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## A PHASE TRANSITION-LIKE INSTABILITY IN STATIC SAMPLES OF TWISTED NEMATIC LIQUID CRYSTAL WHEN THE SURFACES INDUCE TILTED ALIGNMENTS

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**Résumé.** — Ces dernières années on s'est beaucoup intéressé aux structures en hélice dans les cellules à cristaux liquides nématiques (NLC). Cet article rapporte le comportement de telles structures lorsque les surfaces induisent non pas l'orientation planaire classique mais des alignements homogènes inclinés. On montre alors que la torsion totale est égale à  $\Pi$ , il existe une valeur critique de l'angle d'inclinaison aux surfaces pour laquelle la structure en hélice se transforme spontanément en une structure non *twistée*. Cette transformation présente toutes les caractéristiques d'une transition de phase qui peut être soit du premier soit du deuxième ordre suivant les valeurs des constantes élastiques du matériau. La confirmation expérimentale a pu être obtenue pour le MBBA.

**Abstract.** — There has been, in recent years, a great interest in twisted orientation patterns in static samples of nematic liquid crystals (NLC). Here we investigate the behaviour of such structures when the limiting surfaces induce not planar alignment but homogeneously tilted alignment. It is shown that when the overall twist is equal to  $\Pi$ , there exists a critical value of the tilt angle at the surface where the expected twisted structure spontaneously transforms into a non-twisted orientation pattern. This transformation presents all the features of a phase transition, which can be either of first or of second order depending on the set of elastic constants of the material. Experimental confirmation has been obtained with MBBA.

**1. Introduction.** — In a theoretical investigation [1], Leslie showed that in a classical twisted nematic cell with planar alignment on the limiting surfaces, non-parallel distorted twisted orientation patterns might be observed instead of the classical parallel twisted orientation pattern when the relative values of the elastic constants of the nematic material lie in a certain range. That is to say that in such a case, the equilibrium conformation of the nematic medium is obtained when the optic axis in the bulk is not parallel to the limiting surfaces but slightly inclined. However such a situation will not be obtained unless the twist elastic constant is large compared to the other two and thus is not to be expected with common nematic materials.

But if one allows the surface alignment to be tilted rather than planar, such non-parallel twisted patterns will be obtained with materials as common as MBBA.

In a recent paper [2], it is reported that by suitable prior treatment of the solid surfaces, it is possible to produce homogenous alignment of the NLC where the tilt angle  $\theta_0$ , with respect to the normal of the surface, is not  $\pi/2$  (planar alignment) but may vary over the whole range  $0 \leq \theta_0 \leq \pi/2$ , depending on the surface treatment. If one now rotates one plate in its

own plane through an angle  $2\varphi_0$ , the alignment directions of the two surfaces no longer coincide and a conformation which is both twisted ( $2\varphi_0$  overall twist) and tilted, is obtained. It is clear that since  $\theta_0$ , the tilt angle on the surface, is no longer  $\pi/2$ ,  $\theta(z)$ , the tilt angle in bulk, has no reason to remain equal to  $\theta_0$ . And, although the set of elastic constants of the material certainly influences  $\theta(z)$ , our main parameters are the surface tilt angle  $\theta_0$  and the overall twist  $2\varphi_0$ , and our problem appears quite different from Leslie's. This communication aims to describe the behaviour of such conformations while  $\theta_0$  and  $\varphi_0$  vary.

More precisely the purpose of this work is to determine under which conditions ( $\theta_0$ ,  $\varphi_0$ ),  $\theta_m$ , the tilt angle at the centre of the gap, reduces to zero : it is clear that when such conditions are obtained the expected twisted conformation III described in figure 1a is replaced by the untwisted orientation pattern III' given in figure 1b.

A first, rather straight-forward exact calculation of  $\theta_m$  as a function of ( $\theta_0$ ,  $\varphi_0$ ) can be performed in the ideal case where the Frank-Oseen constants of the material are such that :

$$K_{11} = K_{33} = 2.K_{22}$$

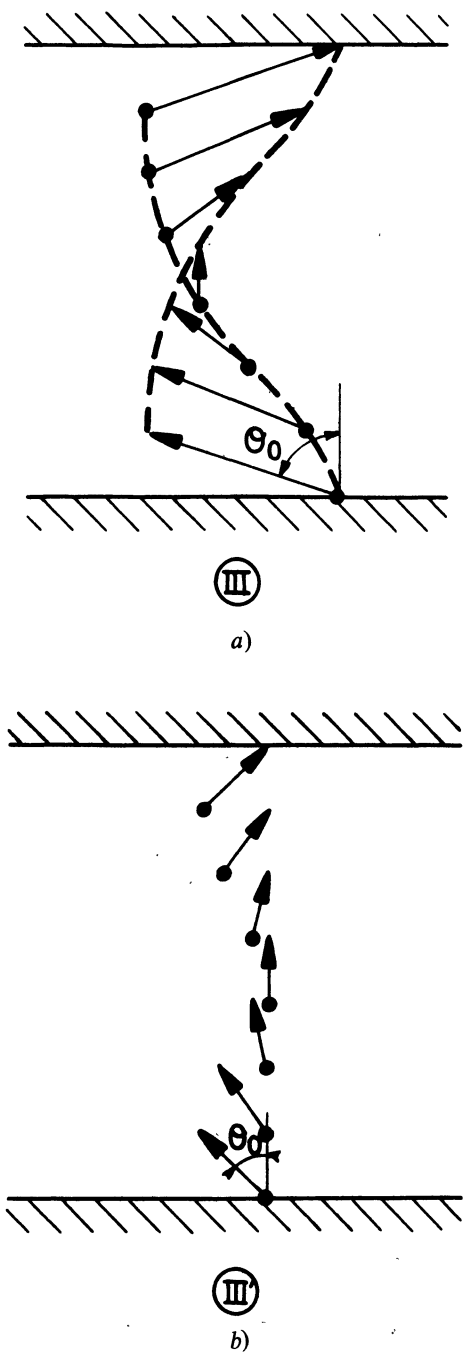


FIG. 1. — a) Description of the twisted configuration III; b) Description of the non-twisted configuration III'.

It is then possible to derive what happens when  $K_{11}$  is allowed to differ from  $K_{33}$  as occurs in the case of MBBA ( $K_{11} = 0.62 K_{33}$ ,  $K_{22} = 0.5 K_{33}$ ). The required conditions are :

- $2 \varphi_0 = \pi$ ,
- $\theta_0$  smaller than a critical value  $\theta_{0c}$  which depends on the elastic constant of the nematic material.

Otherwise it is shown that the transformation of conformation III into conformation III' is similar to a second-order phase transition.

Good experimental agreement is obtained with MBBA sandwiched between glass plates treated with octyl amine at low surface concentration.

In a later section we briefly give some insight into the behaviour of this transition in the general case, and show that it definitely becomes first-order when  $2 K_{22} > K_{33}$ .

**2. General equations.** — Since the criterion of existence of III or III' is energetic one has to study the elastic energy of the NLC sandwiched in the cell. The existing configuration is then the one of lower energy.

It is convenient to choose a right-handed coordinate system with the  $z$ -axis perpendicular to the plates, and such that the origin is equidistant from the solid boundaries.

