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Smectic Ordering of 8CB Liquid Crystal Confined to a Controlled-Pore Glass

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We study the temperature evolution of smectic ordering of 8CB liquid crystal confined to various CPG matrices. The characteristic diameters of matrices ranged from 24 nm to 128 nm. The CPG voids were either left non-treated or were treated with silane. A weakly 1st order N-SmA transition in bulk 8CB, which could be attributed to the Halperin-Lubensky-Ma (HLM) effect, is broadened in confined samples. In confined samples substantial pretransitional anchoring was also observed, particularly in the silane-treated samples.

Keywords: confined geometry; controlled-pore glass (CPG); Halperin-Lubensky-Ma (HLM) effect; octylcyanobiphenyl (8CD); small-angle X-ray scattering (SAXS); smectic ordering

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I. INTRODUCTION

Phase behavior of various liquid crystal (LC) phases confined to porous matrices is interesting both from fundamental and practical point of view. As porous matrices, aerogels, Russian glasses, Vycor glasses, and controlled-pore glasses (CPGs) are commonly chosen [1]. The porous environment imposes a kind of disorder to confined LC phases. The phase behavior of confined LC phases is influenced by finite size effects, surface interactions and geometrically imposed randomness. In the list given above the lowest degree of disorder is imposed by CPG matrices [2,3], which are also the focus of our study.

It is known that even a weak disorder can dramatically influence the structural properties of phases possessing a Goldstone mode. According to the Imry-Ma theorem [4] even an arbitrary weak disorder breaks the system into a domain type pattern. The characteristic linear length of domains should depend on the disorder strength. In analogy one could therefore in CPG confinement expect a domain type pattern in the orientational ordering. The reason behind this is the broken continuous symmetry at the isotropic-nematic phase transition. In an average domain, a bulk-like ordering is roughly realized. Because the degree of disorder is relatively weak it influences only structural LC properties, while the phase behavior is affected only quantitatively (e.g., shift of phase transition temperatures). However, the phase behavior can be drastically qualitatively influenced if the characteristic linear confining size R becomes comparable to the relevant LC phase correlation length [1].

In this paper we study the influence of CPG-confinement on the phase behavior of 8CB liquid crystal using the method of small angle X-ray scattering (SAXS). We focus on the nematic-smectic A phase transition. The CPG voids are either non-treated or treated with silane, imposing a qualitatively different LC orientational ordering. The plan of the paper is as follows. In Sec. II we describe the experimental set-up and list experimental results. In Sec. III we present a simple model needed for a qualitative explanation of the results. In Sec. IV we discuss our measurements. In the last section we summarize our findings.

II. EXPERIMENT

The molecules of the liquid crystal octylcyanobiphenyl (8CB) consist of two phenyl rings and the octyl tail. In the bulk state the 8CB exhibits a second order SmA-N phase transition at temperature $T_{NA} \approx 307\,\mathrm{K}$. Note that some authors claim this transition to be very weakly 1st

order [5–10]. Here the term very weakly 1st order transition is used to distinguish the character of this transition from the weakly 1st order character of the isotropic to nematic phase transition, where the enthalpy change is very small, but the change of the order parameter at the transition is relatively large. In the case of discontinuous N-SmA phase transition both the order parameter and enthalpy changes are small.

As a confining medium we use the Controlled-Pore Glass (CPG) matrices [2,3]. The scanning electron micrograph (SEM) of an empty CPG matrix is shown in Figure 1. The CPG voids resemble curved and strongly interconnected cylinders of radii R. We use CPG matrices of the mean pore diameter ranging from 24 to 128 nm and having a standard deviation of 5–10%. The void surface of the CPG is smooth down to the nm scale [3].

The CPG matrices were filled with 8CB in the isotropic phase. The non-treated CPG void surfaces enforce isotropic tangential orientational anchoring of the LC molecules [3,11]. Because of steric effects the orientation along the voids, long axes are chosen as easy axes among the degenerate set of easy axes. In silane treated CPG samples the pore surface enforces homeotropic orientational anchoring of the LC molecules [12].

