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Biaxial Nematics

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The biaxial nematic phases are completely anisotropic liquids which present translational disorder like the ordinary liquids, but with the molecules statistically oriented along the three directions of space. They appear to be the generalisation of the uniaxial nematics, and may be understood as having a second (and then a third) director, the three directors being perpendicular to one another.

The biaxial nematics have been experimentally discovered only recently in lyotropic mixtures (Saupe, 1980), and in thermotropic and polymer compounds (1986). They thus have been the subject of few theoretical and experimental studies. However we can mention some interesting physical properties already evidenced:

—The disclination lines in the biaxial nematics are observed to make spontaneous zig-zags with a definite angle. (The explanation is that the order on the defect lines is lowered to the uniaxial order, making the lines to bear a director which couples to the biaxial bulk, and orients to a preferred angle if referred to it).
—The phase transition between the uniaxial and biaxial nematic phases is second order (because this transition may be reduced to the 2D-plane perpendicular to the uniaxial director). This allows in principle, one to approach the phase transition as close as possible. Different experimental means, like light scattering and light interferences, have been employed to study this particular transition.
—Dissolving a small amount of a chiral compound in a biaxial nematic has led one to obtain the biaxial cholesteric phase. This phase presents only one cholesteric pitch, with its cholesteric axis along a director while the other chiral axes remain frustrated.
—Indirect informations on the shape of the micelles and the structures they build, have been obtained in the lyotropic nematic phases by means of high resolution X-ray measurements associated to light scattering experiments.

These short insights give some ideas on the physical properties of the biaxial nematic phase. They also show that this domain of the Liquid Crystals is not closed yet, and that progresses are expected for the next years.

I. INTRODUCTION

In contrast to the nematic liquid crystals which have been first observed a long time ago, the biaxial nematic phase is a quite recent

discovery. Indeed, the biaxial nematic phase (N_b) has only been predicted in 1970 by Freiser[1] in a generalization of the Maier-Saupe theory of the nematic state.[2] It has then effectively been observed in 1980 by Yu and Saupe in the lyotropic mixtures.[3] The N_b phase may be defined as a completely anisotropic liquid, exhibiting translational disorder like ordinary liquids, but with the elementary objects statistically oriented along the three directions of space. The N_b phase thus have three directors, perpendicular to one another, instead of one in the classical uniaxial nematics (N_u). It is therefore a more ordered phase than the N_u phases which, in that sense, it appears to generalize. Since the N_b phase has been discovered, the subject has performed consistent progresses in both the theoretical and experimental areas which are shortly presented in the following sections II and III, respectively.

II. THEORIES OF THE BIAXIAL NEMATIC PHASE

1. Microscopical theories

Before the N_b phase has experimentally been discovered, its possible existence has been theoretically investigated for a system of hard rectangular plates using lattice models,[4] Landau approaches,[5] and Maier-Saupe treatments.[6] These different studies reached about the same conclusions that the N_b phase should exist as an intermediate phase between two N_u phases of opposite signs, the rodlike (N_c) and platelike (N_d) nematics. They also predict the N_u—N_b phase transitions to be second order along critical lines which cross in a sharp cusp, at the first-order boundary of the isotropic phase (I) (Figure 1).

However, the synthesis of molecules which are rectangular enough to produce the N_b phase, is not an easy task, and the subject did not progress for years in this direction. The reflections then moved towards apparently more available systems made of mixtures of rodlike and platelike molecules, using different theoretical methods. Mean field lattice models have been applied to this problem leading to various investigations, e.g.: Flory-type calculations[7] by Alben,[8] a Potts-Ising approach by Caflisch et al[9] and a Van der Waals-type treatment by Chen and Deutch.[10] Furthermore, extensions of the Onsager theory[11] to solutions of rodlike and disklike particles have been developed by Rabin et al,[12] and by Stroobants and Lekkerkerker.[13] All these studies lead to the same conclusion that mixtures of rods and plates should

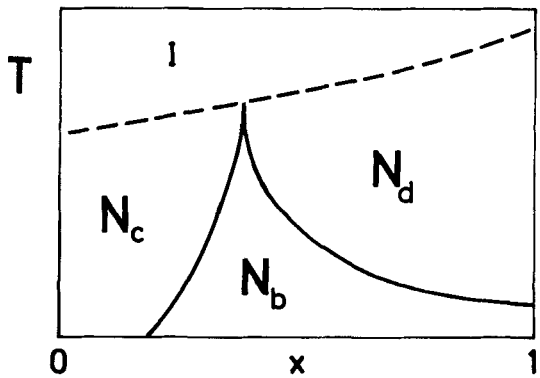

FIGURE 1 Phase diagram of the uniaxial (calamitic, N_c and discotic, N_d) and biaxial (N_b) nematic phases as predicted by the microscopical theories. In the case of systems of hard rectangular plates, the parameter x is the shape anisotropy of the elementary units (i.e. the width to length ratio of the rectangles). In the case of mixtures of rodlike and disklike particles, x is the relative concentration of the disklike particles. The first-order transition to the isotropic phase is marked as a dashed line. The second order N_u—N_b phase transitions are represented with solid lines.

produce the N_b phase, with about the same phase diagram as already proposed on the basis of a single species of biaxially shaped molecules. The major change is the replacement of the intrinsic biaxiality of the molecules by the relative concentration of the plates (or the rods) as the pertinent parameter in the phase diagram (Figure 1). However, following an interesting remark by Palffy-Muhoray *et al.*,[14] the N_b phase could not be formed with mixtures of rods and plates, because it is thermodynamically unstable if compared to uniaxial phase separation. This conclusion is reached under the reasonable assumption of average interactions between the rods and the plates. It could explain why the experimentalists did not succeed to observe the N_b phase by mixing elongated with disk-like molecules.