The director vector  $\mathbf{n}$  which defines the local orientation of the NLC, is projected on the three axes :

$$\begin{aligned} n_x &= \sin \theta(z) \cos \varphi(z) \\ n_y &= \sin \theta(z) \sin \varphi(z) \\ n_z &= \cos \theta(z) . \end{aligned} \tag{1}$$

The thickness  $2h$  of the sample is small compared to the dimensions of the plates and variations of the orientation parallel to the solid surfaces seem unlikely. Therefore the elastic energy of the NLC reduces classically to :

$$W_{el} = \int_{-h}^{+h} F(\theta) \theta'^2 + G(\theta) \varphi'^2 dz \tag{2}$$

with

$$\begin{aligned} F(\theta) &= K_{11} \sin^2 \theta + K_{33} \cos^2 \theta \\ G(\theta) &= (K_{22} \sin^2 \theta + K_{33} \cos^2 \theta) \cdot \sin^2 \theta . \end{aligned} \tag{3}$$

Writing that  $W_{el}$  is extremum leads to the equations :

$$\begin{aligned} 2 F(\theta) \theta'' + \frac{dF}{d\theta} \theta'^2 - \frac{d}{dz} \cdot G(\theta) \varphi'^2 &= 0 \\ G(\theta) \varphi'' + \frac{dG}{d\theta} \cdot \theta' \varphi' &= 0 , \end{aligned} \tag{4}$$

where the prime denotes differentiation with respect to the  $z$  coordinate.

In our problem, both surfaces induce the same tilt angle  $\theta_0$  on the NLC ; we must write :

$$\theta(h) = \theta(-h) = \theta_0 . \tag{5}$$

The second pair of boundary conditions is given by  $2 \varphi_0$ , the total twist angle from one plate to the other.

While the conditions in our experiments correspond to  $\varphi_0 = \pi/2$ , we prefer, as a first step, not to restrict this angle to that particular value and to write :

$$\varphi(h) = -\varphi(-h) = \varphi_0 . \tag{5'}$$

As was suggested [2] by the observation of configuration III', a solution  $\theta(z)$ ,  $\varphi(z)$  which satisfies the particular equations (6) :

$$\left. \begin{aligned} G(\theta) \varphi' &= 0 \\ F(\theta) \theta'^2 &= b \end{aligned} \right\} b = \text{integration constant} \quad (6)$$

would *a fortiori* satisfy the general equations (4). Thus whatever the boundary conditions  $(\theta_0, \varphi_0)$  are, configuration III' always appears as an extremum for  $W_{el}$ .

On the other hand, a configuration where  $\theta(z)$  remains constant while  $\varphi(z)$  varies alone would lead to the following set of equations :

$$\frac{dG}{d\theta} \cdot \varphi'^2 = 0; \quad G(\theta) \cdot \varphi'' = 0 \quad (7)$$

which can be simultaneously satisfied only if :

$$\left. \frac{dG}{d\theta} \right|_{\theta_0} = 0. \quad (8)$$

Thus, except in the case of very special boundary conditions ( $\theta_0 = \pi/2$  for instance), an orientation pattern where  $\theta$  remains constant with respect to the  $z$  coordinate will not be an equilibrium configuration.

In the general case where both  $\theta(z)$  and  $\varphi(z)$  may vary, the equations (4) integrate to yield :

$$G(\theta) \varphi' = a; \quad F(\theta) \theta'^2 + G(\theta) \varphi'^2 = b. \quad (9)$$

Since our problem is symmetrical with respect to the  $z = 0$  plane, a regular solution for equations (9) will have the properties :

$$\theta(z) = \theta(-z); \quad \varphi(z) = -\varphi(-z) \quad (10)$$

and thus :

$$\theta'(0) = 0; \quad \varphi(0) = 0. \quad (12)$$

Clearly, equations (9) remain different from (6) as long as  $a$  is strictly positive. The regular solution  $\theta(z)$  of (9) must then satisfy the condition :

$$\theta(z) > 0 \quad (13)$$

and in particular :

$$\theta_m = \theta(0) > 0. \quad (14)$$

Given such a solution, if one continuously modifies the boundary conditions so that  $\theta_m \rightarrow 0$ , the finite boundary conditions imply that simultaneously  $a \rightarrow 0$ . Then (9) continuously reduces to (6) and the equilibrium configuration III continuously transforms into III'.

If one combines equations (9), it follows that :

$$F(\theta) \cdot \theta'^2 = a^2 [1/G(\theta_m) - 1/G(\theta)]. \quad (15)$$

A necessary condition for a solution of this type is that the right hand side of equation (15) remains

positive, and thus holds in the range where  $G(\theta)$  increases monotonically with  $\theta$ . This condition implies :

$$\theta_0 < \theta_n \quad (16)$$

where  $\theta_n$  is defined by :

$$\sin^2 \theta_n = \frac{K_{33}}{2 K_{33} - 2 K_{22}}. \quad (17)$$

Since solutions where  $\theta_0 > \theta_n$  will be such that  $\theta_m > \theta_0$  our transition will not occur in this latter range, and solutions corresponding to equation (15) are the only ones of interest. (15) yields solutions in which  $\theta(z)$  decreases monotonically from  $\theta_0$  at the surface to  $\theta_m$  at the centre of the gap ; and they take the form [1] :

$$\begin{aligned} az &= G(\theta_m)^{1/2} \int_{\theta_m}^{\theta_0} \left[ \frac{F(u) G(u)}{G(u) - G(\theta_m)} \right]^{1/2} du \\ \varphi &= G(\theta_m)^{1/2} \int_{\theta_m}^{\theta_0} \left[ \frac{F(u)}{G(u) [G(u) - G(\theta_m)]} \right]^{1/2} du. \end{aligned} \quad (18)$$

Within our boundary conditions :

$$ah = G(\theta_m)^{1/2} \int_{\theta_m}^{\theta_0} \left[ \frac{F(\theta) G(\theta)}{G(\theta) - G(\theta_m)} \right]^{1/2} d\theta \quad (19)$$

$$\varphi_0 = G(\theta_m)^{1/2} \int_{\theta_m}^{\theta_0} \left[ \frac{F(\theta)}{G(\theta) [G(\theta) - G(\theta_m)]} \right]^{1/2} d\theta. \quad (20)$$

As in Leslie's problem, (20) is important since it determines  $\theta_m$  as a function of  $\theta_0$  and  $\varphi_0$ . Since equation (20) is rather difficult to manipulate when  $F(\theta)$  and  $G(\theta)$  are fully developed, we prefer as a first step to study an ideal case where :

$$K_{11} = K_{33} \quad \text{and} \quad K_{22} = \frac{K_{33}}{2}. \quad (21)$$

From the solution of this case, we then derive the behaviour of the transition when  $K_{11}$  is allowed to differ slightly from  $K_{33}$ , as it does for MBBA :

$$K_{11} = 0.6 K_{33} \quad \text{and} \quad K_{22} = 0.5 K_{33} \quad (22)$$

**3. The ideal case where  $K_{11} = K_{33} = 2 K_{22}$ .** — With such elastic constants, equation (20) takes the rather simple form :

$$\begin{aligned} \varphi_0 &= \sqrt{2(1 - \cos^4 \theta_m)} \times \\ &\int_{\theta_m}^{\theta_0} \frac{d\theta}{\sqrt{(1 - \cos^4 \theta) (\cos^4 \theta_m - \cos^4 \theta)}}. \end{aligned} \quad (23)$$

With the aid of the first substitution :

$$\cos^2 \theta = u : 0 < \cos^2 \theta_0 < u < \cos^2 \theta_m < 1$$

the integral becomes :

$$J = \frac{1}{2} \int_{\cos^2 \theta_m}^{\cos^2 \theta_0} \frac{du}{(1-u) \sqrt{u(1+u)(u_m+u)(u_m-u)}} \tag{24}$$

and with the aid of the second substitution :

$$u = \frac{u_m \sin^2 \Phi}{2 - \sin^2 \Phi}, \quad k^2 = \frac{1 - u_m}{2} = m \tag{25}$$

