

Preliminary observations of defects in a polymeric nematic phase

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Some optical observations of defects (disclination lines) in a polyester nematic phase are presented. These observations clearly show the predominance of lines of half integer strength. This result, as well as other observations, seem to fit in with large values of the splay and bend constants K_1 and K_3 compared with the twist constant K_2 . However, K_1 seems to be much larger than K_3 . Interesting phenomena related to disclination core structure and to the surface lines, involving a particular molecular distribution in the surface, are described.

Keywords Defects; disclination lines; polyester; nematic phase; core structure

INTRODUCTION

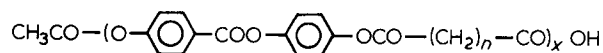
Recently a growing number of polymers forming nematic phases have been discovered, thanks to the efforts of chemists in the search for potential applications of high modulus fibres. Preliminary investigations into the physics of defects of these new materials are few but new questions have arisen concerning the influence of the molecular structure on the properties of defects. We shall discuss some results that have been obtained.

According to Millaud *et al.*, who prepared some sulphuric acid solutions of various polymers¹, there is a predominance of disclinations of integer order ($S = \pm 1$) as is usual in a nematic monomer, but with a very different core structure, namely the core being singular with lines appearing very thin under polarizing microscopy. These authors propose a pure radial splay model, which avoids bend energy; they claim that K_3 is large compared with K_1 and K_2 . They also claim that the core region has a larger density of polymeric chain ends and that the diffusion process of chain ends towards core regions is possible only if the molecular weight is sufficiently low. It is only if such a diffusion process can take place that the core thins down.

In investigations Mackley *et al.*² made on a *p*-hydrobenzoic acid copolyester, a number of integer disclinations in the classical 'plage à noyaux' texture were observed. Looking closely at their pictures, it does not seem that the core is thin and as such these results do not corroborate with the evidence from the previous authors¹. Note however, that the contrast is much fuzzier than in usual 'plage à noyaux', which could be due to the chain ends effect mentioned above. Unfortunately we have no data enabling us to compare the molecular weights in both of the above investigations (refs. 1 and 2).

In both investigations, the textures look like familiar nematic textures and can be used without fear for characterization of the phase (see also ref. 3), but the observed samples displayed large differences as compared with classical samples related to the differences in the molecular structure. We have reached similar conclusions

from a systematic study of a new nematic polymer and these conclusions are presented here. However our observations and models are at variance with both refs. 1 and 2, but seem to corroborate well with observations made in ref. 3 (Noël, private communication). These differences might be due to the different type of polymer we have used (note that the polymer used in ref. 1 is lyotropic); this puts stress on the large variety of new phenomena we expect to find in investigating the physics of liquid crystalline polymers. Our nematic polymer⁴ belongs to a series of polyesters whose general formula is



with $3 < n < 12$, 14 and 20. Here we report results concerning the compound with $n = 5$, for various samples with differing values of x , dispersity, and the state of purity. These may be distinguished as:

Sample A: short chains; product obtained after a short polymerization time ($\sim \frac{1}{2}$ h), showing a small inherent viscosity^{5,9}, with small x (a few units) (x estimated by comparing inherent viscosities of various polymers of different lengths), the inherent viscosity η_i being defined here as the viscosity of a solution of 0.5 g of material in 100 ml of dichloroacetic acid.

Sample B: very polydisperse, with a mixture of short and long chains.

Sample C: purified product obtained after a long polymerization (~ 3 h)¹⁰, $x \sim 24$, calculated from a series of high resolution n.m.r. counts of the CH_3 terminal groups⁶. Inherent viscosity was a few times greater than in sample A.

