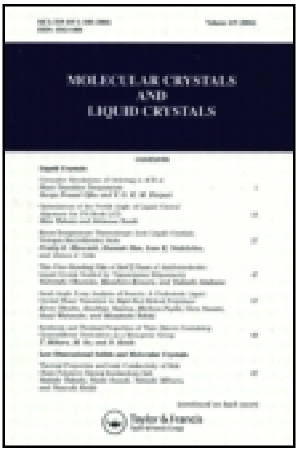

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Smectic-A-Like Ordering Induced by the Free Surface of 4,n-Ocyloxybenzoic Acid Liquid Crystal Droplets

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SMECTIC-*A*-LIKE ORDERING INDUCED BY THE FREE SURFACE OF $4,n$–OCYLOXYBENZOIC ACID LIQUID CRYSTAL DROPLETS

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Abstract We report on onset of a surface induced phase in droplets of $OOBA$ liquid crystals desplaying optical properties typical for the smectic-A state. The latter state does not exist in the bulk phase diagram of the system. The surface phase appears in a temperature range close to the bulk nematic-smectic-C transition temperature T_{NC}. The results are interpreted through a Landau-de Gennes type model with additional δ-function terms.

The surface phenomena in liquid crystals are characterized by a wide variety of properties. Verious interesting surface effects are observed near the bulk transition temperatures: Smectic-A layering was indicated just above the nematic-smectic-A bulk transition temperature T_{NA} [1,2]. Recently, Ocko and co-workers have studied, using a X-ray technique, the smectic-A ordering induced by a free surface in the isotropic phase of nCB/n-cyanobiphenyl/ and $nOCB/n$-oxycyanobiphenyl/ homologous series that have direct phase transitions from isotropic to smectic-A phase. They found series of surface phase transitions which correspond to the addition of single layers of the smectic phase.

The surface smectic ordering mentioned above appears just above T_{NA} or T_{IA}. In this paper we study another possibility for smectic layering localized near the free surface appearing just above the nematic-smectic-C transition temperature T_{NC}. Recent polarizing microscope [4] and small angle X-ray scattering experiments [5] indicated a smectic-A phase in homeotropically oriented films of the homologous $p-n$-octyloxy ($OOBA$) and nonyloxy benzoic acids ($NOBA$) liquid crystals. These systems do not possess smectic A bulk phase, i.e., the smectic-A phase is entirely induced by the surface forces. Here we study surface instabilities near T_{NC} in droplets of $OOBA$ and $HOBA$ liquid crystals. A smectic layering with optical textures typical for smectic-A state just above T_{NC} is observed by a polarizing microscope technique. The surface tilt angle θ_s jumps at T_{NC} from zero to a finite value which is very small as compared to the bulk tilt angle θ_B ($\theta_B \approx 47.5 \pm 1^0$ for $OOBA$ [5]). Another instability indicated in $OOBA$ occurs at $T \equiv T^* \approx T_{NC} - 0.8\ deg$, when the surface tilt angle θ_s jumps from a relattively small value to a value slightly less than θ_B. It is interesting that the last instabilities are absent in $OOBA$ droplets when the surface tension is reduced by lecitine dopping.

Experimental results: The microtextural experiments were accomplished on $OOBA$ and $HOBA$ droplets deposed on glass substrates. The average thickness of droplets, measured perpendicular to the substrate, was approximately $60\mu m$. The cooling and heating rates ($0.1\ deg/min$) were controlled by Mettler FP82 hot stage. In order to reduce possible vertical temperature gradients, the glass substrate together with droplets were placed in the middle of the oven by heat isolating spacers. The optical measurements were made by a polarizing microscope $NU-2$. The textural analysis reveals three optically distiguishable pictures near T_{NC}, Fig.1.

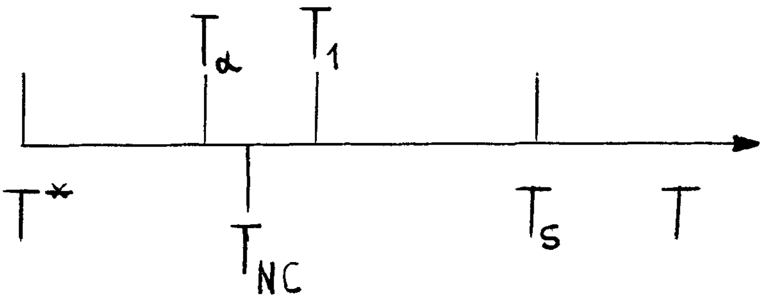

FIGURE 1. Characterictic temperatures in the texture experiment: $T_1 = T_{NC} + 0.2deg$, $T_\alpha = T_{NC} - 0.1deg$, $T^* = T_{NC} - 0.8deg$

