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Structural disjoining pressure in thin film of liquid crystals

I.: Thermodynamics and Frederiksz transition with surface fields*)

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With 8 figures

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List of symbols

h_T	:	film transition thickness
h_S	:	critical film stability thickness
φ superscript	:	film phase
A	:	area
f	:	force per unit area
h	:	film thickness
T	:	temperature
V	:	volume
F	:	free energy
η	:	disjoining pressure
$d\tau$	:	work performed in varying h
P_c	:	capillary pressure
s	:	specific surface entropy
Δ	:	film tension
μ	:	chemical potential
σ	:	surface tension
$\Gamma(h)$	:	number of molecules per unit surface of film at thickness h
ϖ	:	film perimeter
subscript h	:	upper surface
subscript o	:	lower surface
w	:	surface free enthalpy
G	:	free enthalpy
W'	:	specific bulk free enthalpy in film of L.C.
W_b	:	specific bulk free enthalpy of L.C.
$W(h,z)$	:	specific excess free enthalpy in thin film of L.C.
$\vec{n}$	:	liquid crystal director
θ	:	angle between director and x, y plan
ϕ	:	azimutal angle
W'_d	:	elastic energy density
W'_u	:	specific bulk free enthalpy of the undistorted film
w', $\Delta w'$	:	isotropic and anisotropic contribution to the interfacial tension of L.C.
K	:	average elastic constant of nematic liquid crystal
Δ_u	:	non elastic contribution to the film tension
Δ_d	:	elastic contribution to the film tension
Γ_{el}	:	elastic torque
Γ_s	:	surface torque
η_d	:	classical disjoining pressure
η_s	:	structural disjoining pressure
$B(h)$	:	Van der Waals parameter
Δn	:	optical anisotropy of the liquid crystal
δ	:	optical retardation
I	:	light intensity
h^+	:	reduced thickness

Introduction

The properties of disperse systems in liquids depend on the nature and state of their interfaces and of the thin films separating the particles of the dispersion.

Although intermolecular forces are short-range, there is increasing belief that next to these interfaces, the initial perturbation of the two phases in contact takes place over a finite thickness of the liquid intermediate film. It has been assumed that the perturbation may structure (1, 2) or destructure (3, 4) the liquid. The effect of the dispersion constituents polarities has been emphasized, although recent experiments (4, 5) have demonstrated that this particular property is not essential for interfacial structuring.

For thin films, *Derjaguin* (1, 2) has postulated the occurrence of a structural disjoining pressure related to the interfacial structuring.

The polar thermotropic liquid crystals or L.C., which have a strong molecular field,

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are systems appropriate for the study of interfacial structuring. Elastic forces resist any structure perturbation or distortion in bulk so that an interfacial structuring will propagate away from the interface.

The properties of LC in bulk have been extensively studied (6, 7). A review of the recent results on the effect of surface forces on LC orientation specificity may be found in ref. (7). In the present paper we deal only with the surface forces of physical chemical nature.

A direct approach to the study of these forces is the study of wettability or adhesion of the system LC-substrate solid (8, 9, 10, 11) or liquid (12) which provide information on LC substrate interfacial tension variation with changes in interfacial structure.

Finally, surface structuring and orientation in thin films on solid substrates has been considered as an epitaxial growth (2).

In the present paper, the thermodynamics of asymmetric nematic liquid crystal, NLC, thin films on water are discussed, using the concept of surface tension anisotropy (13, 14) i.e. variation of NLC interfacial tension with molecular orientation at the interface.

Derjaguin (1), *Sheludko* (15) and *Everett* (16, 17) thermodynamic approaches are used to deduce the appropriate film thermodynamic potential and disjoining pressure. Using the formalism of *Jenkins* and *Barratt* (13) and the results of *Parsons* (14), we discuss the particular equilibrium disjoining pressure for NLC films of various thicknesses for various surface orientations under two alternative assumptions:

A) thickness independent surface orientation

B) thickness dependent surface orientation.