$J$  becomes :

$$J = \frac{1}{2 a \sqrt{2} m'} \int_{\Phi_0}^{\pi/2} \frac{d\Phi}{\sqrt{1 - m \sin^2 \Phi}} \times \left[ 1 + \frac{2 m' - 1}{1 - m' \sin^2 \Phi} \right] \quad m' = 1 - m$$

where  $\Phi_0$  is such that :

$$\cos^2 \theta_0 = \frac{u_m \sin^2 \Phi_0}{2 - \sin^2 \Phi_0} \tag{25'}$$

Introducing elliptic integrals of first and third kind :

$$J = \frac{1}{2 m' \sqrt{u_m} \times 2} \{ K(m) - F(\Phi_0 | m) + (2 m' - 1) [\Pi(1 - m | m) - \Pi(1 - m; \Phi_0 | m)] \} \tag{26}$$

Then, for any given value of  $\theta_0$ , one can draw the curve

$$\varphi(\theta_0, \theta_m) = \sqrt{2(1 - \cos^4 \theta_m)} \times J(\theta_0, \theta_m), \tag{27}$$

and the expected solutions for equation (23) will be given by the intersection of curve (27) with the horizontal straight line :

$$\varphi = \varphi_0 \tag{28}$$

Since the existence and nature of the expected transition depends on the behaviour of (27) around  $\theta_m = 0$ , we derived the following limited development of  $\varphi(\theta_0, \theta_m)$  :

$$\varphi(\theta_0, \theta_m) = \frac{\pi}{2} + \sqrt{m} \left( \frac{\pi}{2} - \Phi_0 - \text{tg } \Phi_0 \right) + 0(m) \tag{29}$$

around  $\theta_m = 0$ .

From (29) one immediately obtains the following results :

—  $\lim_{\theta_m \rightarrow 0} \varphi(\theta_0, \theta_m) = \frac{\pi}{2} = \varphi_{0K}$  and does not depend on  $\theta_0$ ;

—  $\lim_{\theta_m \rightarrow 0} \partial \varphi(\theta_0, \theta_m) / \partial \theta_m$  is a monotonically increasing function of  $\theta_0$  in the range  $[-\infty, \pi/2]$ . The value  $\theta_{0K}$  where it changes its sign is given by the equation :

$$\frac{\pi}{2} - \Phi_{0K} - \text{tg } \Phi_{0K} = 0 \Rightarrow \theta_{0K} \cong 58^\circ 43' \tag{30}$$

—  $\lim_{\theta_m \rightarrow 0} \partial^2 \varphi(\theta_0, \theta_m) / \partial \theta_m^2 = 0$  for any value of  $\theta_0$ . (31)

At the opposite end of curves (27) one can show that :

$$\lim_{\theta_m \rightarrow \theta_0} \varphi(\theta_0, \theta_m) = 0$$

while

$$\lim_{\theta_m \rightarrow \theta_0} \frac{\partial \varphi(\theta_0, \theta_m)}{\partial \theta_m} = -\infty$$

With these results, the set of curves given in figure 2 have been drawn with the aid of an electronic calculator.

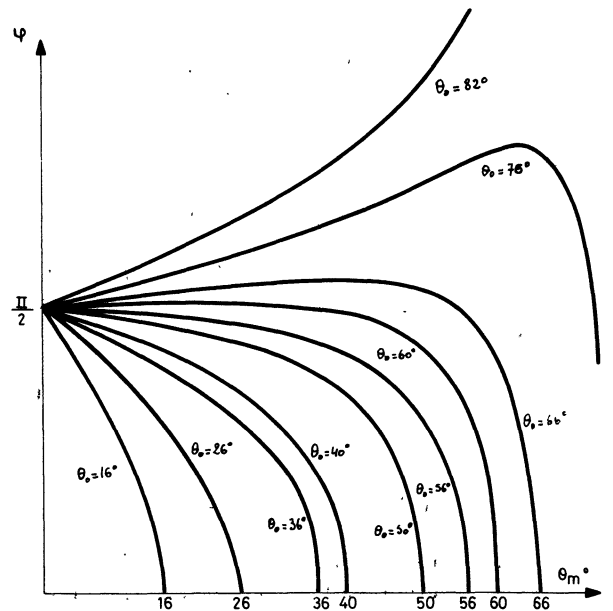


FIG. 2. — Curves  $\varphi(\theta_0, \theta_m)$  corresponding to the ideal case where  $K_{11} = K_{33} = 2 K_{22}$ .

We clearly have to consider two independent parameters i.e.  $\theta_0$  and  $\varphi_0$  corresponding to the boundary conditions.  $\theta_0$  defines the curve  $\varphi(\theta_0, \theta_m)$  while  $\varphi_0$  defines the straight horizontal line  $\varphi = \text{constant} = \varphi_0$ .

The intersection of those two curves gives the values of  $\theta_m$  where  $W_{el}$  is an extremum.

Since our problem is to find what happens when  $\theta_0$  varies while  $\varphi_0$  is fixed, we treat the three following cases separately :

a)  $\varphi_0 < \varphi_{0K} = \pi/2$ . — The line  $\varphi = \varphi_0$  will cut cross the curves  $\varphi(\theta_0, \theta_m)$  in one only point where  $\theta_m = \theta_{m2}(\theta_0)$ .

Thus in case where  $\varphi_0 < \varphi_{0\kappa}$  we clearly have two extrema for  $w_{el}(\theta_m)$  respectively :

$$\theta_m = 0 \quad \text{and} \quad \theta_m = \theta_{m_2}(\theta_0).$$

The problem is then to know which one is the minimum. The comparison could be performed by using equation (9) and injecting the obtained value of  $\theta_m$  in the expression of  $W_{el}$ . Since such an operation is forbiddingly complicated it is more convenient to make the following continuity considerations.

$W_{el}(\theta_m)$  may reasonably be considered as a continuously differentiable function of  $\theta_m$ . On the other hand the case where  $\varphi_0 = 0$  is obvious and we have :

$$\left. \frac{\partial W}{\partial \theta_m} \right|_{\varphi=0} > 0 \quad \text{if} \quad \theta_m > \theta_0$$

and

$$\left. \frac{\partial W}{\partial \theta_m} \right|_{\varphi=0} < 0 \quad \text{if} \quad \theta_m < \theta_0.$$

Within the preceding continuity assumption, it can be deduced that  $\partial W / \partial \theta_m |_{\theta_0, \varphi \neq 0}$  is negative on the right hand side of the curve  $\varphi(\theta_0, \theta_m)$  and positive on the other. Then points of the curve  $\varphi(\theta_0, \theta_m)$  where this function increases with  $\theta_m$  are maxima for  $W_{el}$  while the minima correspond to the points of  $\varphi(\theta_0, \theta_m)$  where  $\partial \varphi / \partial \theta_m < 0$ .

Since  $\partial \varphi(\theta_0, \theta_m) / \partial \theta_m |_{\theta_{m_2}}$  is negative,  $\theta_{m_2}$  is the minimum for  $W_{el}(\theta_m)$  while  $\theta_m = 0$  is the maximum, and the energy diagram given in figure 3 can be drawn. Clearly as long as  $\varphi_0 < \pi/2$ ,  $\theta_{m_2}$  reaches 0 while  $\theta_0$  itself decreases to zero : a phase transition may not be expected for such overall twists.

b)  $\varphi_0 = \varphi_{0\kappa} = \pi/2$ . — As long as  $\theta_0 > \theta_{0\kappa}$  the point  $\theta_{m_2}$  still exists and for the same reason as in the

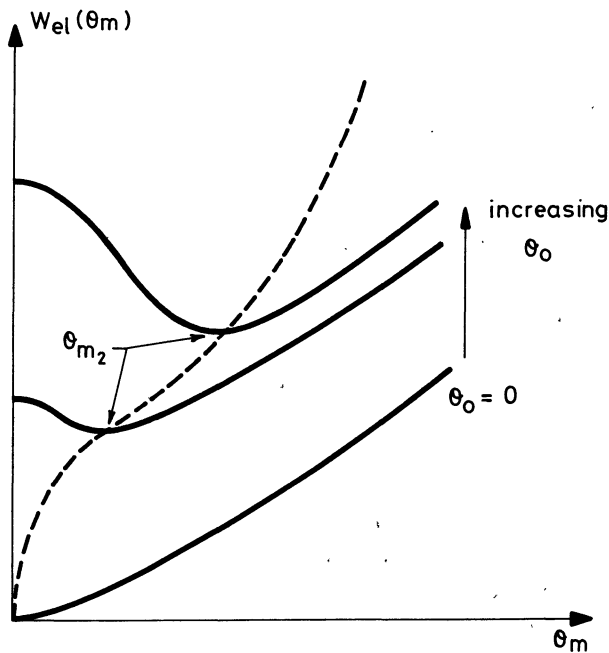


FIG. 3. — Energy diagram  $W_{el}(\theta_m)$  when the overall twist  $2\varphi_0$  is smaller than  $\pi$ .

preceding case, it represents the absolute minimum for  $W_{el}(\theta_m)$ .

