Wetting Transition and Divergence of the Extrapolation Length near the Nematic-Isotropic Transition

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We report an investigation of the wetting behavior of 5CB drops on silicon wafers. Nematic drops exhibit a characteristic mesoscopic thickness that diverges as the nematic-isotropic transition is approached. This divergence may be associated with the vanishing of the anchoring strength, or equivalently, to a wetting transition occurring near the nematic-isotropic transition. Pretransitional effects due to the structuring of the drop close to the solid surface can be observed in the isotropic phase. [S0031-9007(98)06597-1]

Surface-induced effects in liquid crystals (LC's) are of interest from both an industrial and a fundamental-physics perspective. A better knowledge of interfacial properties of liquid crystals may lead to improvements in liquid- crystal displays, and correspond to an increasing general interest in the physics of surface phenomena and of confined systems. For the last two decades, important phenomena like surface-induced orientational order [1–3] or orientational wetting [4–6] have been the object of intensive study. A lot of attention has also been addressed to the anchoring mechanism [7]. In this Letter, we present new results about the wetting behavior of 5CB (4-*n*-pentyl-4′-cyanobiphenyl) on silicon wafers near the nematic-isotropic transition by combining spatially resolved ellipsometry (well adapted for complete wetting situations) and "macroscopic" observations using polarized optical microscopy (partial wetting situations). Our aim is to study a model system to achieve a more fundamental understanding of the influence of surface-induced effects on the wetting properties of LC's. Detailed knowledge of the oxidized-silicon-wafer/LC interface is also a necessary first step before the processes involved during the wetting of a LC on anisotropic silicon substrates coated with evaporated silicon oxide (which is of more interest for industrial applications [8]) may be understood.

5CB exhibits solid (S), nematic (N), and isotropic (I) phases. In the bulk, 5CB molecules form dimers whose length reaches 25 Å [9] while the length of individual molecules is 18.7 Å. Samples of 5CB were purchased from BDH Ltd., and used without any further purification (according to the manufacturer, the purity of the compound is better than 99%). Small droplets of the LC were deposited on silicon wafers [type *n*, dopant *P*, orientation (100) purchased from Siltronix] bearing a natural oxide layer of 2 nm. These substrates were cleaned by an UV-ozone exposure [10]. Such surfaces are known to promote quasiplanar anchoring of 5CB, the anchoring at the air-nematic free interface being homeotropic [11]. These silicon wafers thus allow us to easily study LC films under elastic stress (due to antagonist anchoring conditions at

both interfaces). We observe that the 5CB nematic phase completely wets such surfaces while the isotropic phase wets them only partially; the nematic-isotropic transition is accompanied by a wetting transition. The detailed experimental setup has been described elsewhere [12]. We note that our spatially resolved ($25 \times 100\ \mu\text{m}^2$) single wavelength ($\lambda = 6328$ Å) ellipsometer is phase modulated and works at Brewster incidence with a typical time constant of 20 ms per experimental point. The thickness resolution is 0.2 Å on silicon wafers thanks to the large optical index contrast between the solid surface and the thin liquid layer.

In a previous Letter [11], we discussed the structure of a 5CB-nematic drop close to the solid surface. First let us reexamine the main results from the previous work. The thickness profile of the drop, measured by ellipsometry, exhibits two characteristics thicknesses L_2 and L_1. During the spreading, the drop thickness decreases until L_2 is reached. Then the drop breaks into islands on top of L_1 and the ellipsometric profile becomes irregular (cf. Fig. 1). The higher L_2 terrace, belonging to the mesoscopic scale, results from a balance between elastic, anchoring, and spreading energies. Using a simple model, we showed that the thickness L_2 is related to the well known extrapolation length [13] $L_c = K/W_1$ where W_1 is the anchoring energy and K an elastic constant associated to the elastic distortion owing to antagonist anchoring conditions. The lower L_1 terrace belongs to the molecular scale. It is a trilayer (tilted monolayer bearing a smectic-like bilayer) with a very well defined thickness of 33 Å that remains constant as the temperature changes. This structure is actually completely determined by the specific short-range interaction between the LC and the solid. Our model is no longer valid below a cutoff thickness, which is of the order of the specific LC-solid interaction range. L_1 then appears as a natural cutoff thickness. This explains why L_2 is taken from the top of the trilayer and not from the solid surface. While L_1 does not change with temperature, L_2 is highly sensitive to any temperature variation. We have therefore performed a systematic study of this dependence.
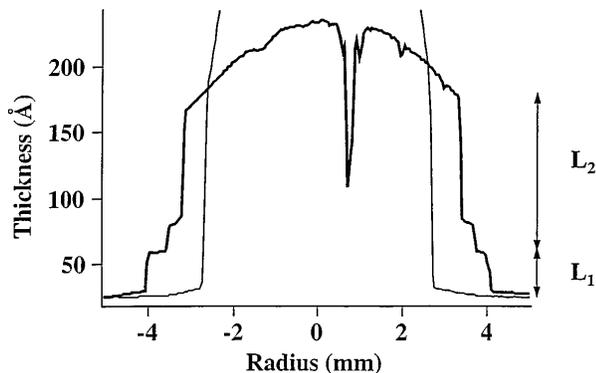
FIG. 1. Ellipsometric thickness profiles of a nematic drop ($T = 26.0\,°C$) 5.5 h and 20.5 h after drop deposition. The baseline at 20 Å is the silica layer on top of the silicon wafer. Two characteristic thicknesses L_1 and L_2 appear. Note the structure (bilayer) just above L_1, at the edge of the drop.