In both cases, it is predicted that very thin films adopt a non-distorted, epitaxial, structure whereas thick films are distorted.

However, the transition thickness h_T from the undistorted to the distorted NLC film is different in cases (A) and (B).

This difference originates specifically in the different behaviour of the disjoining pressure in the two cases (A) and (B). This transition in structure, analogous to the well known Frederiksz transition (18) observed when external electric or magnetic fields are applied to NLC slabs, is directed by surface forces in the case of asymmetric thin films of NLC on substrates.

In the conclusion, we compare our results with those obtained by different methods for different systems.

Thermodynamic potential thin films and structural disjoining pressure of liquid crystals

The system of figure 1 is analogous to that of *Ash*, *Everett* and *Radke* (16, 17).

The thickness h of fluid corresponds to a force Af exerted on the plates. Work is performed to vary h: $d\tau = —Afdh$. *Derjaguin*'s disjoining pressure (1, 2) is by definition: $\eta = -(1/A)\ (\partial F/\partial h)_{A,T,V}$. As $dF = d\tau$, it follows that $\eta = f$ and is measured by the capillary pressure (1, 2) P_c.

The variation of the free energy F^ϕ of the film phase, noted ϕ, is equal to

$$dF^\phi = S^\phi dT + \Delta dA - fAdh + \mu dn^\phi - pdV^\phi \qquad [1]$$

where Δ is the film tension defined by *Sheludko* (15). Integration at constant T, h, μ, Δ leads to

$$F^\phi = \Delta A + \mu n^\phi - pV^\phi. \qquad [2]$$

A relevant thermodynamic potential Φ for film phases is therefore:

$$\Phi = F^\phi + pV^\phi - n^\phi\mu = \Delta A = 2\sigma^\phi A$$
$$= G^\phi - n^\phi\mu \qquad [3]$$

where σ is the surface tension of the film (16, 17) and Φ corresponds to defined values of T, P, μ. From [2] and [3] the variation of Φ is:

$$d\Phi = -S^\phi dT + \Delta dA - fAdh - n^\phi d\mu$$
$$+ V^\phi dp \qquad [4]$$

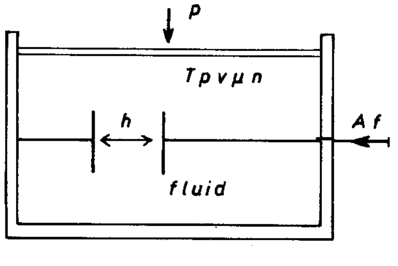

Fig. 1. Film of fluid between two surfaces. Uniform temperature T, pressure p, chemical potential μ; volume V, n mole number, A surface area, h separation, f force on plates

and the definition of the equilibrium disjoining pressure is deduced:

$$-\frac{1}{A}\left[\frac{\partial\Phi}{\partial h}\right]_{T,A,\mu,p} = f = \eta. \qquad [5]$$

A corresponding Gibbs-Duhem equation for films is obtained from [3] and [4]

$$-s^{\Phi}dT - d\Delta - fdh - \Gamma(h)d\mu + hdp = 0 \qquad [6]$$

which leads to a second expression for η

$$\eta = -\left[\frac{d\Delta}{dh}\right]_{T,p,\mu} = -2\left[\frac{d\sigma^{\varphi}}{dh}\right]_{T,p,\mu} \qquad [7]$$

when either Φ or Δ are known, the disjoining pressure η may be deduced using [5] or [7].

Nematic liquid crystal (NLC) thin films

a) Thermodynamic potential and equilibrium of structure

Jenkins and *Barratt* (13) formalism is used to find for a domain of NLC of thickness h, cross section A and perimeter $\bar{\omega}$ as shown in figure 2.

The film domain area is large compared to its thickness. Except on the perimeter, where a defect occurs, the molecules are uniformly oriented on each molecular layer of the NLC film. It is assumed that the contribution of the defect free enthalpy to the free enthalpy of the domain is negligible. The film is asymmetric and has an upper surface free enthalpy $w_h(h)$ and a lower surface free enthalpy $w_o(h)$ dependent on the local molecular orientations which may vary with h.

