N \frac{\xi}{R}, \quad (4)$$

which offers a consistent explanation of the observed $\Delta\nu$ in 5CB (Fig. 3). In some nematic materials, the NMR line splitting can be explained well by a slightly different profile of the degree of order consisting of a thin (≈ 1 nm) layer of constant S and the usual exponential tail [9,16], but in our case such an ansatz does not improve the fit.

The line splitting in 8CB obviously does not conform to this simple model in the entire temperature range studied. The data reveal at least two distinct regimes of wetting behavior separated by a discontinuity of the slope of the line splitting at about 5 K above the clearing point (Fig. 2). Well above T_{NI} , the line splitting in 8CB does not depart signifi-

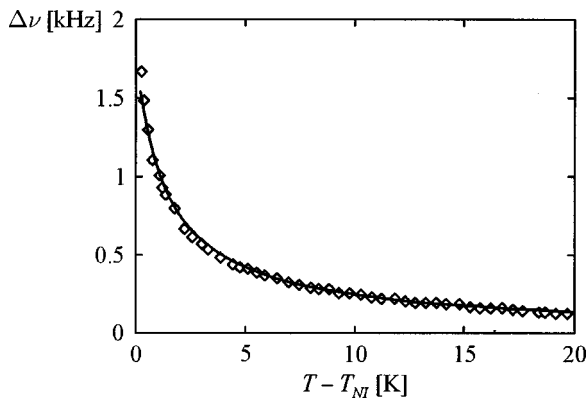


FIG. 3. Line splitting in confined 5CB (diamonds) is described accurately by the Landau–de Gennes theory of orientational wetting (solid line). The best-fit parameters of the model [Eq. (12) with $l=0$, which basically reduces to Eq. (4)] read $g=1.08$ mJ/m² and $S_S=0.41$; the material parameters used read $a=0.13$ MJ/m³K, $L=17$ pN, and $T^*=34.2^\circ\text{C}$ [17].

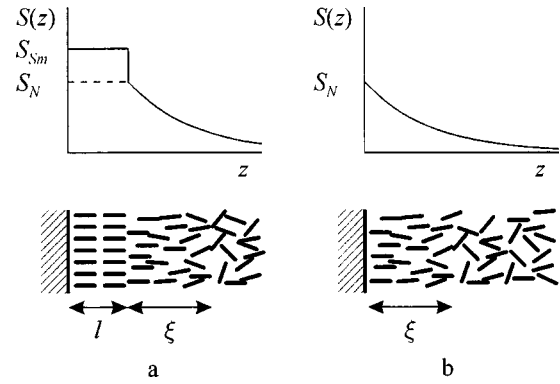


FIG. 4. Schematic representation of molecular order in the sample above T_{NI} : wetting layer with substrate-stabilized smectic order (a) and purely nematic wetting layer (b).

cantly from its 5CB counterpart, and it seems to follow the temperature dependence predicted by Landau–de Gennes theory of orientational wetting. However, at approximately $T_{NI}+10$ K, it starts to increase much faster than in 5CB and close to the phase transition, $\Delta\nu$ in 8CB is considerably larger than in 5CB. This indicates that in the immediate vicinity of the clearing point, the boundary layer does not consist solely of the region characterized by the exponentially decaying profile of the degree of order. The extra line splitting may be related to the onset of the smectic layering which is known to result in an enhanced orientational order. This hypothesis is substantiated by the observed discontinuity of the slope of the splitting, which can be regarded as another fingerprint of the presmectic order within the wetting layer.

Substrate-stabilized presmectic order has been observed in many liquid-crystalline materials, and its evolution is often associated with a discrete growth of the smectic layer [3,4,6,18] which should result in a discontinuity of $\Delta\nu$ rather than $d(\Delta\nu)/dT$. However, it seems that discrete layering transitions are observed only in long-chain liquid crystals with the smectic-A phase immediately below the isotropic phase, such as 11CB and 12CB [3,4,6], whereas in short-chain compounds, which are characterized by a phase sequence crystal \leftrightarrow smectic-A \leftrightarrow nematic \leftrightarrow isotropic, the discontinuous layering transitions disappear. Another important feature of the surface-induced smectic order is that the layering transitions at solid substrates are not as sharp as at the air interface [4]. These two notions imply that in our experiment, we could not really expect to observe a jump of the adsorption parameter.