Most of the samples were prepared by introducing the material, by capillarity, between two glass plates previously cleaned in a sulphochromic solution and heated in a Mettler FP 52 hot stage at $\sim 200^\circ\text{C}$. The polymer aligns in the flow direction and maintains this orientation for sufficient time to allow complete observation of defects. There is a tendency for the samples

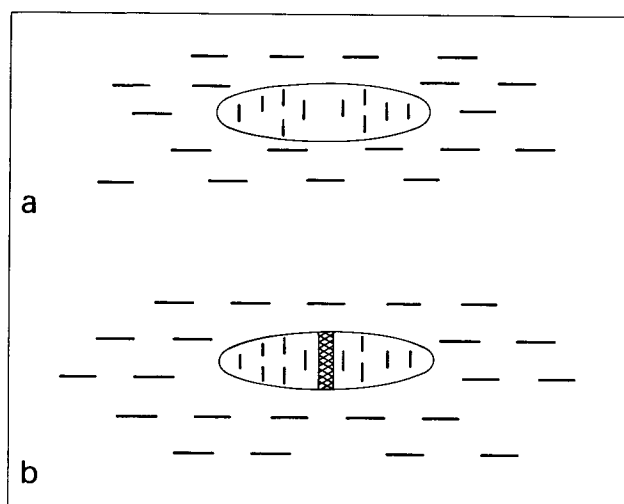


Figure 1 Disclination loops in sample C (schematic) (a) thin thread $|S| = 1/2$; (b) thin thread with a thick thread ($|S| = 1$) attached

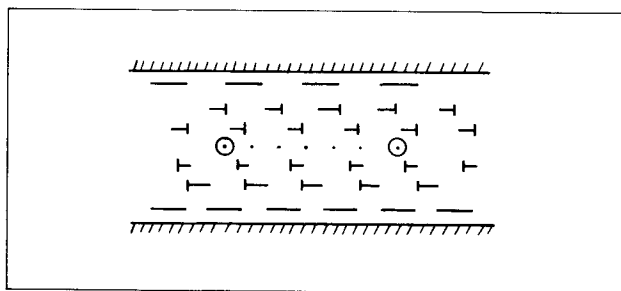


Figure 2 Twist character of a disclination loop in a sample of type C

to become homeotropic with ageing, the homeotropy being quite complete after 2 days annealing in a closed oven at 190°C . The sample thickness varies between $10\ \mu\text{m}$ and $50\ \mu\text{m}$. Some samples were prepared after having coated the glass plates with a solution of polyimide in *N*-methylpyrrolidone, heating at 150°C , rubbing in a fixed direction (*à la Châtelain*), and heating again at 220°C . For these samples the polymer aligns along the direction of rubbing quite easily. We also observed free droplets.

For samples A, the textures display thin lines of strength $|S| = 1/2$ and thick lines of strength $|S| = 1$. In the course of time the threads have a tendency to disappear and give way to a texture with a well resolved Friedel's 'noyaux'. In all respects, there is no difference between this polymeric phase and the usual thermotropic nematic phase. This result is explained by the shortness of the molecules.

Samples B: in this type of specimen we have observed a phase separation at 210°C , some areas remaining isotropic, others becoming nematic, but we have not yet studied in detail the corresponding textures but expect to do so in the near future.

Samples C: they are typical of polymeric nematics and are comparable in molecular weight ($M \sim 12\ 000$) with the polymers already studied. Let us state immediately the conclusions we shall reach: the twist constant K_2 is definitely smaller than K_1 and K_3 , hence most of the geometry tends to avoid bend and splay; K_1 is larger than K_3 ; most of the disclinations observed are of the half-integer type; the nature of the core remains an open and

interesting problem, of a different nature from that in usual nematics.

We will discuss only the textures of samples C in this paper.

PLANAR SAMPLES, INSTABILITIES, TRANSITION TO THE HOMEOTROPIC GEOMETRY

Immediately after introduction of the specimen by capillarity between the two glass plates, a large number of thin loops elongated in the flow direction were observed, which disappear after a few minutes by decreasing their size; they are clearly half integer lines and this is recognized by the fact that some of these lines are sometimes conjugated to an internal thick line (see Figure 1) which is necessarily of integral character.* The essentially twist-bend geometry which exists around such loops is drawn on Figure 2. In the final stage near collapse, the loops persist for a very long time at a size in the order of $0.5\ \mu\text{m}$, which is practically indistinguishable under the microscope.

