Superstructures in magnetically oriented lyotropic nematics, a hydrodynamic effect ?

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Superstructures in magnetically oriented lyotropic nematics, a hydrodynamic effect ?

J. Charvolin and Y. Hendrikx

Laboratoire de Physique des Solides (*), Bât. 510, Université Paris-Sud, 91405 Orsay, France

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Résumé. — Des études de diffraction de la lumière montrent l'existence d'une organisation périodique à grande échelle des agrégats dans des phases nématiques lyotropes orientées par un champ magnétique. Ces observations furent d'abord interprétées structuralement, en termes de fluctuations de la concentration des agrégats. L'étude décrite ici suggère plutôt une interprétation texturale, en terme d'une distribution périodique de l'orientation des directeurs. Cette organisation correspond aux rouleaux formés par les écoulements associés à la rotation des directeurs dans le champ magnétique. Ces expériences constituent les premières observations de phénomènes hydrodynamiques cohérents dans des cristaux liquides lyotropes.

Abstract. — Light scattering studies have demonstrated the existence of a large scale periodic organization of the amphiphilic aggregates in magnetically oriented lyotropic nematic samples. This was first interpreted structurally, in terms of fluctuations of the concentration of the aggregates. The study described here rather suggest a textural interpretation, in terms of a periodic angular distribution of the directors. This organization corresponds to the roll structure associated with the backflow induced by the orientation of the aggregates in the magnetic field. These experiments constitute the first observations of coherent patterns of hydrodynamic origin in lyotropic liquid crystals.

1. **Introduction.** — We have recently characterized a « nematic » lyotropic phase of type I (water-decanol-sodium decyl sulfate [1]) as an anisotropic aqueous solution of cylindrical aggregates of amphiphilic molecules [2]. These cylinders are packed with orientational order and the average direction of their axes defines the director. Light scattering studies of magnetically oriented samples have also demonstrated the existence of a large scale organization of the aggregates with a characteristic length of several μm [3]. This was interpreted as being due to intrinsic periodic fluctuations of the aggregate concentration [3] and the term « macromicelles » was proposed to characterize such a superstructure [4]. However, optical studies of the orientation process of a sample in a magnetic field show the transient appearance of a periodic orientational distribution of the directors in domains of several μm [2, 5] and, therefore, suggest an extrinsic textural interpretation of the light scattering patterns. We present here a study of the formation of the periodic domains and we show that their organization is due to the onset of a convective effect ; we also show that the light scattering patterns are in fact related to the growth of the domains under the application of the field.

The conditions to investigate this phenomenon are those for the study of the Freedericksz transition in thermotropic nematic liquid crystals. The nematic phase is prepared in a planar configuration between glass plates, then a magnetic field is applied normal to the plates. The resulting competition between the magnetic susceptibility (which tends to align the director along the field) and the elastic energies (which tend to retain a uniform orientation of the directors consistent with the orientation at the surface of the samples) create a distortion of the field of directors at small magnetic fields. Beyond a certain threshold a convective instability develops which has been considered in detail for thermotropic liquid crystals [6].

Such experiments are in fact the first observation of a flow coupled with the orientation of the director in a lyotropic liquid crystals. In the following discussion it will be shown that the analogy with the similar situation in thermotropic liquid crystals is qualitatively though not quantitatively correct, as can be expected from the structural difference between both systems.

(*) Laboratoire associé au C.N.R.S. (L.A. n° 2).

2. **Experimental methods.** — 2.1 PREPARATION OF THE SAMPLE. — The lyotropic phase is a mixture of 40.5 % sodium decyl sulfate, 7.1 % decanol and 52.4 % water (% in weight). At room temperature it forms a nematic phase of cylindrical aggregates with positive anisotropy of diamagnetic susceptibility. This nematic phase is introduced by capillarity between glass plates separated by spacers from 20 to 1 000 μm. The directors tend to align parallel to the glass plates and nearly planar domains, with a distribution of their orientations, are observed. A magnetic field is then applied parallel to the glass plates in order to obtain a planar single domain with uniform director $\mathbf{n}_0$ [7].

