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A.M. Figueiredo Neto

Instituto de Física, Universidade de São Paulo

L. Liebert

Université de Paris-Sud, Lab. Physique des Solides Bât. 510 et  
Laboratoire pour l'Utilisation du Rayonnement  
Electromagnetique - LURE, Bât. 209C, 91405 Orsay -  
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## FERROFLUIDS IN LIQUID CRYSTALLINE SYSTEMS

A.M.Figueiredo Neto\*, L.Liebert<sup>†</sup>

\*Universidade de São Paulo, Instituto de Física

CP: 20516, CEP: 01498 São Paulo, Brazil

<sup>†</sup>Université de Paris-Sud, Lab. Physique des Solides Bât.510

et Laboratoire Pour l'Utilisation du Rayonnement

Electromagnetique - LURE, Bât.209C, 91405 Orsay-France.

(I) General Considerations

It is a well-known fact that intermediate or mesomorphic phases may exist between the crystalline and the isotropic liquid phases. The symmetry properties of these mesophases are intermediate between those of a crystal and a liquid<sup>(1)</sup>: order in one or even in two dimensions coexists with fluidity. Liquid crystals are essentially made of anisotropic units and are classified<sup>(1)</sup> as thermotropic or lyotropic. Thermotropic liquid crystals are systems constituted of elongated<sup>(1)</sup> or disk-like<sup>(2)</sup> molecules which may exhibit a few transitions through a change of the system's temperature. Lyotropic liquid crystals<sup>(3,4)</sup> are mixtures of amphiphilic molecules and a solvent (usually water) in appropriate temperature concentration conditions. These amphiphilic molecules form anisotropic aggregates (micelles) which are the basic units to the mesophase. These systems may go through a few phase transitions if both the temperature and the relative concentrations of the different compounds are changed.

According to the molecular (or micellar) order, liquid crystals are classified upon their symmetry in three

major classes<sup>(1)</sup>: nematics, cholesterics and smectics. We shall restrict our discussion to the first two classes. Three types of nematic order, two uniaxial and one biaxial, are known<sup>(5)</sup>. In the uniaxial nematic phases<sup>(3,4,6)</sup> the preferred direction of alignment (the director  $\vec{n}$ ) coincides with the optical axis of the phase, i.e. there is an infinite-fold axis, whereas the biaxial nematic phase has three orthogonal two-fold symmetry axes<sup>(6,7)</sup>. The cholesteric order may be understood<sup>(1)</sup> as constituted of successive nematic planes, parallel to each other, with  $\vec{n}$  twisting around an axis perpendicular to these planes.

Liquid crystals are oriented<sup>(1)</sup> by electric and magnetic fields ( $\vec{H}$ ) or by shear stress. Since the anisotropic part of the diamagnetic susceptibility is small<sup>(1)</sup> ( $\sim 10^{-7}$ ), high magnetic fields<sup>(8)</sup> ( $\sim 10$ K Gauss) are usually needed. In order to reduce the strength of H in practical experiments, ferromagnetic grains (ferrofluids) are introduced<sup>(8,9)</sup> in the liquid crystalline system. In this way, fields of about 10 Gauss are enough to orient the mesophases<sup>(9)</sup>. Nematic and cholesteric liquid crystals doped with ferrofluids are called<sup>(8)</sup> "ferro-nematics" and "ferrocholesterics", respectively. A ferrofluid is a colloidal suspension of small ferromagnetic particles dispersed in a liquid medium<sup>(10)</sup>. It has the fluidity of a homogeneous liquid and high magnetic susceptibility. The magnetic particles ( $\text{Fe}_2\text{O}_3$ , Fe, Co,  $\text{Fe}_3\text{O}_4$ , etc...); with dimensions of about  $100\text{\AA}$ , are coated with a dispersive agent (a long chain surfactant or a polymer) to prevent the aggregation of the particles dispersed in the solvent (water, oleic acid, etc...) <sup>(11)</sup>.

The introduction of ferrofluids in liquid

crystals serves the purpose not only of reducing the strength of H necessary to orient the phases, but also allows the study of the physics of the liquid crystalline system itself.

In this paper, we shall discuss some aspects of the use of ferrofluids in thermotropic and lyotropic systems, concerning both the experimental difficulties as well as the fundamental physical phenomena involved.

