Binary separation in very thin nematic films: thickness and phase coexistence

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The behavior as a function of temperature of very thin films (10 to 200 nm) of pentylcyanobiphenyl (5CB) on silicon substrates is reported. In the vicinity of the nematic/isotropic transition we observe a coexistence of two regions of different thicknesses: thick regions are in the nematic state while thin ones are in the isotropic state. Moreover, the transition temperature is shifted downward following a $1/h^2$ law ($h$ is the film thickness). Microscopic observations and small angle X-ray scattering allowed us to draw a phase diagram which is explained in terms of a binary first order phase transition where thickness plays the role of an order parameter.

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The effect of confined geometry on the phase transitions of liquid crystals has attracted much attention over the years, from both theoreticians and experimentalists [1–8]. In particular Sheng [1] first predicted a shift in the nematic to isotropic transition temperature for a thin nematic film held between two ordering surfaces and a change from first order to second order transition under a critical thickness. This theoretical work has since been extended by Shuckin and Poniewierski [2] to the case of disordering surfaces and to situations where the sandwiching surfaces present either identical or competing orientations. In the meantime, experimental studies on liquid crystals in porous media [3–5], in submicron-sized droplets [6] or in thin films by Yokoyama [7] and more recently by Wittebrood et al. [8] have shown confinement induced shifts in the transition temperature consistent with theoretical predictions. Yet in most experimental cases, no conclusion could be drawn firmly on the order of the transition. Liquid crystalline films have also attracted much attention recently in dewetting studies [9–12].

In this letter, we study the case of very thin films, the thickness $h$ ranging from 10 to 200 nm, and report the first experimental evidence of a coexistence between two phases at equilibrium corresponding to two different thicknesses. This possibility of the system to adapt the thickness, as one boundary is a free surface, has neither been observed previously nor been predicted theoretically, yet it is a very striking effect of the surface on phase transitions. The decrease in the transition temperature shows a $1/h^2$ dependence consistent with Shuckin predictions, but the system adopts a binary state, here interpreted as a first order phase transition coupled with an elastic distortion field. This observation may be relevant to explain experimental data of some other groups as it shows that an important parameter -the thickness- may, in certain cases, not be fixed by the experiment.

For these experiments we use 4-n-pentyl-4’-cyanobiphenyl (5CB) (purchased from BDH Ltd., purity 99.5 %), a liquid crystal that undergoes a bulk phase transition from the nematic to the isotropic state at 35°C. The solid substrates we use are silicon wafers (type $n$, dopant $P$, purchased from Siltronix), bearing a natural, 2 nm thick, amorphous silica layer. They are used with no further cleaning or chemical treatment. The substrate roughness measured by X-ray reflectivity is about 35 nm. The anchoring of 5CB molecules on the substrate is known to be planar (i-e parallel to the surface) [13] while the anchoring at the air is homeotropic (perpendicular to the surface). The homogeneous film is obtained by spin-coating a solution of 5CB diluted in ultra-pure chloroform and the thickness is controlled by adjusting the concentration of the solution or the velocity of the spin-coater (typically 3000 rpm). All the films are formed at room temperature (23°C), where the 5CB is in the nematic phase in the bulk. The thickness is then measured very accurately either by Small Angle X-Ray Scattering (SAXS) or ellipsometry while the film is being observed under a reflection microscope, the image being acquired and analyzed on a computer. The experimental set-up includes a temperature controller able to maintain the temperature and its homogeneity in the film to better than $0.5^\circ$C.

