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Magnetic Field Effects in Nematic and Cholesteric Droplets Suspended in an Isotropic Liquid†

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Abstract—The structure of spherical droplets of nematic and cholesteric materials floating in an isotropic liquid is experimentally investigated by microscopic observation with polarized light.

In nematic droplets either a star configuration or a bipolar configuration have been observed depending on the nature of the isotropic liquid. Cholesteric droplets adopt a spiral shaped structure whenever the radius of the droplet is much larger than the helical pitch. Changes in optical patterns induced by a magnetic field are analysed.

A theoretical investigation of the structure of droplets of nematic materials floating in an isotropic liquid has been carried out a few years ago by E. Dubois-Violette and O. Parodi.[1] By assuming an anisotropic surface energy, these authors predicted two possible configurations depending on whether surface tension induces a normal or a tangential orientation of the molecules at the nematic–isotropic liquid interface.

a) When the molecules are tangential to the surface, the stable configuration is bipolar with two opposite singularity points (Fig. 1(a)). In a magnetic field the whole droplet would rotate and orient itself with the polar axis parallel to the direction of the field (Fig. 1(b)).

b) When the molecules are perpendicular to the surface one should observe a radial configuration with a point disclination at

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the center of the droplet (Fig. 2(a)). In a high magnetic field a first order transition is expected in which the droplets would adopt an aligned configuration with an equatorial disclination (Fig. 2(b)).

The critical field should be obtained when the radius R of the droplet is of the same order of magnitude as the coherence length ζ

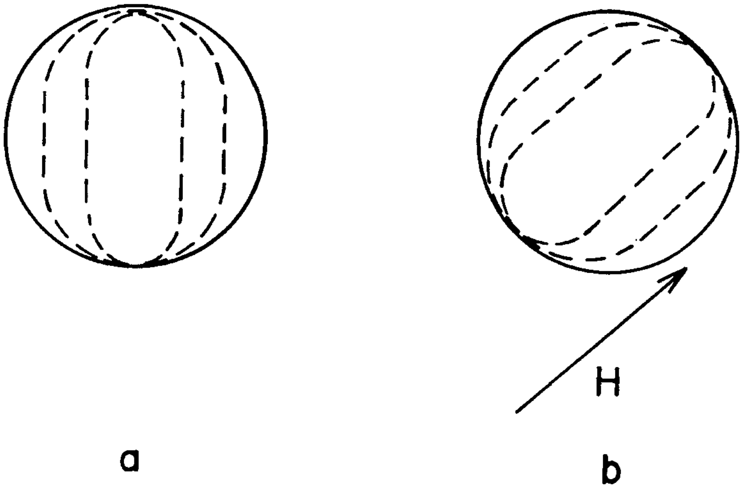


Figure 1. (a) Bipolar configuration; (b) Configuration in a magnetic field.

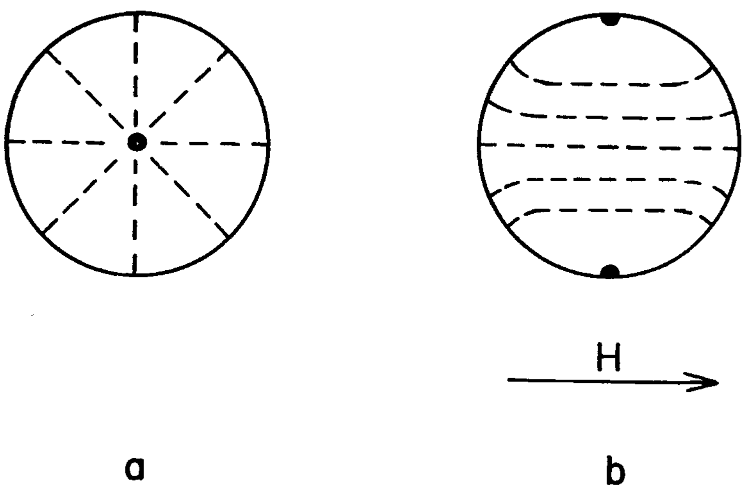


Figure 2. (a) Star configuration; (b) Configuration in a high magnetic field.

defined by the relationship[2]:

$$\zeta = \sqrt{(K/\chi_a)}\,\frac{1}{H}$$

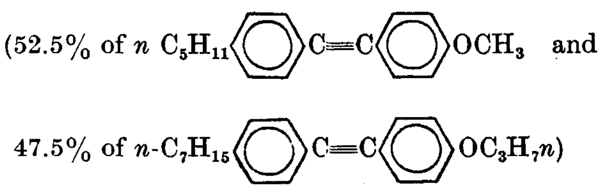
where K is an average of Frank's elastic constants, χ_a is the anisotropy of diamagnetic susceptibility and H the magnetic field.