## (II) How do ferrofluids orient liquid crystals?

Ferrofluids are introduced in the mesophases in small quantities in order to prevent strong modifications of the physical properties of the liquid crystals (12,13). In lyotropics, in particular, the water base ferrofluid doping introduces an additional amount of water in the system, which may change the transition temperatures. A doping with about  $10^{-2}$  weight% (or equivalently  $10^{12}$  magnetic grains/cm<sup>3</sup>) of ferrofluid does not sensitively, for our purposes, modify the transition temperatures, the refraction indices or the X-ray diffraction patterns of the lyotropic mesophases (12,13). The minimum concentration (8) above which the liquid crystalline medium follows the orientation of the magnetic grains is about  $\frac{1}{LD^2}$ , where L and D are typical dimensions of the grain and the sample, respectively.

Two different forms of the coupling between the ferrofluid and the liquid crystalline system have to be considered: the effect of the magnetic field of the grain (with magnetic moment  $\vec{\mu}$ ) and the mechanical coupling. At this point we will summarize the theoretical considerations of Brochard and de Gennes (8) of 1970:

- (a) The magnetic effect - the strength of the magnetic effect may be estimated by comparing the changes introduced in the free energy (F) of the crystalline medium for  $\vec{n}$  and  $\vec{\mu}$  (the magnetic moment of a particle of volume V) either parallel or perpendicular to each other. The free energy may be written, to first order, as (1)

$$F = F_0(\vec{n}) - \frac{1}{2} \chi_a \int (\vec{n} \cdot \vec{H})^2 dv,$$

where  $\chi_a$  is the anisotropic part of the diamagnetic susceptibility of the liquid crystal. Then

$$\Delta F \sim \frac{1}{2} \chi_a \frac{\mu^2}{V}$$

and for typical values  $\chi_a \sim 10^{-6}$ ,  $V \sim 10^{-18}$  cm<sup>3</sup>,  $\mu \sim 10^{-13}$  uem;  $\Delta F \sim 10^{-19}$  erg  $\ll k_B T$  for  $T \sim 300$  K.

- (b) Mechanical coupling - to evaluate the magnitude of this effect, we compare the free energy of two different configurations corresponding to arrangements of the anisotropic magnetic grains either parallel or perpendicular to  $\vec{n}$ . The elastic free energy is written as (1)

$$F = \frac{1}{2} \int [K_{11} (\text{div} \vec{n})^2 + K_{22} (\vec{n} \cdot \text{rot} \vec{n})^2 + K_{33} (\vec{n} \times \text{rot} \vec{n})^2] dv,$$

where  $K_{ii}$  are the Franck elastic constants.

For  $K_{11} = K_{22} = K_{33} = K$  we have

$$F = \frac{1}{2} K \int (\text{grad} \theta)^2 dv,$$

where  $\theta$  is the angle between the long axis of the molecules and  $\vec{n}$  (14). For an anisotropic particle of length L (and form anisotropy of about 10) one therefore has

$$\Delta F \sim \frac{K L^3}{L^2} = KL.$$

For typical values of K ( $\sim 10^{-6}$  dynes) and L ( $10^{-5}$  cm),

$\Delta F \sim 10^{-11} \text{erg} \gg k_B T$  for  $T = 300^\circ\text{K}$ .

We may conclude<sup>(8)</sup> that the mechanical coupling is by far the predominant effect in the orienting process in the liquid crystalline systems doped with ferrofluids.

### (III) Thermotropic ferronematics

Several attempts have been made at obtaining a thermotropic ferronematic with the liquid crystal p-methoxybenzilidene-p-n-butylaniline, usually called MBBA<sup>(15,16,17)</sup>. This liquid crystal has<sup>(1)</sup> a solid-nematic transition around  $20^\circ\text{C}$  and a nematic-isotropic transition at  $47^\circ\text{C}$ . However, a major difficulty arises in experiments with thermotropic materials when one tries to obtain a homogeneous distribution of the individual magnetic grains in the liquid crystal matrix. The attempts to dope MBBA with small ( $L \sim 150\text{\AA}$ ) magnetic particles have not, to our knowledge, attained any success. Rault and co-workers<sup>(15)</sup> have doped MBBA with  $\gamma\text{-Fe}_2\text{O}_3$  magnetic grains of  $0.35\mu\text{m}$  length and  $0.04\mu\text{m}$  diameter. Large remanent magnetizations,  $M(H=0)$ , were observed in the nematic phase, which disappear at the nematic to isotropic phase transition. In high magnetic fields ( $\sim 1\text{KG}$ ), long magnetic needles ( $\sim 50\mu\text{m}$ ) were observed, indicating the aggregation process of the magnetic grains. In 1976, Hayes<sup>(16)</sup> doped MBBA with almost circular magnetic platelets of  $\text{Fe}_3\text{O}_4$  in a hydrocarbon base. These platelets had typically  $50\mu\text{m}$  diameter and the director  $\vec{n}$  perpendicularly oriented to the platelet surfaces. The molecules of MBBA were oriented by two parallel rubbed surfaces. It was observed that the magnetic platelets change the orientation of the nearby molecules in the bulk of the sample, as a function of the

magnetic field direction. The resultant magnetic field gradients promote transport and further aggregation of the magnetic platelets.

