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Characterization of lyotropic nematics in cylindrical capillaries

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Procedures for characterization of lyotropic nematics in cylindrical capillaries by optical microscopy in orthoscopic geometry are presented. Typical textures due to surface alignment allow unambiguous characterization of N_c (cylindrical micelles) and N_d (discotic micelles) phases. Typical textures due to the compromise between surface and magnetic alignment allow unambiguous definition of the sign of the diamagnetic anisotropy susceptibility $\Delta\chi$. The textures allow also estimates of anisotropies of elastic constants for N_d lyomesophases.

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1. Introduction

Lyotropic nematic liquid crystals are usually characterized by polarized optical microscopy (OM) of samples conditioned in thin planar capillaries (0·1–0·3 mm). Uniaxial phases show typical textures in orthoscopic geometry associated with surface anchoring: N_c phases (cylindrical micelles) show planar birrefringent textures while N_d phases (discotic micelles) show pseudo-isotropic textures [1, 2]. This occurs because of the interactions of micelles with the vitreous surface. The surface is covered with at least one layer of surfactant molecules adsorbed that produce a hydrophobic surface. Micelles near this surface orient with their surfactant molecular axes perpendicular to the surface. Cylindrical micelles of N_c phases orient with their symmetry axes parallel to the surface, while discotic micelles of N_d phases orient with their symmetry axes perpendicular to the surface.

The signal of the diamagnetic anisotropy susceptibility ($\Delta\chi = \chi_{\parallel} - \chi_{\perp}$) determines the response of the director to an applied magnetic field **H**. For amphiphiles with hydrocarbon chains, magnetic orientation is defined by the anisotropy of the chain, which align with chain axis perpendicular to **H**. So usually N_c phases have $\Delta\chi > 0$ (N_c^+) and N_d phases have $\Delta\chi < 0$ (N_d^-). It is possible however to have N_c^- and N_d^+ for other types of amphiphiles [3, 4]. It is important therefore to characterize nematic phases by determination of the director direction in magnetically oriented samples, thus obtaining the sign of $\Delta\chi$. Procedures to identify this sign by OM observation of samples in thin planar capillaries have also been reported [5].

On the other hand, X-ray diffraction (XD) studies of these systems are performed with samples conditioned in cylindrical capillaries (inner diameter 0·5 to 2·0 mm). Planar cells are inconvenient because they have thick walls, that attenuate the X-ray beam and produce undesirable scattering. It is thus not routine to follow by OM observations exactly the same sample that is being studied by XD. Usually the sample used for OM characterization and the sample used for XD studies come from the same test tube where the sample was prepared.

This paper addresses to situations in which it is desirable to observe by OM the same capillary (and thus exactly the same lyonematic sample) that is being studied by

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XD in cylindrical capillaries. Examples of such situations are: studies of ageing effects, that may be followed over months [6]; studies of bulk magnetic orientation in thicker samples, and competition with surface effects; analysis of effects of damage due to X-ray irradiation. All these studies are made with much more confidence if observations by both OM and XD are made on the same cylindrical capillary.

Cylindrical configuration for thermotropic nematics with homeotropic surface alignment has been discussed previously [7–10].

Effects of surface and magnetic orientation of nematic lyomesophases in cylindrical capillaries have been studied previously [11], but no systematic characterization of lyotropic nematic phases in cylindrical capillaries by OM has been so far reported.

The purpose of this article is to describe simple procedures for characterization of lyotropic nematic phases by OM of samples conditioned in cylindrical capillaries. A comparison with results previously obtained for thermotropics is discussed. Estimates of anisotropies of elastic constants of lyonematics are also made.

2. Materials and methods

OM observations have been made with a Wild orthopol microscope equipped with photomicrograph facility and also with a horizontal axis simple microscope equipped with polarizers.

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Direct observation of cylindrical capillaries in orthoscopic geometry is difficult due to a convergence effect of lens type. This effect was eliminated by observation of the cylindrical capillary embedded in a planar diopter of refractive index close to that of the sample (water may be used). A specially designed sample holder has been constructed for this purpose [12].

The simple microscope allows direct observation of the capillary placed between the poles of a permanent magnet. The convergent lens effect was eliminated by using an extense source of illumination.