We therefore conjecture that the growth of the wetting layer is described by the following scenario: (i) at temperatures above $T_2 \approx T_{NI}+14$ K the wetting layer is purely nematic throughout the sample; (ii) from T_2 to $T_1 \approx T_{NI}+5$ K the smectic order gradually builds up; and (iii) at temperatures from T_1 down to T_{NI} the wetting behavior is characterized by a smectic film in addition to the usual nematic wetting layer, which is present at all temperatures (Fig. 4). Having no information on the mechanisms that drive the gradual evolution of the adsorption parameter, we do not attempt to describe the midtemperature regime from T_1 to T_2 . We can, however, construct a self-consistent phenomenological model of wetting in the low-temperature regime

from the clearing point to T_1 and in the high-temperature regime (above T_2), which we present in the next paragraphs.

III. THEORY

Since the first experimental studies of wetting in nematic liquid crystals [12], the Landau–de Gennes continuum theory of the substrate-stabilized order has proved to offer a rather complete description of the phenomenon [11,14,15], and it also represents the basis of our model of wetting in the isotropic phase of 8CB. However, it has to be extended to describe the enhanced orientational order within the pre-smectic film that separates the nematic wetting layer from the substrate in the low temperature regime.

As a zeroth-order approximation, we assume that the thickness of the smectic film is small, which in turn implies that the degrees of smectic and nematic order within the layer can be considered homogeneous. The bulk free energy of the orientational order within the smectic film consists of the usual quadratic Landau-type term and the smectic-nematic interaction

$$F_{Sm}(S) = A \left[\frac{1}{2} a(T - T^*) S^2 - D \Psi^2 S \right] l, \quad (5)$$

where A is the internal surface area of the channel, a is the coefficient in the Landau expansion, T^* is the so-called supercooling temperature, D is the strength of the smectic-nematic coupling, Ψ is the degree of smectic order, and l is the thickness of the layer, which is assumed to be temperature-independent [19]. Needless to say, $D\Psi^2$ enters the above model as a single parameter; Ψ itself depends primarily on the steric interaction between the molecules and the substrate and can also be treated as independent of temperature.

The degree of orientational order depends also on the surface free energy described by

$$F_S(S) = \frac{1}{2} A g (S - S_S)^2, \quad (6)$$

where g is the strength of the surface interaction and S_S is the preferred value of the degree of order at the wall [20,21]. In the mean-field approximation, the equilibrium value of S within the smectic film corresponds to the minimum of the total free energy, $F_{Sm} + F_S$, and it reads

$$S_{Sm} = \frac{D\Psi^2 l + g S_S}{a(T - T^*) l + g}, \quad (7)$$

which approaches S_S if the surface coupling is very strong [$g \gg a(T - T^*) l, D\Psi^2 l$] and $D\Psi^2 / a(T - T^*)$ if it is very weak [$g \ll a(T - T^*) l, D\Psi^2 l$].

Beyond the smectic film (Fig. 4), the degree of orientational order falls off very quickly with the distance from the substrate and the cylindrical symmetry of the sample is not really important. The free energy of the purely nematic part of the wetting layer is given by

$$F_N + F_S(S(z=l)) \quad (8)$$

with

$$F_N = A \int_l^\infty \left[\frac{1}{2} a(T - T^*) S^2 + \frac{1}{2} L \left(\frac{dS}{dz} \right)^2 \right] dz, \quad (9)$$

where z is the distance from the substrate and L is the effective elastic constant [14,15]. The corresponding profile of the degree of order is exponential

$$S(z) = S_N \exp(-(z-l)/\xi), \quad (10)$$

where

$$S_N = \frac{g S_S}{a(T - T^*) \xi + g} \quad (11)$$

and $\xi = \sqrt{L/a(T - T^*)}$ is the nematic correlation length. We stress that within our model, the degree of orientational order experiences a discontinuity at $z=l$ because S_{Sm} is not equal to S_N . At first sight, this may seem unphysical, but the discontinuity is due to the presence of the smectic film, which is, in fact, a semimicroscopic feature of the system.

