

CHAPTER I

INTRODUCTION

It is now well known that in many organic compounds with long and narrow molecules, the solid phase does not directly go over to the ordinary (isotropic) liquid phase when heated, but passes through one or more intermediate phases. The term 'liquid crystal' is a general name given to these intermediate phases. They are also called mesomorphic phases or mesophases.

A substance in this phase exhibits some 'crystalline' properties such as anisotropy in dielectric and diamagnetic properties, optical and elastic properties, etc. and some 'liquid' properties such as viscosity, surface tension, etc. Hence in general it has properties which are intermediate between those of crystals and liquids.

Liquid crystals which are obtained by varying the temperature of the sample are called thermotropic liquid crystals. Mesomorphism can also be induced by the influence of solvents. Such liquid crystals are called lyotropic liquid crystals. In this thesis, we shall be concerned only with thermotropic liquid crystals.

Friedel (1922) classified thermotropic liquid crystals broadly into three groups (1) nematic, (2) cholesteric, and (3) smectic.

Nematic liquid crystals

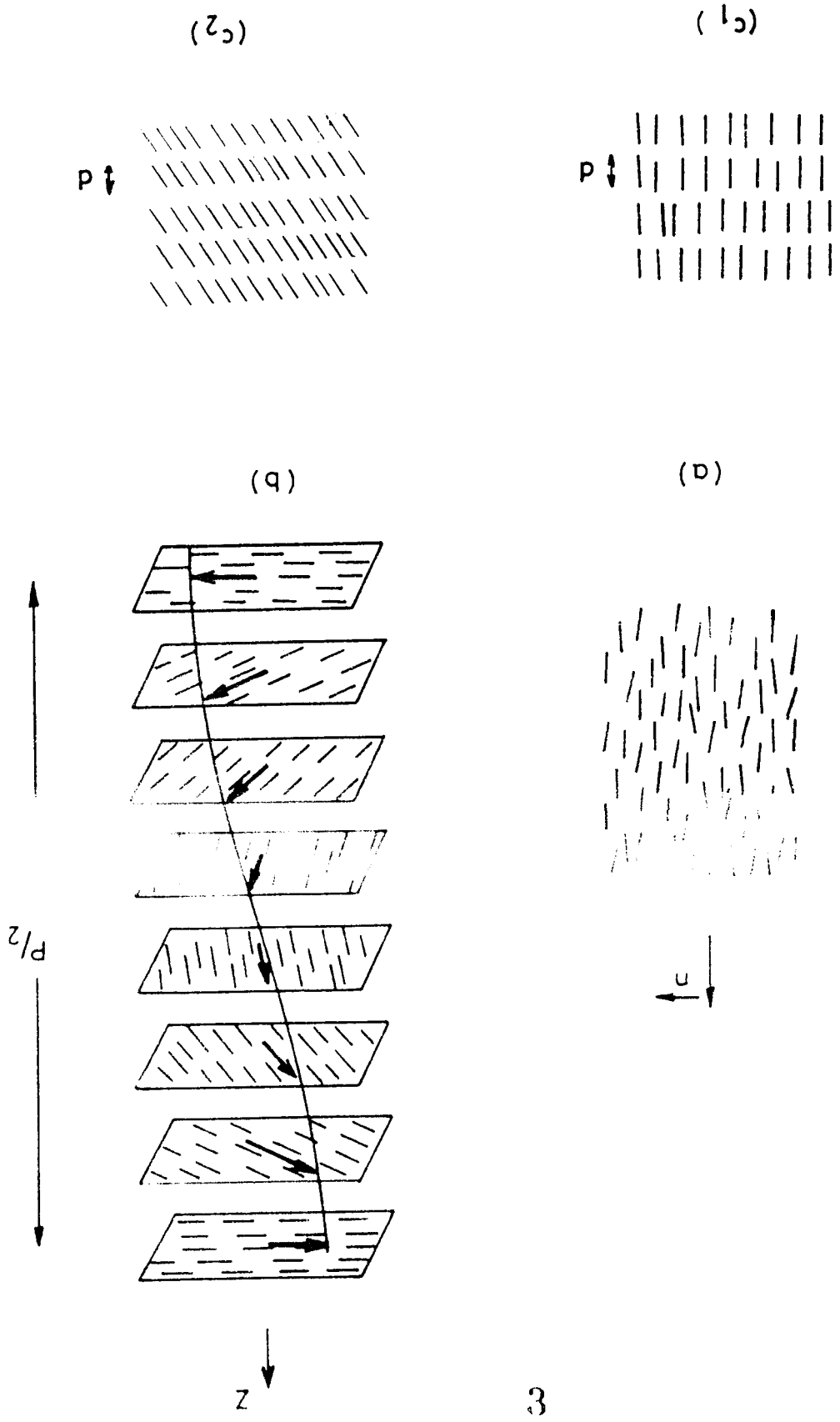
In this phase, the molecules have no long range translational order but have a high degree of orientational order. Hence the molecules tend to be parallel to some common direction called the 'director', a dimensionless unit vector represented by \vec{n} (fig.1.1(a)) Experimental results indicate that \vec{n} and $-\vec{n}$ are indistinguishable. A nematic liquid crystal is optically uniaxial, positive and strongly birefringent.