The (slow) transformation to an homeotropic geometry is controlled by the appearance of loops which separate planar regions from homeotropic regions (Figure 3). The molecules inside the transition region suffer a practically pure twist; this makes these loops akin to 90° Bloch walls in ferromagnets (Figure 4). The pure twist character of the

* Such events are very rare; they involve twist, bend and splay deformation; this last character implies a large energy term, which explains their rarity.

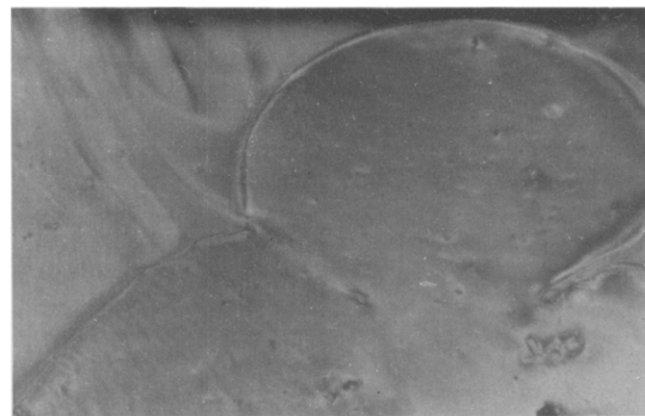


Figure 3 Loop appearing in a planar geometry, separating a planar area (left) from an homeotropic growing one (right). Crossed polars

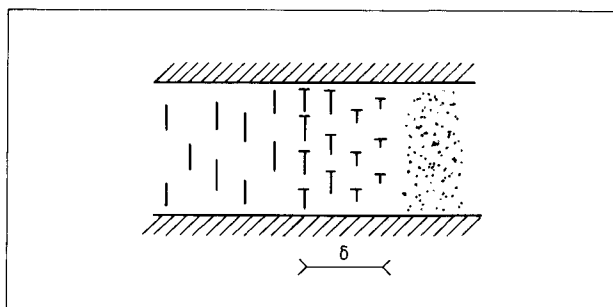


Figure 4 To first approximation, the planar and homeotropic regions are separated by a wall through which the director rotates by an angle of 90° ; the wall is parallel to the direction of the nematically correlated macromolecules in the planar region

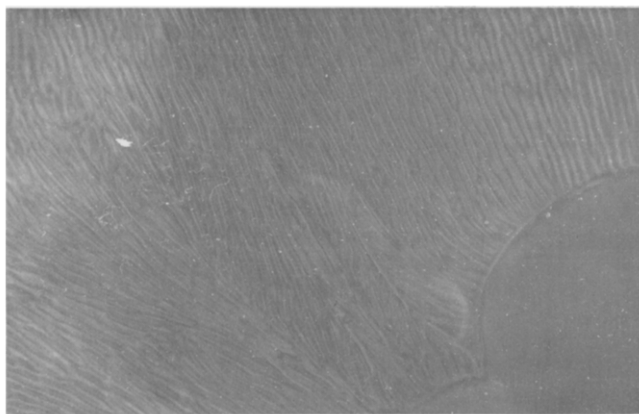


Figure 5 Instabilities perpendicular to the molecular alignment (in the planar area). The loop wall shows a cusp, which is the termination of a quasi-wall of large bend splay deformation in the planar area. Crossed polars

wall is deduced from observation of the instabilities (Figure 5) which appear when one gently presses down on the upper plate (even breathing from the mouth on the upper plate causes a phenomenon) and then release it. These instabilities, as we have been able to show by looking for the slow and fast optical axes of the molecules, are perpendicular to the director. The wall itself is divided in segments which end on sharp cusps at which the orientation of the director in the planar region changes abruptly. It is most probable that the chirality of the 90° wall changes from one segment to the other. These cusps are therefore locations of disclination lines of strength $1/2$, in which splay and bend deformations are concentrated (Figure 5). The distribution of the director itself in the line and its vicinity is probably as is indicated in Figure 6.