The small angle X-ray scattering (SAXS) method is ideal to determine the layered smectic configuration [13,14]. The SAXS patterns of samples have been measured at the SAXS beamline of

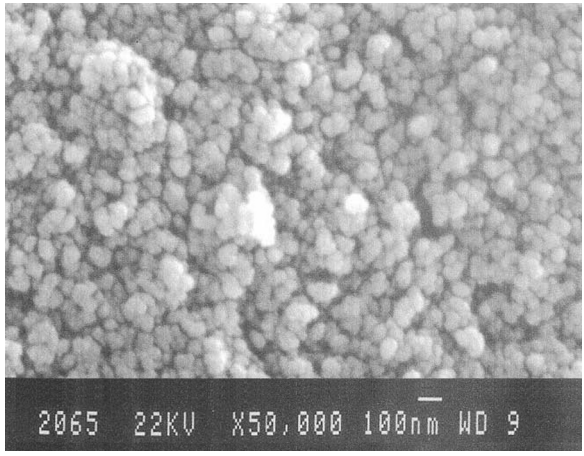

FIGURE 1 The scanning electron micrograph (SEM) of an empty CPG matrix having a pore radius of 24 nm.

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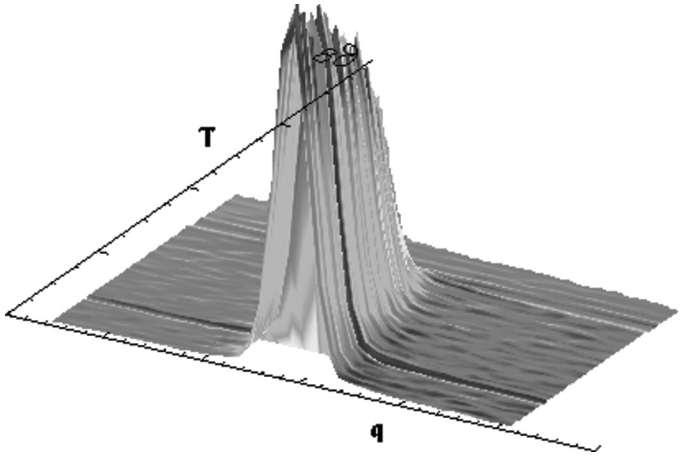

FIGURE 2 A typical small angle X-ray scattering (SAXS) intensity peak $I(q)$, where q is the scattering vector. The peaks are shown in a two-dimensional plot for various temperatures T in bulk 8CB.

the Elettra Synchrotrone in Trieste (Italy). In the smectic phase a peak is observed. Its position reveals the value of the smectic layer spacing d. The amplitude of the peak is proportional to the average value of the smectic order parameter η. The line-width of the peak reveals the X-ray correlation length ξ_x.

The experimental results are shown in Figures 2–5. In Figure 2 we show a typical first order SAXS scattering intensity peak $I(q)$, where q is the scattering vector. The temperature evolution of the degree of smectic ordering for non-treated and silane-treated samples is shown in Figure 3a and Figure 3b, respectively. Figure 4 reveals the influence of confinement on the average thickness of smectic layers. The temperature dependence of the X-ray scattering lengthy ξ_x is plotted in Figure 5.

III. MODEL

To analyze the behavior across the N-SmA phase transition, we use a Landau-Ginzburg phenomenological approach [14,15]. We describe the orientational ordering with the nematic director field $\vec{n}$, pointing along the average orientation of rod-like LC molecules. The smectic ordering is described with the smectic complex order parameter $\psi = \eta e^{i\phi}$. Here η yields the degree of smectic ordering and the phase factor ϕ determines the position of smectic layers.