A permanent magnet of 2 kG was used and three different geometries have been defined for studies of magnetic orientation:

(1) **H** present (geometry $G_\perp$): the capillary is placed between the poles of the magnet, with the capillary axis perpendicular to both **H** and the light beam.

(2) **H** residual (gometry $G_\parallel$): the magnet is removed and the sample turned 90° around its axis. Thus the direction of magnetic orientation coincides with the direction of the light beam. To be sure that magnetic orientation is kept residually it is important, after observation, to turn the sample more 90° and to verify the permanence of the $G_\perp$ condition as well. Good residual orientation is usually kept within at least one day.

(3) Rotating sample in geometry G_{rot}: with the magnet, sample and light beam placed as in $G_\parallel$, the sample is rotated around its axis by a driving motor with angular velocity $\omega = 0{\cdot}5$ turns/min.

Geometries $G_\perp$ and $G_\parallel$ correspond to the geometries used to characterize phases by XD [13]. Geometry G_{rot} corresponds to the original geometry for characterization of lyonematics by N.M.R. [14]. G_{rot} is also particularly convenient for XD studies of N_d samples with $\Delta_\chi < 0$ [12], since the director is then forced to be in the direction of the capillary axis (the alternative of applying **H** perpendicular to capillary axis in two mutually successive directions is not completely reliable for long exposures, since

the result may not be necessarily a sample with complete symmetry around the capillary axis).

The liquid crystalline systems that have been used were the conventional [14] sodium decyl sulfate (SDS) ternary N_c^+ phase (40·0 per cent SDS/53·0 per cent H_2O/7·0 per cent decanol—referred to as SDS-1), and quaternaries N_d^- phases (37·0 per cent SDS/51·0 per cent H_2O/6·0 per cent decanol/6·0 per cent N_a sulphate—referred to as SDS-2), (34·3 per cent SDS/56·5 per cent H_2O/1·4 per cent decanol/2·8 per cent N_a sulphate—referred to as SDS-3, (31·9 per cent SDS/57·6 per cent H_2O/5·3 per cent decanol/5·2 per cent N_a sulphate—referred to as SDS-4). A recently obtained [15] N_c^+ phase of sodium dodecyl sulphate (SLS) (25·0 per cent SLS/70·5 per cent H_2O/4·5 per cent decanol—referred to as SLS-1), a N_d^- phase [6] (24·7 per cent SLS/70·0 per cent H_2O/5·3 per cent decanol—referred to as SLS-2) and N_d^- phase of potassium laurate (KL) (30·5 per cent KL/6·6 per cent decanol/60·9 per cent H_2O/2·0 per cent KCL—referred to as KL-1) were also investigated by OM in cylindrical capillaries. These samples were all characterized also by conventional OM investigation in planar cells and studied by XD in our laboratory.

3. Orthoscopic observations

(*a*) *Surface alignment*

Figure 1 shows the temporal evolution of textures of N_d and N_c phases in cylindrical capillaries until the process of surface orientation is completed (~ 50 hours). The texture, initially similar for N_c and N_d phases, evolves to typical textures that allow unambiguous identification and characterization of the two types of uniaxial phases. For N_c phases the director **n** is in the direction of the capillary axis, as evidenced in figures 1 (*g*) and (*h*). When the direction of polarization coincides with the capillary axis the texture is pseudo isotropic; a turn of 45° related to the polarizers reveals a planar birefringent texture.

The direction of the capillary axis in figure 1 (*g*) is slightly different than the direction of polarization to allow visualization of the capillary, otherwise completely black. The two dark lines of figure 1 (*h*) are coloured and correspond to changes in colour due to changes in thickness of the sample in the cylindrical capillary.

The director field has thus a preferable direction in the whole cylindrical capillary.

For N_d samples the texture is characterized by a black central line (figure 1 (*d*)) when the capillary axis is parallel to the direction of polarization. A turn of 45° results in a texture (figure 1 (*e*)) with a clear central line between two coloured and darker lines. This result shows that only in the central part of the cylindrical capillary the director has the direction of the capillary axis. The texture remains invariant turning the capillary around its axis. The same kind of textures were obtained for the nematic thermotropic MBBA doped with hexadecyl trimethyl ammonium bromide, which promotes normal alignment at the glass surface [9].