Point disclinations in the center or at opposite points of nematic droplets dispersed in the isotropic phase of the same material have already been observed by different authors.[3]

In the present paper some experiments are described in which droplets of nematic and cholesteric materials floating in various isotropic liquids are investigated by microscopic observation with polarized light. Changes in the optical pattern induced by a magnetic field are also analysed.

1. Nematic Emulsions

Three room temperature nematic materials have been investigated: paramethoxybenzylidenebutylaniline (MBBA), the so called "Licristal Merck IV" and a mixture of two tolanes[4]



The isotropic medium in most experiments was glycerol previously doped by different surfactants. The emulsions have been prepared by shaking mixtures of liquid cristalline and isotropic liquids. If the medium is not viscous enough, the emulsion is unstable and the optical observations are difficult. As a consequence it is also quite impossible to investigate high melting point liquid crystals. One way to prepare stable emulsions is to disperse the nematic sample in boiling mixtures of glycerol and agar agar. By cooling down slowly we obtain a more or less soft paste or gel containing trapped birefringent droplets of liquid crystal. If the cooling was too fast the droplets were deformed. A shearing of the gel between two plates

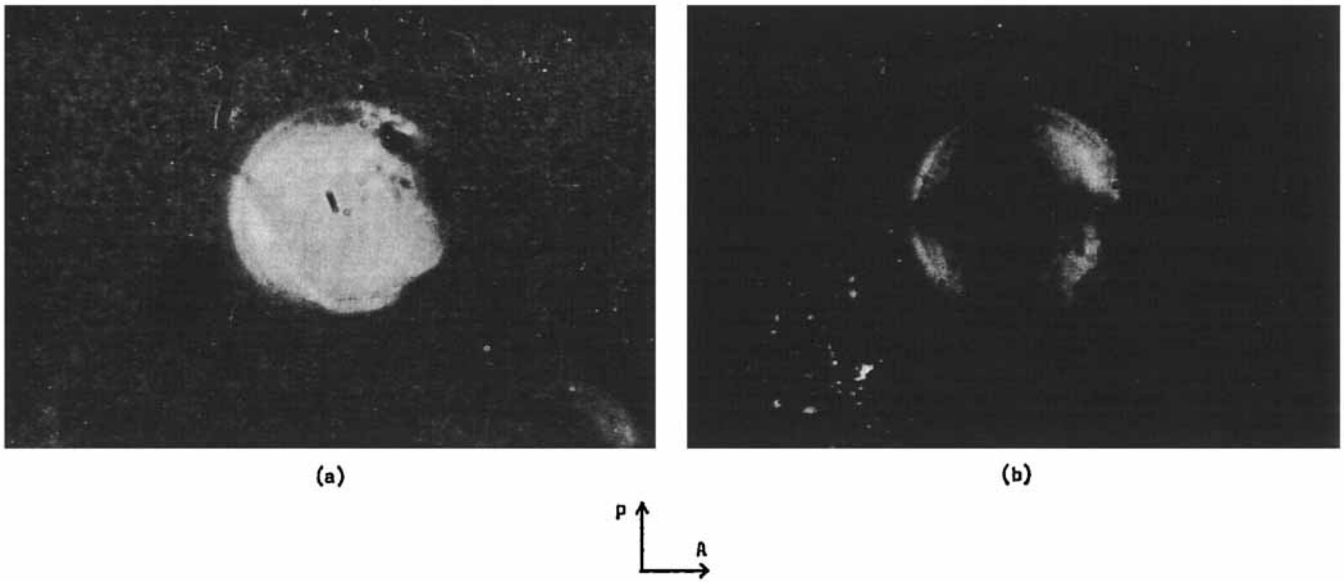


Figure 3. Droplet of MBBA in a gel of glycerol–Teepol–Agar agar, between crossed polarizers. Between photograph (a) and photograph (b) the microscope stage was rotated through an angle of 45°.

then gives rise to the formation of small spherical droplets giving regular optical patterns.

We have observed both tangential and radial configurations depending on the nature of the surfactant used. The former has been found when the glycerol is doped with the so-called " Teepol " commercial detergent.