After forming a film of a given initial thickness $h$ ranging from $\sim$ 10 nm to $\sim$ 200 nm, we observe its behavior when heated from nematic phase or cooled from isotropic phase. For each chosen temperature, we wait a few minutes for the system to reach equilibrium, the state then being stable over hours. A representative example is given on Fig.1 for a film of initial thickness $h = 48.5$ nm, with the associated characteristic temperatures (the dark

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regions here are higher in thickness than the clear ones). For this thickness, when the temperature is lower than $T_1 = 33.1^\circ C$ or higher than $T_2 = 34.5^\circ C$, the film is homogeneous and presents the same thickness as when formed at room temperature. For any temperature between $33.1^\circ C$ and $34.5^\circ C$, the film presents coexisting regions of two different thicknesses. On a short time scale, coalescence modifies the shape and distribution of these regions before stabilization but the thicknesses are not affected. On a much longer time scale (few hours), the system evolves because of a slow dewetting. The temperatures have been given here for this particular film, but both $T_1$ and $T_2$ depend on the initial thickness.

A more detailed observation of the process leading to the stable state when cooling the film from the isotropic phase shows that (Fig.1): i) at temperature $T_2$ -which is below the bulk $T_{NI}$- regions of thicker film ("islands") nucleate, leading to a situation where two different thicknesses coexist, with a certain area fraction (defined as the ratio of thick covered area over total area); ii) decreasing the temperature further, regions of thicker film decrease in thickness and the area fraction increase, while the thinner regions also decrease in thickness; iii) finally the film recovers its initial homogeneous thickness at temperature $T_1$. For example, we observe that for $33.9^\circ C$ (Fig. 1b), the thickness of the dark regions is higher ("darker") than the thickness of the dark regions of a lower temperature $33.4^\circ C$ (Fig.1c) but that the area fraction is smaller. We checked that the variation of the area fraction is compatible with a volume conservation law.

In the same manner, when heating the film from the nematic state, it shows a similar behavior but now regions of thinner film ("holes") nucleate. Moreover a comparison of two films of different initial thickness at the same intermediate temperature shows that both coexisting thicknesses of the two films are similar but that the area fraction is different, the thinner film having a smaller fraction than the thicker one. Out of these qualitative observations we conclude that the two coexisting thicknesses depend only on temperature while the area fraction is a function of the chosen temperature and the initial thickness.

We have used Small Angle X-ray Reflectivity to characterize thickness and roughness. Figure 2 shows the experimental data for a film of initial thickness $42$ nm, for three different temperatures, one below $T_1$, one intermediate, and one above $T_2$ (respectively $25^\circ C$, $33.4^\circ C$ and $37^\circ C$ in this example). For the two extreme temperatures, where the film is homogeneous, we observe typical Kiessig interference fringes.

The data are easily fitted using Parratt’s method [15] by a calculation of the intensity scattered by an homogeneous film of electronic density $\rho_c = 0.33 e \cdot \text{Å}^{-3}$, which corresponds to 5CB electronic density. We obtain a thickness of $42.0 \pm 0.2$ nm with a roughness of $0.50 \pm 0.05$ nm for $37^\circ C$, where the film is in the isotropic phase, and a thickness of $39.8 \pm 0.2$ nm with a roughness of $0.80 \pm 0.05$ nm for $25^\circ C$, where the film is in the nematic phase (the slight difference in the thickness, typically 4%, is only due to the long time necessary to acquire a sequence of X-ray spectra).

As for an intermediate temperature, where the coexistence takes place, the intensity does not present classical oscillations but is the superposition of two systems of fringes, as can be seen on the second curve of Fig.2 ($33.4^\circ C$ in this case). We measure the area fraction (0.44 in this case) on a microscope image of the
film and use it as a fixed value in the model. The best fit, shown on Fig.2, is then obtained with a model of two homogeneous films (with same electronic density \( \rho_e = 0.33 \text{ e} \cdot \text{Å}^{-3} \)), one of thickness 25.8 ± .2 nm and roughness .58±.05 nm, the other of thickness 62.3±.5 nm and roughness .85±.05 nm, with a relative weight corresponding to the area fraction. One can check that volume is conserved (0.56 × 25.8 + 0.44 × 62.3 = 41.8 ± 42 nm).

