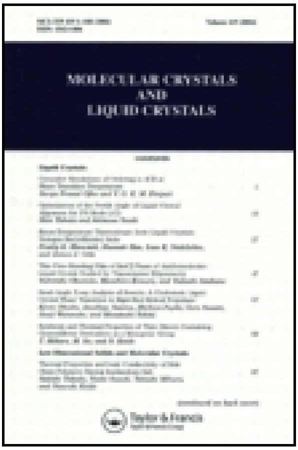

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The Role of Long Range Forces in the Stability of Nematic Films

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The Role of Long Range Forces in the Stability of Nematic Films

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We present an experimental study of the wetting of 5CB in the nematic phase on silicon wafers. A nematic droplet of 5CB wets completely the surface. However a characteristic structure is visible in the mesoscopic range on the thickness profile. The corresponding thickness, typically 200 Å, increases with temperature and "diverges" at the Nematic/Isotropic transition. This is characteristic of a wetting transition: a 5CB droplet in the isotropic phase does not wet the surface. In the discussion, we propose a simple model which takes into account long range interaction and we show that the balance between elastic, anchoring and van der Waals energies may fix the wetting condition.

Keywords: Wetting; Liquid crystal; van der Waals; Thin films

INTRODUCTION

Surface interactions between liquid crystals (LCs) and treated substrates are the most important factor in determining the alignment mechanism of LCs on the surface [1,2]. Studying the wetting of a liquid crystal on a solid substrate is an elegant way to obtain information on the microscopic interactions involved [3]. Wettability and stability of thin films are linked [4] and controlled by intermolecular forces whose interplay may be analyzed in term of disjoining pressure [5, 6]. The disjoining pressure isotherm is generally nonmonotonic and is a combination of long and short range. A thin film of nematic liquid crystal has specific interactions added to the usual structural and van der Waals ones: we mainly think about anchoring and elastic forces the strength of which strongly depends on temperature.

In this paper, we will first summarize the experimental results we obtained on spontaneous wetting and on thin wetting films [3, 7]. The second part will be devoted to the analysis of the free energy per unit area in the case of a thin nematic film, we will discuss the coincidence of a wetting transition with the nematic/isotropic phase transition. In the last part, the choice of the Hamaker constant sign in van der Waals interaction is argued.

EXPERIMENTAL OBSERVATIONS

The LC in our studies is 4-cyano-4'-n-pentylbiphenyl (5CB). With increasing temperature, 5CB undergoes a phase transition at 24°C from crystalline to nematic phase and at 35.3°C from nematic to isotropic phase. In the bulk, 5CB molecules are paired into dimers with antiparallel dipole moments. The apparent thickness of this bilayer is 25 Å [8] while the individual molecule length is 18.7 Å. The solid substrates are silicon wafers (type n, dopant P, orientation (100) purchased from Siltronix) bearing a natural oxide layer of 2 nm. Prior to the experiments, the substrates are cleaned by UV ozone exposure [9]. The 5CB is deposited either from microscopic droplets (spontaneous wetting) or by spin coating from toluene solution (thin wetting film).

Spontaneous wetting

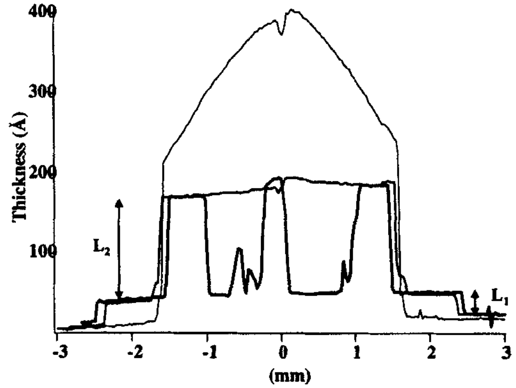

FIGURE1 Ellipsometric thickness profiles of a 5CB drop spreading on a silicon wafer at a temperature of 25 °C. The time t after droplet deposition are t = 4h, 24h and 55h.