The film free enthalpy is equal to:

$$G^{\Phi} = \int_{V} W' dv + \int_{A^{\Phi}} [w_o(h) + w_h(h)]dA. \qquad [8]$$

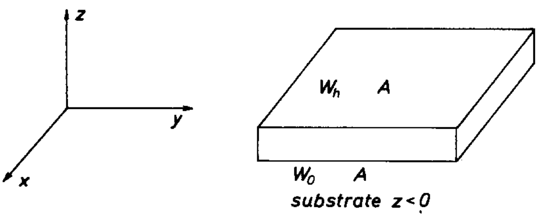

Fig. 2. Domain of thin film on a substrate: A_f = area; V_f = volume. W' = bulk specific free enthalpy; w_h, w_o = surface specific free enthalpy

Let the specific bulk free enthalpy in the film $W' = W'(h,z)$ be:

$$W'(h,z) = W(h,z) + W_b \qquad [9]$$

where $W_b = \varrho\mu$ is the specific bulk free enthalpy of the very thick and extended domain and $W(h,z)$ is the excess free enthalpy density in the thin film.

From [8] and [9] we obtain for G^{Φ} the expression:

$$G^{\Phi} = A^{\Phi}\{\varrho\mu h + \int_0^h W(h,z)dz + w_o(h) + w_h(h)\}. \qquad [10]$$

The specific film potential Φ is obtained from [9] and [10]:

$$(\Phi/A^{\Phi}) = \Delta = [G^{\Phi}(h)/A^{\Phi}] - \varrho\mu h \qquad [11]$$

Δ the specific film thermodynamic potential for unit surface Δ is obtained from [10] and [11]

$$\Delta = \int_0^h [W(h,z)]dz + w_o(h) + w_h(h). \qquad [12]$$

When $h \to \infty$, we have $\Delta_\infty = (w_o + w_h)_\infty$.

The disjoining pressure is obtained from [5] [7] and [12]:

$$\eta = -\left\{\frac{\partial}{\partial h}\int_0^h [W(h,z)dz]\right\}_{T,P,\mu} - \frac{\partial(w_h + w_o)}{\partial h}_{T,P,\mu} = P_c. \qquad [13]$$

When $P_c = O$, the equilibrium thickness of the film domain is given by the solution of the equation:

$$-\left[\frac{\partial}{\partial h}\int_0^h W(h,z)\,dz\right]_{T,p,\mu} - \left[\frac{\partial(w_h + w_o)}{\partial h}\right]_{T,P,\mu} = 0. \qquad [14]$$

b) Expression for Δ and η of NLC

NLC are characterized by the strong mutual alignment of their molecular axis $\vec{n}$ along an axis of uniaxial symmetry. In figure 3, a simplified case (6, 7) is shown.

Figure 4a shows an undistorted domain. Figure 4b shows a distorted domain such that

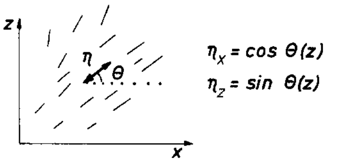

Fig. 3. Orientation of the uniaxial symmetry axis $\vec{n}$; n_x, n_z = components of $\vec{n}$; θ: azimutal angle

the angle θ between $\vec{n}$ and the x direction varies from the base to the top of the film. This distortion adds an elastic positive contribution to the free enthalpy density of the undistorted film of thickness h. This contribution is very roughly (6, 7):

$$W'_d = \frac{1}{2} K \left(\frac{d\theta}{dz}\right)^2 . \qquad [15]$$

Where K is the average elastic modulus of the NLC. Then, if the specific bulk free enthalpy of the undistorted film is $W'_n\,(h,z)$

$$W(h,z) = W'_n(h,z) - \varrho\mu + W'_d(h,z). \qquad [16]$$

Eliminating $W(h,z)$ from [12] and [16]

$$\Delta = \int_0^h [W'_u(h,z) - \varrho\mu]\,dz + \int_0^h W'_d(h,z)\,dh + w_o(h) + w_h(h)\,. \qquad [17]$$

According to references [13, 14], the anisotropy of the interfacial tension is expressed as follows:

$$w_h = w'_h + \Delta w_h \sin^2\theta_h$$
$$w_o = w'_o + \Delta w_o \sin^2\theta_o \qquad [18]$$

where $w_h\,(\pi/2) < w_h(o)$ and $w_o(\pi/2) > w_o(o)$.

