PHYSICAL REVIEW E VOLUME 54, NUMBER 5 NOVEMBER 1996

Thickness-dependent phase transition in thin nematic films

M. M. Wittebrood, D. H. Luijendijk, S. Stallinga, and Th. Rasing
Research Institute for Materials, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

I. Muševič
J. Stefan Institute, Jamova 39, 61000 Ljubljana, Slovenia

(Received 20 November 1995)

Using light scattering, the thickness dependence of the isotropic-nematic phase transition temperature T_{NI} in a thin film of octylcyanobiphenyl (8CB) is studied in two distinct geometries: with and without strain. We observed a large stress induced shift in T_{NI}, as a function of the film thickness d. At $d \sim 0.3$ μm a crossover in the behavior of T_{NI} as a function of thickness is observed, which can be attributed to a competition between strain and anchoring forces. [S1063-651X(96)08311-0]

PACS number(s): 64.70.Md, 61.30.Gd, 68.10.Cr, 68.60.−p

The effects of confinement on the phase transitions in liquid crystals have attracted much attention recently [1–4]. In particular, calorimetric and light scattering experiments on liquid crystals in porous media indicate a shift ΔT_{NI} of the isotropic-nematic transition and a possible change from a first order to a continuous transition. This last observation appears to depend on the type of porous matrix. For example, Iannacchione *et al.* find a second order transition in porous glass [4], whereas in Anopore the transition is of first order [1]. To understand these observations, both the confinement and the randomness of the porous medium are important. Confinement effects will in general lead to a $1/R^2$ depression of the transition temperature, whereas a random field leads to a suppression of the first order character. Both aspects have been observed [1–4].

In this paper we present a study of the confinement effects of the isotropic-nematic phase transition using a well defined planar geometry. This enables us to control the thickness and the surface induced ordering independently. The influence of ordering or disordering of the surfaces on the isotropic-nematic phase transition temperature in 5CB in a cell with two identical boundaries has been studied by Yokoyama [5]. His measurements were consistent with the calculations of Sheng [6] and Poniewierski *et al.* [7], and showed a $1/d$ and $-1/d$ dependence of the ΔT_{NI} for an ordering and disordering surface, respectively.

We have examined the case of two different surface orientations, and have observed a ΔT_{NI} following a combination of $-1/d^2$ and $1/d$ dependence for thicknesses larger than 0.3 μm, and showing a $-1/d$ dependence for smaller thicknesses. Here d is the separation between the two surfaces. In contrast, when both surfaces induce the same orientation, no shift of T_{NI} is observed. The results are in qualitative agreement with a Landau model introduced by Sluckin *et al.* [8], where two competing orientations introduce a stress term that is responsible for the observed $-1/d^2$ dependence. Sluckin *et al.* also predicted a crossover to a $1/d$ thickness dependence for small d. The absence of a measurable shift in the cell with two identical boundaries is consistent with the measurements by Yokoyama [5].

For the experiments we used octylcyanobiphenyl (8CB), which has a bulk nematic-isotropic phase transition at 41 °C. To prepare a homeotropic and planar alignment, the 8CB was spread on a nylon coated glass substrate. The nylon coated surface induces a planar ordering, whereas the free surface gives a homeotropic alignment. The 8CB was deposited using iso-propanol as a solvent and formed flat, pancakelike droplets. For the larger thicknesses, the film thickness was determined by counting Newton's rings; for the very thin films, the thickness was calculated from the known amount of bulk material and the measured size of the 8CB droplet. The accuracy of this determination was checked by also using it for thicker films. For the planar-planar geometry, we used a flat fused quartz substrate on the one side, and a long focal length ($f = 2$ m) glass lens as the other surface. In this way the cell contained a continuous variation of thicknesses from <0.02 μm in the center, to ~ 10 μm (at 7 mm from the center). Here the thickness increases as r^2, where r is the distance with respect to the center. The cell was filled at 50 °C using capillary action in the isotropic phase.