A typical ellipsometric thickness profile of a 5CB droplet spreading at 25 °C is shown on figure 1. On the thickness profile, we observe the formation of two characteristic lengths: L_1 and L_2. The first one, at the edge of the droplet is equal to 3.3 nm and is independent of temperature (in the nematic phase) while the second one ranges from 15 nm to more than 120 nm for temperatures ranging between 24 °C and 35.3 °C. While spreading, the drop becomes a quasi flat film of thickness L_2 extending over millimeters. Later on, this film breaks into islands and a careful analysis of the thickness profile shows that these islands actually connect the thickness L_2 to the thickness L_1. X-ray reflectivity measurements [10] performed on the L_1 terrace have given evidence that the organization of the LC molecules is a trilayer. This trilayer consists of a smectic-like bilayer standing above a "ferroelectric" monolayer with tilted molecules. The higher L_2 terrace results from a balance between anchoring, elastic and van der Waals energies. We will discuss this point further. The temperature dependence of the L_2 terrace has been widely studied [11]: L_2 behaves as $L_2 \propto 1/(T_{NI}-T)$ in the nematic phase while in the isotropic phase the 5CB does not wet the surface anymore. This is characteristic of a wetting transition at the nematic/isotropic transition. In the nematic phase the L_2 film is a metastable equilibrium state of the droplet: at later stages, the spreading leads to a thin film of thickness L_1 and intermediate thicknesses are not permitted. As L_2 depends on temperature we were interested into changes from one metastable state to an other. Assume that the temperature increases from T_1 to T_2 ($T_1 < T_2$) in the nematic phase. The droplet of thickness

$L_2(T_1)$ has to rearrange in order to reach the thickness $L_2(T_2)$ where $L_2(T_1) < L_2(T_2)$. As shown on figure 2, this rearrangement happens with the development of structures analogous to the ones observed in spinodal decomposition in binary mixtures. In order to obtain more information on this process, we went on studying the evolution of a thin film.

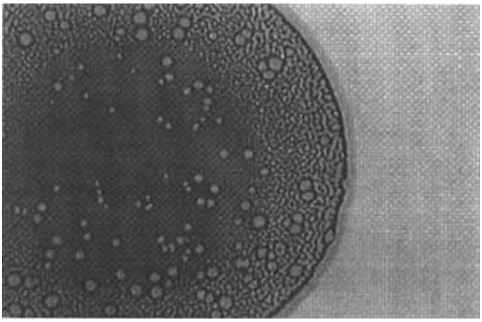

FIGURE 2 Formation of specific pattern as the temperature increases from 24 °C to 32 °C. The size of the image is 1100 μm×840 μm

Thin wetting film

Nematic films are spun cast from toluene solutions at a typical spin rate of 240 rad. s^{-1}. The thickness of the films is controlled by concentration and measured using ellipsometry. Concurrently, we have used a polarized optical microscope coupled to a video camera to capture images of the thin film.

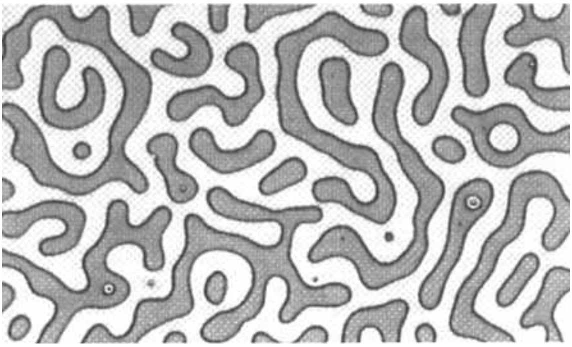

FIGURE 3 Formation of spinodal patterns observed for a 100 nm thick layer film spun cast from a toluene solution at a temperature of 35°C. The size of the image is 1300 μm×770 μm

For a temperature of 25 °C, a 17 nm thick nematic film is not stable and evolves by the formation of patterns while a 42.8 nm thick film remains stable over days; for a temperature of 35 °C even a film of 100 nm is unstable (figure 3). The behavior of the thin film depends on the availability of a liquid reservoir. As one spins cast the solid substrate (diameter ~ 2 cm) with the toluene solution, a rim may form on the edge of the wafer and leads after evaporation to a reservoir of nematic. After a first process of spinodal dewetting (the thickness of the islands increases), either the specific structures start to spread and ultimately merge to give a final thicker stable film, either the structures stop, if no reservoir is available. Spinodal dewetting consists in the growing of a capillary wave driven by dispersion forces across the film. The amplitude of the thickness fluctuation is expected to grow exponentially with time. Usually in the valley of this fluctuations, the liquid surface ultimately reaches the substrate and initiates dewetting, leading to the formation of an array of droplets. Our situation is slightly different : the final state is a thicker film or an inhomogeneous system with the coexistence of two thicknesses.

THE FREE ENERGY PER UNIT AREA OF A THIN NEMATIC FILM

The stability of a thin nematic film or the spreading of a nematic droplet on a solid substrate may be discussed in terms of the free energy F (per unit area) of a film of thickness h.