While  $\theta_0$  decreases down to  $\theta_{0\kappa}$ ,  $\theta_{m_2}$  quickly falls to zero. And when  $\theta_0$  is smaller than  $\theta_{0\kappa}$ ,  $\theta_{m_2}$  no longer exists and the equilibrium configuration is obtained when  $\theta_m = 0$ . Since  $\theta_m$  continuously decreases to zero while  $\theta_0 \rightarrow \theta_{0\kappa}$ , the phenomenon is typically a second-order phase transition. The energy diagram, which can be obtained in the same way as in the preceding case, is also typical of a second-order phase transition (Fig. 4).

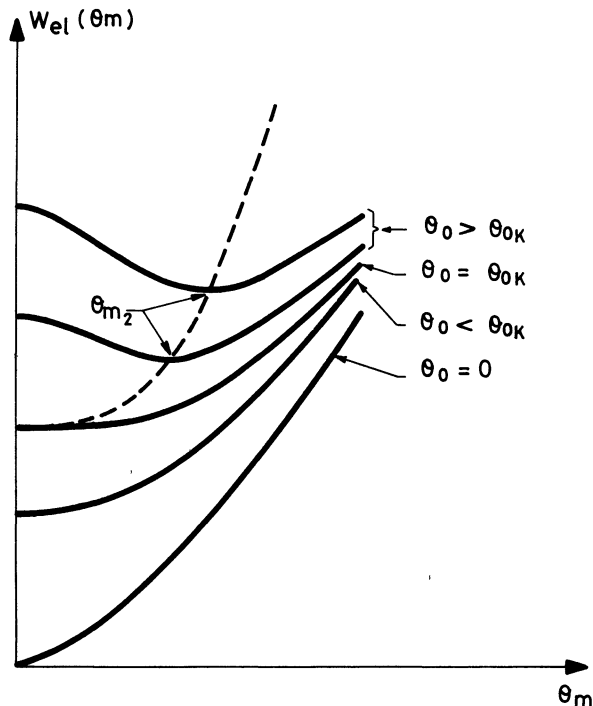


FIG. 4. — Energy diagram  $W_{el}(\theta_m)$  when the overall twist  $2\varphi_0$  is equal to  $\pi$ .

c)  $\varphi_0 > \varphi_{0\kappa} = \pi/2$ . — The same type of considerations would, in this case, indicate a transition of first order.

However the physical significance of such overall twists  $2\varphi_0$  greater than  $\pi$  must first be discussed. Figure 5 describes such a situation for a right-twisted configuration : it immediately appears that the corresponding left-twisted configuration is such that :

$$2\varphi_{0\text{left}} < \pi.$$

This later configuration is therefore less distorted and would take the place of the former through the nucleation and motion of a low energy bulk integral disclination line such as the AB line in figure 8. Through this process we are thus driven back to the case where  $2\varphi_0 < \pi$  and as pointed out in a) no transition can be expected in this case.

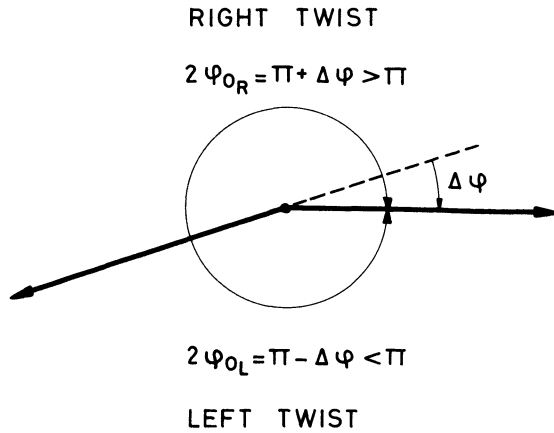


FIG. 5. — Description of a misaligned sample : right twist  $2\varphi_0 = \pi + \Delta\varphi > \pi$ ; left twist  $2\varphi_0 = \pi - \Delta\varphi < \pi$ .

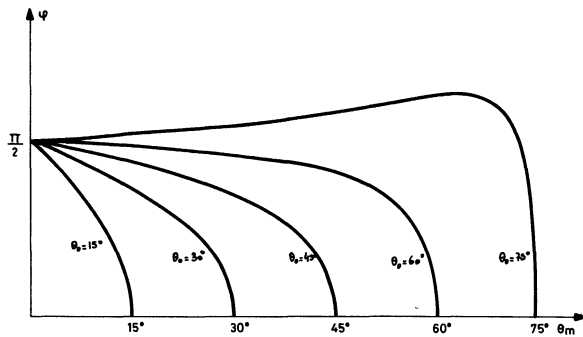


FIG. 6. — Curves  $\varphi(\theta_0, \theta_m)$  for the material MBBA ( $K_{11} = 0.62 K_{33}$ ;  $K_{33} = 2 K_{22}$ ).

The results of this discussion can be summed up as it follows :

—  $\varphi_0 < \pi/2$  : configuration (III) is stable for any value of  $\theta_0$  and there is no transition.

—  $\varphi_0 = \pi/2$  : (III) is stable when  $\theta_0 > \theta_{0K}$  while (III) is stable when  $\theta_0 < \theta_{0K}$ , and the transition is of second order.

—  $\varphi_0 > \pi/2$  : spontaneously transforms into  $\varphi_0 < \pi/2$  by changing the sign of the order parameter.

**4. The case where  $K_{11} \neq K_{33}$ ;  $2 K_{22} = K_{33}$ .** — These conclusions have been obtained in the ideal case where  $K_{11} = K_{33}$  and  $K_{22} = 0.5 K_{33}$ . There are a number of recent measurements of the Frank-Oseen coefficients for the material MBBA (see for example Haller [5] and Leger [6]) and typically one finds that :

$$K_{11} = 0.62 K_{33}, \quad K_{22} = 0.5 K_{33}.$$

This material is not far from our ideal case since its coefficients verify the second relation. We must however discuss what happens when  $K_{11}$  is allowed to be different from  $K_{33}$ .

Since we failed to obtain a somewhat manageable solution of equation (20) in such a case, we have to derive it from the ideal case.

Where we had :

$$F(\theta) = K_{33}$$

we now have

$$F(\theta) = K_{11} \sin^2 \theta + K_{33} \cos^2 \theta.$$

Introducing

$$\beta = \frac{K_{11} - K_{33}}{K_{33}} > -1.$$

$F(\theta)$  becomes :

$$F(\theta) = K_{33}(1 + \beta \sin^2 \theta). \quad (33)$$

At this point it is helpful to introduce the notation :

$$H(\theta, \theta_m) = \frac{\sqrt{2(1 - \cos^4 \theta_m)}}{\sqrt{(1 - \cos^4 \theta)(\cos^4 \theta_m - \cos^4 \theta)}}. \quad (34)$$

The equation (23) for the ideal case becomes :

$$\varphi_0^i(\theta_0, \theta_m) = \int_{\theta_m}^{\theta_0} H(\theta, \theta_m) d\theta \quad (35)$$

where the index *i* denotes the ideal case.