In those experiments, homogeneous isotropic films (\( T > T_2 \)) systematically show a lower roughness (from .45 to .55 nm) than homogeneous nematic ones (\( T < T_1 \)) (from .75 to 1.2 nm). The roughness of the film is thus an important parameter and is characteristic of the phase. The typical value found for an isotropic phase is in good agreement with what we expect from the thermal fluctuations of an isotropic liquid free interface. The roughness \( \bar{\sigma} \) calculated from a capillary wave model [16] is given by \( \bar{\sigma}^2 = \langle z^2 \rangle = \frac{2\pi}{\log \frac{Q_{\text{max}}}{Q_{\text{min}}} \cdot \frac{\gamma}{\pi \gamma}} \) where \( \gamma \) is the surface tension of the liquid and \( Q_{\text{max}} \) and \( Q_{\text{min}} \) are two cut-off wave vectors depending on the system, respectively the size of the molecules and the coherence length of the X-ray beam. Taking experimental values: \( \gamma = 29 \text{ mN} \cdot \text{m}^{-1} \), \( Q_{\text{max}} = 4.1 \times 10^6 \text{ m}^{-1} \) (which corresponds to an average molecular size of 16 nm) and \( Q_{\text{min}} = 8.1 \times 10^5 \text{ m}^{-1} \) (which corresponds to a measured coherence length of 80 \( \mu \text{m} \)), one finds \( \bar{\sigma} = .49 \text{ nm} \). The higher roughness in the case of a nematic film may be explained by the distortion of the director field: the degenerate planar anchoring at the substrate (i.e isotropic in the azimuthal direction) induces defects in the configurations of molecules near the lower surface that propagate through the film to protrude from the upper free surface, which is thus distorted.

The important point is now that, for intermediate cases, the film of smaller thickness has the characteristic roughness of the isotropic phase and the one of higher thickness has the characteristic roughness of the nematic phase. Simultaneous observations using crossed-polarizers made on films \( \gtrsim 40 \text{ nm} \) show birefringence in thick regions contrary to thin regions [17]. Moreover we have checked that in thinner regions the film does not present a uniform homeotropic nematic state but truly an isotropic state, using the following method: knowing the exact thickness by SAXS, the apparent optical refractive index of the film was then measured by ellipsometry for different incident angles at temperatures just above \( T_2 \). As in the case of the isotropic phase and contrary to the case of the nematic phase, the apparent refractive index in this region remains constant with respect to the angle. The convergence of those observations shows that for intermediate temperatures, the film is composed of thin regions of isotropic phase and thick regions of nematic phase. The description in terms of coexistence of two films of different thickness can now be understood as the coexistence of nematic and isotropic phase.

Repeating the procedure at different temperatures for each initial film thickness, one is able to build up a phase diagram, as shown in Fig.3. This diagram gathers all the different points (\( h, T \)) corresponding to a state with coexistence of two thicknesses. It presents three parts: the upper part where the film is homogeneously in the isotropic phase, the lower part where the film is homogeneously in the nematic phase and the intermediate part where there is separation in two phases. We notice that for thick films (\( > 200 \text{ nm} \)) both characteristic temperatures tend towards the bulk transition temperature, as expected from bulk behavior.

This situation is reminiscent of the phase separation in a binary mixture of two miscible nematogens at initial concentration \( c_0 \) when it is quenched to a temperature between the two pure transition temperatures: a smaller concentration \( c_1 \) in the isotropic phase coexists with a higher concentration \( c_2 \) in the nematic phase, with a ratio \( \varphi \) such that \( c_0 = \varphi \cdot c_1 + (1 - \varphi) \cdot c_2 \). In the same manner, the description made above of the behavior of the film with temperature can be followed on the phase diagram when following a vertical line at constant \( h = h_0 \). The diagram has to be read as a first order phase transition in a binary mixture, where the thickness plays the role of the concentration, where \( h_0 = \varphi \cdot h_1 + (1 - \varphi) \cdot h_2 \), with \( h_1(T), h_2(T) \) and \( \varphi(h_0, T) \). Here \( h_1 \) and \( h_2 \) are also two different phases.