2. Macroscopical theories

The macroscopical theories describe the nematic phases in terms of the continuous field of the order parameter. Following Saupe[15] and de Gennes,[16] the order parameter of the nematic phases may be defined as the average tensor

$$S^{ij}_{\alpha\beta} = \frac{1}{2}\langle 3\, i_\alpha j_\beta - \delta_{ij}\, \delta_{\alpha\beta}\rangle,$$

where $\mathbf{i}, \mathbf{j} = \mathbf{X}, \mathbf{Y}, \mathbf{Z}$ are orthogonal unit vectors linked to the elementary object (molecule or micelle) of the nematic phase, while $\alpha,\beta = x,y,z$, refer to the laboratory frame axes. As shown by Priest and Lubensky[17] and Straley,[6] the tensorial order parameter $S^{ij}_{\alpha\beta}$ depends only on the average quantities:

$$S = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle,$$

$$T = \langle \sin^2\theta \cos 2\varphi\rangle,$$

$$U = \langle \sin^2\theta \cos 2\psi\rangle,$$

$$V = \frac{1}{2}\langle (1 + \cos^2\theta)\cos 2\varphi \cos 2\psi\rangle,$$

where θ,φ,ψ are the Euler angles of the molecular frame $\{\mathbf{X}, \mathbf{Y}, \mathbf{Z}\}$ relative to the laboratory frame. In systems composed of uniaxial objects, only S can be non zero. The local environment is then uniaxial. For systems of biaxial objects, *i.e.* having the symmetry of rectangular parallelopipeds, nonzero values of S or/and U (with $T = V = 0$) indicate uniaxial nematic phases, while, if moreover T or V (or both of them) are non zero, the nematic phases are biaxial. The different combinations of the independent components of the order parameter $S^{ij}_{\alpha\beta}$ could thus correspond to different N_u and N_b phases, with phase transitions between them.[18]

For most purposes however, it is reasonable to assume, without too much loss of generality, that the angle ψ is equally distributed. Then $U = V = 0$, and the order parameter reduces to the second-rank tensor $Q_{\alpha\beta} = S^{XX}_{\alpha\beta}$ (when taking the local axes $\mathbf{X}, \mathbf{Y}, \mathbf{Z}$, along the symmetry axes of the elementary object). $Q_{\alpha\beta}$ is convenient to describe most of the physical properties of the N_b phase. In particular, the coupling energy to external fields like the magnetic field H, may be written as:[16]

$$F = \frac{1}{2}\chi_0 Q_{\alpha\beta} H_\alpha H_\beta, \tag{1}$$

where χ_0 is a susceptibility coefficient independent of the nematic order $\sim 3\ 10^{-9}$ cgs[56] (with a positive or negative sign depending on the choice of the axes, see also § III.4.a). For symmetry reasons, $Q_{\alpha\beta}$

is diagonal in the laboratory frame of the symmetry axes of the N_b phase. Its elements depend only on the scalar order parameters, S the usual scalar order parameter of the uniaxial nematics, and T the scalar order parameter specific to the N_b phase:

$$Q_{xx} = -\frac{1}{2}(S - T);\ Q_{yy} = -\frac{1}{2}(S + T);\ Q_{zz} = S.$$

Various methods have been employed to derive the elastic energy density of the N_b phase.[19–25] It may be expended in terms of the gradients of $Q_{\alpha\beta}$ as:[25]

$$f = K_{\alpha\beta\gamma}\,\partial_\alpha Q_{\beta\gamma} + K_{\alpha\beta\gamma\mu\nu\rho}\,[\partial_\alpha Q_{\beta\gamma}][\partial_\mu Q_{\nu\rho}] + K_{\alpha\beta\gamma\mu}\,\partial_\alpha\partial_\beta Q_{\gamma\mu}, \quad (2)$$

where $K_{\alpha\beta\gamma}$, $K_{\alpha\beta\gamma\mu\nu\rho}$, $K_{\alpha\beta\gamma\mu}$ are elastic tensors characteristic of the biaxial (possibly chiral) nematic. Considering now that the degree of ordering is unaffected throughout all the medium, *i.e.* that S and T are constant, the expression (2) may be transformed to the generalized Frank elastic energy of the nematics, including the case of chiral biaxial nematics.[26] There are now 12 bulk elastic constants, 3 surface elastic constants and 3 chiral constants to describe the N_b phases, instead of respectively 3 bulk electric constants, 1 surface term and 1 cholesteric constant for the uniaxial phases. It is to be noticed that, though the three chiral distortions cannot simultaneously occur on large scales (because rotations of different axes do not commute)[27] their elastic contributions have nevertheless all to be considered in the total free energy of the chiral N_b phase, at least to determine which will be the effective cholesteric axis among the three possible ones.[28] Such an ambiguity does not exist in the chiral N_u phases where the cholesteric axis is, for symmetry reasons, perpendicular to the director.