2.2 EXPERIMENTS. — The domains are created by applying a magnetic field, $\mathbf{H}_0$ (several kG), perpendicular to the director, $\mathbf{n}_0$, of the planar sample, i.e. perpendicular to the glass plates. The geometry of the experiments is defined in figure 1, the optical observations

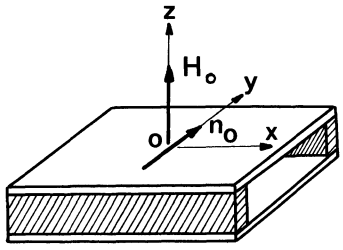

Fig. 1. — The configuration of the experiments : $\mathbf{n}_0$ is the director of the planar sample prior to the application of the magnetic field $\mathbf{H}_0$.

are made along either Oz or Ox. The observed growth and relaxation of the domains are quite slow (time scales of the order of several minutes). This permits to prepare the sample in a conventional electromagnet, then to observe the development of the patterns at various time intervals in a microscope outside the magnet. In order to check that this convenient method of observation does not overlook any fast process we also performed a similar experiment with samples containing 1 % of ferrofluid (A01-200 G from ferrofluidics). In this case the required magnetic field could be created by Helmholtz coils mounted directly on the stage of the microscope [8]; this permitted a continuous observations of the evolutions of those samples. The observed phenomena appeared qualitatively similar for both types of samples, with and without ferrofluid, however a quantitative comparison is prevented by our limited understanding of the interaction between the ferrofluid and the structure.

3. **Observations.** — We shall present them in two steps according to the thickness of the sample :

3.1 THICK SAMPLES (10^3 μm). — The application of the magnetic field along Oz induces the appearance in the (Oxy) plane of a coarsely periodic organization

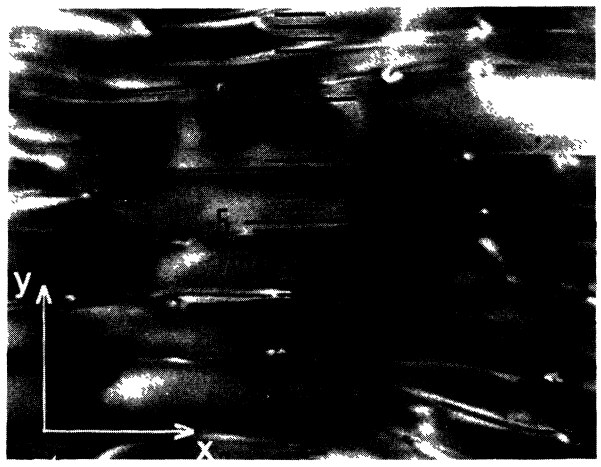

Fig. 2. — View along Oz of a thick planar sample (thickness : 1 mm, with the director $\mathbf{n}_0$ parallel to Oy) submitted to a magnetic field along Oz (H_0 = 15 kG). One large division of the scale is 160 μm.

of isoclines with a wave vector along Oy, as shown in figure 2. (After several hours in the field dark, quasi homeotropic, area develop and the texture evolves toward a more homogeneous one.) The stripes result from the focussing of the light rays by the distortion of the director. This is reminiscent of similar observations in thermotropic nematics [9] but there the organization is more coarse owing to the presence of defects which we did not succeed in eliminating. For this reason also a quantitative study of the organization from plots as functions of field strength and sample thickness is not yet possible. In the lack of samples with perfectly periodic organizations we shall limit ourselves to qualitative considerations. It appears that in a 15 kG magnetic field the distance between two stripes varies from 60 to 80 μm, it decreases when the field increases and does not appear commensurable with the thickness of the samples.