We used static light scattering to determine the temperature of the isotropic-nematic phase transition. The liquid crystal is placed between crossed polarizers, and the scattered intensity is measured under an angle of $\sim 7°$ with respect to the transmitted beam. In this geometry there is almost no scattering in the isotropic phase. In the nematic phase, however, a finite amount of scattering due to order parameter fluctuations is measured. Figure 1 shows the measured scattering intensity as a function of the temperature for several cell thicknesses. At the phase transition we observe a sudden jump in the scattering intensity, which for thicker layers is accompanied by intensity fluctuations.

Even for the smallest thicknesses, the transition appears to be first order judging from the small but discontinuous step in the scattering intensity at T_{NI}. A gradual transition to a more second-order-like transition cannot, however, be excluded within the present accuracy.

Figure 2 shows the shift of the isotropic-nematic phase transition temperature as a function of the film thickness, in the case of two different boundaries. We observe two regimes. For larger thicknesses (>0.3 μm) the shift is a combination of a $1/d$ (surface ordering effect) and a $-1/d^2$ de-

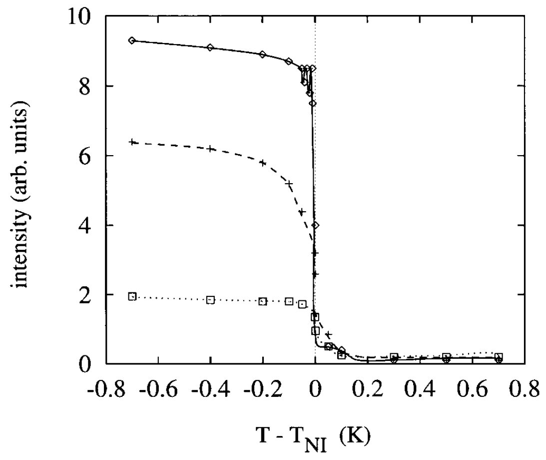

FIG. 1. Light scattering intensity vs temperature for different film thicknesses: $d \simeq 0.5$ μm ($\Diamond$), $d \simeq 0.25$ μm ($+$), and $d \simeq 0.02$ μm ($\square$). T_{NI} is the isotropic-nematic phase transition temperature. The lines are guides to the eye.

pendence (caused by strain). This can clearly be seen in Fig. 3, where $\Delta T d$ is plotted versus $1/d$. Fitting the data yields

$$\Delta T d = A - \frac{B}{d}, \tag{1}$$

with $A = 0.17 \pm 0.10$ μm K, $B = 0.14 \pm 0.05$ μm^2 K, and d in μm. For thicknesses smaller than 0.3 μm, however, the dependence has changed into a $-1/d$ behavior,

$$\Delta T \sim -\frac{C}{d}, \tag{2}$$

with $C = 0.29 \pm 0.03$ μm K and d in μm. In the situation where we have identical boundaries, we observed no shift in the phase transition temperature within the accuracy of our measurements (± 0.1 °C) (Fig. 4). These two observations lead to the conclusion that the temperature shift, observed in the first situation, must be due to stress induced by the forced variation of the orientation within the sample.

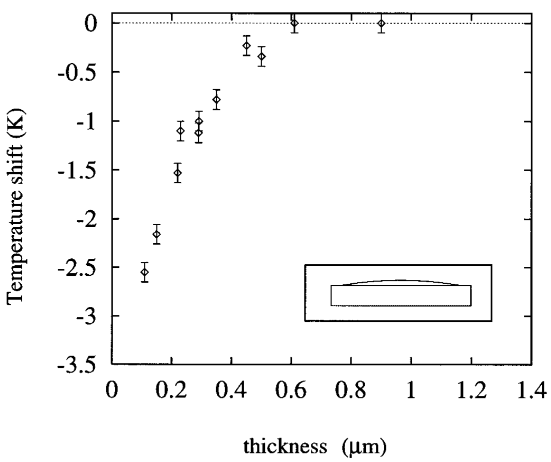

FIG. 2. The isotropic-nematic phase transition temperature, relative to its bulk value (41.2 °C), vs thickness in strained 8CB films. The transition temperature shifts to lower values for $d \leqslant 0.5$ μm. A schematic view of the film configuration is shown in the inset: flat 8CB pancakelike droplets on the substrate.