This thickness transition and the shift in the transition temperature can be interpreted as a competition between the energy that is necessary to melt the sample in the isotropic state before the bulk transition temperature and the distortion energy kept inside the film. Indeed the two antagonists anchoring conditions, planar

![FIG. 3. Phase diagram gathering the two coexisting thicknesses as a function of temperature for different initial thicknesses: the open marks are the thin isotropic phase and the filled ones the thick nematic phase. The error bars are within the points dispersion and are not represented for clarity. The inset presents the same data, plotting \( T - T_{NI} \) as a function of \( 1/h^2 \), with two linear fits.](image-url)
and homoetropic, imply that the director field undergoes an elastic distortion along the normal to the substrate. Assuming there is no anchoring transition, that is to say no change as a function of temperature or thickness in the anchoring angles near both surfaces (an assumption that will be discussed further on), the elastic component of the free energy per unit surface of the film may be written as \[18,19\]:

\[
F_{el}(h) = \frac{1}{2} \frac{K \Delta \theta^2}{h}
\]  

where \(K\) is the elastic constant of the nematic (in the one constant approximation) and \(\Delta \theta\) is the difference between the anchoring angles at the two boundaries.

Following Sluckin et al. \[2\], a balance between this energy and the cost of moving the transition to a temperature \(T_{NI} + \Delta T_{NI}\) gives the Kelvin equation, which describes the variation of the transition temperature with thickness:

\[
\frac{\Delta T_{NI}}{T_{NI}} = -\frac{1}{2 \Delta H_{NI}} \frac{K \Delta \theta^2}{h^2}
\]  

where \(\Delta H_{NI}\) is the latent heat of the transition. The experimental \(-1/h^2\) dependence of both coexisting lines of the transition is shown in the inset of Fig.3, where the fits give \(T - T_{NI} = -\frac{C}{h^2}\) with \(C = 5.04 \times 10^{-15}\) K.m\(^2\) for \(T_1\) and \(C = 0.82 \times 10^{-15}\) K.m\(^2\) for \(T_2\) respectively. Using experimental data given in the literature for 5CB: \(\Delta H_{NI} \sim 10^6\) J.m\(^{-3}\) \[3\], \(K \sim 3 \times 10^{-12}\) N \[20\] and \(T_{NI} \sim 300\) K and \(\Delta \theta \sim \frac{\pi}{2}\), we estimate \(C \sim 10^{-15}\) K.m\(^2\), which is of the correct order of magnitude. The good quantitative agreement between experiments and these theoretical predictions must not hide the fact that the existence of two coexisting thickness is not explained simply by the Kelvin equation: the thickness separation can only be explained once conservation of volume is taken into account. A homogeneous film will have to pay the price of the latent heat to be isotropic or the price of the elastic distortion to be nematic. For a certain range of temperatures depending on the initial thickness, it can be energetically advantageous for the system to separate into two thicknesses: the sum of the energy of a nematic higher regions -favorable because releasing the elastic distortion- and the energy of an isotropic lower regions -unfavorable because isotropic- may be lower than the energy of an homogeneous film, either in the isotropic state or in the nematic state at this temperature. A model within a Landau-de-Gennes framework confirms quantitatively this assumption and will be detailed in a forthcoming paper \[21\]. This also accounts for the fact that no anchoring transition occurs in this system, as this scenario will allow the system to keep any nematic thickness above the extrapolation length \(K/W\) (where \(W\) is the anchoring strength), which describes the critical thickness below which a constrained nematic will prefer to break the anchoring rather than undergo the elastic distortion. This interpretation shows that the thickness plays the role of an order parameter. This reveals the first order nature of the phase transition where a binary state can be observed.