In such emulsions, most of the droplets when viewed between crossed polarizers appear uniform except in the vicinity of surface point disclinations (Fig. 3(a)).

By rotating the microscope stage, one finds for each of these droplets two positions at right angle where the droplet appears dark (Fig. 3(b)). Similar observations have been made in gels of glycerol–Teepol–Agar agar.

If we apply a magnetic field of about 1000 Gauss all the droplets rotate and align themselves in the direction of the magnetic field. All these experimental observations are consistent with the bipolar configuration as described in Fig. 1(a).

The same optical patterns have been observed for droplets of Merck IV floating in a polymeric oil of polytrichlorofluoroethylene.[5] However, at room temperature the polymeric oil is partially soluble in the nematic material. Moreover the emulsion is unstable.

We have also observed radial configurations for the three nematic materials investigated, when dispersed in pure hydrogen bounded liquids. Most of the investigations have been carried out in gels or in mixtures of glycerol with a solution of polyoxyethyleneglycol in water. A typical mixture is composed of 44% of glycerol, 44% of water and 12% of polyoxyethyleneglycol.

Figures 4(a) and 4(b) show droplets of Merck IV dispersed in such a mixture. A singularity located at the center of the droplet is observed. As a matter of fact, it does not seem to be a single defect point but a small twisted area. The twist becomes more apparent when the sample is observed between crossed polarizers (Fig. 4(b)). The characteristic extinction cross does not coincide with the directions of the polarizers but is twisted with respect to these directions at the center of the droplet. When rotating the polarizer and analyser together the extinction arms rotate the same way. This demonstrates the radial nature of the configuration of the liquid crystal within the droplet.

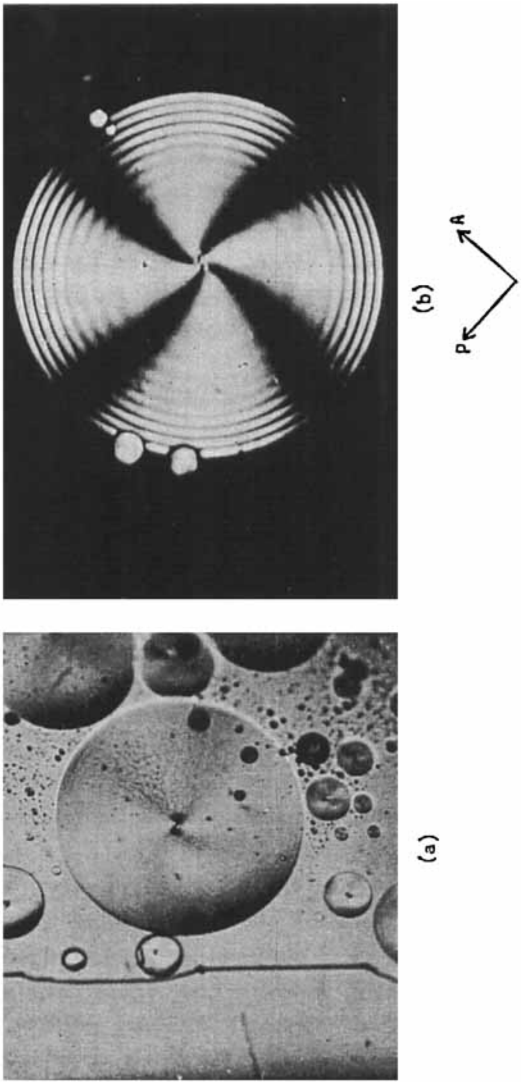


Figure 4. Droplet of Merck IV in a mixture Glycerol, water, polyoxyethylene glycol. (a) Natural light; (b) Between crossed polarizers.

The concentric rings observed in Fig. 4(b) result from changes in the total phase difference between ordinary and extraordinary waves.

Many droplets, especially the largest ones are characterized by a defect which is not located at the center of the droplet. It may even happen that the defect moves to the surface or close to the surface of the droplet. The disclination then is easier to see and looks as if it had the form of a small loop.[6]

However, it is possible to obtain real star configurations when the droplets are dispersed in glycerol doped with a small fraction of N Cetyl–N–N–N trimethylammoniumbromide (CTAB). The CTAB might be partially dissolved in the nematic materials and since the CTAB is a soap which itself is able to form smectic phases, the twist and bend elastic constants could be increased giving rise to a pure splay deformation. As a matter of fact, if the CTAB is in excess, one can see at the center of the droplet a birefringent aggregation growing radially, which could be a smectic cybotactic group (Fig. 5).