Once the profiles of the degree of order have been determined, we can calculate the line splitting [Eq. (1)], which turns out to be given by

$$\Delta\nu = \Delta\nu_0 \left[\frac{D\Psi^2 l + g S_S}{a(T - T^*) l + g} \frac{l}{R} + \frac{g S_S}{a(T - T^*) \xi + g} \frac{\xi}{R} \right], \quad (12)$$

where R is the radius of the channels. At temperatures well above T_{NI} , the smectic order at the wall is absent and $l=0$, whereas l is finite in the immediate vicinity of the clearing point.

IV. DISCUSSION

As mentioned above, our model covers both high-temperature and low-temperature regime. We start fitting the theoretical prediction [Eq. (12)] to the data in the high-temperature regime, where the smectic film is absent and $\Delta\nu$ depends solely on two unknown model parameters, the strength of the surface coupling (g) and the preferred degree of order at the substrate (S_S). Once these two quantities have been found, we analyze the low-temperature regime and determine the remaining two parameters, the thickness of the smectic film (l) and the product of the strength of the smectic-nematic coupling and the degree of smectic order ($D\Psi^2$). In the analysis of the data, we use the values of the material constants in the Landau–de Gennes expansion determined by light scattering and differential scanning calorimetry experiments: $a = 0.19$ MJ/m³K, $T^* = 39.4$ K, and $L = 6.6$ pN [22,23]. The line splitting in a perfectly ordered nematic phase of α -deuterated 8CB is about 90 kHz [24].

The analysis of the high-temperature regime basically tells us what the actual degree of nematic order at the wall is, $g S_S / [a(T - T^*) \xi + g]$ [Eq. (11)]. It turns out that there is a range of sets of g and S_S that give virtually identical values of $\Delta\nu$ and consequently S_N in the whole temperature range. This is, in fact, not very surprising: at temperatures from 14 to 19 K above the clearing point, the correlation length in 8CB is about 1.4 nm, and if g is assumed to be of the order of 1 mJ/m², $a(T - T^*) \xi / g$ is larger than (or at least compa-

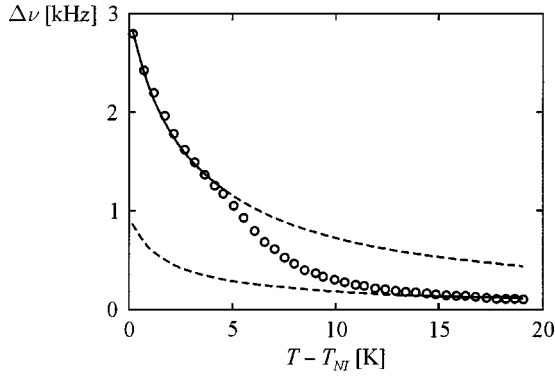


FIG. 5. Fit to the observed line splitting in 8CB corresponding to a two-bilayer presmectic film at temperatures below $T_{NI}+5$ K: $g=2.9$ mJ/m², $S_S=0.26$, $l=6.2$ nm, and $D\Psi^2=0.12$ MJ/m³. In the high-temperature regime wetting is purely nematic with the same g and S_S . The solid part of each curve represents the fitted regime and the dashed part is its continuation to the other two temperature regimes. All other sets of model parameters summarized in Table I yield fits practically indistinguishable from this one.

table to) 1. In this case, the degree of nematic order at the wall can be approximated by $gS_S/a(T-T^*)\xi$, which means that the line splitting actually depends on the product of g and S_S rather than on g and S_S themselves. This effect is enhanced by the narrowness of the temperature range assigned to the high-temperature, nematic wetting regime and the limited variation of the line splitting within this range. The best-fit sets of the strength of the surface coupling and the preferred degree of nematic order are reasonable: for example, 1.2 mJ/m² and 0.49, 1.7 mJ/m² and 0.37, 3.2 mJ/m² and 0.24, etc.

The different sets of g and S_S also give essentially identical fits of the line splitting in the low-temperature wetting regime, each with a different pair of l and $D\Psi^2$; a typical fit to the data is shown in Fig. 5. The low-temperature regime, however, provides a criterion that distinguishes between acceptable and unacceptable sets of g, S_S, l , and $D\Psi^2$. The extra line splitting induced by the substrate-stabilized smectic order is proportional to the *product* of the thickness of the smectic film and the degree of nematic order within it, and some combinations of g and S_S result in small l and large S_{Sm} , whereas others correspond to large l and small S_{Sm} . The criterion is based on the magnitude of the degree of orientational order within the smectic film: (i) in the low-temperature regime S_{Sm} should be larger than S_N , because it does not seem likely that the smectic-nematic coupling would effectively reduce the degree of order, and (ii) S_{Sm} must not exceed 1 for obvious reasons (Fig. 6).