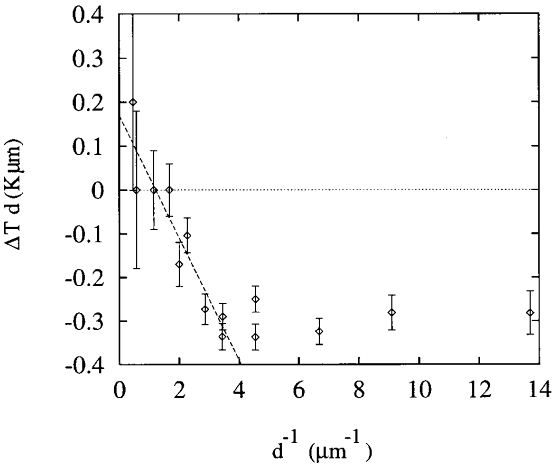

FIG. 3. The temperature shift (ΔT) times the thickness vs the inverse thickness in strained 8CB films. The line represents a fit (for $d^{-1} < 3.3$ μm^{-1}) with $\Delta T \times d = 0.17 - 0.14 \times d^{-1}$ (μm K). At $d^{-1} \simeq 3.3$ μm^{-1} a crossover is observed to a behavior where $\Delta T \times d$ is independent of d.

Following Sluckin *et al.* [8] one expects two thickness regimes for capillary condensation in a restricted planar geometry with different orientations induced by the walls. A crossover between these two regimes occurs at a certain thickness d_c.

For thicknesses larger than d_c two terms are important: (1) a capillary condensation term, which comes from the Kelvin equation and contains the surface tensions γ_N and γ_I, where the subscripts denote the nematic and isotropic phase, respectively; (2) a stress term, which causes a varying director orientation within the nematic layer and is a linear function of the Frank elastic constant K. The phase transition takes place at a temperature $T_{NI} + \Delta T$, where

$$\Delta T = \frac{T_{NI}}{L}\left[\frac{(\gamma_I - \gamma_N)_1 + (\gamma_I - \gamma_N)_2}{d} - \frac{\pi^2}{4}\frac{K}{d^2}\right], \tag{3}$$

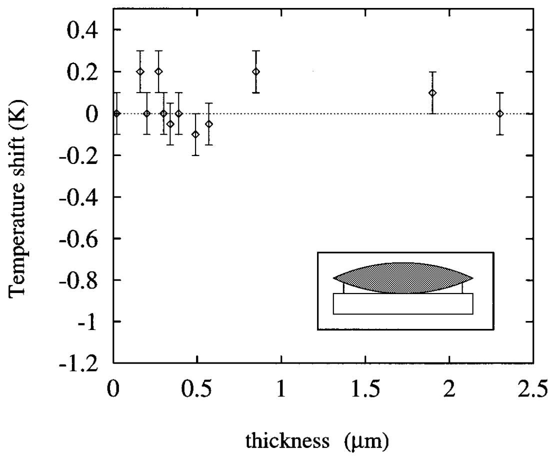

FIG. 4. The isotropic-nematic phase transition temperature, relative to its bulk value (40.8 °C), vs thickness for a strainless 8CB layer. The inset schematically shows the cell configuration: 8CB between a lens and a flat substrate.

where L is the latent heat at the isotropic-nematic transition, and the indices 1 and 2 indicate the two separate boundaries.

At $d \approx d_c$, however, the cost of varying the director is higher than that of changing the boundary condition at the boundary with the smallest anchoring constant W. This means that for $W_1 \ll W_2$, $(\gamma_N)_1$ should be replaced by $(\gamma_N)_1 + W_1$. In the regime where $d \approx d_c \cong (K/W_1)$, we therefore expect

$$\Delta T \cong \frac{T_{NI}}{L}\left[\frac{(\gamma_I - \gamma_N)_1 + (\gamma_I - \gamma_N)_2 - W_1}{d}\right]. \tag{4}$$

Note that d_c equals the extrapolation distance L_1. The crossover between the two behaviors can be gradual or in the form of a phase transition [8].

For the calculation of ΔT we use the Young-Laplace equation for the surface tension at wall i [7]:

$$(\gamma_I - \gamma_N)_i = \gamma_{NI} \cos \theta_i^{NI}, \tag{5}$$

with γ_{NI} the surface tension of the *NI*-interfacial layer and θ_i^{NI} the angle of the *NI* interface with respect to wall i.