The origin of such a periodicity in a nematic sample cannot be looked for in the competition between the magnetic and elastic terms only : it would lead to walls without organization [10]. The distortion of the director has to introduce a third term, for example a flexo-electric coupling, some layer arrangement as in smectic samples, or a hydrodynamic backflow [6], for a periodicity to appear. In order to discriminate between static and dynamic phenomena we completed observations of the samples in the plane ($\mathbf{H}_0$, $\mathbf{n}_0$). Figure 3 shows the evolution of a line of defect initially parallel to $\mathbf{n}_0$. This line is straight before the application of the field (a), it becomes progressively distorted under the field, in an oscillating manner, with a wavelength of about 160 μm (b and c). Such a distortion of the line of defects shows that the field induces alternative displacements of matter within the sample every 80 μm. After several minutes in the field stripes, distant by about 80 μm and which run through the sample one glass plate to another, settle (d). These stripes in the plane ($\mathbf{H}_0$, $\mathbf{n}_0$) are to be

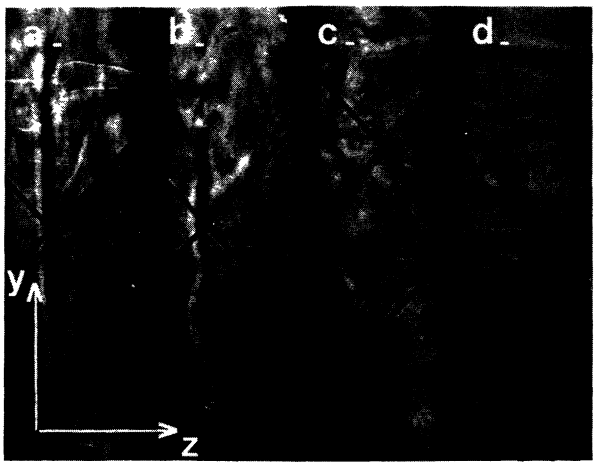

Fig. 3. — Sideviews along Ox of a section of the sample parallel to the ($\mathbf{H}_0$, $\mathbf{n}_0$) plane taken at successive times : a) no field along Oz, a line of defects is visible parallel to $\mathbf{n}_0$ · b) immediately after the application of H_0 = 15 kG along Oz ; c) after 5′ in the field ; d) after 15′ in the field.

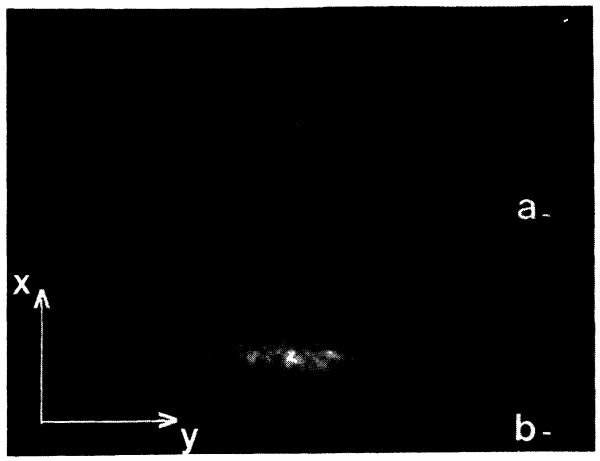

Fig. 5. — Diffraction diagrams obtained with a laser beam (λ = 6 320 Å) parallel to Oz, the analyser is along Oy, the polarizer is along Ox. The sample is planar with $\mathbf{n}_0$ along Oy (a), it has been submitted to the magnetic field $\mathbf{H}_0$ along Oz (b).

combined with those in the plane normal to $\mathbf{H}_0$ in a way which corresponds to the onset of the flow pattern between limiting glass plates represented in figure 4. We are therefore dealing with a hydrodynamic instability with wavelength of about 160 μm, not related to the thickness of the sample which is 10^3 μm.