The first successful attempt to introduce magnetic particles in a thermotropic system and observe collective behaviour of the doped matrix was due to Chen and Amer<sup>(17)</sup>, in 1983. In their experiment, MBBA, placed in a glass cell with parallel plates, was doped with  $\gamma\text{-Fe}_2\text{O}_3$  needles  $0.5\mu\text{m}$  long and aspect ratio of  $\sim 7:1$ , coated with dimethyl octadecyl aminopropyl trimethoxysilyl chloride. The collective behaviour of the liquid crystalline matrix was detected by measuring the birefringence of the sample as a function of the external field. No critical magnetic fields were observed, indicating that  $H < 1\text{G}$  can modify the orientation of the director. At higher magnetic fields, the magnetic grains tend to flocculate in an irreversible way.

### (IV) Lyotropic ferronematics

In the other hand, many experiments with lyotropic systems doped with ferrofluids have been carried out in the uniaxial<sup>(9,13,18,19)</sup> and biaxial<sup>(12,13,19)</sup> nematic phases. Two lyotropic nematic systems have been the object of study: a potassium laurate-decanol-water mixture and a sodium-decylsulphate-decanol-water mixture. These two different mixtures present<sup>(19,20)</sup> nematic phases at ambient temperature. In these experiments, samples were doped with a commercial ferrofluid (Ferrofluidics Corp.) of water base. The magnetic grains of  $\text{Fe}_3\text{O}_4$ , with a mean diameter of  $154\text{\AA}$  (standard deviation of  $94\text{\AA}$ ), were coated with oleic acid and diluted to a concentration

of about  $10^{12}$  grains/cm<sup>3</sup>. Collective behaviour of the liquid crystalline matrix was observed<sup>(9)</sup> with magnetic fields of about 5G. The aggregation of the grains forming needles of about 10 $\mu$ m long was also observed<sup>(18)</sup>. This phenomenon may be explained as due essentially to field gradients at the edges of the small permanent magnets used in the experiments. The movement of these needles may be followed with an optical microscope. The observations described in this and in the next section were obtained in an orthoplan - Pol Leitz microscope, with the sample sealed in glass flat microslides and placed between crossed polarizers.

One of the most interesting properties of the ferronematic system is the existence of depletion layers, i. e., regions where the magnetic grains are segregated<sup>(8)</sup>. In these distorted situations, the condition that the major axis of the anisotropic magnetic grain align parallel to the director cannot be satisfied, for topological reasons (in defects or walls<sup>(1)</sup>). To produce these distorted regions, we create, by means of the application of magnetic fields, nearly ellipsoidal closed walls in a calamitic nematic phase<sup>(18)</sup> (Figure 1). Inside and outside the closed walls,  $\vec{n}$  is parallel to  $\vec{H}$  and in the wall it has a complex configuration<sup>(21)</sup>. In the presence of the magnetic field, the closed walls tend to collapse, thereby, decreasing their dimensions. All the magnetic grains which are surrounded by the walls (with their long axes parallel to  $\vec{H}$ ) are confined inside these walls. The wall acts like a barrier which prevents the passage of the needles from the inside region to the outside. However, the needles are small permanent magnets arranged parallel to another, and therefore a magnetic repulsion arises between them. As a consequence,

the needles are placed at the inside frontier of the closed wall and tend to prevent its complete collapse (Fig.1). This experiment is a confirmation of the predominance of the mechanical coupling<sup>(8)</sup> between the liquid crystal and the ferrofluids, as compared to the magnetic coupling.

The creation of hydrodynamic instabilities is another manifestation of the collective behaviour of the liquid crystalline matrix induced by the movement of the ferrofluid grains. Figure 2 shows one kind of hydrodynamic instability that arises in a calamitic nematic phases<sup>(19)</sup>. Rheological studies may thus be done in ferronematics in an easy and controlled way, with small magnetic fields.