From [15], [18] and [17]:

$$\Delta = \Delta_u + \Delta_d = \int_0^h [W'(h,z) - \varrho\mu]\,dz + w'_h + w'_o + \frac{K}{2}\int_0^h \left(\frac{d\theta}{dz}\right)^2 dz + \Delta w_o \sin^2\theta_o + \Delta w_h \sin^2\theta_h. \qquad [19]$$

Δ_u, Δ_d are respectively the contributions independent or dependent on θ. Distortion or change in θ_h or θ_o modifies the thermodynamic potential Δ_d, the contribution Δ_u being independent of θ_h or θ_o.

The equilibrium value of $(d\theta/dz)$ or $\theta(z)$ is obtained by minimizing Δ_d as usual (6, 7), using the equilibrium boundary conditions discussed in references (13, 14). It is obtained:

$$\theta_z = \frac{\theta_h - \theta_o}{h}\,z \text{ or } \frac{d\theta_z}{dz} = \frac{\theta_h - \theta_o}{h}. \qquad [20]$$

At each surface, the equilibrium orientation of NLC molecules is the result of balance of two torques:

- Γ_{el}: elastic torque opposing disalignment of molecules
- Γ_s: surface torque opposing an increase of surface free enthalpy or surface tension.

The torques are equal respectively to

$$\text{a) } \Gamma_{\text{el}} = K\left(\frac{d\theta}{dz}\right)$$

$$\text{b) } \Gamma_{s,\,h} = \Delta w_h \sin 2\theta_h;\; \Gamma_{s,\,o} = \Delta w_o \sin 2\theta_o. \qquad [21]$$

From [20] and [21] the equilibrium molecular orientation at the film surface are:

$$\text{a) } \frac{K(\theta_h - \theta_o)}{h} = -\Delta w_h \sin 2\theta_h \qquad \Delta w_h < 0$$
$$\text{b) } \frac{K(\theta_h - \theta_o)}{h} = \Delta w_o \sin 2\theta_o \qquad \Delta w_o > 0 \qquad [22]$$

From [19] and [20] we deduce:

$$\Delta = \Delta_u + \frac{K}{2}\,\frac{(\theta_h - \theta_o)^2}{h} + \Delta w_h \sin^2\theta_h + \Delta w_o \sin^2\theta_o \qquad [23]$$

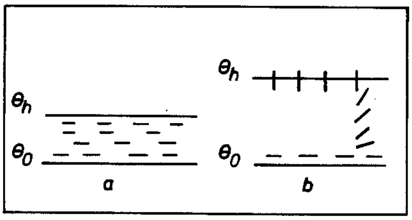

Fig. 4. Thin films of NLC. a) undistorted $\theta_h = \theta_o = O$; b) distorted $\theta_h \neq \theta_o = O$

and from [7] and [24] allowing for [22a] and [22b], the following expression is obtained for the disjoining pressure:

$$\eta = \eta_d + \eta_s = -\left(\frac{\delta \Delta_u}{\delta h}\right)_{T,P,\mu} + \frac{K}{2}\frac{(\theta_h - \theta_o)^2}{h^2} + \frac{2K}{h}(\theta_h - \theta_o)\frac{\theta_o}{d_h}. \qquad [24]$$

η_d is the classical disjoining pressure (1, 2) of the undistorted NLC or $\eta_d = B(h)h^{-3}$. The last terms are standing for η_s, the structural disjoining pressure.

c) Stability and transition critical film thickness

The boundary conditions [22a] have been discussed in reference (14).