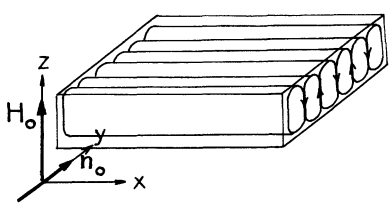

Fig. 4. — Combination of the stripes of figures 2 and 3d showing the flow pattern induced by the application of $\mathbf{H}_0$ in a thick planar sample.

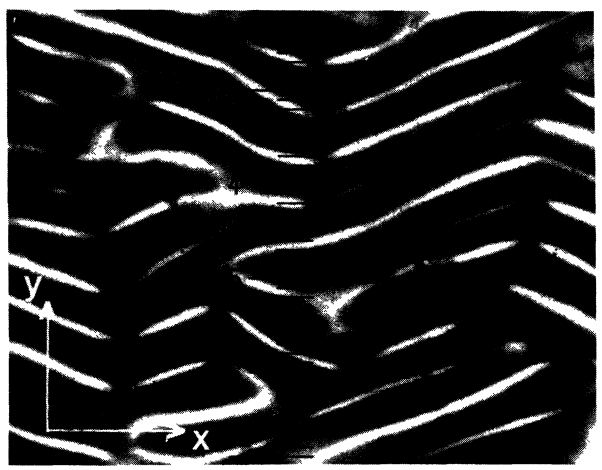

Fig. 6. — View along Oz of a thin planar sample (thickness 180 μm, with the director $\mathbf{n}_0$ parallel to Oy) submitted to a magnetic field along Oz (H_0 = 15 kG). One large division of the scale is 82 μm.

Finally, as shown in figure 5, the periodic light scattering pattern is associated with the growth of the domains when the magnetic field is applied ; from the distance between the spots we recover the characteristic dimension of the domains. We are therefore dealing with a textural, not structural, phenomenon.

3.2 THINNER SAMPLES (320 and 180 μm). — The application of the magnetic field along Oz induces the appearance in the (Oxy) plane of a coarsely periodic organization with two wave vectors, one along Oy as previously and a new one along Ox, as shown in figure 6. The stripe pattern is made of two types of alternating lines : clear lines with soft contours and darker ones with very contrasted black contours. The thickness of the sample which is smaller here than in figure 2 lead to different focussing conditions and the stripes look different. The stripes repeat in the Oy direction every 80 μm ; they present saw-toothed undulations in the Ox direction, the lines changing their type at each edge, with a wavelength of about 360 μm for this sample of thickness 180 μm. The repeat distance along Oy is very close to that measured in the same direction with the thick sample under the same magnetic field ; the periodic organization of the rolls previously described appears therefore not to depend on the thickness of the sample in the range studied up to now. On the other hand the wavelength along Ox is about twice the thickness of the sample, it increases with it and, most likely, the weak undulations of the stripes discernable in figure 2 for the thickest sample studied also reflects the tendency for a periodicity to settle along Ox. This relation of commensurability between the thickness and the wavelength along Ox suggests another type of convective flow along this direction.

Finally we observed qualitatively similar phenomena with much thinner sample (20 and 35 μm),

the patterns are rather disordered but we can say that both wavelengths decrease with the thickness.

4. **Discussion.** — The patterns in figures 2 and 5 have been analysed as resulting from the composition of two flows of convective type induced by the application of the magnetic field. One is in the ($\mathbf{H}_0$, $\mathbf{n}_0$) plane : the distance between the rolls (about 80 μm) does not depend upon the thickness of the sample when it is larger than about 100 μm. The other is in the plane normal to $\mathbf{n}_0$: the distance between the rolls equals the thickness of the sample.