A schematic diagram of the director field in cylindrical capillary for a N_d phase is shown in figure 2. It corresponds to a radial field in the outer part of the capillary, with a changement to an axial field at the capillary centre. The size of the central region corresponds to the thickness of the dark central line in the texture of figure 1 (*d*); it does not correspond however to a 'core'.

This model for the director field corresponds to a non singular screw disclination line of strength $S = +1$ for the case splay-bend [7–10]. It represents a continuous 'escape' into the third dimension, which has been shown to be energetically

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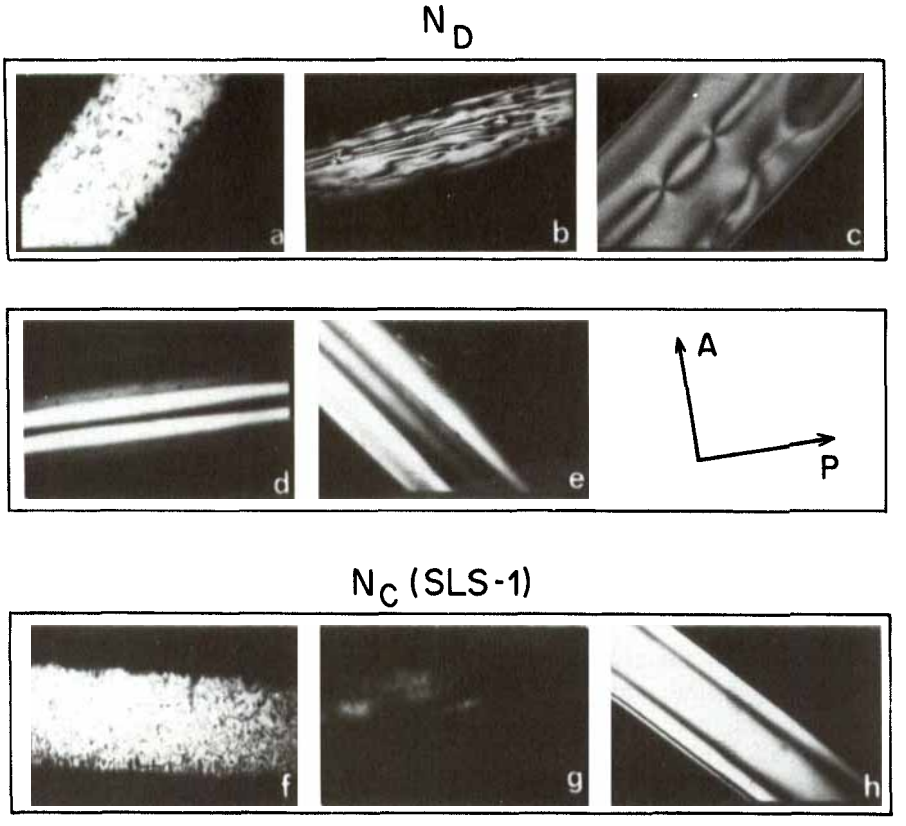

Figure 1. Characteristic textures of lyotropic nematics in cylindrical capillaries of diameter 1 mm under surface alignment. A and P are the directions of the analyser and polarizer. (*a*) N_d disoriented sample (SDS-2). (*b*) N_d sample (SDS-3) just after preparation, showing flux orientation. (*c*) N_d samples (SDS-3) in the process of surface orientation. (*d*)(*e*) oriented N_d sample (SDS-2) with the capillary axis parallel to P(*d*) and at 45° with P(*e*), in the same region. (*f*) N_c disoriented sample. (*g*)(*h*) oriented N_c sample with the capillary axis parallel to P(*g*) and at 45° with P(*h*). All textures of oriented samples are invariant under capillary rotation around its axis.

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more favourable than a +2 disclination line [7, 9] and does not require a 'core' [8].

It should be therefore concluded that OM observations in cylindrical capillaries allow unambiguous characterization of N_c and N_d phases.