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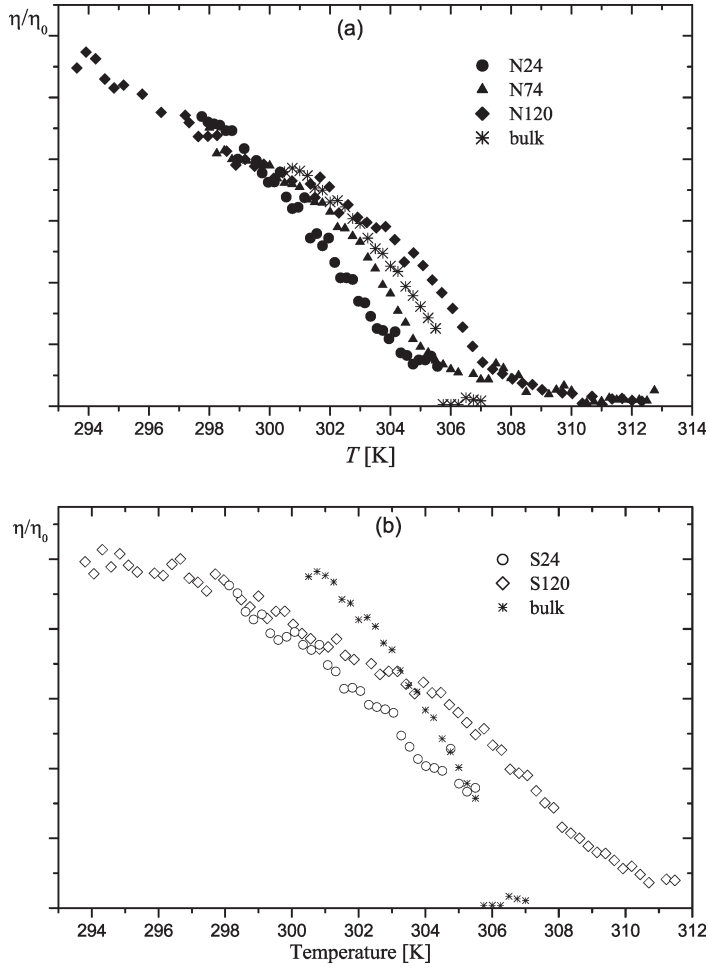

FIGURE 3 The temperature evolution of the degree of smectic ordering for (a) non-treated and (b) silane-treated samples.

The essential contributions to the volume free energy density f are the homogeneous term f_h and the elastic term f_e, i.e., $f \approx f_{\mathrm{h}} + f_e$. The homogeneous term

$$f_{\mathrm{h}} \approx \alpha(T - T_{NA})|\psi|^2 + \beta|\psi|^4 \tag{1}$$

determines the value of $\eta = \eta_0$ at the equilibrium, where α and β are the material constants, and T_{NA} is the temperature of the bulk LC N-SmA phase transition. Above and below T_{NA} the translational order

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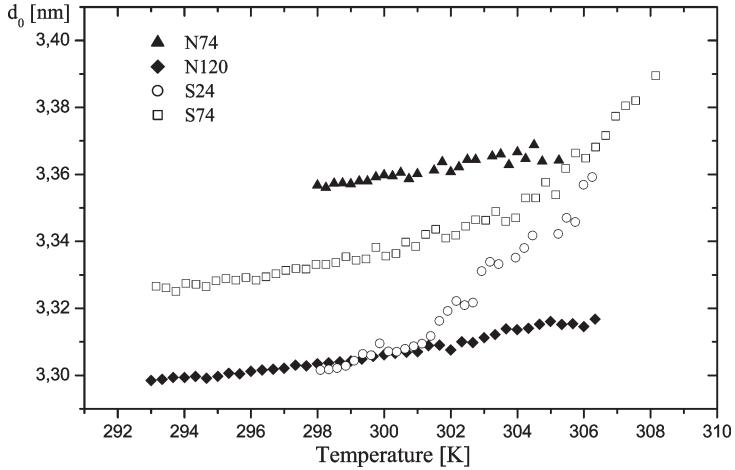