Another important problem in the structural studies (X-ray and neutron diffraction) of lyotropic nematics is the orientation of the sample<sup>(6)</sup>, both in situations where the director orients perpendicular to  $\vec{H}$  (discotic uniaxial nematic phases) and in the biaxial nematic phases. In these cases, turning and oscillating fields, respectively, are needed. The technological problem is conveniently reduced by means of the ferrofluid doping<sup>(6)</sup>, since small magnetic fields can produce a well oriented sample.

#### (V) Lyotropic ferrocholesterics

These systems are obtained by the addition<sup>(22)</sup> of a chiral compound to a ferronematic lyomesophase. Three different ferrocholesteric phases have been observed:

Ch<sub>C</sub> - calamitic ferrocholesteric<sup>(22,23)</sup>  
 Ch<sub>D</sub> - discotic ferrocholesteric<sup>(22,23,24)</sup>  
 Ch<sub>BX</sub> - biaxial ferrocholesteric<sup>(25)</sup>

In a small magnetic field ( $\sim 5G$ ), a  $Ch_D$  (24) (Fig. 3a) phase and a  $Ch_{BX}$  (Fig. 3b) phase are present in which the helicoidal axes aligns parallel to the field (22,25) and in the  $Ch_C$  phase the cholesteric structure is untwisted (22). In systems not doped with ferrofluids the strength of the field necessary to produce the same effect is about 10KG.

The ferrofluid doping is particularly convenient in the measurements of the rotatory power (26) of cholesteric samples in a conventional microscope. In this condition, the helicoidal axis can be oriented parallel to the light beam direction by means of small Helmholtz coils (23).

Hydrodynamic instabilities can be studied by following with an optical microscope the motion of relatively big ferrofluid needles ( $>10\mu m$ ) in a cholesteric matrix. These needles can be formed by the clustering of small magnetic grains in high fields ( $\sim 1KG$ ) or in regions with field gradients. Backflow convective motions were observed in a  $Ch_C$  phase (23) by following the modifications of the form of the needles with time, after removal of the magnetic field. As discussed before, the magnetic field untwist the cholesteric  $Ch_C$  structure and the ferrofluid needles are straightened parallelly to  $\vec{H}$ . When the field is switched off, the hydrodynamic instabilities are induced by the competition between the sample holder walls orientational effect on the micelles and the twisting imposed by the chiral compound (23). Figure 4 shows these backflow convective motions and the big ferrofluid needles deformed by these instabilities.

#### (VI) Concluding remarks

In conclusion, we may say that the ferrofluid

doping of thermotropics and lyotropics is an open field of research. The experimental results obtained with thermotropics indicate that the doping is possible, however, the clustering process of the magnetic grains is the great technological difficulty to obtain a homogeneous ferronematic (or cholesteric) to be used in optical devices. In lyotropics, the doping with a water base ferrofluid forms a stable ferrolyotropic system. Several problems concerning the physics of these systems have been investigated, such as structural and rheological aspects of ferronematics and ferrocholesterics. Using a ferrofluid to prepare ferrolyotropics, good oriented samples are obtained by applying relatively small magnetic fields. As small fields are required, technological problems in practical experiments are sensitively reduced.

As a final remark, we may say that ferrofluids are a very powerful tool to study the physics of the liquid crystalline systems.

#### (VII) Acknowledgments

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## FIGURE CAPTIONS

FIGURE 1: Optical microscopic observation of a closed wall in a calamitic ferronematic lyomesophase (potassium laurate/decanol/water) according to (18).  $\vec{H}$  is the magnetic field ( $\sim 5G$ ). Sample between crossed polarizers. The black points are the ferrofluid needles.  $T = 24^\circ C$ .

- (a) 1:30 hours after the application of the field. Ferrofluid needles at the inside frontier of the closed wall.
- (b) 3 hours after the application of  $H$ . Absence of ferrofluid needles in the region around the closed wall.
- (c) 4:30 hours after the application of  $H$ . Nearly collapsed closed walls.

FIGURE 2: Optical microscopic observation of hydrodynamic instabilities in a calamitic ferronematic lyomesophase (potassium laurate/decanol/water)  $T = 20^\circ C$ . Sample in microslides  $100\mu m$  thick. Crossed polarizers. Initially the magnetic field  $H$  ( $\sim 5G$ ) was in the plane of the figure (planar texture) and later placed perpendicular to the plane of the figure to generate the instabilities.