The fluid dynamics of biaxial nematics have been examined in the details by several authors.[19–20,22–23,29] A rather clear presentation[29] starts with the Rayleigh's dissipation function written in terms of all the possible independent invariants which can be constructed from $Q_{\alpha\beta}$, $\partial_t Q_{\alpha\beta}$, $\partial_\alpha v_\beta$, $\delta_{\alpha\beta}$, where v_α denotes the velocity field and $\delta_{\alpha\beta}$ the Kronecker tensor. The analysis leads to 12 independent viscosity coefficients for the incompressible N_b phase. These 12 coefficients may be distinguished using the Harvard formulation,[16] into 9 proper viscosity coefficients and 3 reactive parameters. They generalize the hydrodynamics of the N_u phase which is described with 5 independent

viscosity coefficients: 4 proper viscosities and 1 reactive parameter. The reactive parameters are coupling coefficients between the velocity gradients and the torques exerted on the N_b phase. They determine the orientation of the directors at equilibrium in a stationary shear flow, without implying energy dissipation by themselves.[30]

In the vicinity of the N_u—N_b phase transition, it is often sufficient to use a reduced order parameter $\zeta_{\alpha\beta}$, specific to the N_b phase, and obtained from the traceless projection of the order parameter $Q_{\alpha\beta}$ in the plane perpendicular to the uniaxial nematic director $\mathbf{n}$.[31] Such a possibility results from the analogy of the N_u—N_b phase transition with the isotropic to nematic phase transition in two dimensions. It expresses that the biaxial orientational order in the 2D-plane perpendicular to the uniaxial director $\mathbf{n}$, is isotropic-like in the N_u phase, and nematic-like in the N_b phase. The eigen-values of $\zeta_{\alpha\beta}$, ζ and $-\zeta$, may be considered as the two scalar biaxial order parameters associated respectively to the biaxial directors $\mathbf{m}$ and $\mathbf{l}$ (Figure 2). They describe the same physical state, *i.e.* they are equivalent, though they have opposite signs. The biaxial free energy is therefore an even function of the biaxial order parameter ζ. Following Landau theory, this indicates that the N_u—N_b phase transition may be second-order.[32] The 2D analogy of the N_u—N_b phase transition moreover allows Jacobsen and Swift[31] to extend the de Gennes analysis[33] of the isotropic-nematic phase transition to the N_u—N_b phase transition, and to predict the behavior of the pretransitional biaxial modes. However, this simplified and fruitful approach neglects couplings between the biaxial and birefringent modes which could sometimes lead to appreciable errors.[32] It also seems to make appear a new elastic term in the free energy, which cross-couples the gradients of the uniaxial

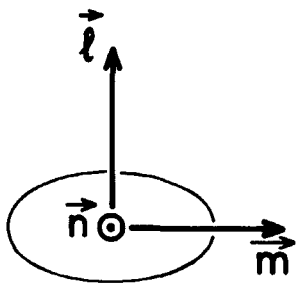

FIGURE 2 The reduced order parameter $\zeta_{\alpha\beta}$ (considered in the vicinity of the N_u—N_b phase transition) may be represented by an ellipsis in the plane perpendicular to the uniaxial director $\mathbf{n}$. Depending on the choice of the biaxial director $\mathbf{n}$ or $\mathbf{l}$, the biaxial order parameter (represented by the corresponding axis of the ellipsis) is ζ or $-\zeta$.

director **n** to the gradients of $\zeta_{\alpha\beta}$.[34] This interesting elastic term is in fact, already present in the $K_{\alpha\beta\gamma\mu\nu\rho}$-terms of Equation (2). As explicitly noticed by Saupe,[22] it has no analogue in the uniaxial nematics. An interesting consequence of these cross-coupling terms is the deviations that they produce on the critical exponents of the N_u—N_b phase transition from those calculated with the three-dimensional XY-model. However, close enough to the transition, these coupling terms become irrelevant and the critical exponents join again the exponents of the XY-model.[35] So, as shown by Cajas *et al.*,[36] the static critical behaviour of the N_u—N_b phase transition is predicted to be isomorphic to the λ-transition in superfluid ^{4}He. On the opposite, the critical dynamics, which is a much more intricate problem, should not follow the XY-model.[36]