The sample temperature was controlled thanks to a temperature regulator (Haake F3) with an accuracy better than 0.1 °C. No thermal gradients between air and the surface were detected and the relative humidity was $(50 \pm 10)\%$. The measurements are presented in Fig. 2. L_2 increases continuously in the nematic phase, and diverges, as the nematic-isotropic transition is approached (cf. Fig. 2). From the wetting physics standpoint, the divergence of the drop characteristic thickness is the signature of a wetting transition [14]. In Fig. 2, we estimate the temperature T^* where the divergence of L_2 occurs; T^* is around 35 °C. Figure 3 is a plot of L_2 as a function of $1/(T^* - T)$. Here, the value of T^* has been adjusted to get the best straight line: $T^* = 34.6 \pm 0.2\,°C$. Thus, our experimental data show that $L_2 \propto 1/(T^* - T)$. L_2 appears as the relevant temperature dependent characteristic thickness. Furthermore, we can estimate the nematic-isotropic transition temperature for our samples, by performing optical observations of 5CB droplets under a polarized microscope: $T_{NI} = 34.8 \pm 0.3\,°C$, which is in good agreement with the value of T^*.
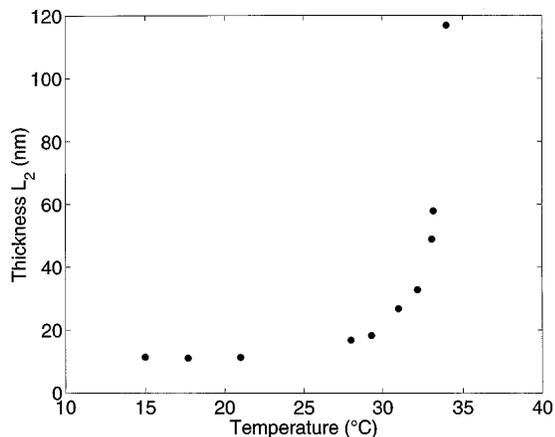
An increase of the extrapolation length close to the nematic-isotropic transition has already been observed [15–17]. But these previous works were related to the study of thick LC cells between plates where a mesoscopic quantity like the extrapolation length is deduced from macroscopic measurements (torque measurements [15], optical retardation measurements [16,17]). In Ref. [16], the authors found a divergence with an exponent of -0.45. They explain that this exponent is not compatible with thermodynamics (which lead to an exponent of -1 [16]), but "is indicative of the occurrence of crossover to a more singular or noncritical behavior". Our system is different because it has a free surface. Moreover, the experimental technique we use (ellipsometry) allows us to directly measure information at a mesoscopic scale. Let us examine the expression of L_2 in this case [11] in order to emphasize its physical meaning:

$$L_2 = \frac{K}{W_1} \frac{\theta_1^2}{S/W_1 - \cos^2 \theta_1}, \tag{1}$$

where K/W_1 is the extrapolation length, θ_1 the director angle at the solid surface, and S the spreading parameter ($S > 0$). As the nematic-isotropic transition is approached, K and W_1 tend to zero. The spreading parameter S also vanishes because a wetting transition takes place in the vicinity of the nematic-isotropic transition. What is the diverging term close to the transition? We have shown [11] that the free energy per unit volume of the drop is $F_v = -(-S + W_1 \cos^2 \theta_1)^2/2K\theta_1^2$. By differentiating this expression with respect to θ_1, one obtains:

$$\cos^2 \theta_1 + \theta_1 \sin(2\theta_1) - S/W_1 = 0. \tag{2}$$

This gives the equilibrium value of θ_1 as a function of S/W_1. The minimum of the free energy per unit volume corresponds to a value of θ_1 varying between $\pi/4$ and $\pi/2$. Thus L_2 exists only if $\pi/2 \geq \theta_1 \geq \pi/4$.