FIGURE 3: Optical microscopic observations of a ferrocholesteric lyotropic mesophase (sodium decylsulphate/Decanol/water/brucine sulphate heptahydrate) according to

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(25). Crossed polarizers.

(a) cholesteric discotic ( $Ch_D$ ).  $T = 14.6^\circ C$ .

(b) cholesteric biaxial ( $Ch_{BX}$ ).  $T = 17.8^\circ C$ . The arrow FF indicates a ferrofluid needle.

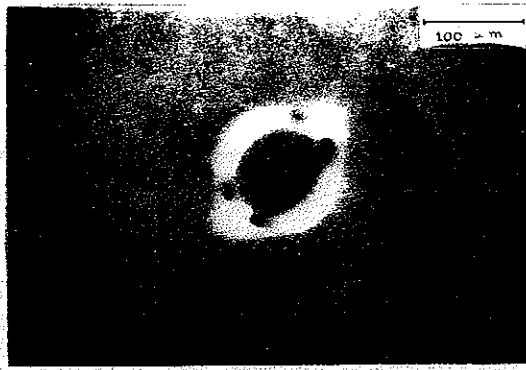
FIGURE 4: Optical microscopic observation of hydrodynamic instabilities in a calamitic ferrocholesteric lyo-mesophase (sodium decylsulphate/decanol/water/brucine sulphate heptahydrate) according to (23).  $T = 24^\circ C$ . Crossed polarizers. Needles of ferrofluid (FF) deformed by the hydrodynamic instabilities.

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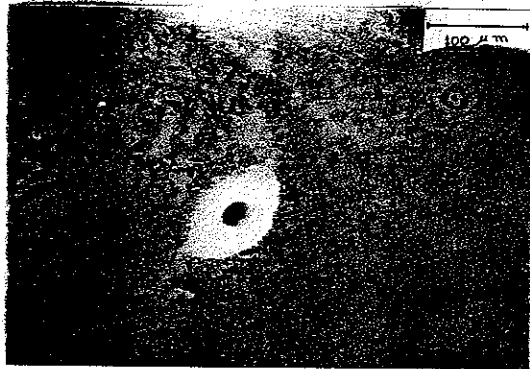


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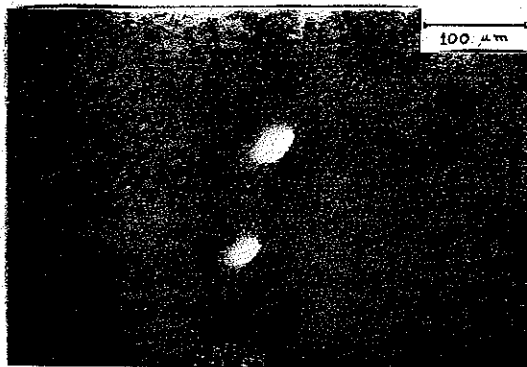
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(a)



(b)



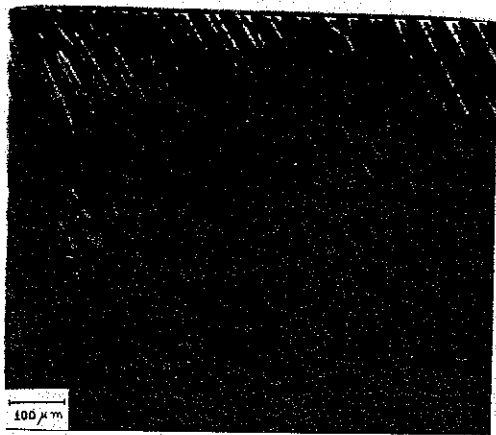
(c)

FIGURE 1

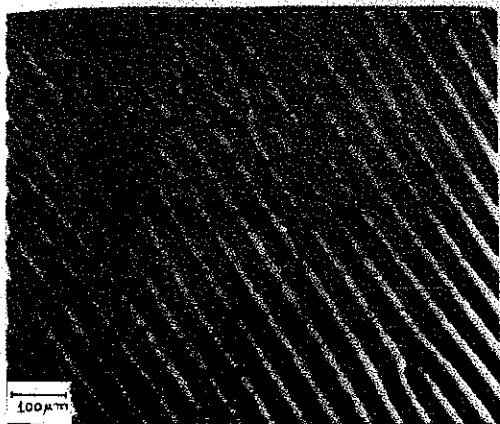


FIGURE 2

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(a)



(b)

FIGURE 3



FIGURE 4

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