When  $K_{11} \neq K_{33}$  we derive :

$$\varphi_0(\theta_0, \theta_m) = \int_{\theta_0}^{\theta_m} H(\theta; \theta_m) \sqrt{1 + \beta \sin^2 \theta} d\theta. \quad (36)$$

We may write :

$$\sqrt{1 + \beta \sin^2 \theta} = 1 + f(\theta, \beta), \quad (37)$$

where  $f(\theta, \beta)$  is either a decreasing negative function of  $\theta$  or an increasing positive function of  $\theta$  with the properties :

$$\lim_{\theta \rightarrow 0} f(\beta, \theta) = 0 \quad \text{and} \quad \lim_{\theta \rightarrow 0} \frac{\partial f}{\partial \theta} = 0. \quad (38)$$

Hence :

$$\varphi_0(\theta_0, \theta_m) = \varphi_0^i(\theta_0, \theta_m) + \int_{\theta_m}^{\theta_0} H(\theta, \theta_m) f(\beta, \theta) d\theta. \quad (39)$$

As in the preceding case, the existence and properties of the transition will be determined by the variations of  $\varphi_0(\theta_0, \theta_m)$  around  $\theta_m = 0$ . We have to calculate the new value of  $\varphi_{0K}(\theta_0)$

$$\varphi_{0K}(\theta_0) = \lim_{\theta_m \rightarrow 0} \varphi_0(\theta_0, \theta_m) \quad (40)$$

$\theta_{0\kappa}$  will then be given by the equation

$$\lim_{\theta_m \rightarrow 0} \frac{\partial \varphi(\theta_0, \theta_m)}{\partial \theta_m} = 0 \quad (41)$$

and the order of the transition depends on the sign of :

$$\lim_{\theta_m \rightarrow 0} \frac{\partial^2 \varphi(\theta_0, \theta_m)}{\partial \theta_m^2} . \quad (42)$$

Combining (39) and (40) yields :

$$\begin{aligned} \varphi_{0\kappa}(\theta_0) &= \frac{\pi}{2} + \lim_{\theta_m \rightarrow 0} \int_{\theta_m}^{\theta_0} H(\theta, \theta_m) f(\beta, \theta) d\theta \\ &= \frac{\pi}{2} + \lim_{\theta_m \rightarrow 0} \left[ \int_{\theta_m}^{\varepsilon} H(\theta, \theta_m) f(\beta, \theta) d\theta + \right. \\ &\quad \left. + \int_{\varepsilon}^{\theta_0} H(\theta, \theta_m) f(\beta, \theta) d\theta \right] \end{aligned}$$

where  $\varepsilon$  is arbitrary, but such that :

$$\varepsilon > \theta_m .$$

Then

$$\lim_{\theta_m \rightarrow 0} \int_{\varepsilon}^{\theta_0} H(\theta, \theta_m) f(\beta, \theta) d\theta = 0$$

and :

$$\begin{aligned} \left| \lim_{\theta_m \rightarrow 0} \int_{\theta_m}^{\varepsilon} H(\theta, \theta_m) f(\beta, \theta) d\theta \right| &< \\ &< |f(\beta, \theta)| \lim_{\theta_m \rightarrow 0} \int_{\theta_m}^{\varepsilon} H(\theta, \theta_m) d\theta \\ &= f(\beta, \varepsilon) \frac{\pi}{2} \rightarrow 0 \quad \text{when } \varepsilon \rightarrow 0 . \end{aligned}$$

Therefore :

$$\varphi_{0\kappa}(\theta_0) = \frac{\pi}{2}$$

whatever the values of  $\beta$  and of  $\theta_0$  are, and the transition (if it exists) will occur only if the overall twist is  $\pi$ .

To get information about  $\theta_{0\kappa}$  compared to  $\theta_{0\kappa}^i$  from equation (41) is rather less obvious : first an integration by parts yields :

$$\begin{aligned} \frac{\partial}{\partial \theta_m} \int_{\theta_m}^{\theta_0} H(\theta, \theta_m) [1 + f(\beta, \theta)] d\theta &= \\ &= \frac{\partial}{\partial \theta_m} \{ [1 + f(\theta_0)] \varphi_0^i(\theta_0, \theta_m) \} - \\ &\quad - \frac{\partial}{\partial \theta_m} \int_{\theta_m}^{\theta_0} \varphi_0^i(\theta, \theta_m) d\theta . \quad (43) \end{aligned}$$

The second term may be written

$$\begin{aligned} - \frac{\partial}{\partial \theta_m} \int_{\theta_m}^{\theta_0} \varphi_0^i(\theta_0, \theta_m) d\theta &= \varphi(\theta_m, \theta_m) \frac{\partial f}{\partial \theta} \Big|_{\theta_m} + \\ &+ \int_{\theta_m}^{\theta_0} \frac{\partial f}{\partial \theta} \cdot \frac{\partial \varphi(\theta, \theta_m)}{\partial \theta_m} d\theta \quad (44) \end{aligned}$$

if this last integral exists.

To prove its existence, it is helpful to write

$$\int_{\theta_m}^{\theta_0} \frac{\partial \varphi^i(\theta, \theta_m)}{\partial \theta_m} \cdot \frac{\partial f}{\partial \theta} d\theta = \lim_{\varepsilon \rightarrow \theta_m} \int_{\varepsilon}^{\theta_0} \frac{\partial \varphi^i(\theta, \theta_m)}{\partial \theta_m} \frac{\partial f}{\partial \theta} d\theta . \quad (45)$$

As long as  $\varepsilon > \theta_m$ ,

$$\int_{\varepsilon}^{\theta_0} \frac{\partial \varphi^i(\theta, \theta_m)}{\partial \theta_m} \frac{\partial f}{\partial \theta} d\theta$$

remains finite and can be written :

$$U(\theta_0, \theta_m) - U(\varepsilon, \theta_m) . \quad (46)$$

When  $\theta$  is close to  $\theta_m$  one can use an equivalent expression for  $H(\theta, \theta_m)$  :

$$H(\theta, \theta_m) \sim \frac{\sqrt{1 - \cos^4 \theta_m}}{\cos^3 \theta_m \sin \theta_m} \cdot \frac{1}{2\sqrt{\theta - \theta_m}} \quad (47)$$

and then obtain an equivalent expressions for  $U(\varepsilon, \theta_m)$  when  $\varepsilon$  is near to  $\theta_m$ , and  $\theta_m$  near to 0 :

$$U(\varepsilon, \theta_m) \sim -\beta \sqrt{\frac{\theta_m}{2}} \cdot 2\varepsilon(\varepsilon - \theta_m)^{1/2} . \quad (48)$$

Thus  $U(\varepsilon, \theta_m)$  is finite,  $U(\theta_0, \theta_m)$  is consequently finite as well, and the integral exists.

Equation (41) then becomes :

$$\begin{aligned} \lim_{\theta_m \rightarrow 0} \left\{ \frac{\partial \varphi^i(\theta_0, \theta_m)}{\partial \theta_m} [1 + f(\theta_0, \beta)] - \right. \\ \left. - \int_{\theta_m}^{\theta_0} \frac{\partial \varphi^i(\theta, \theta_m)}{\partial \theta_m} \frac{\partial f}{\partial \theta} d\theta \right\} . \quad (49) \end{aligned}$$

Although an exact solution of equation (49) cannot be obtained easily, this equation indicates that :

- $\beta < 0$  i.e.  $K_{33} > K_{11}$  and we have  $\theta_{0\kappa} > \theta_{0\kappa}^i$
- $\beta > 0$  i.e.  $K_{33} < K_{11}$  then  $\theta_{0\kappa} < \theta_{0\kappa}^i$

which is rather natural since  $\beta > 0$  obviously favours a twisted configuration while  $\beta < 0$  favours a configuration such as (III).