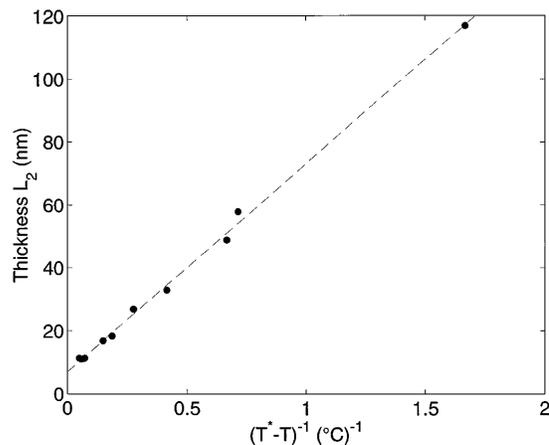FIG. 2.   Thickness L_2 as a function of the temperature.

FIG. 3.   Plot of the thickness L_2 as a function of $1/(T^* - T)$. The value of T^* is adjusted to get the best straight line: $T^* = 34.6 \pm 0.2\,°C$. The dashed line is only a guide for the eyes.

Then S/W_1 is the range $[0, \frac{1}{2} + \frac{\pi}{4}]$. Therefore the term $\theta_1^2/(S/W_1 - \cos^2 \theta_1)$ keeps a finite value when $\pi/2 > \theta_1 \gtrsim \pi/4$. For $\theta_1 = \pi/2$, equation (2) implies that S/W_1 is zero, then $\theta_1^2/(S/W_1 - \cos^2 \theta_1)$ diverges. This case corresponds to the peculiar physical situation where two strong antagonist anchoring conditions are simultaneously satisfied: an homeotropic anchoring at the free interface and a planar anchoring near the solid. It is only possible for an infinite thickness. This situation is not expected for our system because the anchoring is expected to be weak near the solid. Thus we do not expect to have a strong anchoring ($W_1 \gg S$) at the transition. Finally, if we exclude the case $\theta_1 = \pi/2$, the only term, which can be responsible for the divergence of L_2, is K/W_1, the extrapolation length. Thus, the confrontation of our experimental measurements with our theoretical model suggest that the extrapolation length diverges, as the nematic-isotropic transition is approached, with a characteristic exponent -1, which is predicted by thermodynamics [16]. Moreover, since S/W_1 keeps a nonzero finite value at the nematic-isotropic transition, wetting properties and anchoring conditions reflect the same physical process. From the wetting physics standpoint, one could state that L_2 behaves like K/S and thus interpret the observed divergence as a signature of a wetting transition. In term of liquid crystals physics, L_2 behaves like the extrapolation length, and its divergence is due to the vanishing of the anchoring strength. Both descriptions are indeed equivalent. Within the precision of the measurements, the wetting transition and the nematic-isotropic transition coincide. This link between wetting and anchoring is reminiscent of the interpretation of the anchoring energy as the anisotropic part of the surface tension [18] and has been recently studied by Crawford et al. [5] in the case of liquid crystal confined in a cylindrical channel. We conclude our model properly describes the physics of the system at a mesoscopic scale. However, as it can be seen on the thickness profile in Fig. 1, a surface-induced ordering (corresponding to a bilayer) appears at the edge of the drop just above the trilayer, precisely in the part of the LC film supposed to be driven by anchoring, spreading, and elastic energies. Furthermore, we do not know if this structure is preserved in the central part of the drop. So, if our model, which does not take into account specific molecular effects, gives us the physical meaning of L_2, a fine analysis of these molecular effects remains yet to be achieved.