Observations have also been performed in the presence of a magnetic field. The application of a high magnetic field gives rise to a disclination line located in a plane perpendicular to the direction of the field. If the magnetic field is perpendicular to the direction of observation, the disclination line looks superposed on the central defect (Fig. 6(a)). Between crossed polarizers the droplets appear bright (if the magnetic field is at 45° with respect to the direction of the polarizers) except along the disclination line (Fig. 6(b)).

As a matter of fact the magnetic transition occurs gradually. If we apply a magnetic field of increasing strength, we observe at first a deformation of the arm cross, the birefringence rings starting to move simultaneously (Fig. 6(b)). This transition is not as sharp as a Freedericksz transition, implying that there are more than one elastic constant involved. It is however possible to determine a critical magnetic field occuring when the extinction cross starts to change its shape. The disclination line previously mentioned appears for slightly higher magnetic fields. Instead of a removal of the central defect, it seems more likely that two other concentric disclination lines appear (Fig. 7). When the strength of the magnetic field increases, one disclination would move toward the center and the other toward the surface of the droplet.

If the coherence length varies as the radius of the droplet, the

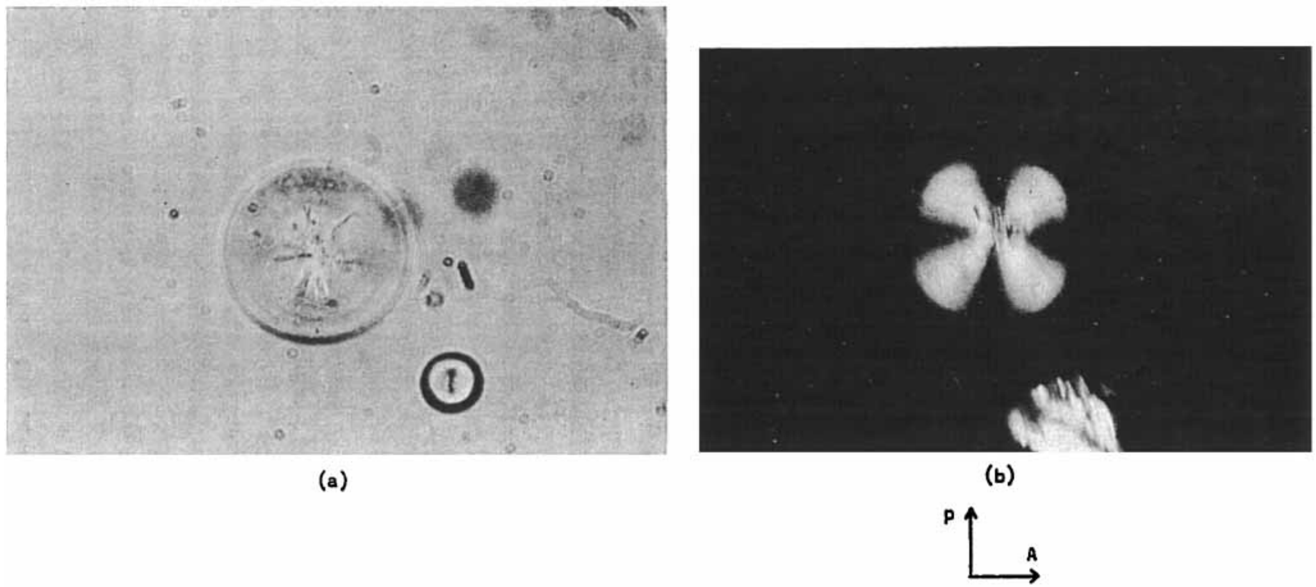


Figure 5. Droplet of MBBA in a mixture Glycerol–CTAB. (a) Natural light; (b) Between crossed polarizers.