It is found that, when $\theta_0 = 0$, according to the figures 4a and 4b, the solution of [22a] is

$$\text{a)}\ \theta_h = 0 \quad h < h_T = -\frac{K}{2\,\Delta w_h}$$

$$\text{b)}\ \theta_h \neq 0 \quad h > h_T = -\frac{K}{2\,\Delta w_h}. \qquad [25]$$

Below a transition thickness h_T the structure of figure 4a is stable. Above h_T the structure of 4b is stable. This thickness h_T depends on the ratio $(K/\Delta w_h)$ i.e. on the magnitudes of the torques Γ_{el} and Γ_s.

From [24] and [25] it follows that the structural transition will modify the disjoining pressure expression as follows:

$$\text{a)}\ \eta = -\frac{B(h)}{h^3} + \frac{K}{2}\frac{\theta_h^2}{h^2} \quad h > h_T$$

$$\text{b)}\ \eta = -\frac{B(h)}{h^3} \quad h < h_T \qquad [26]$$

The structural disjoining pressure is positive and stabilizes the film shown in figure 4b only.

From [22a], [25a and 25b] and [26] a final expression is obtained for [26].

$$\eta = -\frac{B(h)}{h^3} + \frac{1}{2K}\Delta w_h^2 \sin^2 2\,\theta_h \qquad [27]$$

The condition for NLC thin film stability is discussed below. It leads to a critical stability thickness $h_s \neq h_T$.

Material and experimental methods

The NLC: 4–4′-pentylcyanobiphenyl (5CB) has been kindly offered by BDH. Its purity is better than 99%.

The substrate: distilled water 3 X is swept before depositing the NLC. The films are formed by spreading 2–6 μl of NLC on various areas: 4, 10, 40 sq cm, of substrate contained in an optical cell at 23 °C. The cell is examined between crossed Nicols, using a commercial polarizing microscope and transmitted light.

In general, $20X$ and $100X$ magnifications were used and $200X$ exceptionally.

The optical anisotropy of 5CB is $\Delta n \simeq +0{,}15$ (19). The optical retardation for an incident light crossing the film of figure 4a of thickness h is equal to $\delta = h\,\Delta n$.

The figure 5 represents the experimental setup. A compensating plate L equivalent to a retardation on δ_0 is placed between polarizer and sample. For a uniform film, with L absent, the intensity of the light crossing the sample

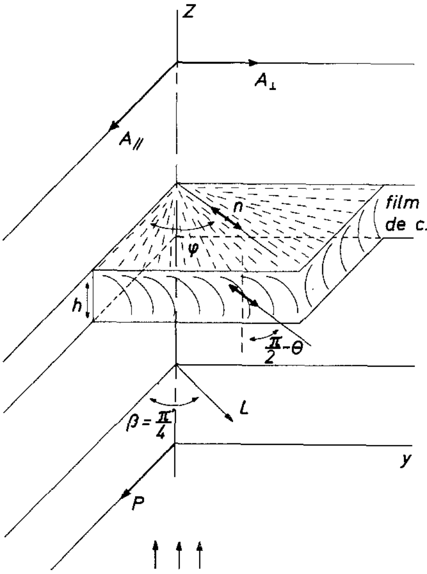

Fig. 5. Experimental device for observation of liquid crystal film; P: polariser; $A_{//}$ or $A_\perp$: analyser parallel or perpendicular to the polariser; h: film thickness; $\vec{n}$: liquid crystal director defining the optical axis; $\frac{\Pi}{2} - \theta$ = polar angle; : azimutal angle

parallel or perpendicular to the polarizer P respectively is equal to

$$\text{a)}\quad I_{//} = I_o \left| 1 - (\sin 2\phi)^2 \sin\left(\frac{2\pi\delta}{\lambda}\right) \right|$$

$$\text{b)}\quad I_{\perp} = I_o \left| (\sin^2 2\phi)^2 \sin\left(\frac{2\pi\delta}{\lambda}\right) \right| \qquad [28]$$

where I_0 is the incident light intensity (fig. 5). When white light is used, a coloured image is obtained.