The existence of the cusp itself (why does the line of transition between the two wall segments of opposite chiralities affect the wall so abruptly?) is not easily understood. The curvature of the wall segments is due to the motion of the wall which tends to extend the homeotropic region; the wall is therefore convex towards the planar region. If we suppose, moreover, that the wall has a larger mobility than the line, then the line stays back and this could explain the cusp. Note also that there is, in the planar region, a 'quasi-wall' which is bordered by the line, through which the nematic correlated molecules** suffer rapid splay and bend deformations (δ' is much smaller than δ , the wall thickness). This quasi-wall is not in the wake of the line, and cannot be explained by the smaller mobility of the line. Therefore we have to imagine a quite complex repartition of the director, whose purpose is, on large scales, not only to decrease splay and bend deformations at the expense of twist deformations, but probably also (since the quasi-wall is a bend-splay wall in a sea of essentially bend deformations) to decrease

* At this stage we do not want to hypothesise on the chain configuration in the nematic state, whether the rigid aromatic cores couple together preferentially and drive the alignment of the flexible $(\text{CH}_2)_5$ chains, or these flexible chains have enough freedom to give the whole macromolecule some kind of random-coil configuration. Probably something intermediary occurs, which strongly depends on the length of the flexible section. For example, a drastic increase in the viscosity with the length of the alkyl chain has been observed (for $n=14$; the sample, although having a normal nematic X-ray diagram, does not crystallize on the scale observed in optical microscopy, and does not show any recognizable defect, which can be understood as due to an increase in the 'random-coil'-ness).

splay contributions to the total energy versus bend contributions. Therefore, K_1 appears to be larger than K_3 . Also, there is a core contribution to the total energy, which requires the elaboration of a core model which has not yet been undertaken.

Note that the measurement of the wall thickness δ tells us something about the anchoring energy W_S (difference in energy between planar and homeotropic anchoring). We clearly have

$$\delta \sim K_2/W_S$$

so that a large value of δ implies a small value of W_S .

Our last remark concerns the model of a wall versus that of a disclination line. In most of our experiments the sample thickness is small and indeed is comparable to the 'wall' thickness δ ($\sim 10 \mu\text{m}$). It is believed that in thicker samples a splitting of the wall in lines parallel to the glass plates is possible. This is a phenomenon which has been described a number of times in nematics⁷.

PERSISTENT PLANAR ANCHORING: SURFACE LINES

In samples with extremely planar anchoring and in which the initial capillary flow is induced along the direction of anchoring, a number of $S = \pm \frac{1}{2}$ disclinations form (see Figures 7 and 8) which are attached to the glass plates. Essentially, both ends are attached to the same glass plate, and the disclinations are at an angle φ_0 of the order of 45° to the flow direction. This remarkable phenomenon is attended by the formation of extended surface objects, whose extension is related to the transition line as follows: their long dimension is equal to the length of the transition line, their transverse dimension seems to depend on what has been, in some earlier oscillating movement of the transition line, the largest displacement of this transition line (with ends attached). In fact, the size of the extended object is able to grow with time, and this growth seems to attend any fluctuation in the transition line. The transition line itself reaches an equilibrium shape which depends on the size of the extended object, as if it were repulsed outside the volume occupied by this object. Also, the growth of the extended surface object proceeds in such a way that it takes a toothed shape, as a rake.* We

* The teeth of the rake grow in the direction of an applied flow, whatever this direction might be.