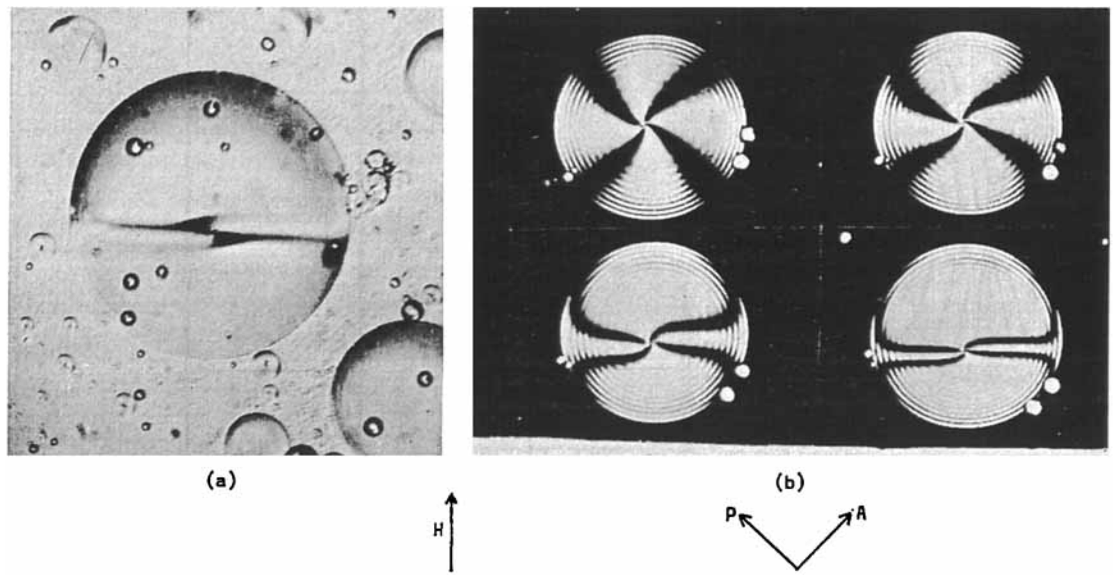


Figure 6. Droplet of Merck IV in a mixture Glycerol–water–polyoxyethyleneglycol. (a) Natural light H = 12,000 G; (b) Between crossed polarizers. The strength of the magnetic field increases from top left photograph to bottom right photograph.

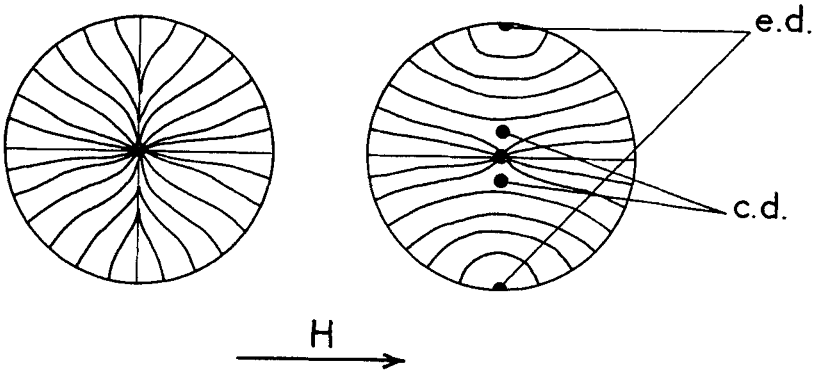


Figure 7. Schematic representation of the deformation induced in a star configuration by a magnetic field of increasing strength. (c.d.) Circular disclination; (e.d.) Equatorial disclination.

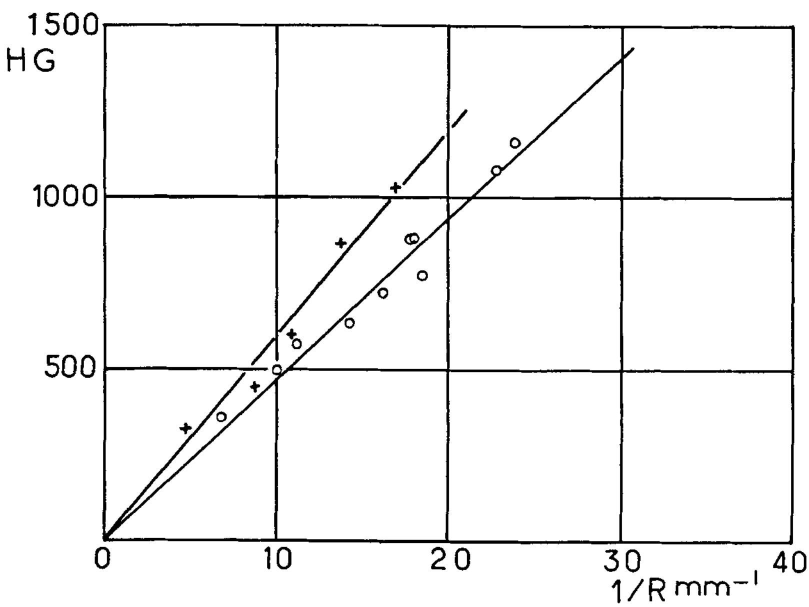


Figure 8. Critical magnetic field versus the inverse of the radius of the droplet (+) MBBA, (○) Merck IV. The isotropic liquid is a mixture of glycerol–water–polyoxyethylene–glycol.

critical magnetic field should be proportional to $1/R$. This is what we have found as shown in Fig. 8.