As noted above, the nature of the transition depends on the sign of :

$$\frac{\partial^2 \varphi(\theta_0, \theta_m)}{\partial \theta_m^2} \Big|_{\theta_m=0} . \quad (42)$$



One can easily see that it will no longer be of second order if this second derivative becomes positive :

$$\left. \frac{\partial^2 \varphi(\theta_0, \theta_m)}{\partial \theta_m^2} \right|_{\theta_m=0} > 0.$$

From above :

$$\frac{\partial^2 \varphi(\theta_0, \theta_m)}{\partial \theta_m^2} = [1 + f(\beta, \theta_0)] \frac{\partial^2 \varphi(\theta_0, \theta_m)}{\partial \theta_m^2} - \frac{\partial}{\partial \theta_m} U(\theta_0, \theta_m).$$

The second term can be written :

$$\frac{\partial}{\partial \theta_m} U(\theta_0, \theta_m) = \frac{\partial}{\partial \theta} [U(\theta_0, \theta_m) - U(\varepsilon, \theta_m)] + \frac{\partial}{\partial \theta_m} U(\varepsilon, \theta_m).$$

When  $\theta_m \rightarrow 0$

$$\int_{\varepsilon}^{\theta_m} \frac{\partial^2 \varphi^i(\theta, \theta_m)}{\partial \theta_m^2} \cdot \frac{\partial f}{\partial \theta} d\theta \rightarrow 0$$

and :

$$\frac{\partial}{\partial \theta_m} \int_{\theta_m}^{\varepsilon} \frac{\partial \varphi^i(\theta, \theta_m)}{\partial \theta_m} \cdot \frac{\partial f}{\partial \theta} d\theta \sim \frac{\beta \varepsilon \sqrt{\theta_m}}{\sqrt{2(\theta - \theta_m)}} \rightarrow 0$$

and thus

$$\lim_{\theta_m \rightarrow 0} \frac{\partial^2 \varphi(\theta_0, \theta_m)}{\partial \theta_m^2} = \lim_{\theta_m \rightarrow 0} \frac{\partial^2 \varphi^i(\theta_0, \theta_m)}{\partial \theta_m^2} = 0.$$

Hence the transition remains of second order.

Figure 6 represents the curves  $\varphi(\theta_0, \theta_m)$  when  $\beta$  is equal to  $-0.38$  (MBBA).

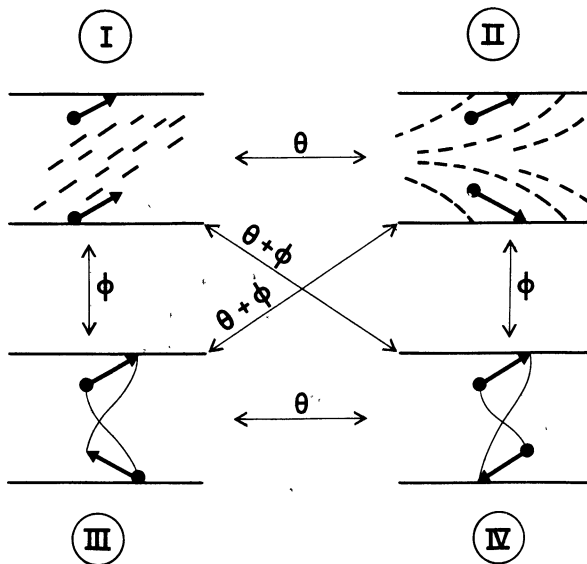


FIG. 7. — The four configurations in bulk which can be obtained when the surfaces induce tilted alignment.

In our physical situation where the nematic material is MBBA,  $K_{11}$  is slightly smaller than  $K_{33}$ . The preceding considerations indicate that the expected transition, when the overall twist is  $\pi$ , will be of second order and that it will occur when  $\theta_0$  decreases to reach the value  $\theta_{0\kappa}$  slightly larger than  $58^\circ 43'$ .

**5. Observations.** — In ref. [3], we studied the configurations in the bulk of a nematic liquid crystal sandwiched between two parallel glass plates previously treated with heptylamine. This treatment of the surfaces leads to a high tilt angle. Figure 7 shows the four configurations in bulk which can be obtained in such a cell. The configuration III is actually observed inside closed surface disclination loops ( $\varphi$ -lines) such as the one given in figure 8. If one point inside the loop is observed in convergent polarized light, the conoscopic pattern obtained is that given in figure 9. The centre of the bright circles may be either on the left or on the right of the observation field depending on the sign of the rotation of  $n$  (left or right twist). Inside the loop, a region where the rotation is left is separated from a right-twisted region by a bulk  $\pm 1$  disclination line such as the line AB in figure 8.

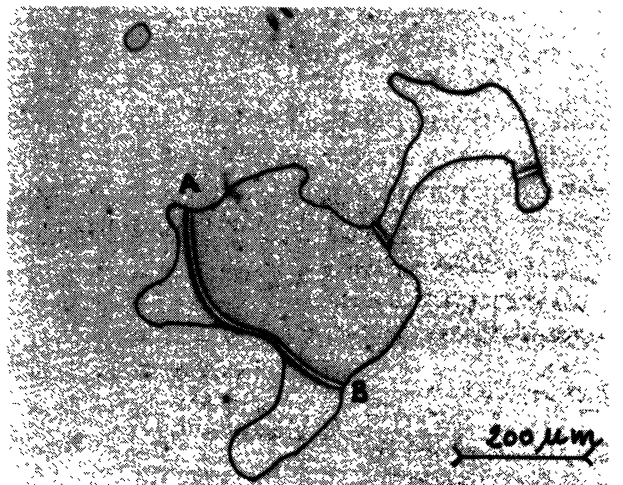
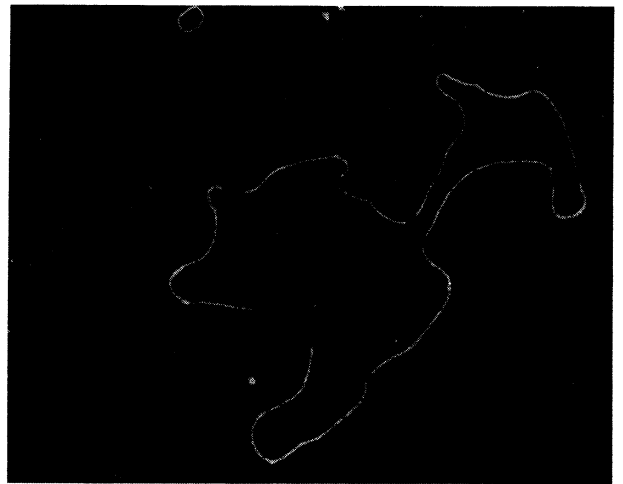


FIG. 8. — A  $\varphi$ -line loop enclosing a region where the configuration is III.

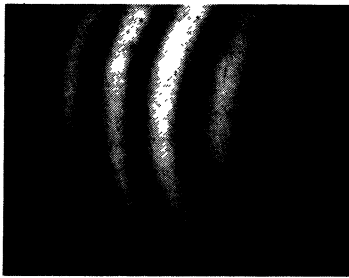


FIG. 9. — Conoscopic pattern corresponding to configuration III.

Some observations have also been performed when the surfaces induce a small tilt angle (glass treated with nonylamine :  $\theta_0 \simeq 20^\circ$ ). As predicted for such cases, configuration III is no longer observed. The conoscopic pattern is given in figure 10. Symmetry considerations (ref. [2]) show that it indeed corresponds to III'.