These two requirements limit the relevant range of the model parameters by the two sets shown in Table I. The first set of parameters corresponds to a thick smectic film characterized by moderate degree of order, and the second one represents a thin but highly ordered smectic film. Any combination of g, S_S, l , and $D\Psi^2$ obtained by linear interpolation between the two limiting sets also gives a good and formally acceptable fit. However, it is well known that the cyanobiphenyls form bilayers of neighboring molecules having overlapping cores at the center of the bilayer [25], and the wavelength of the mass density wave (i.e., the thickness of a bilayer) in the smectic-A phase of 8CB is about 3.1 nm.

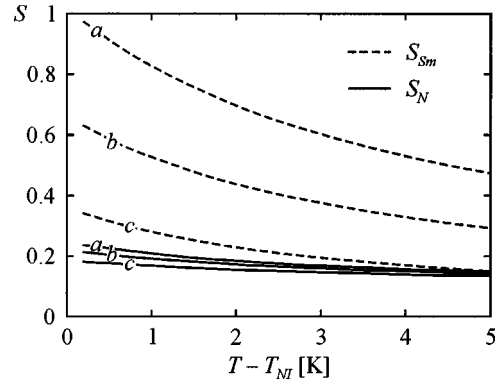


FIG. 6. Temperature variation of the degree of orientational order within the presmectic film (S_{Sm}) and within the nematic wetting layer (S_N) in the low-temperature regime for three sets of model parameters that all give virtually identical fits. Set *a* ($g=1.2$ mJ/m², $S_S=0.49$, $l=1.9$ nm, and $D\Psi^2=0.54$ MJ/m³) is characterized by a thin but highly ordered presmectic film, set *b* ($g=1.7$ mJ/m², $S_S=0.37$, $l=3.1$ nm, and $D\Psi^2=2.9$ MJ/m³) corresponds to a one-bilayer presmectic film, and set *c* ($g=2.9$ mJ/m², $S_S=0.26$, $l=6.2$ nm, and $D\Psi^2=0.12$ MJ/m³) represents a two-bilayer presmectic film. Set *c* is the most probable one because the degree of orientational order within the presmectic film is realistic and the discontinuity $S_{Sm}-S_N$ is small.

This means that in our system, the smectic wetting film includes either 1 bilayer ($g=1.7$ mJ/m², $S_S=0.37$, $l=3.1$ nm, and $D\Psi^2=0.29$ MJ/m³) or 2 molecular bilayers ($g=2.9$ mJ/m², $S_S=0.26$, $l=6.2$ nm, and $D\Psi^2=0.12$ MJ/m³). The former possibility seems rather unlikely because it corresponds to a highly ordered presmectic bilayer with S_{Sm} reaching 0.6 at temperatures just above T_{NI} , which also implies that its discontinuity $S_{Sm}-S_N$ is very large. In case of a double-bilayer film, the degree of orientational order does not exceed 0.35 and the discontinuity is far smaller (Fig. 6). Therefore we can conclude that the presmectic film in our sample consists of 2 molecular bilayers.

This result is in agreement with our initial expectations: the semimicroscopic theoretical model of the ordering is based on the assumption that the smectic part of the wetting film is thin, which implies that the ordering within it can be assumed to be homogeneous. One could argue that the smectic layers are characterized by different degrees of the orientational order, and that the smectic layers melt one after another just as in the x-ray scattering study of wetting of 12CB at alkylsilane-coated silicon substrate [4] and in Anopore

TABLE I. Acceptable range of the best-fit sets of model parameters. All sets of g, S_S, l , and $D\Psi^2$ obtained by linear interpolation between the two limiting sets give indistinguishable fits to 8CB data. However, those corresponding to thick smectic wetting films— l about 6 nm—seem more reasonable because in this case the degree of orientational order within the presmectic film is not too high and the discontinuity $S_{Sm}-S_N$ is small.

	g [mJ/m ²]	S_S	l [nm]	$D\Psi^2$ [MJ/m ³]
Thin smectic film	1.2	0.49	1.9	0.54
Thick smectic film	3.2	0.24	7.2	0.10

membranes treated by aliphatic acid [6]. But our data exhibit only one discontinuity in the slope of the line splitting and it is hard to imagine that its temperature variation could ever be subdivided into distinct regimes other than the three we have proposed.