III. EXPERIMENTAL RESULTS

1. Evidence of the biaxial nematic phase

In 1980, Yu and Saupe[3] give the first experimental evidence of the N_b phase in lyotropic mixtures of potassium laurate (KL), or of sodiumdecylsulfate (SdS) with 1-decanol (DeOH) and D_2O. By means of conoscopic observations and NMR-measurements, they determine the temperature-concentration phase diagrams of these systems. They show that the N_b phase is comprised between the two N_c and N_d uniaxial phases, and that it joins the isotropic phase in a quadruple point topologically equivalent to the theoretical prediction of Figure 1. However, the experimental system presents a more complicated behavior with reentrant N_b and N_c phases.[3] Birefringence measurements repeated later on in the SdS-system, confirm the existence of the N_b phase.[37]

In the same period, Yaniv *et al.*[38] find with NMR experiments, the biaxial nature of the cholesteric phase in thermotropics. The cholesteric phase which is in fact the twisted form of the uniaxial nematic phase, is thus shown to be locally equivalent to the N_b phase. This property of biaxiality arises because the cholesteric axis introduces some difference between the directions perpendicular to the director. The molecular model developed by Lin-Liu *et al.*[39] explains qualitatively well such a biaxial behavior though the amplitude of the effect is not completely understood yet.

These two examples of biaxiality in nematics are naturally not the only biaxial phases encountered in liquid crystals. Let us just mention that the smectic C phases, because of their tilted smectic layers, have

a monoclinic symmetry and thus are biaxial.[40] Similarly, the columnar discotics observed by Sigaud et al,[41] which exhibit two orthogonal broken translational symmetries, seem also to be biaxial.[20]

2. Uniaxial to Biaxial nematic phase transitions

a. Static properties. Experiments have been developed in order first to confirm the existence of the N_b phase, and then to determine the general features of the N_u—N_b phase transitions. Magnetic resonance splittings and optical birefringence measurements have been performed in this way as functions of temperature, and compared to Landau theory.[42] In principle, both the NMR and birefringence measurements yield the correct biaxial order parameter in the vicinity of the nematic transitions, provided that they involve linear physics only. (This condition of linearity is required from the definition of the order parameter as an average tensor (§ II.2)). Because of the large mutual interactions between the induced electric dipoles (which give non-negligible contributions of non-linear order), the optical susceptibility tensor, calculated from the optical indices, does not generally fulfill the linearity conditions. For this reason, in thermotropic liquid crystals, the optical susceptibility is rejected as the order parameter, in profit of the magnetic susceptibility tensor.[16] The case of lyotropics is different because of their very low birefringence ($\sim$ a few 10^{-3}). The anisotropic parts of the induced electric dipoles then do not interact much, and their non-linear contributions may be neglected as in the magnetic interactions. This allows the electrical susceptibility measured at optical frequencies, to be a good candidate as the phenomenological order parameter of the lyotropic nematic phases. In this context, a lot of experiments have been devoted to the measurements of the optical indices in the N_c, N_d and N_b phases of the LK and SdS lyotropic mixtures.[42–44]

Conoscopic experiments have been realized on thick N_b samples (up to 2.5 mm) which were properly oriented by means of a strong magnetic field associated to small oscillations about its average position. They show almost perfect interference patterns, *i.e.* with a good contrast everywhere.[43] Such a quality ensures that the splitting of the conoscopic cross does not result from distortions of the N_u phase, and therefore that biaxiality is real. It may also be argued that the measured biaxiality does not correspond to a coexistence region between the N_c and N_d phases because this would produce smoothings in the measurements of the optical indices versus temperature which are not observed.[43] The index measurements moreover show that the

N_u—N_b phase transitions are second-order following the theoretical predictions (§ II.1), and present a mean-field behaviour[42] clearly evidenced on the linear variations of the invariants of the order parameter, $Q_{\alpha\beta}Q_{\alpha\beta}$ and $Q_{\alpha\beta}\ Q_{\beta\gamma}\ Q_{\gamma\alpha}$,[43] as functions of temperature. However, closer from transition than 30 mK, a Ginzburg crossover to a critical XY-regime is experimentally observed.[44]

The mean-field behaviour of the N_u—N_b phase transitions have indirect consequences. It introduces for instance, correlations between the optical birefringence and the temperature range of the N_b phase.[45] Such a particular property may be explained with the natural idea that the N_b phase is favored by an increase of the order parameter. Practically, this correlation provides a guide for preparing samples of the desired biaxial temperature range.[46]

b. Dynamic properties. The dynamic properties of the nematic phases have experimentally been investigated first by measurements of light transmission versus temperature near the N_u—N_b phase transitions.[47-48] These measurements integrate the contributions of all the modes of the thermodynamically excited fluctuations of the order parameter $Q_{\alpha\beta}$ in the sample. On approaching near to the N_u—N_b phase transitions, the biaxial modes exhibit diverging amplitudes[31-32] which strongly scatter depolarized light and thus reduce light transmission.[48] A more detailed study of the fluctuation modes of the order parameter has then been performed by means of the Rayleigh-scattering technique in the three nematic N_d, N_c and N_b phases.[49-50] Because the N_u—N_b phase transitions are second-order, it is possible to follow the behavior of the pretransitional modes as close to the transition as desired. (Let us notice that this is not the case at the 3D-analogous nematic-isotropic transition which is first order). Using light-beating spectroscopy, Lacerda *et al.*[49-50] thus observe the critical slowing-down of the two pretransitional relaxation modes of the amplitude and of the orientation of the order parameter. In Figure 3 are sketched the temperature variations of the relaxation frequency $1/\tau$ of the biaxial bend mode (orientational fluctuations) that have been measured on recording the depolarized light. This result is consistent with Landau theory which predicts that in the N_b phase, the relaxation frequency of the biaxial bend mode is proportional to the temperature distance to the transition[32] ($1/\tau \propto \Delta T$), while in the N_u phase:

$$\frac{1}{\tau} = \frac{a + K q^2}{\nu}, \tag{3}$$

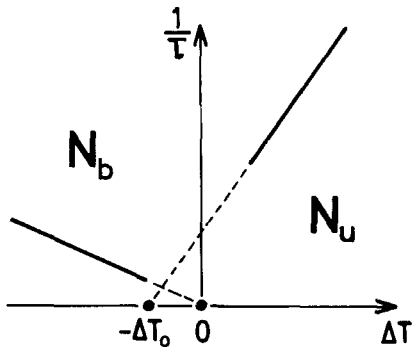

FIGURE 3 Temperature variations of the relaxation frequency $1/\tau$ of the biaxial bend mode of q wave-vector according to Landau theory (heavy lines), in the N_b and N_u phases. Their extrapolations to zero frequency respectively yield the transition temperature and $-\Delta T_o$. This construction thus gives a simple evaluation of the bare correlation length ξ_0.

In this expression, q is the wave-vector of the measured mode, K and ν are the average elastic and viscosity constants relative to the order parameter, and $a = \alpha \Delta T$ is a Landau coefficient which vanishes at the considered N_u—N_b phase transition. From expression (3), one may define the correlation length ξ of the order parameter in the N_u phase by:

$$\xi = \sqrt{\frac{K}{a}} = \xi_0 \left(\frac{\Delta T}{T_c}\right)^{-1/2}$$

where $\xi_0 = \sqrt{\dfrac{K}{\alpha T_c}}$ is the bare correlation length. Denoting ΔT_o, the temperature for which $q\xi = 1$, one has also:

$$\xi_0 = \frac{1}{q}\left(\frac{\Delta T_o}{T_c}\right)^{1/2} \tag{4}$$

This expression allows direct determination of ξ_0 from the measurements sketched in Figure 3 where $-\Delta T_o$ may readily be read from the extrapolation of the orientational (or off-diagonal) mode in the N_u phase to zero frequency. (It is just an extrapolation because on this temperature range, the Landau theory is no more valid).[32] From the Figure 5 in Reference 50, one thus finds that $\xi_0 \sim 200$–400 Å, depending on the measurements. This result is different from the one

announced in Reference 50 probably because of a wrong choice of the transition temperature T_c.

3. Microscopic structure

From X-ray[51] and neutron[52] diffraction measurements, the lyotropic N_c and N_d phases have been first analyzed to be respectively made of rodlike and disklike micellar aggregates dispersed in water. Within this scheme, the N_b phase has been imagined to be a mixture of both types of micelles. Except maybe the hydrodynamic experiments suggested by Pleiner and Brand[53] (for measuring the coupling constant between the directors of the disklike and rodlike micelles), most of the macroscopic experiments give integrated results which cannot learn about the microscopic structure of the lyotropic N_b phase. In particular, they cannot directly answer to the question whether the N_b phase is made of only one kind of biaxial micelles or made of a mixture of rodlike and disklike micelles. They however provide sometimes very interesting indications. For instance, the light scattering experiments are able to show that the correlation length ξ, concerning the biaxial order, is always much larger (§ III.2.b) than the micellar size ($\sim$ 50 Å). This result indicates that the second-order N_u—N_b phase transitions are never encountered at the microscopical scale of the micelles,[54] and therefore, that the micellar aggregates cannot suddenly change their shape at the N_u—N_b phase transitions. In this view, the different nematic phases are just the macroscopic consequence of different orientational fluctuations of almost invariant micelles. The orientational fluctuations thus give rise to the N_u phases when they are full rotations around the director, and they generate the N_b phase when they are restricted to small amplitude oscillations. This simple view is corroborated by X-ray diffraction measurements which prove the same pseudo-lamellar ordering in the three neighbouring nematic phases of the KL-mixtures.[54] A more detailed analysis of the X-ray diffraction patterns indicates that the micelles may reasonably well be sketched as biaxial platelets (Figure 4) of typical dimensions:[55] 85 Å, 55 Å, 26 Å. (Let us notice that this estimate is consistent with the conductivity measurements by Photinos *et al.*[56] in the N_c and N_d phases of the KL-mixtures when analyzed with the assumption that the uniaxial order parameters S = 0.6).