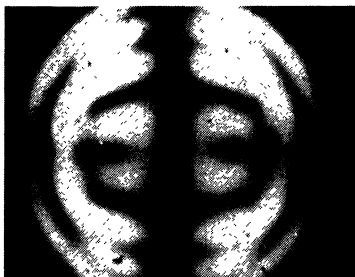


FIG. 10. — Conoscopic pattern corresponding to configuration III'.

One can observe that the observed conoscopic figure in case of configuration III allows one to determine physically whether the overall twist is right or left ; while this distinction is impossible in the case of III'. III then appears as the ordered state and III' as the disordered one.  $\theta_m$  may thus be considered as the order parameter  $\xi$  with the following convention :

$$\begin{aligned} \xi &= \theta_m && \text{for right twist III} \\ \xi &= \theta_m = 0 && \text{for III'} \\ \xi &= -\theta_m && \text{for left twist III.} \end{aligned}$$

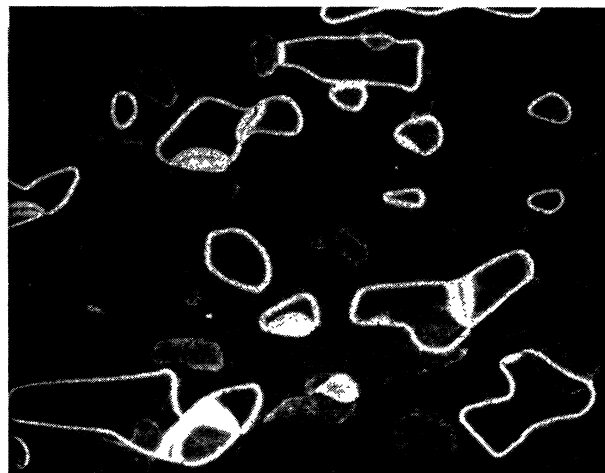
Furthermore it is rather significant that in figure 8, III configurations of opposite twist are separated by an integral disclination line.

From the work of the Orsay group [4], it is known that such lines in NLC media are not singular : the director vector in the core lies parallel to the remaining direction (here the direction normal to the surfaces) and in this manner avoids the expected discontinuity.

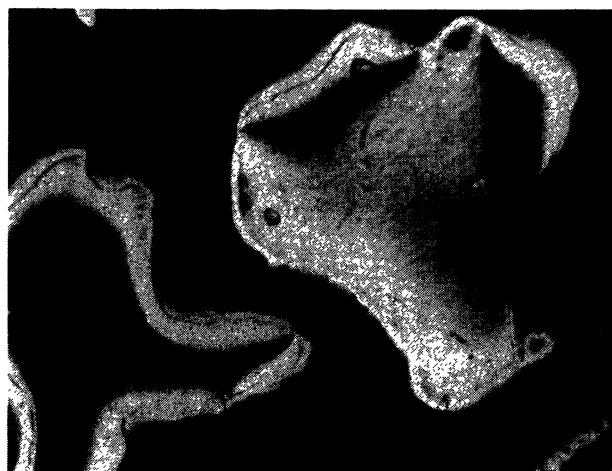
Thus at the centre of such a line  $\theta_m$  is equal to zero. Across the interface (i.e. the line) which separates the two ordered states of opposite sign, the order parameter continuously increases (or decreases) through the value  $\xi = 0$ . The optical width of this

line therefore corresponds to the fluctuation length and is expected to increase and diverge when the boundary conditions  $(\theta_0, \varphi_0)$  approach the transition conditions  $(\theta_{0K}, \pi/2)$ . This condition is not so easy to obtain experimentally : the technique of alignment by short-chained surfactants (ref. [2]) yields a discrete series of tilt angles  $\theta_0$  depending on the number  $n$  of  $\text{CH}_2$ -groups in the chain. None of the tilt angles of the series is near enough to  $\theta_{0K}$  to yield an unambiguous confirmation of the transition : when  $n = 7$  the configuration is definitely (III) while for  $n = 8$  it is definitely (III'). However we approached  $\theta_{0K}$  (MBBA) with the aid of octylamine dissolved in very weak concentrations in nitromethane. With such concentrations the tilt angle obtained depends sharply on the temperature during adsorption. The patterns obtained in figure 11a-b are the result of good luck rather than of reproducible experimental conditions.

In figure 11a inside the small closed  $\varphi$  line loops, left twisted and right twisted (III) configurations are still stable. But the integral bulk lines which separate them appear drastically widened compared to the one which is seen in figure 8. This sharp increase of



a)



b)

FIG. 11a), b). — Experimental observations of the transition.

the fluctuation length indicates that  $\theta_0$  is larger than, but rather close to,  $\theta_{0K}$ .

In figure 11b,  $\theta_0$  is still closer to  $\theta_{0K}$  : (III) is no longer stable while (III') is not yet stable either ; and some kind of critical opalescence fills the whole  $\varphi$ -line loop. This feature confirms the second-order character of the transformation.

6. **The general case.** — As long as  $K_{11}$  is equal to  $K_{33}$ , the integration of equation (20) through elliptic integrals remains possible whatever the relative values of  $K_{22}$  and  $K_{33}$  are. However the calculations are difficult and tedious and we briefly indicate the main results.

The interesting range for  $K_{22}$  where the transition can occur is :

$$0 \leq K_{22} \leq K_{33} . \quad (50)$$

In the close vicinity of  $\theta_m = 0$ ,  $\varphi(\theta_0, \theta_m)$  can be approximated by the Taylor expansion :

$$\begin{aligned} \varphi(\theta_0, \theta_m) = & \frac{\pi}{2} + \frac{\theta_m}{\sqrt{t(t+1)}} \left( \frac{\pi}{2} - \Phi_0 - t \operatorname{tg} \Phi_0 \right) \\ & + \theta_m^2 \cdot \frac{\pi}{4t} \cdot \frac{t-1}{t+1} + o(\theta_m^2) \end{aligned} \quad (51)$$

where  $t$  stands for :

$$t = \frac{K_{22}}{K_{33} - K_{22}} \quad (52)$$

and  $\Phi_0$  is related to  $\theta_0$  and  $\theta_m$  by :

$$\cos^2 \theta_0 = \frac{\cos^2 \theta_m \sin \Phi_0}{2 - \sin^2 \Phi_0} . \quad (53)$$

From (51), it is possible to derive the main pieces of information about the transition :

— as in the preceding cases, it may occur only if  $2\varphi_0 = \pi$  ;

— here again, the slope of  $\varphi(\theta_0, \theta_m)|_{\theta_m=0}$  is a strictly increasing function of  $\theta_0$ . The value of  $\theta_k$  is now given by the equation :

$$\frac{\pi}{2} - \Phi_0 - t \operatorname{tg} \Phi_0 = 0 \quad (54)$$

it may be shown that, whatever the value of  $t$ , this equation always has a solution  $\theta_{0K}$  which lies in the range :

$$\frac{\pi}{4} \leq \theta_{0K} < \theta_n \leq \frac{\pi}{2} .$$

— However, paying attention to the sign of the second derivative of  $\varphi(\theta_0, \theta_m)$ , one can show that the value of  $t$  may also affect the order of the transition :

$$\left. \frac{\partial^2 \varphi(\theta_0, \theta_m)}{\partial \theta_m^2} \right|_{\theta_m=0} = \frac{\pi}{4t} \cdot \frac{t-1}{t+1} \quad (55)$$

does not depend on  $\theta_0$  but only on  $t$ . Clearly as long as  $t$  is such that  $t < 1$ , this derivative is negative : the same discussion as in the ideal case remains valid ; the transition occurs when  $\theta_0$  is equal to  $\theta_{0K}$  and it is of second order.