2. Cholesteric Emulsions

We have also investigated the change in optical pattern due to a cholesterization of a nematic sample. This cholesterization has been achieved by doping the nematic materials with a cholesteric compound. A very small fraction (less than 0.5%) of the additive is sufficient to induce a pitch smaller than the average radius of the droplets ($\sim 10\,\mu$) and therefore would not change considerably the interfacial tension. In the present case we have used the cholesteryl propionate (CP) as a doping agent. The concentration in weight of CP ranged from 0 to 2.28%. The variation of the pitch with concentration in CP has been determined by the Cano wedge method[7] and is reported in Fig. 9.

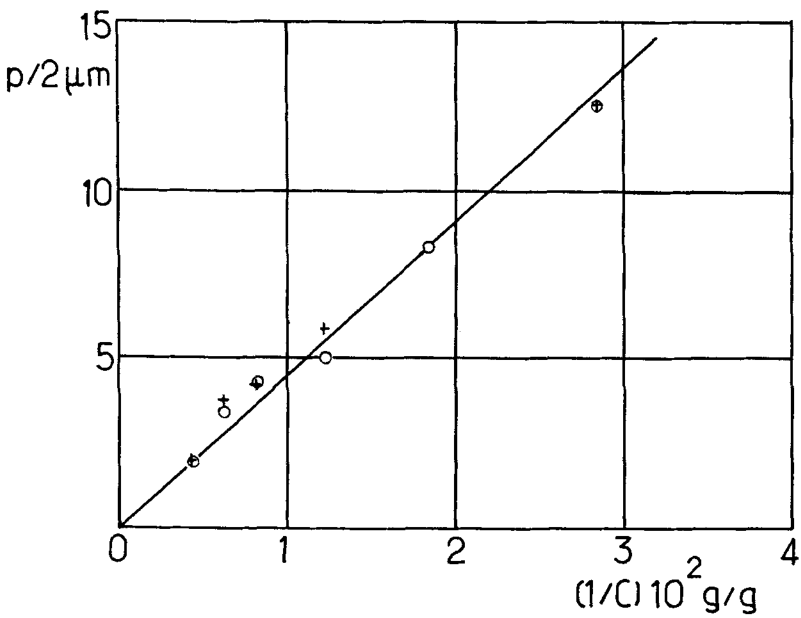
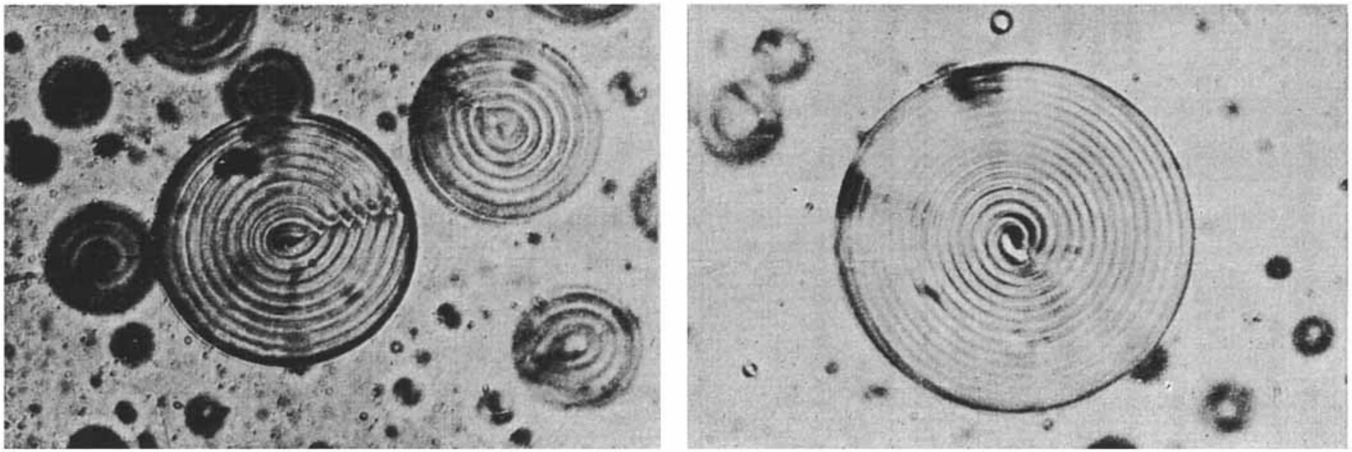