Comparison between these calculations and our measurements shows a good qualitative agreement. Furthermore, the ratios between the three terms caused by capillary condensation, strain and anchoring, respectively, are consistent with the expectations, when we use $\gamma_{NI} = 9.5 \times 10^{-6}$ J/m^2 [9], $K = 3 \times 10^{-12}$ N [10], $W \cong 2.5 \times 10^{-5}$ J/m^2 [values measured by others are $W = (1.0 \pm 0.5) \times 10^{-5}$ J/m^2 [11] and $W > 6 \times 10^{-5}$ J/m^2 [9]], and $\cos\theta_1^{NI} + \cos\theta_2^{NI} \cong 1$ (i.e., slightly ordering surfaces). From these values of K and W we can calculate d_c to be 0.12 μm, which is in reasonable agreement with the experimentally found value of 0.3 μm. However, our measured temperature shifts are almost two orders of magnitude larger than calculated, using $T_{NI} = 314$ K and $L = 1.36 \times 10^6$ J/m^3 (value for 5CB [5]).

These observations seem to lead to the conclusion that for a film with one free surface there is an effective latent heat which is much smaller than the bulk value, given above. In systems containing two cell walls [5] temperature shifts have never been observed for thicknesses as large as 0.4 μm and the latent heat equals the bulk latent heat. This is also confirmed by our measurements on 8CB layers in a cell, where the bulk latent heat should be used to account for the absence of a measurable temperature shift.

At this moment it is not clear why a free surface would lead to such a small latent heat. We can only refer to experiments done in porous media where the measured latent heat is found to be slightly smaller than the bulk value [12].

In conclusion, we have observed the competition between capillary condensation, strain and anchoring. The measured behavior of the shift in the *IN*-phase transition temperature as a function of thickness is qualitatively consistent with the theoretical predictions of Sluckin *et al.* [8]. Also the ratios between the different terms: capillary condensation, strain and anchoring and the observed critical thickness agree with the expectations. However, the free surface of the 8CB films seems to lead to a temperature shift that is much larger than the temperature shifts measured in strainless cells.

We gratefully acknowledge A.F. van Etteger for valuable assistance with the experimental equipment. Part of this work was supported by the PECO/Copernicus programme ERBCIPACT930159.

---

[1] G.S. Iannacchione and D. Finotello, Phys. Rev. Lett. **69**, 2094 (1992).
[2] N.A. Clark, T. Bellini, R.M. Malzbender, B.N. Thomas, A.G. Rappaport, C.D. Muzny, D.W. Schaefer, and L. Hrubesh, Phys. Rev. Lett. **71**, 3505 (1993); T. Bellini, N.A. Clark, C.D. Muzny, L. Wu, C.W. Garland, D.W. Shaefer, and B.J. Oliver, *ibid.* **69**, 788 (1992).
[3] A. Golemme, S. Žumer, D.W. Allender, and J.W. Doane, Phys. Rev. Lett. **61**, 2937 (1988).
[4] G.S. Iannacchione, G.P. Crawford, S. Žumer, J.W. Doane, and D. Finotello, Phys. Rev. Lett. **71**, 2595 (1993).
[5] H. Yokoyama, J. Chem. Soc. Faraday Trans. 2 **84**, 1023 (1988).
[6] P. Sheng, Phys. Rev. Lett. **37**, 1059 (1976).
[7] A. Poniewierski and T.J. Sluckin, Liq. Cryst. **2**, 281 (1987).
[8] T.J. Sluckin and A. Poniewierski, Mol. Cryst. Liq. Cryst. **179**, 349 (1990).
[9] S. Faetti and V. Palleschi, Phys. Rev. A **30**, 3241 (1984).
[10] M.J. Bradshaw, E.P. Raynes, J.D. Bunning, and T.E. Faber, J. Phys. (Paris) **46**, 1513 (1985).
[11] O.D. Lavrentovich and V.M. Pergamenshcik, Phys. Rev. Lett. **73**, 979 (1994).
[12] G.S. Iannacchione and D. Finotello, Phys. Rev. E **50**, 4780 (1994).