FIGURE 4 The temperature evolution of the average thickness of smectic layers of 8CB in CPG matrices of various pore radii R.

parameter takes on the values $\eta_0 = 0$ and $\eta_0 = \sqrt{\alpha(T_{NA} - T)/(2\beta)}$, respectively. The elastic term is given by

$$f_e = C_{II}|(\vec{n}\,.\nabla - iq_0)\psi|^2 + C_\perp|(\vec{n} \times \nabla)_\psi|^2. \qquad (2)$$

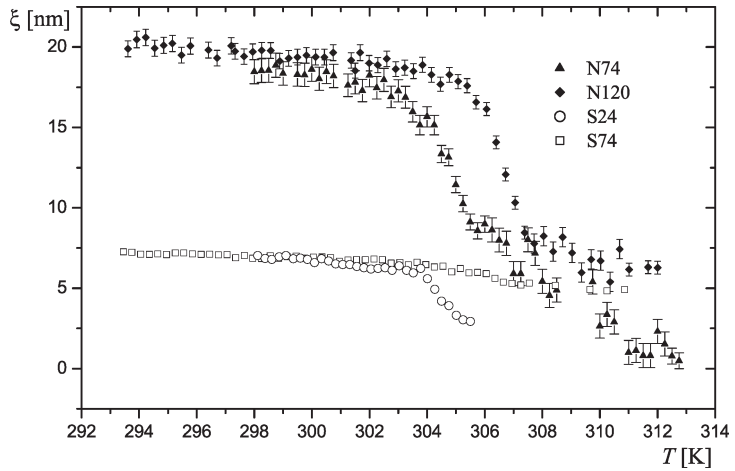

FIGURE 5 The temperature dependence of the X-ray scattering length ξ_x of 8CB in CPG matrices of various pore radii R. Estimated experimental error is shown with error bars for the non-treated samples and with the size of the symbol for silane-treated samples.

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where the positive quantities C_{II} and $C_{\perp}$ stand for smectic compressibility and smectic bend elastic constant. These terms tend to enforce smectic layering with layer spacing $d_0 = 2\pi/q_0$ and the nematic director field pointing along the layer normal.

The influence of the confining surface on smectic ordering is described with the surface free energy density contribution [16]

$$f_s = -W(\psi + \psi^*). \tag{3}$$

Here the quantity W describes the smectic anchoring properties of the CPG-LC interface.

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IV. RESULTS AND DISCUSSION

In Figure 3 we show the temperature evolution of the degree of smectic ordering in bulk and as a function of R and CPG treatment. Most studies predict a 2nd order character of the N-SmA phase transition, but some more recent studies [6–10] suggest that it is of a very weakly 1st order transition. Our measurements are in agreement with these recent studies. The cause for the discontinuous behavior could be the coupling between η and fluctuations in $\vec{n}$, the so called Halperin-Lubensky-Ma (HLM) effect [5]. It has been shown that the presence of $\vec{n}$ fluctuations could alter the analytic form of the free energy as a function of ψ. Namely, the integration over $\vec{n}$ fluctuations results in the effective free energy in which also a negative cubic term of ψ is present (i.e., $f_{\mathrm{h}} \approx \alpha(T - T_{NA})|\psi|^2 - \gamma|\psi|^3 + \beta|\psi|^4$). Note that in confined samples this discontinuous jump disappears in line with expectations that confinement in general suppresses some fluctuation modes.