The first characteristic temperature T_1 for $OOBA$ is $\approx 0.2deg$ above T_{NC} when the typical for the nematic-smectic-A interface "stripe" picture, described by Cladis and Torza [7], appears. This picture indicates the first stage of growth of smectic layers initiating from the free surface. The second picture, appearing in the temperature interval $T_{NC} - 0.8deg < T < T_{NC} - 0.1deg$ for $OOBA$ droplets, is the so-called "honeycomb" texture, Fig.2. This texture indicates a phase optically close to the smectic-A state.

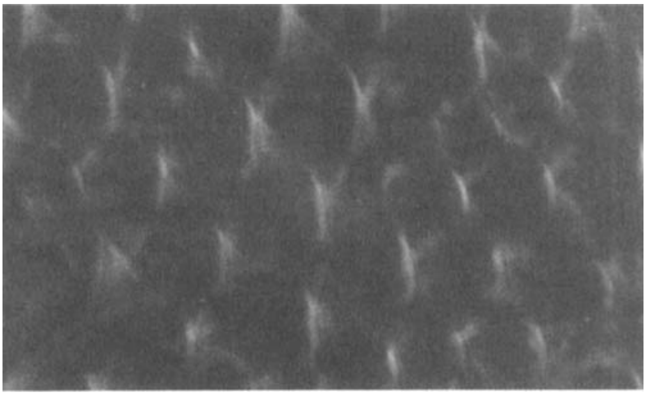

FIGURE 2. "Honeycomb" texture of $OOBA$ at $T = 108°C$. Magnification 125X.

The thirth surface instability in our *OOBA* droplets appears at $T^* \approx T_{NC} - 0.8deg$ when the "honeycomb" texture transforms into the picture shown in Fig.3. This picture corresponds to a smectic-C phase because of the brokening of the "honeycomb" texture. Presumably at T^* the surface tilt angle jumps to $\theta \approx \theta_B$. For the cooling and heating rates mentioned above, we have not indicated any temperature hysteresis.

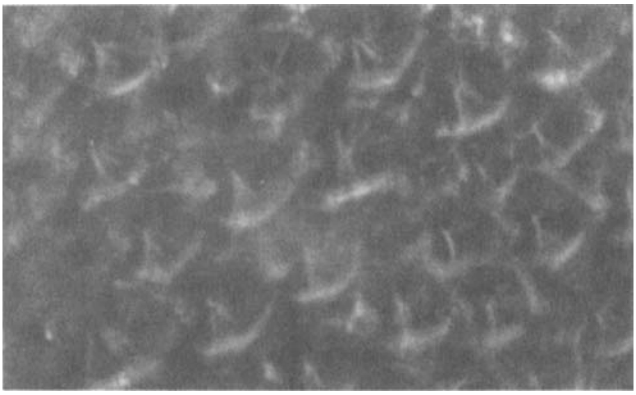

FIGURE 3. The broken "honeycomb" texture of *OOBA* at $T = 107.3°C$. Magnification 125X.

The same optical measurements were accomplished on *HOBA* droplets characterized by large latent heat $h/k_B T_{NC} = 3.5$. In *OOBA* liquid crystals the ratio $h/k_B T_{NC} \approx 0.26$ is by an order of magnitude smaller. The whole temperature interval (T^*, T_1) is reduced to $T_1 - T^* \approx 0.2deg$. In order to check the role of the surface energy, we dopped *OOBA* with 0.05% lecitine, thus reducing the surface tension. The whole region (T^*, T_{NC}) disappeared, so that the characteristic temperatures T^*, T_1, and the corresponding textures, were not observed.

Landau-de Gennes description: One can get a qualitative understanding of the observed surface instabilities from a Landau-de Gennes phenomenological description with additional terms localized near the free surface:

$$F_s(\psi,\theta) = \int_0^\infty \left[\frac{C}{2}\left(\frac{d\psi}{dx}\right)^2 + \frac{K}{2}\left(\frac{d\theta}{dx}\right)^2 + F(\psi,\theta) - F(\psi_B,\theta_B)\right] dx + f_s(\psi_s,\theta_s). \tag{0.1}$$

Here $F(\psi,\theta) = f(\psi) + g(\theta) - (k/2)\psi^2 sin^2\theta$ is a free-energy density similar to Benguigui's one used to describe the NC phase transition [8]. $f(\psi) = (\alpha/2)\psi^2 + (\beta/4)\psi^4$ $(\beta > 0)$ is the "pure" smectic A term (ψ is the density-wave amplitude) and $g(\theta) = (a/2)sin^2\theta + (b/4)sin^4\theta + (c/6)sin^6\theta$, $(a,b,c,> 0)$; $(-k/2)\psi^2 sin^2\theta$ $(k > 0)$ is the coupling between the order parameters ψ and θ ensuring a finite tilt angle θ in the smectic-C phase; $\psi_B \equiv \psi(x = \infty)$, $\theta_B \equiv \theta(x = \infty)$. x is a co-ordinate perpendicular to the surface.