When polarizer and analyzer are parallel, the zeroth order of the colour sequence is white (silver). It is black for perpendicular polarizer and analyzer. The other colours are determined by (δ/λ), the respective intensity depending on ϕ. When L is inserted (fig. 5), corresponds to the following values of:

$$\delta' = \delta + \delta_o \quad \text{for} \quad \phi = \frac{\pi}{4} \pm \pi$$

$$\delta'' = \delta - \delta_o \quad \text{for} \quad \phi = -\frac{\pi}{4} \pm \pi.$$

For distorted films (fig. 4b), the average optical retardation is calculated using the variation of the polar angle of molecular axis $\theta(z)$ in the film given by [20].

For uniform samples, $\delta_\theta = \delta \cos^2\theta$ (20). We assume that for a distorted sample the average retardation $\bar{\delta}$ is equal to:

$$\bar{\delta} = \Delta n \int_0^h \cos^2\theta(z)\, dz \qquad [29]$$

where h is the real film thickness.

Results

a) Orientation of NLC molecules at the film interfaces

The thin films studied display many defects of orientation. These are described in reference (12). However, the extension of the uniform domains of the order of 1 mm is large compared to the width of the defect walls or lines which are of the order of 10 μm. We can assume that their contribution to the free enthalpy of the uniform domains is negligible. To find the value of θ_h, we measured $\bar{\delta}$ for various known values of h and used equations [20] and [29].

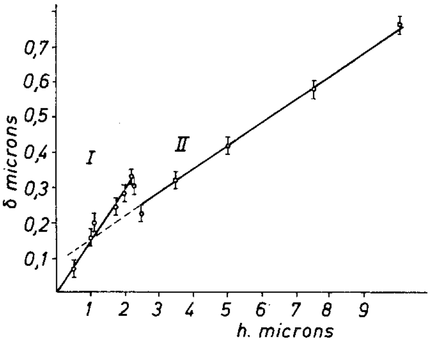

Fig. 6. Variation of the average retardation $\bar{\delta}$ with the film thickness h. I) undistorted. II) distorted films

The values of h were deduced from the known volumes v of spread NLC and the area a of the substrate. The error on h is smaller than 15%. The range of values of h is 0.5—10 μm.

The optical retardation $\bar{\delta}$ measured is smaller than 1 μm. The observed colours correspond to the 1st, 2nd, 3rd orders in Newton colour sequence. They allow for the evaluation of $\bar{\delta}$ with a satisfactory accuracy as $\delta \simeq N \frac{\lambda_o}{2}$ where $\lambda_o \simeq 0{,}56$ μm for white light. The figure 6 represents the results.

The slope of I in figure 6 is equal to $\Delta n = 0.15$. The slope of II in the same figure is equal to 0.07 and close to $(\Delta n/2) = 0.075$. The intercept of II with the ordinate airs is equal to 0.08. The transition $I \rightarrow II$ occurs at h=2.2 ±0,1 m.

Interpretation of the results

From [29], [20] and [25], we obtain the average retardation

$$\bar{\delta} = \frac{1}{2}\,\Delta n\, h + \frac{1}{4}\,\frac{\Delta n\, h}{\theta_h}\,\sin 2\theta_h. \qquad [30]$$

Two cases are considered for the distorted films shown in figure 4b.

A) $\theta_h = \pi/2$ independent of h. Then

$$\bar{\delta} = \frac{1}{2}\,\Delta n\, h.$$

B) $0 < \theta_h < \pi/2$ when h varies. [31]

These cases correspond respectively to weak surface forces or "anchoring" of molecules at the film free surface. The substrate anchors strongly the molecules. We eliminate sin 2 θ_h from [30] using [22] and [25] and obtain:

$$\bar{\delta} = \frac{\Delta nh}{2}\left(1 - \frac{K}{2h\,\Delta W_h}\right) = \frac{\Delta n}{2}\,(h + h_T) \qquad [32]$$

in which the definition [25] of h_T has been used.

