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Possible smectic A ordering in a droplet of 4-*n*-octyloxybenzoic acid liquid crystal

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Our microtextural as well as depolarized light scattering analyses of 4-*n*-octyloxybenzoic acid liquid crystal droplets provide evidence for a possible smectic A ordering induced by the free surface. This appears near the bulk smectic C–nematic transition at T_{S_CN}. A simple mean field analysis, based on a Landau–de Gennes–Benguigui free energy functional with an additional surface parameter K_s, allows, in principle, the possibility for a smectic A surface phase at temperatures slightly above T_{S_CN}.

It is well-known that the bulk phase diagram of 4-*n*-octyloxybenzoic acid (OOBA) contains nematic and smectic C phases, while the smectic A state is absent [1]. Recent polarizing microscopy and small angle X-ray scattering experiments [2] demonstrate, however, a possible smectic A ordering in homeotropically oriented films of OOBA near T_{S_CN}. Smectic layering can also appear just above the smectic A–nematic transition temperature T_{S_AN} [3], as well as near the smectic A–isotropic transition temperature T_{S_AI} [4].

Recently, Selinger and Nelson have proposed a density-functional theory of nematic and smectic A order near a surface [5], in order to explain the X-ray experiments [3, 4]. An alternative lattice model has been developed by Pawlowska *et al.* [6]. The microscopic approach seems to be effective in that it obtains the discreteness observed in the layering transitions. On the other hand, this approach does not predict such transitions when the bulk is nematic; instead the surface smectic order grows smoothly from the nematic phase. The surface forces, restricted to the first layer in the lattice model, are in accord to the Landau–de Gennes type description with δ function surface terms. Recent X-ray experiments by Ocko [7] seem to show a critical behaviour near the layering transition, so that the problem remains open. These theories do not discuss the growth of the surface-induced smectic ordering near the first order smectic C–nematic transition.

In the present communication we report on a possible presurface smectic A ordering near T_{S_CN} in droplets of OOBA induced by the free surface. We have used two different experimental methods to indicate the presurface ordering, namely optical microtextural analysis, and depolarized light scattering analysis. The experiments were performed on OOBA droplets deposited on a glass substrate. The special treatment of the substrate (homeotropic or planar orientation) had no effect on the optical textures which appeared on cooling or heating around T_{S_CN} ($T_{S_CN} = 108{\cdot}1^{\circ}C$). The average thickness of a droplet measured perpendicular to the substrate, was approximately

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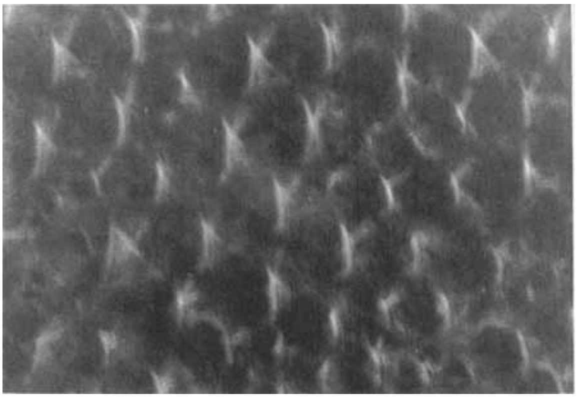

Figure 1. The honeycomb texture of OOBA, at 107·8°C; magnification ×80.

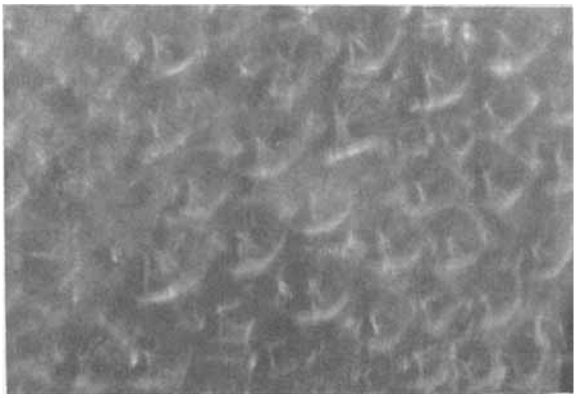

Figure 2. The broken honeycomb texture of OOBA at 106·9°C; magnification ×80.

60 μm. The cooling and heating rates (0·1°C min^{-1}) were controlled by a Mettler FP 82 hot stage. In order to reduce possible vertical temperature gradients, the glass substrate, together with the droplets, were placed in the middle of the oven by heat isolating spacers.

The optical measurements were made with an NU-2 polarizing microscope. The analysis reveals three well-pronounced and optically different textures around T_{S_CN}: (i) approximately at $T_1 - T_{S_CN} = 0{\cdot}2$°C we see a typical striped picture, characteristic of the smectic A–nematic interface [8]; (ii) at $T_2 - T_{S_CN} = -0{\cdot}1$°C the so-called honeycomb texture appears (see figure 1) which is typical of a smectic A phase [8]; (iii) finally, at $T_3 - T_{S_CN} = -0{\cdot}8$°C the honeycomb texture changes into that shown in figure 2 (a broken honeycomb). The broken honeycomb indicates a significant increase of the smectic C tilt angle. Similar experiments were done with 4-n-heptyloxybenzoic acid (HOBA) droplets, characterized by a significantly higher latent heat $\Delta H = 10{\cdot}9$ kJ mol^{-1} ($\Delta H = 1{\cdot}2$ kJ mol^{-1} for OOBA) for the smectic C–nematic transition but the corresponding textures were not observed.