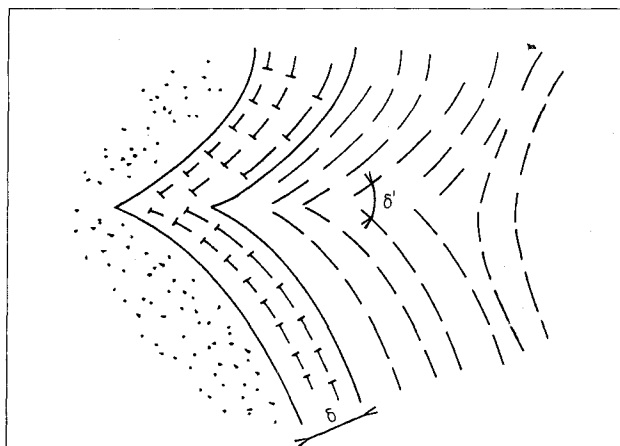


Figure 6 Structure of the 90° wall at a cusp; view from above, in a plane parallel to the glass plates (see Figure 5)

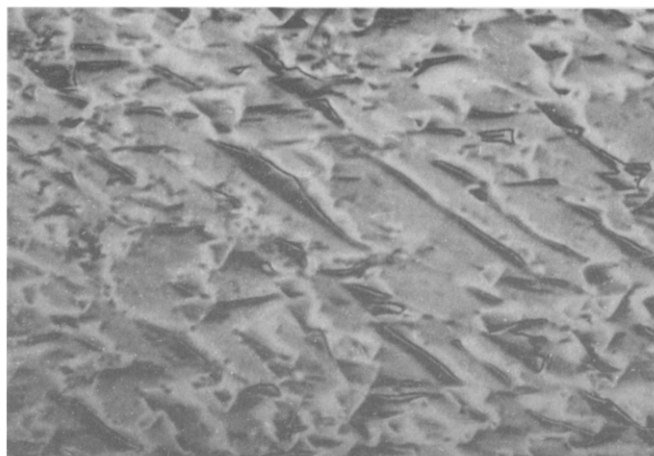


Figure 7 Formation of surface disclination lines joining two points of attachment to the surface of a $S = 1/2$ line. The surface line shows up a complex core structure in the form of a 'rake' of crystallization; the bulk line is at an angle of 45° approximately with the general alignment, which is horizontal

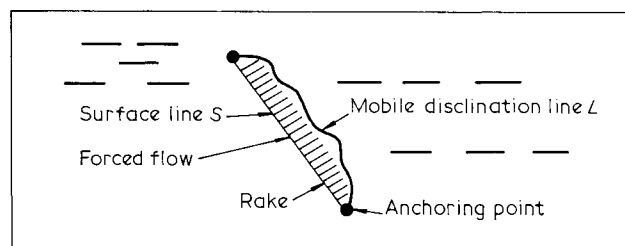


Figure 8 Extended surface object and mobile $|S| = 1/2$ line attached to the glass plate; view from above

propose the following interpretation for these phenomena:

(i) the disclination is at an angle to the general direction of alignment (see *Figure 9* for definitions) because of a balance between twist deformation on one hand, bend and splay on the other, with the necessity of minimizing splay deformations. A rough estimation of the relative values of K_1 and K_3 can be extracted from the measurement of the angle φ_0 (see *Figure 9*) by working out the following model; take the disclination along the Oz axis, assume the general alignment at an angle φ_0 from the normal to the transition line in the plane yz (which is the plane of the sample). Then assume that \vec{n} is confined to the plane xY (this assumption seems to fit with the observed contrast; the plane xY is perpendicular to the sample and can be chosen as the plane of polarization of the incident light, for example: in such a case very little intensity should be transmitted between crossed polars, exception the near vicinity of the line L); call θ a polar angle in this plane. Then

$$n_x = \cos \psi \quad n_y = \cos \varphi_0 \sin \psi \quad n_z = \sin \varphi_0 \sin \psi$$

where $\psi = \psi(x, y)$. When $\psi = \pm \theta/2$, one gets either a wedge line ($\varphi_0 = 0, \pi$) or a twist line ($\varphi_0 = \pi/2$). Minimizing the total Frank energy with respect to φ_0 yields:

$$\int \left[-K_2 \cos \varphi_0 \left(\frac{d\psi}{dy} \right)^2 + (K_1 \cos^2 \psi + K_3 \sin^2 \psi) \cos \varphi_0 \left(\frac{d\psi}{dy} \right)^2 + (K_3 - K_1) \frac{\sin 2\psi}{2} \frac{d\psi}{dx} \frac{d\psi}{dy} \right] dx dy = 0$$