With decreasing R the smectic growth in all samples apparently changes. The suppression of the N-SmA phase transition temperature is governed mostly by ordering at the CPG-LC interface, what has been treated in detail in Ref. [11]. The pre-transitional ordering is caused by the surface wetting term that exhibits linear dependence on ψ, see Eq. (3). In case that the bulk N-SmA transition is of second order, this surface wetting converts the continuous transition into a gradual onset of smectic ordering as temperature T is decreased. In case that transition is weakly discontinuous, the gradual evolution is obtained for sufficiently strong surface wetting strength W [11,12]. The relative importance of the surface term with respect to the volume free energy terms scales as W/R [11,12], and hence gains on importance as R is decreased. In the silane-treated samples the pre-transitional effects are stronger because of stronger smectic coupling at the CPG-LC interface. Namely, in non-treated samples only the "outer" molecules within a smectic layer are in direct contact with

the interface. In the silane-treated samples on average the smectic layers grow from the interface towards the void interior.

We next consider the $d = d(R)$ dependence, shown in Figure 4. In general the confinement relatively weakly alters the $d(T)$ dependence in comparison to the bulk behavior because any changes in layer spacing are extremely energetically expensive. The $d = d(R,T)$ changes are larger in silane-treated samples. We believe that the $d = d(R,T)$ behavior is governed by qualitatively different mechanisms in non-treated and silane-treated samples, respectively. In the non-treated case we believe that the CPG surface gains imprinted and frozen-in periodicity when the smectic ordering becomes sufficiently strong on lowering temperature from the nematic phase [17]. With decreasing temperature the layer thickness shrinks and the mismatch with respect to frozen-in surface ordering increases. The balance of this competition results in the $d(T)$ dependence, that slightly differs from the bulk one. On the contrary, in silanized samples the smectic layers grow from the surface. In this case memory effects are expected to be absent (or at least relatively less important). Depending on the ratio R/d the smectic layers are either compressed or dilated on the average. Hence in this case the $d(R)$ behavior is expected to have subsatantially different behavior what is indeed observed.

In Figure 5 we plot $\xi_x = \xi_x$ (R, T, surface treatment). Above T_{NA} the X-ray length coincides with the smectic order parameter correlation length [14] and its behavior is dominated by thermal fluctuations. On decreasing T the pinning of smectic domains at geometrically imposed pinning centers becomes increasingly important. Bellow T_{NA} the pinning becomes dominant, saturating ξ_x to a nearly constant value. Our measurements suggest that deep in the smectic phase ξ_x saturates to a value that is almost independent of R. Note that this observation is not the consequence of limited experimental resolution. Namely, the width of $I(q)$ dependence was in all cases larger than the resolution width. The reason for such behavior can be described in terms of a random anisotropy type phenomenological approach and will be presented in our future work.

V. CONCLUSIONS

We have studied the temperature evolution of the smectic ordering of 8CB LC confined to various CPG matrices. The CPG voids were either left non-treated or treated with silane. In the former case the isotropic tangential anchoring is realized and the layers are on average stacked along the voids longer dimension. In silane-treated samples the

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smectic layers grow from the surface in case of a strong enough surface anchoring potential.

While the bulk N-SmA transition is very weakly discontinuous [5–10], in CPG voids the transition becomes continuous or gradual. In case that HLM effect is present, the change of transition character could be explained by assuming that confinement suppresses fluctuations responsible for this effect.

In all CPG samples a pre-transitional smectic growth was observed, suggesting the presence of the surface interaction term linear in η. The pre-transitional effects are much stronger in silanized samples, where the coupling between the CPG matrix and smectic layers is substantially stronger. The smectic layer distance is only weakly influenced by confinement in non-treated samples. On the contrary, in silanized samples apparent change in LC behavior is observed as R is varied. We predict qualitatively different mechanisms controlling $d(R,T)$ dependence in non-treated and silane-treated samples, respectively. In non-treated samples memory effect are important, causing the competition between different periodicities in the system below T_{NA}. On the other hand, in silanized samples the smectic growth is more exposed to confinement effects. Depending on the value of R/d the smectic layers could either experience dilatation or compression with respect to the bulk equilibrium spacing. The X-ray length ξ_x in the SmA phase reveals the average pinning length of smectic clusters. Deep in the SmA phase this length exhibits weak dependence on R and T.

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