Naturally, the micellar dimensions slowly change with the temperature and concentrations. These continuous changes could consequently trigger the different nematic and isotropic phase transitions of the phase diagram (Figure 1) with a similar mechanism as proposed

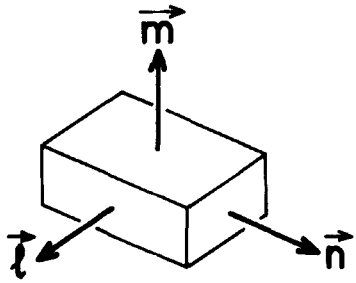

FIGURE 4 Schematic micellar aggregate. The micelles are approximately placed parallel to one another. Full cooperative rotations of the micelles around the directors **m** or **n** respectively yield the N_d or N_c phases. Small amplitude oscillations keep the N_b phase.

for the N_d—I phase transition.[57] However, these changes of the micellar sizes are negligible close enough to the second order N_u—N_b phase transitions. Therefore, it seems reasonable, contrary to the opinion of Boden *et al.*,[58] to neglect the influence of the micellar changes when calculating the order parameter from the optical birefringence measurements in the vicinity of the N_u—N_b phase transitions (§ III.2.a). In this case, the order parameter calculated from the birefringence measurements should be proportional and equivalent to the order parameter directly obtained from X-ray measurements.

Direct experimental evidences of the local biaxiality in the N_u phases of the KL-mixtures nearby the N_b phase have been obtained by means of neutron scattering with contrast variations.[59] These experiments confirm the information originally obtained from the light scattering measurements. It is to be noticed that the same local structure seems also to extend to the isotropic phase of the KL-mixtures as shown with magnetically-induced birefringence measurements,[60] and X-ray scattering analysis.[57]

4. Recent aspects of the N_b phase

a. Biaxial cholesteric phase. The addition of some amounts of a chiral agent *e.g.* brucine sulfate heptahydrate (BS), to the lyotropic SdS or KL systems, is well known to transform the nematic phases into cholesteric phases, *i.e.* into spontaneously twisted nematic phases.[61] This property naturally extends to the N_b phase which becomes the biaxial cholesteric phase (Ch_b).[62] The whole nematic phase diagram (roughly sketched in Figure 1) is thus changed, though with slight modifications in temperature and concentrations, into a similar cho-

lesteric phase diagram where the Ch_c, Ch_d, Ch_b phases have replaced the N_c, N_d and N_b phases respectively.

Applying a strong magnetic field makes the three cholesteric phases to orient in the following manner: the Ch_c phase is completely untwisted, similar to the N_c phase, and the Ch_d and Ch_b phases (Photo 1), are twisted around one cholesteric axis only (parallel to **H**), as evoked in § II.2. The three cholesteric phases exhibit different textures when observed between crossed polarizers. This makes them easily distinguishable: the Ch_c phase is uniform, and the Ch_d and Ch_b phases present stripes which are the marks of the vertical cholesteric planes (imposed by the horizontal magnetic field). The stripes are heavy black lines in the Ch_d phase at the homeotropic places (Photo 1a). They become lighter in the Ch_b phase when biaxiality has suppressed the homeotropic regions (Photo 1b).

Conoscopic[3,43] and X-ray diffraction[54] experiments have shown that the micelles in the N_b phase of the SdS and KL-mixtures prefer to orient in such a way that **n** (Figure 4) be parallel to **H**. (The macroscopic consequence of this effect is expressed in Equation 1. It may be explained from the diamagnetic susceptibility of the amphiphilic molecules which makes the molecules, being perpendicular to the micellar surfaces, tend to maximize the micellar surfaces parallel to **H**). From Photo 1 b, one thus observes that in the N_b phase, the cholesteric axis chooses to be along **n**, while the other chiral axes remain frustrated.[62] In the N_u phase, the problem is different in that sense that the cholesteric axis cannot choose another direction than perpendicular to the uniaxial director.

As discussed in § III.1, the uniaxial cholesteric phases (Ch_u) are in fact intrinsically biaxial (thus, strictly speaking, the terms "uniaxial cholesteric" sound like a contradiction), and therefore both the Ch_u and Ch_b phases have the same symmetry. The order parameter which describes the Ch_u—Ch_b phase transition is then non-zero on both sides of the transition. According to Landau analysis, this indicates that the Ch_u—Ch_b phase transition, like the liquid-gas transition, cannot be second-order.[63] The Ch_u—Ch_b phase transition should thus be first order or continuous. Preliminary experiments seem to favor this latter possibility.[64]

b. Disclinations in the biaxial nematic phase. Maybe the most interesting subject in the physics of the N_b phase concerns the defects, *i.e.* the disclination lines. Theoretical studies have shown that they have unusual properties related to the non-Abelian character of the fundamental group of the N_b phase.[65] In principle, the N_b phase