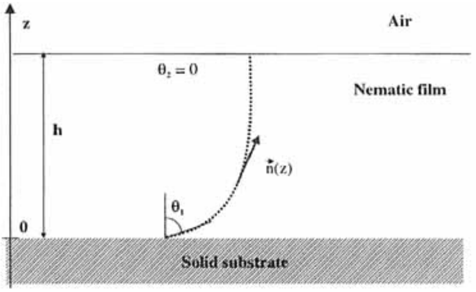

FIGURE 4 Schematic drawing of the 5CB molecules in a thin mesoscopic film of thickness h.

5CB molecules are known to have a strong homeotropic anchoring at the air interface ($\theta_2 = 0$) and a weaker and quasi planar anchoring on the silicon wafer. The angle θ_l on the surface may be different from $\pi/2$ and the anchoring energy [1,12] is $\frac{1}{2} w_l \cos^2 \theta_l$ which can also be interpreted as the anisotropic part of the nematic/solid interfacial tension. The result of this antagonist anchoring condition is an elastic distortion of the director $\vec{n}$ across the film. The last contribution to the energy is the van der Waals one. At this stage we assume that the Hamaker constant A has a positive value so that the van der Waals contribution tends to thin the film and opposes the wetting. The detailed structure of A is discussed in the last part. The free energy per unit area can now be written

$$F(\theta_l, h) = \gamma_{SN}(\theta_l = \frac{\pi}{2}) + \frac{1}{2} w_l \cos^2 \theta_l + \gamma(\theta_2 = 0) + \int_0^h \frac{1}{2} K \left(\frac{\partial \theta}{\partial z} \right)^2 dz - \frac{A}{12 \pi h^2} \qquad (1)$$

where z is the thickness coordinate, K the elastic constant (in a one constant approximation), $\theta(z)$ the angle which the director makes with the z-axis, γ_{SN} and γ the interfacial tensions solid/nematic and nematic/air.

The function θ(z) that minimizes the free energy per unit area and satisfies the boundary conditions :

$$\theta(z=h)=0 \tag{2}$$

$$-K\dot{\theta}(z=0)-\frac{1}{2}w_l\sin(2\theta_l)=0 \tag{3}$$

is

$$\theta(z)=\theta_l\left(1-\frac{z}{h}\right) \tag{4}$$

where θ_l is determined by the second boundary condition (3):

$$\sin(2\theta_l)=\frac{2K}{w_l}\frac{\theta_l}{h}=\frac{L}{h}2\theta_l \tag{5}$$

$L = K/w_l$ is usually called the surface extrapolation length. Equation (5) shows that the anchoring angle is different from zero only if $h > L$. For film thicknesses below L, the sample undergoes an homeotropic orientation. By putting (4) into (1) we obtain :

$$F(\theta_l,h)=\gamma_{SN}+\frac{1}{2}w_l\cos^2\theta_l+\gamma+\frac{K\theta_l^2}{2h}-\frac{A}{12\pi h^2} \tag{6}$$

We introduce the quantity P which represents the interaction energy of the substrate with air across the nematic film of thickness h. P(h) is also defined as the excess free energy necessary to approach this two media from infinity to thickness h :

$$P(\theta_l,h)=\frac{1}{2}w_l\cos^2\theta_l+\frac{K\theta_l^2}{2h}-\frac{A}{12\pi h^2} \tag{7}$$

and we define an adimensional function in order to compare the relative importance of the term due to van der Waals interaction and terms due to the specific liquid crystal character :

$$f(x)=\frac{P(h)}{w_l}=\frac{1}{2}\frac{\theta_l^2}{x}+\frac{1}{2}\cos^2\theta_l-\frac{\tilde{A}}{x^2} \tag{8}$$

where $x = h/L$ and θ_l are coupled by the relation $x\sin(2\theta_l) = 2\theta_l$ and $\tilde{A} = \frac{A}{12\pi K}\frac{w_l}{K}$. For $K = 0.5\ 10^{-11}$ kg.m.s^{-2}, one obtains the figure 5 for values of $\tilde{A} = 0, \tilde{A} = 0.1$ and $\tilde{A} = 1$ which correspond respectively to values of the Hamaker constant around 0, 4 10^{-19} and 4 10^{-18} Joules if the anchoring energy is estimated to be $w_l \approx 0.25\ 10^{-3}$ kg.s^{-2}.