To simplify the analysis a number of assumptions are made in eq.(1): (i) One-constant approximation for Frank's elastic energy ($K_{11} = K_{22} = K_{33} \equiv K$). This assumption seems to be reasonable in the nematic, and even in the smectic-C phase, when all the elastic constants diverge $K_{ii} \propto \xi^2$ near the NC transition [9]; ξ is the correlation length). In the smectic-A phase, however, diverge only K_{22} and K_{33}, so that, such a simplification is not reasonable. (ii) The tilt angle θ between the director **n** and the normal to the smectic layers **N**, as well as the smectic-A order-parameter ψ, are supposed to depend only on the co-ordinate normal to the surface $\theta = \theta(x)$. Thus, we neglect, e.g., possible smectic layer distortions. (iii) It is suposed that the smectic layers grow parallel to the free surface, that is, the surface and layer normals coinside. This assumption is confirmed in a number of previous experiments, and seems being a characteristic feature of verious liquid crystals [1,10].

The surface forces can be modelled by the folloing δ-function terms:

$$f_s(\psi_s,\theta_s) = \frac{\sigma}{2} sin^2\theta_s - \frac{k_s}{2}\psi_s^2 sin^2\theta_s - \frac{\delta}{2}\psi_s^2, \tag{0.2}$$

where $\psi_s = \psi(x)\ |_{x=0}$; $\theta_s = \theta(x)\ |_{x=0}$. Here the first term represents the well-known Rapini-Papoular surface energy [11]. The easy axis is parallel to **s**, $\sigma > 0$. The symmetry of the system allows two additional terms which enforce the smectic layering near the surface provided that k_s, $\delta > 0$. Especially the term $(-\delta/2)\psi^2$ with $\delta > 0$ in a natural way describes the tendency of the presurface cybotactic groups to orient their smectic layers parallel to the surface. For small θ and ψ the coupling term can be neglected.

The mean-field analysis of eq.(1) leads to the following equations:

$$C\frac{d^2\psi}{dx^2} = \frac{\partial F(\psi,\theta)}{\partial \psi}, \tag{0.3}$$

$$K\frac{d^2\theta}{dx^2} = \frac{\partial F(\psi,\theta)}{\partial \theta}, \tag{0.4}$$

and the boundary conditions

$$C\left(\frac{d\psi}{dx}\right)_0 = \frac{\partial f_s}{\partial \psi_s}, \tag{0.5}$$

$$K\left(\frac{d\theta}{dx}\right)_0 = \frac{\partial f_s}{\partial \theta_s}, \tag{0.6}$$

$$\left(\frac{d\psi}{dx}\right)_\infty = \left(\frac{d\theta}{dx}\right)_\infty = 0, \qquad \psi(\infty) = \psi_B, \qquad \theta(\infty) = \theta_B. \tag{0.7}$$

In general, eqs.(3-7) can be solved only numerically. However, one can derive some analytical results near T_{NC} and in some special regions of the parameter space (σ, k_s, δ).

As an example, let us assume that $\sigma, \delta > 0$, $k_s = 0$. It is convinient to use the first integral of eqs.(3,4)

$$-F(\psi_B,\theta_B) = \frac{C}{2}\left(\frac{d\psi}{dx}\right)^2 + \frac{K}{2}\left(\frac{d\theta}{dx}\right)^2 - F(\psi,\theta). \tag{0.8}$$

The boundary conditions read:

$$C\left(\frac{d\psi}{dx}\right)_{x=0} = -\delta\psi_s, \qquad \left(\frac{d\psi}{dx}\right)_{x=\infty} = 0. \tag{0.9}$$

$$K\left(\frac{d\theta}{dx}\right)_{x=0} = \sigma sin\theta_s cos\theta_s, \qquad \left(\frac{d\theta}{dx}\right)_{x=\infty} = 0 \qquad (0.10)$$