The primary effect to the field $\mathbf{H}_0$ is to reorient the director $\mathbf{n}_0$ of the planar sample in the ($\mathbf{n}_0$, $\mathbf{H}_0$) plane. In principle in a nematic sample where the magnetic energy should be stored as elastic energy the uniform mode of the Freedericksz transition should be observed alone [10]. The appearance of a periodic mode along $\mathbf{n}_0$ calls for the intervention of a term relaxing the elastic energy and the flow of matter, demonstrated in figure 3, suggests that it is a viscous relaxation. This aspect has been already considered in the case of thermotropic nematics [6] : the backflow associated with the rotation of the director makes an unstable periodic mode grow faster than the stable uniform mode, the period increases with the thickness in a bounded medium and stabilizes to a finite value in an unbounded medium, it decreases when the field increases. This description qualitatively agrees with our observations on the first family of rolls, our thinnest samples (20 and 35 μm) would correspond to the bounded situation whereas the thickness ones (180, 320 and 1 000 μm) would correspond to the unbounded situation, as well as the larger samples used for the first light scattering study [3]. The occurrence of a second family of rolls is not foreseen in this model; similar experimental situations also exist in thermotropic samples but this second mode, which has a larger wavelength than the first, is a weak correction which has not been considered theoretically.

5. **Conclusion.** — According to our study the existence of superstructures in the organization of the aggregates, i.e. periodic fluctuations of their concentration, cannot be inferred from light scattering experiments at the moment. Those lyotropic liquid crystal can still be depicted as assemblies of anisotropic aggregates with some orientational order of the nematic type. A central question for the understanding of lyotropic nematics is : how do they differ from ordinary nematics ? In other words : the basic structural element is no longer one molecule but an aggregate of molecules, does this have any qualitative, or at least quantitative, consequence for the properties of the phase ? So far static studies of birefringence, texture and alignment in a magnetic field suggest the properties of the director to be qualitatively similar in both cases [11, 7]. The observation of hydrodynamic instabilities described here does not invalidate this point of view. Therefore we are left at the moment with the eventuality of quantitative differences for the constants characterizing the materials. We may attempt some comparisons. A first information readily obtainable is the relaxation time, $\tau = \gamma_1/\Delta\chi H^2$, of the orientation in a magnetic field ; it is about 0.1 s in thermotropics and one minute or more in lyotropics. As the anisotropy of susceptibility, $\Delta\chi$, may be smaller in lyotropics by a factor 10, [12], the rotational viscosity, γ_1, may be larger. This is conceivable owing to the large dimensions of the cylindrical aggregate [7]. A second information concerns the elastic constant and may be deduced from the wavelength, λ, of the first family of rolls studied above. Following [6] in the unbounded situation $\lambda^2 \simeq D_e \tau$, where the diffusivity D_e is the geometrical mean between the diffusivity of orientation K/α and the viscous one η_2/ρ. For thermotropic [9] and lyotropic samples in a 15 kG field $\lambda/2$ are respectively 16 and 80 μm so that D_e is larger in the first case than in the second one by more than one order of magnitude. If we consider that η_2 and α_2 are of the same order of magnitude and that $\rho \sim 1$ in both cases it ensues that the elastic constant, K, is smaller in the lyotropic phase by about two orders of magnitude. This is supported by a rough estimation of K considering that it is the ratio of the interaction energy between nematic objects and their typical dimension [13] : here the energy which maintains the orientational order is about 300 K, or

$$0.4 \times 10^{-13} \text{ erg [14]},$$

the dimension 40 Å, so that K would be about 10^{-7} dynes whereas it is 10^{-6} dynes in a thermotropic nematic; moreover the flexibility of amphiphilic aggregates might also contribute in decreasing K.

Indeed the interest of lyotropic materials, when compared to thermotropic ones, would be their extreme variability : the shape, size and packing of the aggregates are very sensitive to the nature, concentration and temperature of the constituants in a way which might affect greatly the constants of the material.

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sition or temperature lead to a « Type II » phase with discoidal aggregates and negative anisotropy of susceptibility which, under the application of a magnetic field parallel to the director of a thick homeotropic sample, exhibits a two-dimensional square pattern similar in nature to the one-dimensional pattern of the type I sample studied here.

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