The molecular effects we have invoked for the nematic phase are also appreciable in the wetting behavior of the isotropic phase close to the nematic-isotropic transition. Let us report now systematic measurements of the contact angle of 5CB isotropic drops on silicon wafers as a function of temperature. Contact angles are measured by optical interferometry. The experimental conditions are the same as for ellipsometric measurements: temperature control, relative humidity of $50 \pm 10\%$. As we transfer the LC on the solid substrate, the drop always reaches

its equilibrium state by spreading. Hence, the contact angle we measure is an advancing contact angle. The dynamic spreading laws, in the case of partial wetting, lead to an exponential relaxation of the contact angle to its equilibrium value (for moderate angles). The relaxation time is

$$\tau \approx R \frac{\eta}{\gamma} \theta_0^{-10/3}, \qquad (3)$$

where η is the viscosity of the liquid, γ its surface tension, R the drop radius, and θ_0 the equilibrium contact angle. Note that this relaxation time strongly depends on θ_0. If one takes typical values of $\eta \approx 0.01$ P, $\gamma \approx 0.03$ N m^{-1}, $R \approx 0.1$ mm, and $\theta_0 \approx 10°$, one obtains $\tau \approx 200$ ms. For $\theta_0 \approx 0.5°$, τ is about 6 h. For 5CB isotropic drops, the observed contact angles are between 5 and 15°. Hence, contact angles have been measured after a duration (typically 1 h) which is very large compared to τ in order to obtain equilibrium values. The graph (a) that we present in Fig. 4 is a plot of the contact angle versus temperature. Using the values of the 5CB nematic surface tension γ measured by Gannon and Faber [19], we can calculate the spreading parameter $S = \gamma(\cos \theta_0 - 1)$. Figure 4 also includes a plot of S^2 as a function of the temperature T. We find that the spreading parameter vanishes at the temperature $T^{**} = 34.9 \pm 0.1$ °C. The value of T^{**} is once again compatible with the value of T_{NI}. Therefore, the variation of the spreading parameter close to the nematic-isotropic transition may be characterised by the scaling law $-S \propto (T - T^{**})^{0.5}$. This behavior is consistent with the existence of a wetting transition in the vicinity of the nematic-isotropic transition.

How long does the equilibrium value of the contact angle persist? This question may appear rather surprising. However, we noticed, as the temperature approached the nematic-isotropic transition (typically $T - T_{NI} < 10$ °C), the value of the contact angle started to decrease after a characteristic time of several hours
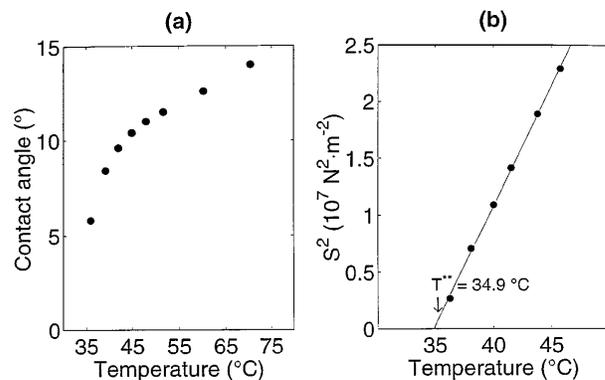

FIG. 4. (a) Contact angle of isotropic drops versus the temperature; (b) plot of S^2 as a function of T. The spreading parameter vanishes at the temperature $T^{**} = 34.9 \pm 0.1$ °C. The solid line is only a guide for the eyes.
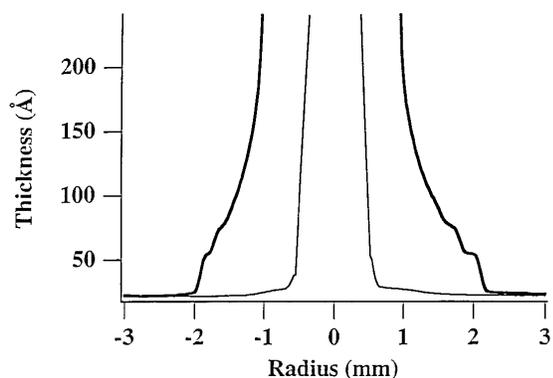
FIG. 5. Ellipsometric profiles of an isotropic drop ($T = 37.9\,°C$) 30 min and 24 h after drop deposition. Once the drop has wetted the solid substrate, the same structure (bilayer on top of L_1) as for nematic drops develops.

(about 6 h at $38.7\,°C$, for example) and ultimately vanished. The final state observed is a complete wetting of the isotropic phase. This pretransitional effect can be associated with the decrease of the surface tension with decreasing temperature. It is well known that a gradient of the surface tension is related to the surface excess entropy per unit area σ: $\partial \gamma / \partial T = -(\sigma_{surface} - \sigma_{bulk})$ [20]. Thus, a positive slope for γ is associated to an excess order near the solid surface. Ellipsometric thickness profiles reveal indeed, as it can be seen in Fig. 5, a surface-induced ordering. We can distinguish, in the molecular part of the profile, a trilayer bearing a bilayer; it is the same structure as for nematic droplets close to the nematic-isotropic transition. This change in the wetting behavior of isotropic drops close to the nematic-isotropic transition may be linked to a slow drop structuration near the solid surface. This structuration seems to be faster as the temperature approaches T_{NI}. This explains why the contact angle value typically remains constant over several days for $T - T_{NI} > 10\,°C$. Therefore, we have here another experimental evidence of molecular effects on the wetting behavior of LC's.