(*b*) *Quantitative comparison with thermotropics*

The darker lines in figure 1 (*e*) for N_d correspond to the region where the projections of the director, in a plane perpendicular to the incident line, form an angle of 45°, shown in figure 3.

If r is the distance to the capillary centre, R the capillary radius and φ the angle between the director and a diametral plane, it is possible to calculate r/R from [7]

$$\frac{r}{R} = \left| \frac{\cos k \sin \varphi - \sqrt{[1 - \sin^2 k \sin^2 \varphi]}}{\cos k \sin \varphi + \sqrt{(1 - \sin^2 k \sin^2 \varphi)}} \right|^{1/2} \cdot \exp \{ -\psi \tan k \}$$

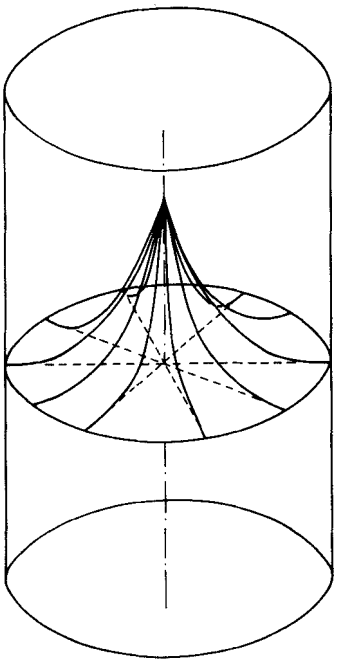

Figure 2. Representation of the director field for N_d samples in cylindrical capillaries.

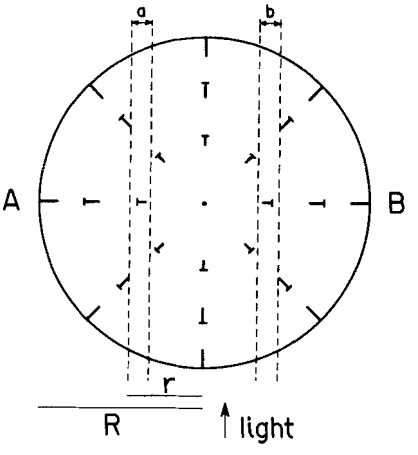

Figure 3. The projections of the director in the regions which correspond to the darker lines (*a*, *b*) of figure 1 (*e*) form an angle of 45° with a plane perpendicular to the incident light and the plane *AB*.

where $\sin\psi = \sin k \sin\varphi$, $K_{11} < K_{33}$ and

$$\tan^2 k = \frac{K_{33} - K_{11}}{K_{11}}.$$

For thermotropic nematic MBBA, we measured the ratio $r/R \cong 0{\cdot}30 \pm 0{\cdot}1$ in figure 9 (*c*) of Meyer's [9], which leads to $K_{11}/K_{33} \cong 0{\cdot}46 \pm 0{\cdot}3$ for $\varphi = 45°$.