The plot of $\bar{\delta}$ vs. h according to [31] or assumption 1 should provide a line with zero intercept at the origin and slope equal to $(\Delta n/2)$. The analogous plot according to [32] or assumption 2 should provide a line with a positive intercept equal to $(\Delta n/2)h_T$.

For undistorted films or $\theta_h = \theta_0 = 0$ (see fig. 4a) the retardation becomes:

$$\bar{\delta} = \Delta nh. \qquad [33]$$

The slope of the plot $\bar{\delta}$ vs h is equal to Δn.

In the figure 6 we show this plotting. It is seen that:

a) For $h < 2.2$ μm, the films verify the equation [33] (line I).

b) For $h > 2.2$ μm the results verify the equation [32] corresponding to the distorted films with θ_h varying with h. From the intercept it is obtained for the structural transition thickness: $h_T = 1.1$ μm. From the definition [25] of h_T, we find for the anisotropy factor of surface tension of 5CB, $\Delta w_h = 4.5 \times 10^{-6}$ Jm^{-2}, for $K = 10^{-11}$N.

Therefore the expression of the surface tension of 5CB may be written:

$$\text{(18bis)}\quad w_h = w_h' - 4{,}5 \times 10^{-6} \sin^2\theta_h\ [\mathrm{Jm}^{-2}].$$

The anisotropic contribution is negligible compared to the first isotropic contribution of the order of 38, 10^{-3}Jm^{-2}.

However, the observed structural transition thickness h_T is smaller than the discontinuity in $\bar{\delta}$ observed at $h = 2.2$ μm (fig. 6). This disagreement may be due to our method of averaging the orientations in equation [29].

The structural disjoining pressure exists only for $h > 2.2$ μm.

It has a maximum value for $\theta_h = \pi/4$, according to its expression [27] and assuming that $\eta_d << \eta_s$.

At a thickness called h_s of mechanical stability limit, $\theta_h = \pi/4$, the structural disjoining pressure is maximum and equal to η_s^s.

$$\eta_s^s = \frac{\Delta w_h^2}{2K} = \frac{K}{2}\,\frac{(\pi/4)^2}{(h_s)^2} \qquad [34]$$

From [34] and $\Delta w = 4.5 \times 10^{-6}$ Jm^{-2} we find $h_s = 1{,}78$ μm and $\eta_s^s = 1$ Jm^{-3}.

For $0 < \theta_h < \pi/4$ and $h < h_s$, according to the mechanical stability condition and to [34], the stability criterium.

$$-\frac{d\eta}{d_h} \simeq = -\frac{2\,\Delta w_h^2}{K}\cos 2\,\theta_h$$

$$\sin 2\,\theta_h\,\frac{d\theta_h}{dh} > 0. \qquad [35]$$

The distorted film of figure 4b verifies [35] for $\frac{\pi}{4} < \theta_h < \frac{\pi}{2}$ i.e. for $h > h_s = 1.8$ μm while according to [25] distorted structures may persist in the range $h > h_T = 1.1$ μm. The lower limit of distorted films is determined by their mechanical stability, rather than by the stability of their structure (conditions [26]).

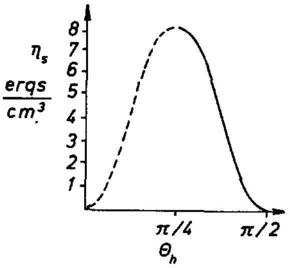

Fig. 7. Variation of the structural disjoining pressure η_s with film molecular orientation θ_h at the free surface of film. I) Stable distorted film; unstable mechanically. II) Mechanically stable distorted films

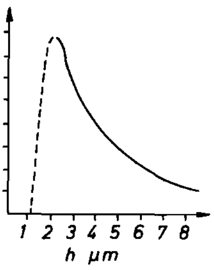

Fig. 8. Variation of structural disjoining pressure η_s of 5CB with the reduced thickness $h^+ = (h/h_c)$

The "Frederiksz" transition in asymmetric thin films may have to conform two sets of conditions: mechanical [35] and thermodynamical or physicochemical: [22] and [25].