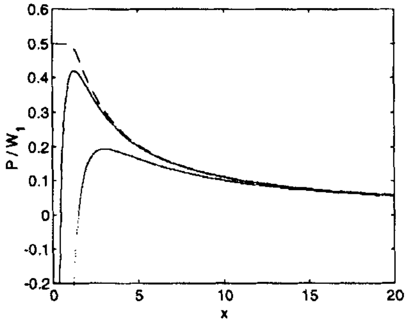

FIGURE 5 Influence of the strength of the van der Waals interaction versus h/L. (--) $\tilde{A} = 0$, (—) $\tilde{A} = 0.1$ and (...) $\tilde{A} = 1$.

The antagonist anchoring conditions leads to an elastic distortion with repulsive interaction between interfaces while van der Waals interactions are attractive and tend to thin the film. In figure 5 we have not drawn the short range interaction because no explicit formulation is available. From the existence of a thin film of thickness L_l in the 5CB spontaneous spreading, we can conclude that short range interaction are repulsive. A schematic shape of the total interaction energy is drawn on figure 6.

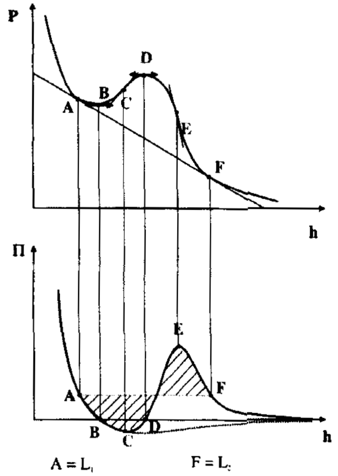

FIGURE 6 Schematic shape of the interaction energy and of the disjoining pressure of a thin nematic film (solid line: nematic phase, doted line: isotropic phase).

The interpretation of wetting experiments requires information on P(h) and $\pi(h)$ also called the disjoining pressure: $\pi(h) = -\frac{dP}{dh}$. This force per unit area is linked to the spreading parameter by the relationship: $S = \gamma_{SO} - \gamma_{SN} - \gamma = \int_0^{\infty} \pi(h)dh$ (γ_{SO} being the solid/air interfacial tension). A positive value of the spreading parameter is equivalent to a wetting situation : the droplet spreads all over the solid substrate. A negative value of the spreading parameter is associated to a non wetting situation and the equilibrium shape of the drop is a spherical cap. On figure 6 is drawn the schematic shape of the disjoining pressure. The solid line is the one expected for the nematic case and the doted one for the isotropic case. As the L_1 film is not modified with temperature we do not expect any major changes in the short range interaction and so in their contribution to the integral of the disjoining pressure. On the contrary, if the temperature is increased from the nematic to the isotropic phase, the elastic contribution goes to zero and the long range contribution of the disjoining pressure becomes negative. This explains the changes in the sign of the spreading parameter and the wetting transition at the nematic/isotropic transition temperature. The L_1 and L_2 films may be qualitatively understood from the disjoining pressure curve. During the spreading, only thicknesses corresponding to a stable part of the disjoining pressure can develop. The condition is $\frac{d\pi}{dh} < 0$, unstable parts are not observed and give rise to a thickness transition (L_1 to L_2) determined by the Maxwell rule. A useful picture is to say that a plateau in the disjoining pressure curve is equivalent to a vertical part in the thickness profile of the drop. The shape of the disjoining pressure or of the effective interaction potential P(h) explains the spinodal dewetting observed for thin film with thickness below h*. By analogy with spinodal decomposition in a mixture, long wavelength capillary waves are amplified if the second derivative of the free energy with respect to the thickness is negative or if the first derivative of the disjoining pressure is positive. This leads in a first approximation (θ_1 independent of h) for the upper value to $h^* = \frac{A}{2\pi K\theta_1^2}$ (point E on the curve) but no expression can be given for the lowest value (point C on the curve) as we do not know the short range interactions. The expression of h* can also be found by a simple hydrodynamic model in which Navier Stokes equations are solved for a viscous fluid in a lubrication approximation [7]. h* is inversely proportional to the elastic constant and goes to infinity when K goes to zero i.e. when the temperature crosses the nematic/isotropic transition. In the isotropic phase even a thick film is unstable, which has been confirmed by experiments.