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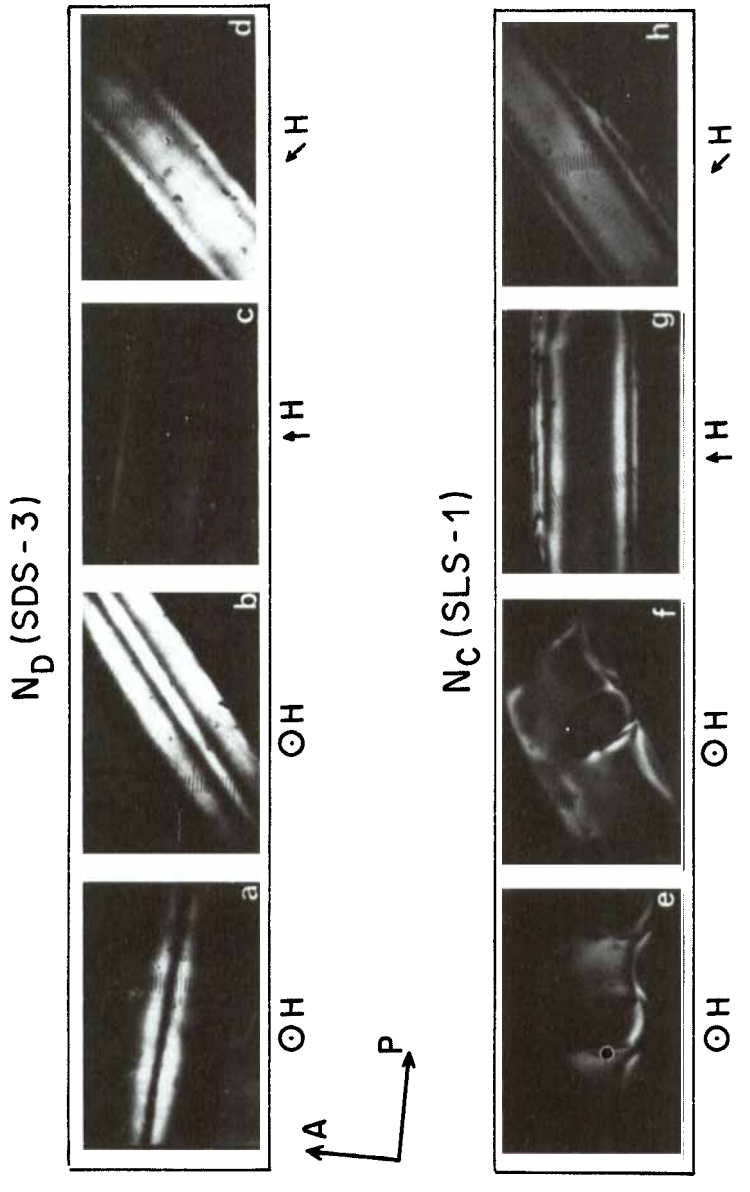

Figure 4. Characteristic textures of magnetically oriented lyotropic nematics in cylindrical capillaries of 1 mm. Sets indicate the directions of the polarizer (P) and analyser (A); ↑ and ⊙ indicate the direction of the magnetic field **H**. (*a*) and (*e*) **H** parallel to observation light and capillary axis parallel to P. (*b*) and (*f*) **H** parallel to observation light and capillary axis at 45° with P. (*c*) and (*g*) **H** perpendicular to observation light and capillary axis parallel to P. (*d*) and (*h*) **H** perpendicular to observation light and capillary axis at 45° with P.

Taking into account that the ratio between splay and bend elastic constants is strongly dependent on temperature [16], this result can be considered compatible with the value 0·7 used by Williams *et al.* [8] for MBBA.

OM observations may therefore give a rough estimate of the anisotropies of elastic constants for N_d nematic lyomesophases. Results obtained at (25·0 ± 0·2)°C are shown in the table.

Table. Anisotropies of elastic constants (K_{11}/K_{33}) at (25·0 ± 0·2)°C for N_d^- nematic lyotropics sodium decyl sulphate (SDS-4), sodium dodecyl sulphate (SLS-2) and potassium laurate (KL-1). Remark that capillaries with different diameters give same values of K_{11}/K_{33}.

Sample	$2R$ (mm)	$2r$ (mm)	r/R	K_{11}/K_{33}
KL-1	1·06 ± 0·01	0·234 ± 0·01	0·22 ± 0·01	0·28 ± 0·04
KL-1	0·51 ± 0·01	0·12 ± 0·01	0·24 ± 0·02	
SDS-4	0·57 ± 0·01	0·18 ± 0·01	0·315 ± 0·02	
SDS-4	0·70 ± 0·01	0·23 ± 0·01	0·33 ± 0·02	0·50 ± 0·04
SDS-4	1·13 ± 0·01	0·34 ± 0·01	0·30 ± 0·01	
SLS-2	0·82 ± 0·01	0·19 ± 0·01	0·23 ± 0·01	0·29 ± 0·02
SLS-2	1·09 ± 0·01	0·26 ± 0·01	0·24 ± 0·01	

These results show that the anisotropies of elastic constants is of the same order of magnitude for thermotropic nematics as MBBA and for lyotropic nematics, as observed already for lyomesophases of decyl ammonium chloride [16].

(*c*) *Magnetic orientation*

OM observations of N_d^- and N_c^+ samples in cylindrical capillaries in geometries $G_\perp$ and $G_\parallel$ are shown in figure 4. Those obtained with rotating sample (G_{rot}) are shown in figure 5.