Cholesteric liquid crystals

The molecules in this phase are optically active. Hence the molecules are arranged in a helix with the screw axis (2) perpendicular to the preferred molecular direction (\vec{n}) (fig. 1.1(b)). Locally a cholesteric is similar to a nematic but \vec{n} is not constant in space. The structure is periodic along Z with a period L (half the pitch). The spiral arrangement gives rise to some unique properties such as selective reflection of circularly polarized light and very large optical rotatory powers.

Schematic diagram showing the molecular arrangement in different types of liquid crystals, viz., (a) nematic, (b) cholesteric, (c₁) smectic A, (c₂) smectic C.

Figure 1.1



Smectic liquid crystals

The molecules are arranged in layers with $\frac{a}{2}$ wall defined interlayer spacing. There are many types of smectics depending upon the molecular arrangement within the layer. We will describe only those, which will be referred to in later Chapters.

In Smectic A the molecules are arranged normal to the layers (fig. 1.1(c₁)). Inside each layer the molecular centres of gravity have no long range translational order. The system is optically uniaxial, the optic axis being normal to the layers.

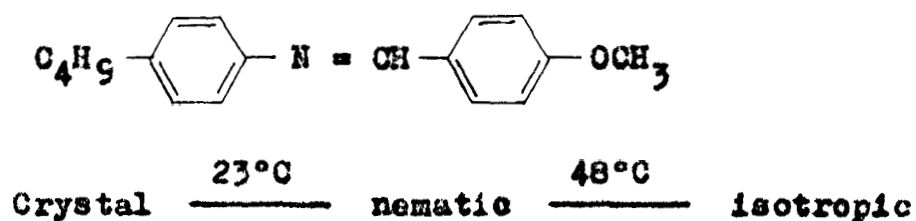
Smectic C (fig. 1.1(c₂)) can be considered as a tilted smectic A. The molecules in each layer are tilted with respect to the layer normal Z . The system is optically biaxial.

In addition to these two types of smectic liquid crystals, a number of other modifications have been identified and classified on the basis of miscibility studies (Sackmann and Demus 1975) and X-ray diffraction studies (de Vries 1975). The structures of many of the newly discovered phases are not yet known with any certainty.

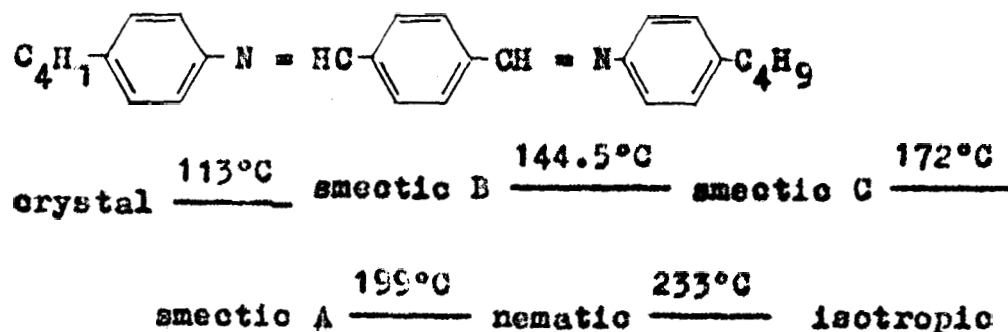
An essential requirement for mesomorphism is

the anisotropic shape of the molecules (usually long and narrow). ~~isotropic~~ Usually, a nematogenic compound has molecules containing a rigid aromatic part with alkyl or alkoxy group attached to one or both ends.