If the contact angle varies with time close to the transition, the same must be true for hysteresis effects. Hysteresis phenomena in this system, close to the nematic-isotropic transition, represent a further expansive field of study. Let us just mention, however, that a receding contact angle of nearly $0°$ has been observed at $58.5\,°C$ (while the advancing contact angle is about $12°$). This seems consistent with the previous discussion; isotropic drops wet the surface when the macroscopic reservoir lies on a well structured molecular film.

In this Letter, we discussed the temperature evolution of 5CB nematic drops thickness profiles near the nematic-isotropic transition, where a wetting transition also takes place. We observe the divergence of a drop characteristic thickness. On both sides of the wetting transition, the behavior of the spreading parameter seems specific to liquid crystals, which can structure close to the solid surface. In the nematic phase, wetting and anchoring reflect the same physical process. In the isotropic phase, the wetting behavior is influenced by a slow drop structuring near the solid. Experimental features are well understood at a mesoscopic scale using a continuum medium model. However, a fine analysis of molecular effects as surface-induced ordering is not yet achieved.

[1] K. Miyano, Phys. Rev. Lett. **43**, 51 (1979); J. Chem. Phys. **71**, 4108 (1979); J. Tarczon and K. Miyano, *ibid.* **73**, 1994 (1980).

[2] G. P. Crawford, R. Stannarius, and J. W. Doane, Phys. Rev. A **44**, 2558 (1991).

[3] H. Hsiung, Th. Rasing, and Y. R. Shen, Phys. Rev. Lett. **57**, 3065 (1986); X. Zhuang, D. Wilk, L. Marrucci, and Y. R. Shen, Phys. Rev. Lett. **75**, 2144 (1995).

[4] W. Chen, L. J. Martinez-Miranda, H. Hsiung, and Y. R. Shen, Phys. Rev. Lett. **62**, 1860 (1989); Mol. Cryst. Liq. Cryst. **179**, 419 (1990).

[5] G. P. Crawford, R. J. Ondris-Crawford, S. Zumer, and J. W. Doane, Phys. Rev. E **53**, 3647 (1996).

[6] G. P. Crawford, R. Ondris-Crawford, S. Zumer, and J. W. Doane, Phys. Rev. Lett. **70**, 1838 (1993); Liq. Cryst. **14**, 1573 (1993).

[7] B. Jerome, Rep. Prog. Phys. **54**, 391 (1991).

[8] M. Monkade, M. Boix, and G. Durand, Europhys. Lett. **5**, 697 (1988); B. Jerome, P. Pieranski, and M. Boix, *ibid.* **5**, 693 (1988).

[9] A. J. Leadbetter, R. M. Richardson, and C. N. Colling, J. Phys. **36** C1, 37 (1975).

[10] J. R. Vig, J. Vac. Sci. Technol. A **3**, 1027 (1985).

[11] M. P. Valignat, S. Villette, J. Li, R. Barberi, R. Bartolino, E. Dubois-Violette, and A. M. Cazabat, Phys. Rev. Lett. **77**, 1994 (1996).

[12] F. Heslot, A. M. Cazabat, P. Levinson, and N. Fraysse, Phys. Rev. Lett. **65**, 559 (1990).

[13] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1993).

[14] M. P. Valignat, N. Fraysse, and A. M. Cazabat, Langmuir **9**, 3255 (1993).

[15] S. Faetti, M. Gatti, V. Palleschi, and T. J. Sluckin, Phys. Rev. Lett. **55**, 1681 (1985).

[16] H. Yokoyama, S. Kobayashi, and H. Kamei, J. Appl. Phys. **56**, 2645 (1984).

[17] J. Chen *et al.,* Mol. Cryst. Liq. Cryst. **275**, 49 (1996).

[18] J. D. Parsons, Mol. Cryst. Liq. Cryst. **31**, 79 (1975).

[19] M. G. J. Gannon and T. E. Faber, Philos. Mag. A **37**, 117 (1978).

[20] S. Chandrasekhar, *Liquid Crystals (Second Edition)* (Cambridge University Press, Cambridge, 1992).