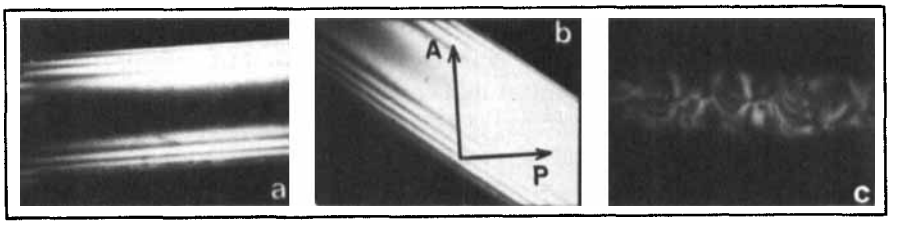

Figure 5. Characteristic textures of lyotropic nematics in cylindrical capillaries of diameter 1 mm after permanence under a magnetic field **H** orthogonal to the axis of the rotating capillary. Sets indicate the directions of the polarizer (P) and analyser (A). (*a*)(*b*) N_d sample (SDS-3) with capillary axis parallel to P(*a*) and at 45° with P(*b*). (*c*) N_c sample (SDS-1). N_d textures (*a*) and (*b*) are invariant under rotation of the capillary around its axis while N_c texture (*c*) is not invariant.

Such magnetically oriented samples display always a superposition of surface and magnetic orientation effects.

N_c^+ samples have the director oriented preferentially in the direction of **H** in the central part of the capillary. Figures 4(*e*), (*f*), (*g*), (*h*) evidence that $\mathbf{n} \parallel \mathbf{H}$ and thus $\Delta\chi > 0$. Results with G_{rot} (figure 5(*c*)) are typical of a disoriented sample.

The director field for a N_c^+ phase magnetically oriented in cylindrical capillaries with **H** perpendicular to the capillary axis is shown in figure 6. Near the surface the

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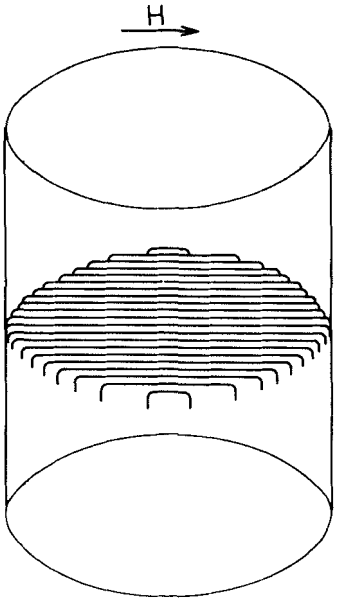

Figure 6. Representation of the director field in N_c^+ samples in cylindrical capillaries oriented with **H** orthogonal to the capillary axis. The alternative of field lines turning downwards is arbitrary; the reverse situation is possible and boundaries between the two possibilities may be observed.

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director is parallel to the capillary axis, and becomes parallel to the applied field (perpendicular to capillary axis) in the central part of the capillary. The extent of the border effects can be seen in figure 4 (*g*) in the white stripes at the capillary border.

For N_d^- samples results are more complex. Results with geometries $G_{\parallel}$ and $G_{\perp}$ for N_d^- samples indicate a director field as displayed in figure 7. Application of **H** perpendicular to the capillary axis deforms the director field in relation to that due only to surface orientation (figure 2). A planar region with director **n** parallel to the capillary axis is formed in the diameter that coincides with the direction of **H** (*AB* in figure 7). When viewed in the direction of **H** (residual), corresponding to the projection of the director field in a plane perpendicular to **H**, the director field is similar to the **n** field of a N_d sample with only surface orientation. Thus in figures 4 (*a*) and (*b*) the texture resembles that obtained only with surface orientation, but are more refringent. When viewed in the direction perpendicular to **H** the sample is black (figure 4 (*c*)) and turning 45° becomes refringent (figure 4 (*d*)).

The director field of figure 7 is reforced by observations made visually in thicker cylindrical capillaries (2·0 mm). When viewed with naked eyes between crossed polarizers these thicker capillaries showed a plane, containing **H** and the capillary axis, that divided the sample in two half cylinders [11]. When the capillary axis is parallel to the polarizer and the incident light is parallel to the direction of **H**, a central dark line can be seen; turning the capillary axis 90° around its axis the capillary becomes almost black.