Figure 9. Half pitch versus the inverse of the concentration in cholesteryl propionate (○): data obtained by the CANO wedge method; (+): distance between two consecutive rings of the optical pattern observed in a droplet.



(a) (b)

Figure 10. Droplets of Merck IV–cholesterylpropionate in glycerol. Natural light: (a) $p/2 = 4.4\ \mu$m; (b) $p/2 = 3.4\ \mu$m.

When the radii R of the droplets are smaller or of the same order of magnitude as the helical pitch the surface energy still governs the internal configuration of the molecules.

For instance, droplets of cholesteric materials dispersed in glycerol–CTAB mistures display the star configuration if $p/R > 1$. On the other hand, if $p/R \ll 1$ whatsoever the surface conditions, we observe a spiral shaped optical pattern with a radial disclination (Fig. 10). Such a pattern has already been observed by Robinson and Ward[8] on droplets of concentrated solutions of polypeptides. The explanation of the corresponding configuration has been given by Pryce and Frank.[9] According to the model given by these authors, the optical pattern would look like a spiral or a series of concentric rings, depending on whether the radial disclination points out along the direction of observation or in a plane perpendicular to it. We have indeed observed both patterns (Figs. 10(a) and 10(b)).

When the microscope objective is sharply focused on the center of the droplet, the observed white and black rings represent the arrangements of the cholesteric planes in a thin slab of material. The distance between two consecutive rings should therefore be equal

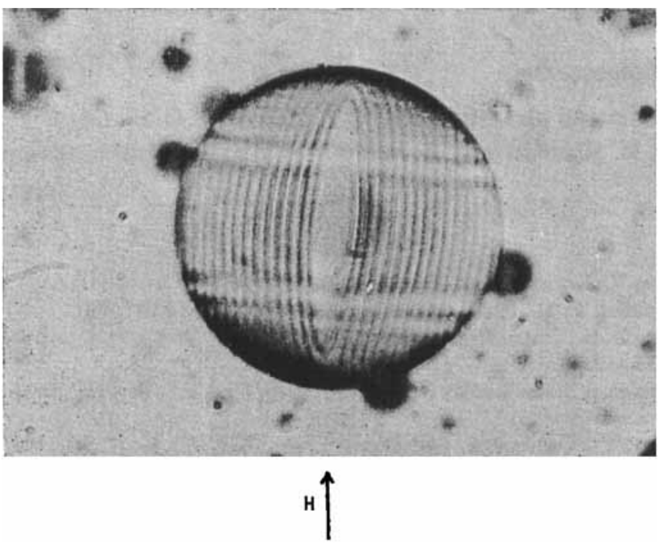


Figure 11. Droplet of Merck IV–cholesterylpropionate in glycerol. Natural light: H = 12,000 G; $p/2 = 3.4$ μm.

to half the helical pitch. Experimental evidence of this last point is given in Fig. 9.

However, according to the same model, the molecules of cholesteric sample should be arranged in a helical fashion along the radial disclination. As a matter of fact when we apply a magnetic field the droplets rotate so that the disclinations align themselves along the direction of the magnetic field. This suggests that the molecules in the vicinity of the disclination converge to give rise to a nematic core. Similar observations have been made for disclinations occuring in the bulk of the cholesteric phase.[10]

It must be noticed that the Pryce and Frank model implies a tangential orientation of the molecules at the interface. Therefore when the surface tension induces the molecules to be normal to the surface of the droplet, there should be additional defects to satisfy boundary conditions.

If we apply a high magnetic field (~12,000 Gauss) the rings become oval (Fig. 11). This change of shape characterizes the tendency of cholesteric axes to orient themselves perpendicularly to the direction of the magnetic field. For even higher magnetic fields one would expect a cholesteric–nematic transition.

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