V. CONCLUSIONS

In this study of wetting behavior of 8CB in the isotropic phase, we have observed a discontinuity of the slope of the deuteron NMR line splitting at about 5 K above the clearing point. Assuming that the discontinuity may be related to the presmectic order within the wetting layer, we have developed a phenomenological semimicroscopic model of the ordering. The model provides a consistent description of the wetting behavior both in the immediate vicinity of the clearing point, where the wetting layer is characterized by a substrate-stabilized presmectic film with positional and orientational order in addition to the nematic wetting layer, and at temperatures above $T_{NI} + 14$ K, where the wetting layer is purely nematic. However, we cannot account for the mid-temperature regime, which corresponds to evolution of the smectic order within the wetting layer.

The parameters of the surface coupling—the strength of the interaction and the preferred degree of order at the substrate—obtained by analyzing the experimental data are compatible with the results of earlier studies of wetting in related systems [11]. The most important new quantitative results of the study are the thickness of the smectic film, which consists of two smectic bilayers of total thickness of 6.2 nm, and the strength of the nematic-smectic coupling. We stress that the observed line splitting in 8CB cannot be explained satisfactorily in terms of purely orientational wetting behavior, i.e., without the onset of the positional order at the wall.

There are a couple of open questions that will require further experimental as well as theoretical investigations. First, is the smectic order stabilized solely by the impenetrability of the substrate and by the organic coating? We have carried out a parallel study with identical host medium but with a nonsmectogenic liquid-crystalline compound 5CB. There are no signatures of presmectic order in the wetting behavior of this system which is in agreement with earlier analyses [6,11,18,26], and the temperature variation of the line splitting can be described very well by a purely nematic adsorption parameter. A recent NMR analysis of wetting of 8CB in an untreated host medium, which favors planar orientation of the molecules, showed no discontinuities in the slope of the line splitting [27]. These findings imply that the smecticity of the wetting film depends both on intermolecular interactions within the liquid crystal and on the ordering

power of the wall, which seems to be enhanced considerably by chemical treatment that induces homeotropic anchoring.

The second issue to be addressed in the future is related to the mechanisms that govern the apparently continuous evolution of the order in the midtemperature regime. As suggested by several complementary studies [4,6,26], this is most likely an intrinsic feature of the liquid-crystalline material in question, specific for compounds with neither short nor long aliphatic chains. The continuous evolution of the presmectic order in 8CB seems to be driven by smectogenic intermolecular interaction, which is definitely weaker than in long-chain compounds such as 10CB, 11CB, or 12CB: after all, the phase sequence of 8CB includes crystal, smectic-A, nematic, and isotropic phase, whereas in its long-chain homologs the nematic phase is absent.

Another possible explanation of the midtemperature regime is that upon cooling the smectic order actually develops in one or two layering transitions, and that the corresponding discontinuities of the adsorption parameter are smeared out by some kind of inhomogeneities of the substrate. The resulting inhomogeneity of the line splitting is undetectable by NMR, which is, in its nature, an integrative rather than local probe. This hypothesis could be checked by studying the wetting behavior in systems with very homogeneous substrates, such as planar samples bounded by glass, silicon, etc. However, in view of the 12CB layering experiment where discontinuous jumps in $\Delta\nu$ are clearly visible [18] the decisive role of the inhomogeneities of the substrate in smearing out the adsorption parameter is less likely.

In summary, the experiment reported indicates that at temperatures up to 5 K above the nematic-isotropic phase transition, the wetting behavior of 8CB at a chemically treated wall is characterized by a substrate-stabilized layer with both positional and orientational order. The positional order within the wetting layer seems to be induced both by the smectogenic character of 8CB and by the organic coating agent. The evolution of the adsorption parameter is continuous rather than discrete like in long-chain homologs, and at temperature approximately 14 K above the clearing point, the wetting layer becomes purely nematic. At present, our insight into the midtemperature regime is limited: it may involve either a truly continuous growth of the presmectic order or one or two smeared layering transitions. This process will be analyzed in detail in a forthcoming study.

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