In figure 8, the results η^s shown in figure 7 have been plotted $h^+ = h/h_T$. For $1 < h^+ < 1.64$. The film of figure 4b and corresponding to a θ_h changing with h would be unstable according to [34] unless the first in [24] has a significant contribution. However, if $\theta_h = \pi/2$, according to [26a] in this region the positive contribution of η^s enhances the film stability. Therefore the validity of assumption 1 and 2 may be checked by operating in the range $1 < h^+ < 1.64$.

In this range which is of the order of 1 μm for 5CB, letting $[B(h)] \simeq 10^{-20}$ J. The dispersive contribution would be of the order of 10^{-2} Jm^{-2} and much smaller than the values shown in the figures 7 and 8,

If the results display a decrease in η^s for $1 < h^+ < 1{,}64$, the orientation of molecules changes with film thickness and the interfacial tension or the enthalpy verifies equation (18bis). If the limit of film stability *and* film distortion structure disappear at the same film thickness h^+, the orientation of the surface molecules θ_h is fixed. These two cases corresponding to assumptions A and B above are named weak and strong anchorages respectively.

Discussion and conclusion

A Frederiksz transition is found in the absence of external electrical or magnetic macroscopic fields which in our case are replaced by surface short range forces acting at the boundary of asymmetric thin films of 5CB formed at the surface of water.

Evidence is found that the interfacial tension anisotropy at the film–water interface is stronger than at the film vapour interface.

At the last interface, the weaker anisotropy is balanced by the bulk elastic anisotropy. Then the molecular orientation at this interface is dependent on film thickness beyond a predicted transition thickness $h_T = 1{,}1$ μm and observed one at $h_T = 2{,}2$ μm. This variation of molecular orientation allows asymmetric equilibrium distorted NLC films to be formed on water. It corresponds to an anisotropic factor contribution to the free surface tension of NLC equal to $\Delta w_h = 4{,}5 \times 10^{-6}$ Jm^{-2} *independent of film thickness and structure.* Therefore, we deduce that Δw_h is relevant to local, *short range surface forces only.* As two of us (25) have found that 5CB has no polar contribution to its surface tension, we may tentatively conclude that balance between bulk elastic and surface orientation forces is achieved only when surface polar forces are small.

When the short range polar forces are present and much stronger than elastic ones, they fix the surface molecular orientation [9, 25, 26]. They are much larger than the long-range Van der Waals interaction energies film-substrate according to recent theoretic estimations [27, 28, 29] without exception [24].

Surface molecular orientation in asymmetric NLC films is also very important for thin film mechanical stability [30].

The disjoining pressure expression as a function of the angle of molecular orientation at the film surface has been deduced.

For the NLC film studied, 5CB, characterized by a small interfacial anisotropy, lower disjoining pressures and equilibrium thicker films can be predicted, contrary to asymmetric NLC films strongly anchored at both surfaces.

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Note added in proof

Subsequent studies of the structural disjoining pressure under different conditions – small area films – have shown that the surface molecules of L. C. may be anchored more strongly than in the present experiments.

Summary

Thin films (0,2 – 10 μm) of a nematic liquid crystal NLC: 4–4′-pentylcyanobiphenyl (5CB) have been spread on large surfaces of water.

The orientation of the molecules has been examined between crossed polarizer and analyzer and by studying the average retardation of white light as a function of film thickness. At $h_T \simeq 2.2$ μm a Frederiksz transition takes place owing to the balance of elastic and surface forces acting on the film and determining the molecular orientations in bulk at the surface as a function of films thickness. From this variation and h_T, an anisotropy of surface tension of 5CB of the order of 10^{-6} Jm^{-2} is found. This weak anisotropy

determines also the variation of the structural disjoining pressure and the film stability which is discussed at length. A thermodynamic potential for this films is suggested.

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