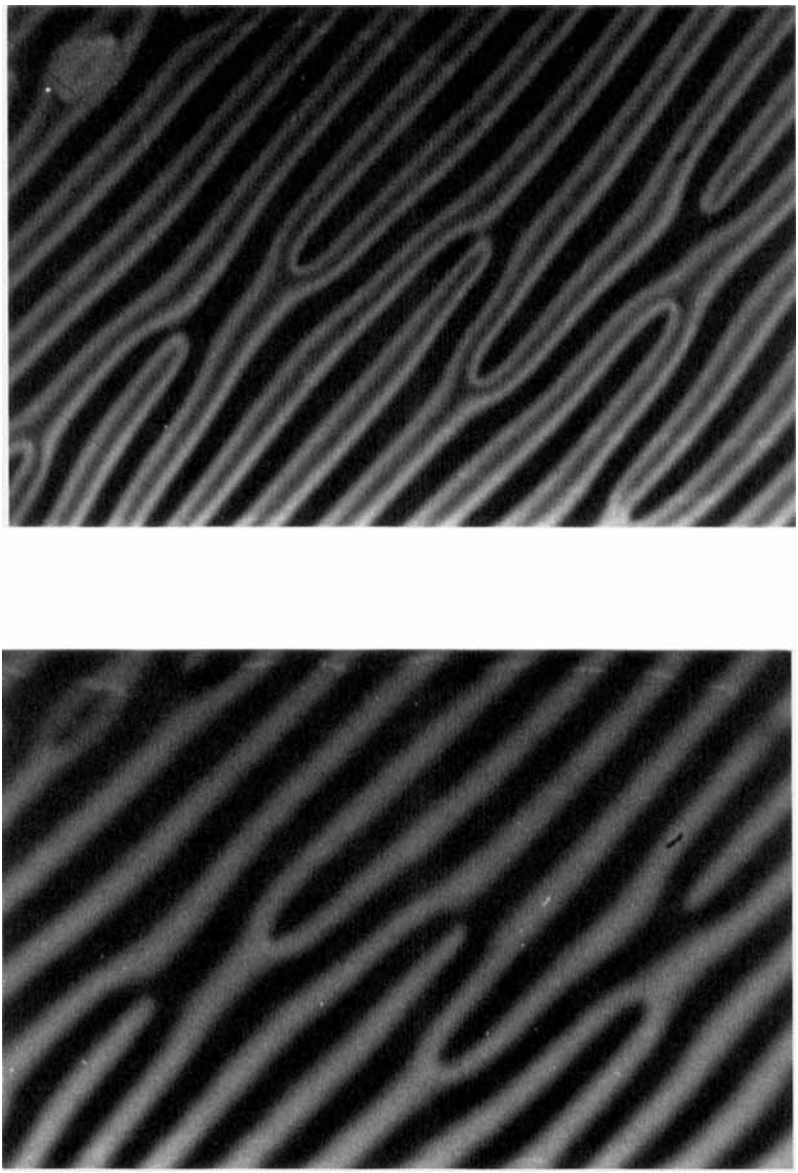

Photo 1 Cholesteric sample observed under crossed polarizers, and oriented with an horizontal magnetic field. The stripes are the marks of the cholesteric planes perpendicular to **H**.

a - Ch_d phase. The heavy black stripes correspond to the homeotropic places.

b - Ch_b phase. The stripes become lighter. The cholesteric pitches ($\sim$ 100 μm) are the same in both the Ch_d and Ch_b phases.

exhibits three types of 1/2-disclinations (of both signs), corresponding to each director **n**, **m** or **l**, and one 1-disclination. As in the N_u phase, the 1/2-disclinations rotate the nematic around them by a $+\pi$ or $-\pi$ rotation. In the N_b phase, the rotation axis is one of the directors **n**, **m**, or **l**. Because rotations of different axes do not commute, 1/2-disclinations of different types, i.e. corresponding to different directors, cannot cross themselves and should thus remain tied up as predicted by Toulouse.[66] However, this particularity has not yet been experimentally verified. The reason is that the biaxial 1/2-disclinations are very difficult to control experimentally, and when they are produced in an undefined fashion, it is quite impossible to determine their type and to tell around which director they make the rotation. However, it may happen sometimes that some entanglement persists in the preparation and seem to be due to the effect announced by Toulouse, but this is not sure because binded disclination lines may also be observed in the same experimental conditions in the N_u phases. Naturally such binded lines in the N_u phases have not the topological origin proposed by Toulouse[66] and could be broken with some energy, but this fundamental difference is difficult to prove experimentally.

It is nevertheless possible to produce disclination lines, one per sample, under reproducible conditions.[67] A method consists in making a competition between two different N_b orientations. Naturally this method requires to control two directors in two parts of the sample. This is not straightforward, but it may be achieved rather satisfactorily when combining the surface effects (which favor the homeotropic orientation of the director **n**), with the magnetic field coupling and the edge effects (which both act on the director **m**).[67] The disclination lines have a core along which the order is lowered down to the isotropic order in the N_u phases, and to the N_u order in the N_b phase. The disclination line in the N_b phase therefore bears a director, parallel to it for symmetry reasons. The director of the line (*e.g.* **m** on the disclination line of Figure 5) elastically interacts with the homologous (**m**) directors in the neighbouring bulk of the N_b phase. This interaction makes the disclination line to orient along preferred directions ($+\theta$ and $-\theta$) and to keep the shape of zig-zags (Photo 2). The line (which bears an uniaxial order) is thus broken at the peaks of the zig-zags, making point defects melted into the isotropic order. It is to be noticed that this mechanism of zigzagging disclination lines implies two directors: one to be broken on the line, and the other one to couple the line to the bulk. In fact, such a condition may be released, and as recently shown, zigzagging disclination lines may also exist in the N_u phases.[68] The observation of