By taking reasonable averages, one gets

$$\frac{K_1 + K_3}{2} \cos \varphi_0 - K_2 \cos \varphi_0 \frac{+\alpha}{\sqrt{2}} (K_3 - K_1) = 0$$

where α is some constant which is larger than $\frac{\cos \varphi_0}{\sqrt{2}}$ if K_1 is larger than K_3 (K_2 small); For $\varphi_0 = \pm \pi/4$, one obtains:

$$K_1 \sim K_3 \frac{2\alpha + 1}{2\alpha - 1} + \frac{2K_2}{1 - 2\alpha}$$

α vanishes for the usual solution $\psi = \pm \theta/2$; α of the order of unity indicates a solution much distorted with respect to the usual one, corresponding to $K_1 \sim 3K_3$ (K_2 small), as expected. A detailed calculation, as indicated here, is in progress.

(ii) the straight boundary of the rake (see *Figure 8*) is, in our opinion, a surface disclination line S which forms in order to counterbalance the topological deformation imposed by the presence of the disclination line L with ends attached. This is explained in *Figure 10* which represents, in a plane perpendicular to the line, the integral lines of the projection of the director on this plane (i.e. the presence of a wedge-type configuration does not mean that we have a wedge line in space).

(iii) it is most probable that the physical properties of the surface line S are governed by its core properties. We propose, as in ref. 1, (but we restrict this proposal to surface lines), that the core is a region with a high density of ends of macromolecules. This decreases locally the entropy of the nematic phase bringing it closer to a

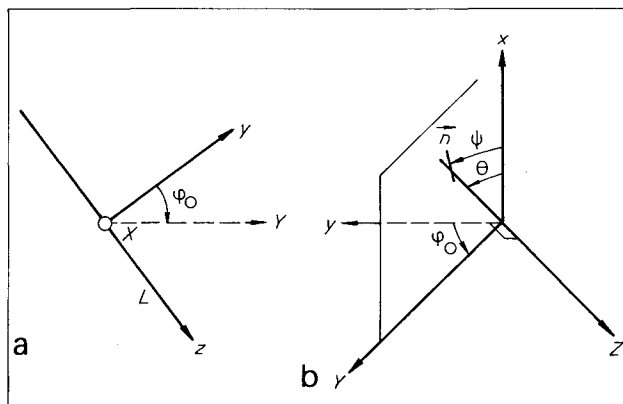


Figure 9 Set of coordinates for the mobile disclination L at an angle to the alignment. (a) In the plane of the sample; the line is along the z axis, at an angle $\pi/2 - \varphi_0$ to the alignment imposed by the anchoring at the glass plates; (b) the macromolecules are assumed to lie in the plane xY perpendicular to the sample

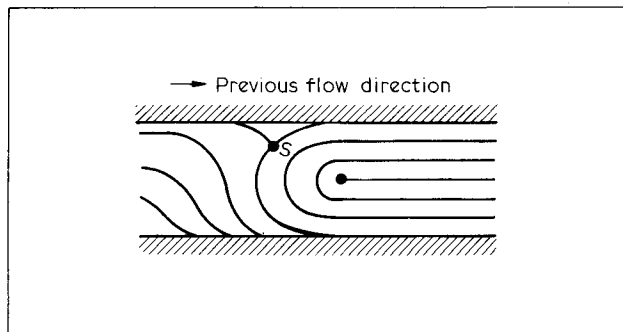


Figure 10 Vertical cut of the situation in *Figure 8*



Figure 11 Free drop; formation of disclination lines more or less parallel to alignment (as inferred by contrast investigation between crossed polars); their length increases with time. Unpolarized light

smectic phase. This decrease is counterbalanced by a decrease in internal energy which can manifest itself as a local tendency to crystallization. This might be the reason for the formation of the rake, the combs of the rake being related to some anisotropic growth process, with larger growth velocity in the direction of alignment.