In conclusion, we have shown in this letter that for very thin cyanobiphenyl films the nematic to isotropic phase transition is coupled with a thickness transition, leading to intermediate states where thin regions of isotropic phase coexist with thick regions of nematic phase. We have been able to build experimentally a phase diagram describing this transition and showing the dependence of the transition temperature with the thickness. We have interpreted this behavior as the result of a competition between the elastic energy and the latent heat of the transition, coupled with a volume conservation law. We have also observed this behavior for compounds of the same family (nCB) and it is certainly more general. It may play a significant role in the stability of LC films, in the sense that we can not impose an arbitrary thickness at any temperature for such systems. Moreover it may also mean that in such systems and in certain cases, a continuous variation of a measured parameter (light scattering, birefringence . . . ) with temperature may not be the signature of second order phase transition but the result of mixing of two signals coming from two coexisting regions in a different state, during a first order phase transition. Being aware of this behavior may be relevant for the fundamental or theoretical study of these systems.

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[1] P. Sheng, Phys. Rev. Lett. 37, 1059 (1976).
[2] T.J. Sluckin, A. Poniewierski, Mol. Cryst. Liq. Cryst. 179, 349 (1990).
[3] M. Kuzma and M.M. Labes, Mol. Cryst. Liq. Cryst. 100, 103 (1983).
[4] G.S. Iannacchione and D. Finotello, Phys. Rev. Lett. 69, 2094 (1992); G.S. Iannacchione, G.P. Crawford, S. Zumer, J.W. Doane, and D. Finotello, ibid. 71, 2595 (1993).
[5] T. Bellini, N.A. Clark, C.D. Muzni, L. Wu, C.W. Garland, D.W. Shaefer, and B.J. Oliver, Phys. Rev. Lett. 69, 788 (1992).
[6] A. Golemme, S. Zumer, D.W. Allender, and J.W. Doane, Phys. Rev. Lett. 61, 2937 (1988).
[7] H. Yokoyama, J. Chem. Soc. Faraday Trans. 2 84, 1023 (1988).
[8] M.M. Wittebrood, D.H. Luijendijk, S. Stallinga, Th. Rasing, and I. Musevic, Phys. Rev. E 54, 5232 (1996).
[9] S. Herminghaus, K. Jacobs, K. Mecke, J. Bischof, A. Fery, M. Ibn-Elhaj and S. Schlagowski, Science 282, 916 (1998).
[10] F. Vandenbrouck, M.P. Valignat, and A.M. Cazabat, Phys. Rev. Lett. 82, 2693 (1999).
[11] A. Ziherl, R. Podgornik, and S. Zumer, Phys. Rev. Lett. 84, 1228 (2000).
[12] O. Ou Ramdane, PhD Thesis, University Paris VI, 1998;
[13] F. Vandenbrouck, S. Bardon, M.P. Valignat, and A.M. Cazabat, Phys. Rev. Lett. 81, 610 (1998).
[14] A. Sharma and R. Khanna, Phys. Rev. Lett. 81, 3463 (1998).
[15] I.G. Parratt, Phys. Rev. 95, 359 (1954).
[16] P.S. Pershan, Faraday Discuss. Chem. Soc., 89, 231 (1990); A. Braslau, P.S. Pershan, G. Swislow, B.M. Ocko, and J. Als-Nielsen, Phys. Rev. A 38, 2457 (1988).
[17] for $< 40$ nm films, birefringence is too weak.
[18] P.G. de Gennes and J. Prost, The Physics of Liquid Crystals (Clarendon Press, Oxford, 1993).
[19] J. Proust, E. Perez, and L. Terminassian-Saraga, Coll. Pol. Sci. 255, 1003 (1978).
[20] M.J. Bradshaw, E.P. Raynes, J.D. Bunning, and T.E. Faber, J.Phys. (Paris) 46, 1513 (1985).
[21] D. van Effenterre, D. Roux, and M.P. Valignat (to be published).