The effect of the magnetic field should be thus first analysed in the plane *AB* that contains **H** and the capillary axis. In this plane the condition **H** perpendicular to **n** leads to **n** parallel to the capillary axis over an extended core, with a continuous change towards an homeotropic anchoring near the surface. In the plane *CD*

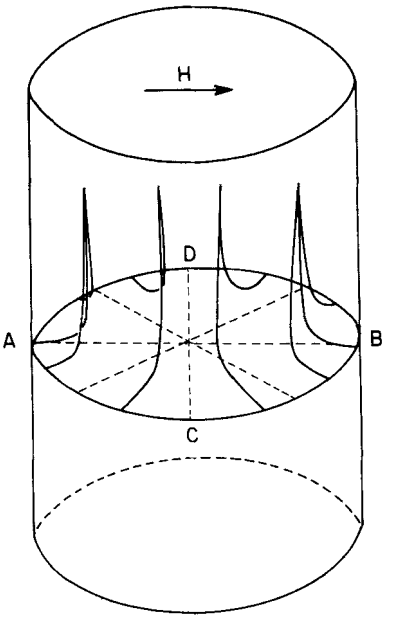

Figure 7. Representation of the director field in N_d^- samples in cylindrical capillaries oriented with **H** orthogonal to the capillary axis.

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perpendicular to **H**, on the other hand the homeotropic anchoring satisfies **n** perpendicular to **H** and thus magnetic orientation induces **n** perpendicular to the capillary axis, except at the centre where the two planes cross each other and there is an escape of the director field along the capillary axis.

The thickness of the central dark line indicates that this escape is also continuous, but very inclined. As a result, in the bulk of the two half-cylinders **n** will be normal to both **H** and the capillary axis; this is the typical result obtained from X-ray diffraction in geometries $G_{\parallel}$ and $G_{\perp}$ [13] [11].

The plane with **n** parallel to the capillary axis is clearly seen by OM, but it is not revealed in usual XD diffraction photographs, that correspond essentially to scattering from the bulk.

Results with geometry G_{rot} figures 5(*a*) and (*b*)) correspond essentially to a rotation of the plane *AB* that contains both **H** and the capillary axis; the extended core becomes tridimensional. In this core the degeneracy due to **n** perpendicular to **H** is removed; the director **n** is parallel to the capillary axis and the sample has axial symmetry (figure 8). This result evidences that **n** is perpendicular to **H** and $\Delta\chi < 0$. This geometry is useful for XD studies of N_d^- lyonematics.

It should be concluded that OM observations of nematic lyomesophases in cylindrical capillaries oriented in magnetic fields allows unambiguous definition of the sign of $\Delta\chi$. The results here obtained by OM and discussed for N_d^- lyonematics in presence of magnetic fields have not yet been obtained with thermotropic nematics, that have usually $\Delta\chi > 0$. Discotic thermotropics with $\Delta\chi < 0$ [17] could probably show similar effects.

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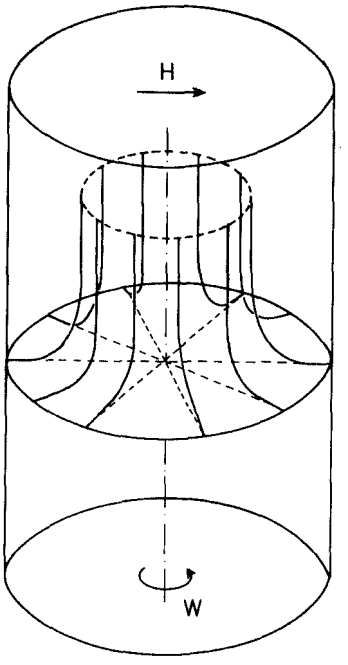

Figure 8. Representation of the director field in N_d^- samples in cylindrical capillaries with geometry G_{rot}.

for the skilful preparation of mesophases. Thanks are also due to Dr. A. M. Figueiredo Neto and T. Kroin for helpful discussions.

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