A parallel measurement of the depolarized light scattering intensity $I^s(T)$ was also made (see figure 3). We see a pronounced reduction of I^s starting slightly above T_{S_CN}, where the striped texture appears ($T \approx T_1$). According to the well-known expression

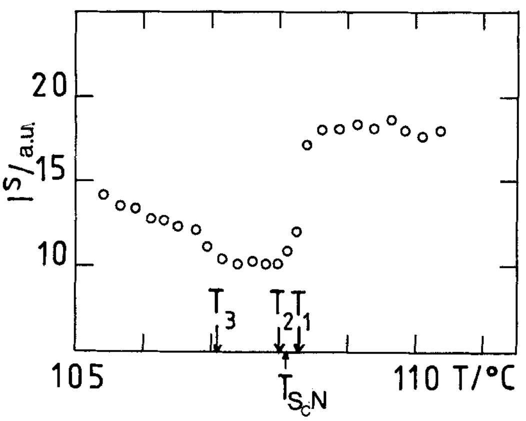

Figure 3. The depolarized light scattering intensity versus temperature for OOBA.

$I^s \sim (\Delta\varepsilon)^2/K$ ($\Delta\varepsilon$ is $\varepsilon_{\parallel} - \varepsilon_{\perp}$, where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the dielectric permittivities and K is the effective elastic constant), this reduction could result from both the increase of K and/or the freezing of the fluctuation in the nematic order parameter, characteristic of smectic layer formation [9]. We believe that the second reason obtains because of the establishment of the honeycomb texture, which is characteristic of the smectic A phase. From symmetry considerations, we would not expect the existence of a smectic A phase below T_{S_CN}. Probably, just below T_{S_CN} we observe a smectic C phase with an extremely small tilt angle, θ, not typical for OOBA (for such materials $\theta \approx 45°$). The increase of θ is revealed both by the breaking of the honeycomb texture (see figure 2) and in the increase in I^s (see figure 3).

An open question remains as to whether a pure smectic A surface phase is observed at $T > T_{S_CN}$. In principle, this is not excluded, as it can be deduced from the following Landau–de Gennes–Benguigui free energy model

$$F_s\{\psi, \theta\} = \int_0^\infty \left[\frac{c}{2}\left(\frac{d\psi}{dx}\right)^2 + \frac{g}{2}\left(\frac{d\theta}{dx}\right)^2 + F(\psi, \theta) - F(\psi_B, \theta_B)\right] + f_s(\psi_s, \theta_s). \qquad (1)$$

Here the droplet is modelled as a semi-infinite system and the x axis is perpendicular to the free surface. C and g are elastic constants for the smectic A order parameter $\psi(x)$ and the tilt order parameter $\theta(x)$, respectively. $F(\psi, \theta)$ is the Benguigui two order parameter free energy model [10] $(F(\psi_B, \theta_B) \equiv F(\psi, \theta)|_{x=\infty})$. The term

$$f_s(\psi_s, \theta_s) = -\frac{K_s}{2}\psi_s^2 \cos^2 \theta_s \qquad (2)$$

takes into account the influence of the free surface $(\psi_s = \psi(x)|_{x=0}, \theta_s \equiv \theta(x)|_{x=0})$. The model embodied in equation (1) is of a form which is widely used in the literature on surface phase transitions [11]. Equation (2) is a surface term analogous to the Benguigui bulk interaction term. A term proportional to ψ_s^2 is also allowed by symmetry. K_s is a phenomenological surface constant. For small θ_s and $K_s > 0$, the surface favours an induction of smectic A ordering, and simultaneously depresses the appearance of a tilt angle. A mean field analysis of equation (1) yields the following picture: at $T = T_s = T_{S_CN} + K_s^2/(\alpha_0 C)$ a surface phase transition takes place, when an exponentially decaying smectic A presurface phase arises ($\psi(x)=\psi_s \exp(-x/l)$, $l=(c/\alpha)^{1/2}$), α_0, α are bulk parameters. This phase exists for $T_{S_CN}<T<T_s$ and $\psi_s \sim (T_s-T)^{1/2}$. The model leads to a finite characteristic length l at $T=T_{S_CN}$ because the constant α in the bulk term $(\alpha/2)\psi^2(x)$ does not change its sign at $T=T_{S_CN}$. We would expect a critical behaviour of some of the elastic constants at $T=T_s$, in analogy with the critical behaviour of the diamagnetic susceptibility in superconductors with plane defects [12]. The preliminary analysis of the model shows that it also describes the system for $T \lesssim T_{S_CN}$. Since the striped texture is known to result from a smectic A–nematic interface instability [8] we are inclined to suppose that its appearance could be related to a smectic A surface phase at $T>T_{S_CN}$. A high resolution X-ray scattering analysis is needed to answer this question. Such an analysis is expected to be effective just below T_s when the striped texture has still not set in.

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