For $T \geq T_{NC}$ the size of the cybotactic groups compares with the coherence length $\xi \propto (C/\alpha)^{1/2}$, whears the penetration depth of elastic deformations of n reads $\lambda \propto (K\beta/C\alpha)^{1/2}$. Then $\lambda/\xi \propto K^{1/2} \propto \xi$, that is, for week first order transitions near T_{NC} $\lambda \gg \xi$. The last two equations (9,10) define the following surface extrapolation lengths

$$\lambda_\theta = \frac{K}{\sigma}, \qquad \lambda_\psi = \frac{C}{\delta}, \qquad (0.11)$$

which caracterize the behavior of order parameters near the surface. Since $K \propto \xi^2$ one expects $\lambda_\theta \gg \lambda_\psi$, Fig.4.

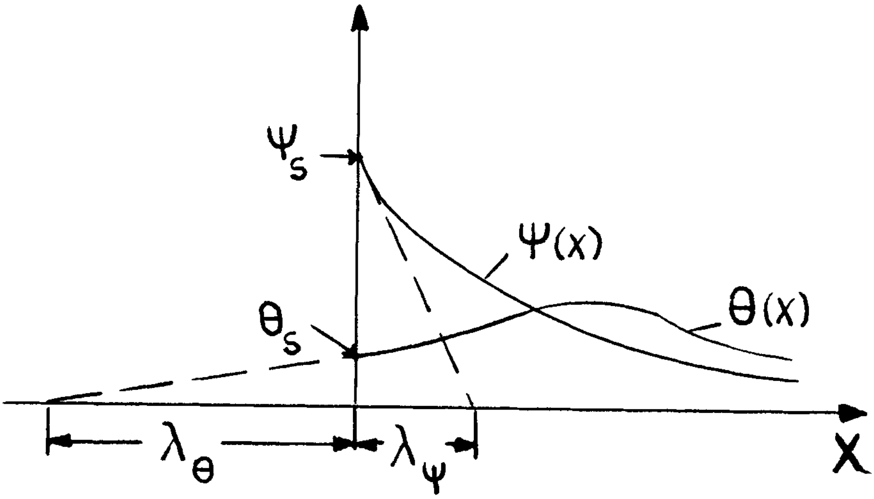

FIGURE 4. The order parameters $\psi = \psi(x)$ and $\theta = \theta(x)$ near T_{NC}, $T > T_{NC}$.

From the above discusion follows that one can expect a surface smectic layering for $T > T_{NC}$ provided that $\delta > 0$ (if $\delta = 0$, then $(d\psi/dx)_{x=0} = 0 \Longrightarrow \psi(x) \equiv 0$). A possible solution for $T > T_{NC}$ is $\theta(x) \equiv 0$, $\psi(x) \neq 0$, when ψ decays exponentionally in the bulk with a characteristic length ξ. In this case, there is a surface phase transition at $T = T_s \equiv T_\alpha + \delta^2/\alpha_0 C$ ($T_\alpha \approx T_{NC}$, $\alpha \equiv \alpha_0(T - T_\alpha)$).

In any case, it is clear, from the boundary conditions for θ, that there is a region near the surface where $\theta(x)$ should increase because ($\sigma > 0$), and this region penetrates deep in the bulk for large elastic constants K. On the other hand, the increase of σ sould diminish the tilt angle at the free surface θ_s.

Conclusion:

The qualitative analysis can explain why the surface instabilities considered above disply in substances with small latent heat of the NC transition ($OOBA$)- this is because of the large penetration length λ of elastic deformations near T_{NC} and the large size of the cybotactic groups ($\sim \xi$). In the analysis an important point is the well pronounced tendency (confirmed also in previous studies) for the smectic layers to grow parallel to the free surface. In such a geometry the Rapini-Papoular term acts towards decreasing of θ in the presurface cybotactic groups. The dopping of a surface active substance (lecitine), which directly reduces the surface tension (and, respectively, σ), supports the latter suggestion. In addition, the above picture leads to the conclusion that the splay elastic constant K_{11} will not be srtongly renormalized near the surface (as it should be near T_{NC} deep in the bulk). As a result, the smectic layer distortions should be favorized in a presurface region with a characteristic length ξ. This can explain the experimentally observed optical microtextures typical for the smectic-A state. The same conclusion has recently been drawn from depolarized light scatterring experiments which also give results typical for the smectic-A state just above T_{NC} [12]. Notice that the optical and X-ray studies of thin $OOBA$ cells demonstrate also results typical for smectic-A state [5]. These techniques, however, can hardly distinguish the true A state from a smectic-C state with extemely small tilt angles θ.

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