MORE ABOUT VAN DER WAALS ENERGY

In the following, the Lifshitz [13] theory simplified by Israelachvili [14] is used to give an estimation of the Hamaker constant A_{021} in the case of two semi-infinite (0 and 1) media in interaction across a third one (medium 2). The non retarded Hamaker constant is the sum of two contributions : $A_{021} = A_{021}\ (\nu=0) + A_{021}\ (\nu>0)$ with

$$A_{021}(\nu = 0) = \frac{3}{4}kT\left(\frac{\varepsilon_1(0)-\varepsilon_2(0)}{\varepsilon_1(0)+\varepsilon_2(0)}\right)\left(\frac{\varepsilon_0(0)-\varepsilon_2(0)}{\varepsilon_0(0)+\varepsilon_2(0)}\right) \tag{9}$$

and

$$A_{021}(\nu > 0) = \frac{3h\nu_e}{8\sqrt{2}} \frac{(n_0^2 - n_2^2)(n_1^2 - n_2^2)}{(n_0^2 + n_2^2)^{\frac{1}{2}}(n_1^2 + n_2^2)^{\frac{1}{2}}\left[(n_0^2 + n_2^2)^{\frac{1}{2}} + (n_1^2 + n_2^2)^{\frac{1}{2}}\right]} \qquad (10)$$

where the ε_i are the static dielectric constants, the n_j are the optical index of the medium and ν_e the electronic absorption frequency.

The first term gives the zero-frequency energy of the van der Waals interaction and includes the Keesom and Debye dipolar contributions. The second term gives the dispersion energy and includes the London energy contribution. In our system, the order of magnitude of the second term is twice larger than the first one. In the following, we will thus neglect it and give a rough estimation of the second one. The sign of $A_{021}(\nu>0)$ depends on the product $(n_0^2 - n_2^2)(n_1^2 - n_2^2)$: a negative value of the Hamaker constant is obtained for an optical index of medium 2 inferior to the one of medium one. This suggests that to account for the attractive contribution of solid substrate and air interaction across the nematic film (i.e. a positive value of the Hamaker constant), we have to introduce the effect of the oxide layer in the expression of the disjoining pressure.

Table 1 gives the value of the Hamaker constant for the two systems : silica/5CB/air and silicon/5CB/air.

Silica SiO_2 $n_0 = 1.46$	5CB $n_2 = 1.7$	Air $n_1 = 1$	$A_{123} = 4.2\ 10^{-20}$ J
Silicon Si $n_0 = 3.88$	5CB $n_2 = 1.62$	Air $n_1 = 1$	$A_{021} = -2.4\ 10^{-19}$ J

TABLE 1 Hamaker constants for two systems : Silica/5CB/air and Silicon/5CB/air

A silicon substrate promotes wetting and cannot induce the spinodal dewetting observed experimentally while a silica substrate is unfavorable to wetting. Our experimental system has to be modeled as a four-layer system: 0, silicon; 1: air; 2: 5CB, 3: silica (thickness d). The van der Waals contribution to the disjoining pressure can be expressed as a function of the Hamaker constants of the three-layer systems air-5CB-silicon A_{021}, Silica-5CB-air A_{123} and the various thicknesses:

$$\pi(h) = -\frac{A_{021} - A_{123}}{6\pi(h+d)^3} - \frac{A_{123}}{6\pi h^3} = -\frac{A(d,h)}{6\pi h^3} \qquad (11)$$

where A(d,h) is the effective Hamaker 'constant' which depends on the oxide thickness. For a silica layer of 20 Å, the effective Hamaker constant goes to zero for h = 30 Å. A positive value happens for thicker h and plays the same role as elasticity.

To summarize, the thin layer of silica is the only candidate counteracting the elastic term. It is responsible for the dewetting process. Even if the numerical values are estimated ones, they illustrate the main behavior of long range interaction in our experimental system. We also think that short range interaction introduced by the silica layer may play a role in dewetting. The main experimental demonstration of the role of the oxide layer has been obtained by getting rid of it: we exposed the silicon substrate to a sulfuric acid solution [15]. The wafer was then kept in a box under a nitrogen flow and we deposed a small drop. We observed a wetting situation even in isotropic phase when the elastic force is not present anymore to balance a negative contribution.

CONCLUSION

We have shown in this paper that wetting is a sensitive process: a weak change in the surface properties may induce a wetting transition. In our specific 5CB/silicon wafer system, the thin layer of silica is responsible for the dewetting observed at the nematic/isotropic transition temperature: the negative contribution of the silica layer to the disjoining pressure is not balanced anymore by the elastic positive contribution. Wetting studies give a new insight on microscopic interaction involved between LC and solid: van der Waals energie may play an important role added to the usual anchoring and elastic ones. As already pointed out by Dubois-Violette and de Gennes [16,17], van der Waals interaction should not be isotropic for LC. We are nowadays investigating this specificity by studying the wetting of LC on an anisotropic substrates.

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