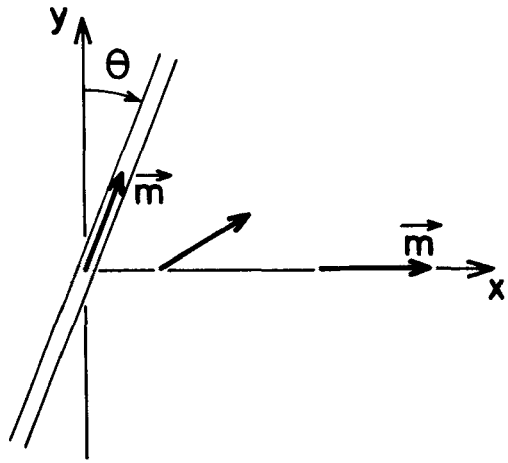

FIGURE 5 Disclination line of **m**-type in the N_b phase. The elastic couplings with the bulk make the line to tilt by an angle $+\theta$ or $-\theta$.

zigzags is therefore not sufficient to prove biaxiality as believed a moment.[69]

c. New N_b phases. Recently, a new thermotropic liquid crystal, made of approximately diamond-shaped molecules (with four branches),

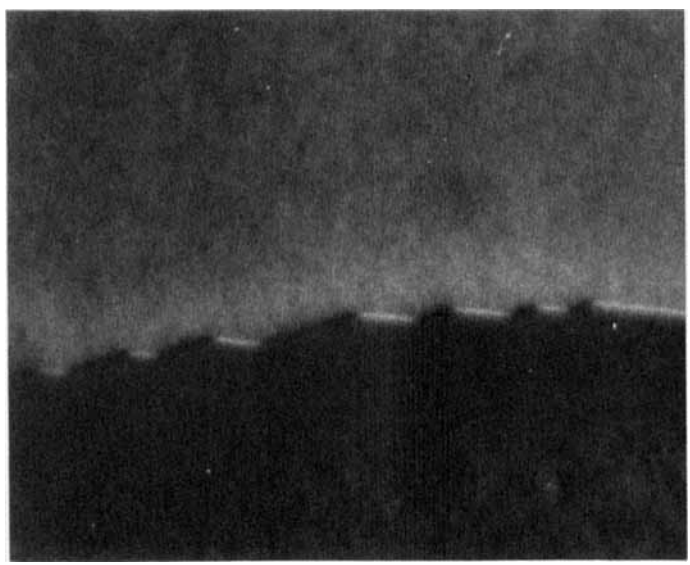

Photo 2 Zigzagging disclination line in the N_b phase.

has been shown to exhibit a N_b phase.[69] The N_b nature of this new thermotropic compound is just qualitatively determined for the moment, with preliminary X-ray diffraction experiments and optical microscopy observations. Tentative measurements of the biaxiality by means of conoscopic interferences failed up to now because this thermotropic N_b phase seems to be very difficult to orient. The conoscopic interference patterns therefore present poor contrasts at least in some part of a ring, and thus yield unreliable results.[70] More tries should be undertaken in order to orient correctly this new phase, for instance with the help of an external electric field.

Recently also, a nematic polymer constituted of mesogenic groups laterally connected to a polymer backbone, has been shown to be biaxial by means of conoscopic observations.[71] The idea is that the mesogenic groups undergo hindered rotations around their long axis which favor biaxial order. However, the polymer N_b samples, like the thermotropic samples, are difficult to orient and they give conoscopic patterns with irregular interferences. This could be a problem, because similar incomplete patterns with a splitten conoscopic cross can also be obtained in distorted uniaxial samples.[72] They thus are unsufficient by themselves to prove biaxiality.[73] More experiments therefore seem necessary to confirm the existence of the thermotropic and polymer N_b phases.

IV. CONCLUSIONS

These short insights on the physical properties of the N_b phases show the sometimes surprising consequences of the existence of a second nematic director. They also show how some progresses have indirectly been performed on the understanding of the neighbouring lyotropic N_u phases, for instance, about their constitutive micelles. Naturally, other physical properties of the N_b phase have to be explored yet. When the thermotropic and polymer N_b phases will be definitely proved, and their anchoring properly controlled, the action of an electric field onto the N_b phases, and its frequency dependence, could be experienced without fears of producing electrolysis as in the lyotropics. This is a promising perspective. It would extend the rich effects of the electric fields in the nematic phases. The thermotropic N_b phases could also be convenient systems to make experiments in other well-known domains of the physics of the N_u phases, as in the hydrodynamics, flexo (and ordo) electricity, surface anchorings, etc..

All these forthcoming progresses could thus bring complements to the somewhat ageing physics of the nematic liquid crystals.

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