However we do not claim to have here a complete understanding of this observation (in particular the unsymmetry of the rake with respect to its boundary S), and more work has to be done.

FREE DROPLETS

Very thin free droplets show marked sets of disclination lines of strength $S = 1/2$ (see Figure 11). The length of these lines increases with time, which probably means that these lines terminate on the free surface, rather than on the glass plate (where the ends would not move easily). The position of the black arms indicates that the configuration of the molecules, in projection in a plane parallel to the glass plate, is different at both ends of the line (this also applies to the observation made in the previous subsection). Figure 12 shows a possible interpretation of these configurations, which are representative of the molecules at the free surface.

To understand this observation, let us first assume that the free drop does not contain any disclination, and that the anchoring conditions on the glass plate and on the free surface are in competition. There is, therefore, a strong bend-splay deformation in the thickness, which is relaxed by the formation of lines involving twist deformation. This explains why their length increases with time. Also some competition between bend and splay can occur. A similar observation has been made by Meyer *et al.*⁷, in PBLG solutions, with a specific model concerning the anchoring conditions.

CONCLUSION

One of the clearest conclusions of this study is obtained from the predominance of $|S| = \frac{1}{2}$ lines; this implies, as it is reaffirmed by other observations, that K_1 and K_3 are definitely larger than K_2 , so that any splitting of the core of an $|S| = 1$ line tending to remove the core singularity⁸, is not favoured. Therefore, since the transition line energy is proportional to $|S|^2$ when a core singularity is present, $|S| = \frac{1}{2}$ lines are favoured.

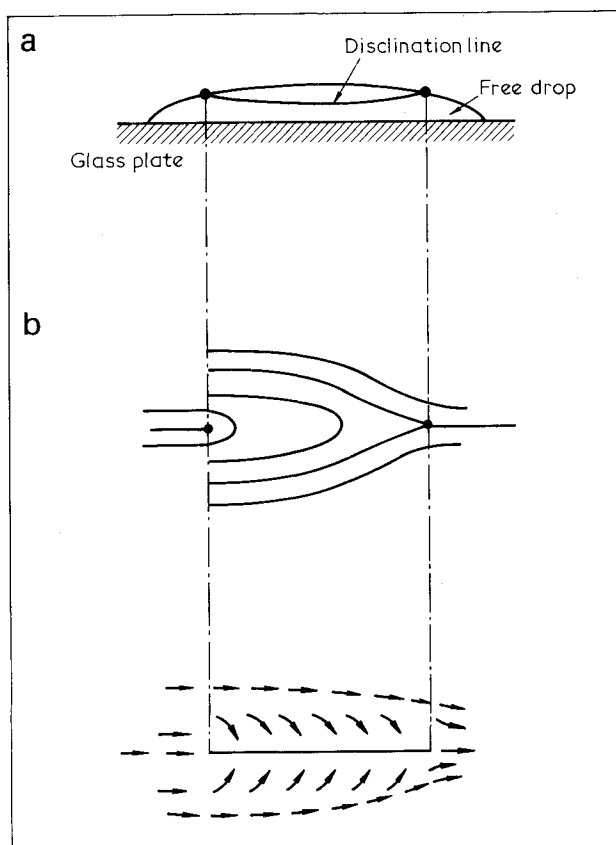


Figure 12 Disclination lines in a free drop; (a) vertical cut; (b) probable directions of the nematic molecules in a plane parallel to the glass plate; (c) twist bend deformation near the free surface (no specification of the component of the director along the normal to the surface)

Concerning the nature of the core, a model like that described in ref. 1, involving a large density of chain ends, seems to be coherent with our observations of surface lines, and might be compatible with our other observations. Concerning the instabilities, their existence probably implies that the medium responds elastically (like a solid) at short times, like a liquid (nematic) at longer times.

It appears clear, therefore, that only a complete investigation, involving the influence of monomer length, molecular weight and dispersity can bring about a greater understanding of such phenomena.

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