In the opposite case where  $t > 1$ , this derivative is positive and the concavity of the curve  $\varphi(\theta_0, \theta_m)$  points upward. Then, as shown in figure 12, there exists a certain range for  $\theta < \theta_{0K}$  such that the curve intersects the straight horizontal line  $\varphi = \varphi_0$  for three values of  $\theta_m$  i.e. :

$$\begin{aligned} \theta_m &= \theta \\ \theta_m &= \theta_{m_1} \\ \theta_m &= \theta_{m_2} . \end{aligned}$$

One must consider  $W_{el}(\theta_m)$  to determine which of these values of  $\theta_m$  are maxima or minima of this elastic energy. Since  $\varphi(\theta_0, \theta_m)$  increases when  $\theta_m = \theta_{m_1}$ , this value leads to a maximum, while  $\theta_m = 0$  and  $\theta_m = \theta_{m_2}$  lead to minima for  $W_{el}(\theta_m)$ . One may derive the energy diagram of figure 12b, which is typical of a transition of first order : while  $\theta_0$  decreases there exists a value  $\theta_{0c} < \theta_{0K}$  where the equilibrium value of  $\theta_m$  abruptly falls down from  $\theta_{m_2}$  to zero.

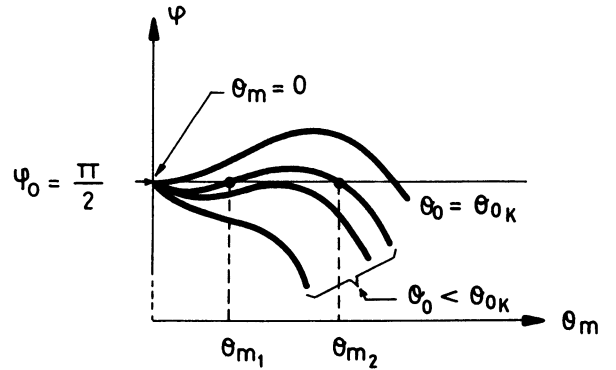


FIG. 12a). — Illustration of the three intersection points  $\theta_m = 0$ ,  $\theta_m = \theta_{m_1}$ ,  $\theta_m = \theta_{m_2}$  when  $t > 1$ .

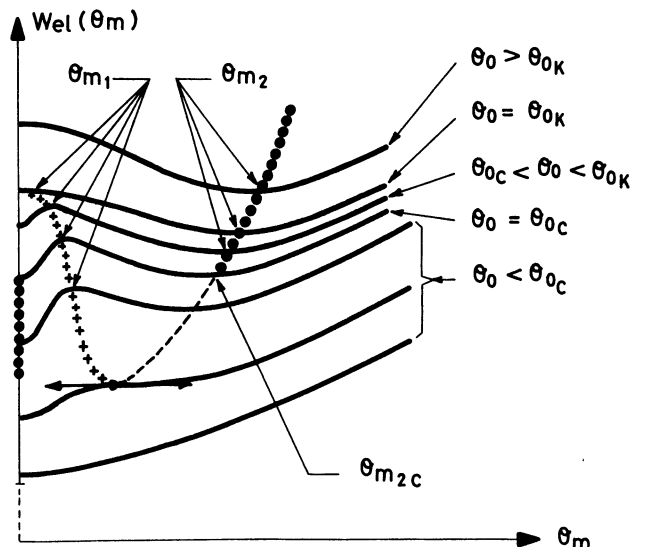


FIG. 12b). — Corresponding energy diagram.

If now  $K_{11}$  is allowed to be different from  $K_{33}$  the same discussion as in a former section is again valid. It is known that this affects the value of  $\theta_{0\kappa}$  but leaves  $\varphi_{0\kappa} (= \pi/2)$  and the concavity of  $\varphi(\theta_0, \theta_m) |_{\theta_m=0}$  unchanged.

Thus the order of the transition depends only on the relative values of  $2K_{22}$  and  $K_{33}$ .

And, with the set of elastic constants given above [5, 6], MBBA just stands at the boundary between the range where the transition is of second order and the range where it becomes of first order. Then, although our experiments actually confirm a second-order transition (or at most weakly first-order), this material is not well suited to prove the results of this last section. Since relation (55) indicates that the concavity of  $\varphi(\theta_0, \theta_m) |_{\theta_m=0}$  reaches its maximum value when  $t = 2.4$ , one may expect clearer evidence of a first-order transition with a material for which  $K_{33} = 1.42 K_{22}$ . However two difficulties arise for such a confirmation : first, measurements of the elastic constants have been given in the literature for a small number of materials only. And, should the required material be available, the possible occurrence of tilted orientations at the surface must first be examined.

**7. Conclusion.** — The aim of this work was to determine the conditions  $(\theta_0, \varphi_0)$  required for a twisted orientation pattern such as (III) to spontaneously transform into a wedge conformation such as (III').

Although a complete exact calculation in the general case was not possible, important information was derived from the discussions :

— Whatever the values of  $K_{11}$ ,  $K_{22}$  and  $K_{33}$  are, this transformation may occur only if the overall twist  $2\varphi_0$  is equal to  $\pi$ . And it has the characteristic features of a phase transition for which the order parameter is  $\theta_m$ , the tilt angle at the centre of the gap.

— This transition may be either of first or of second order depending on the relative values of  $K_{22}$  and  $K_{33}$  (i.e. : on twist and bend Frank-Oseen constants only).

— However the critical value  $\theta_{0c}$  of the surface tilt angle depends on all three elastic constants  $K_{11}$ ,  $K_{22}$  and  $K_{33}$ .

As presented here, this transition has a somewhat unclassical feature : it appears to be induced through the variations of geometrical parameters rather than through those of some intensive thermodynamical quantity (such as temperature, electromagnetic field, force...). It is possible to go back to a more classical description, since the prescription of the orientation of the optic axis at the solid surface is somewhat

unrealistic, and should be replaced by the introduction of a surface energy as proposed by Leslie, Papoular and Rapini [1, 7]. This essentially gives rise to a couple stress condition at the interface, and the critical values of  $\theta_0$  and  $\varphi_0$  obtained appear as the consequence of a critical couple stress at the surface.

However, although this configuration transformation shares many common features with phase transitions, it does not involve the main role of entropy, and the analogy (used throughout this report) stays rather formal just as in the classical Fredericks transition.

One other point needs to be discussed further : from the early works of Mauguin it is commonly assumed that the total rotation in a twisted conformation may not exceed  $\pi/2$ . The explanation which is given for such an assumption is that, in the case of total rotations bigger than  $\pi/2$ , the liquid crystal may relax by an integral multiple of  $\pi$  to a state of lower free energy.

However, observations of overall twists as big as  $\pi$  have been reported [8] inside certain surface disclination loops. The present work is also concerned with experimentally observed overall twists of  $\pi$ . The discrepancy between these observations and the former common sense interpretation may be removed by the following remark : in the case of an overall rotation lying in the range  $[\pi/2, \pi]$  the relaxation of the nematic medium requires the nucleation of a  $\pm 1/2$  bulk disclination line. From the works of the Orsay group [4] it is known that such lines are singular and impose high local distortion on the nematic material. For these reasons (topological barrier and high energy gap) such conformations may last indefinitely as metastable states.

On the other hand, as noted in a former section, when the overall twist exceeds  $\pi$ , a relaxation of the nematic medium is possible through the nucleation of a  $\pm 1$  bulk line. Compared to the former, these lines are not singular (no topological barrier) and impose small distortions on the material (low energy gap). This relaxation is therefore very easy to initiate and thus very likely to occur.

Finally, we remark that a striking feature of our transition is that a necessary condition for its occurrence is a  $\pi$  overall twist whatever  $K_{11}$ ,  $K_{22}$  and  $K_{33}$  are (i.e. whatever the nematic material is). However we failed to deduce this invariant feature as a direct consequence of the particular shape of the elastic energy of nematic media.

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