A well known compound which shows the nematic phase is N-p-methoxy benzylidene-p-butylaniline (MBBA) (Kelker, Scheurle 1969)



There are compounds which show poly mesomorphism also. For example, Terephthal-bis(-p-butylaniline) (TBBA) (Doucet *et al.* 1971)



Order parameter

The order parameter characterising a nematic liquid crystal is the orientational order parameter S

defined as (Zwetkoff 1942)

$$S = \frac{1}{2}(\overline{3\cos^2 \theta} - 1) \quad (1.1)$$

where θ is the angle that ~~that~~ the long axis of the molecule makes with the direction of average orientation of the molecules in the medium, i.e., the director and the bar represents a statistical average.

As the temperature of a nematic liquid crystal is increased, S decreases continuously and at the nematic-isotropic transition point falls discontinuously to zero. Most of the properties characteristic of a nematic can be related with the order parameter.

In this thesis we shall be mainly concerned with the elastic properties of nematic liquid crystals.

Elastic properties

A nematic liquid crystal possesses curvature elasticity. In a uniformly oriented, monodomain sample of nematic liquid crystal, the director \vec{n} is in the same direction throughout the medium. When a weak distortion is induced in the medium $\vec{n} = \vec{n}(r)$ and the derivatives of \vec{n} exist. When an elastic restoring torque comes into play tending to restore \vec{n} to the undistorted state. The distortions in a nematic can be described by a continuum theory.

Elasticity theory

Oseen (1933) gave a theory of elasticity assuming that the intermolecular forces are of short range nature and the density of the substance is constant throughout the medium. The theory was reexamined later by Frank (1958).

With a further assumption that the local value of S remains constant in a weakly distorted medium, we can write down the theory of elasticity. We choose a coordinate system such that the Z axis is along \vec{n} at the origin. For weak distortions n_z can be assumed to be a constant ≈ 1 in the first approximation.

We can now write, at any point (x, y, z)

$$n_x = \frac{\partial n_x}{\partial x}x + \frac{\partial n_x}{\partial y}y + \frac{\partial n_x}{\partial z}z \equiv a_1x + a_2y + a_3z$$

$$n_y = \frac{\partial n_y}{\partial x}x + \frac{\partial n_y}{\partial y}y + \frac{\partial n_y}{\partial z}z \equiv a_4x + a_5y + a_6z$$

$$n_z = 1 .$$

The elastic free energy *par* unit volume can be expressed in the form

$$W_e = k_1 a_1 + \frac{1}{2} k_{1j} a_1 a_j \quad (1.2)$$

$$i, j = 1, 2, \dots, 6 \quad k_{1j} = k_{j1}$$

k_1 has the dimension of force/distance and k_{1j} , of farce.

In a medium where there are no intrinsic deformations $k_1 = 0$. In a cholesteric liquid crystal where there is intrinsic twist $k_2 \neq 0$. Meyer (1969) considered wedge shaped and banana shaped polar molecules forming a nematic liquid crystal and predicted flexo-electric behaviour in them (analogous to piezo-electricity in certain crystals). In such cases, when the director is oriented uniformly in one direction, neighbouring molecules arrange in such a way as to annul their shape anisotropy. However, when a distortion is induced in the medium, the states \vec{n} and $-\vec{n}$ are no longer strictly equivalent. Gruler (1974) has shown that Pa these cases the splay and bend (contributed by the molecular shape anisotropy) affect the elastic constants.

However, for the purpose of this thesis we shall ignore this effect and also assume $k_1 = 0$ (Frank 1958). Taking into account the cylindrical symmetry of the medium about \vec{n} and the equivalence of \vec{n} and $-\vec{n}$ the expression for the elastic free energy density reduces to

$$\begin{aligned}
 w_e = & \frac{1}{2}k_{11}(\nabla \cdot \vec{n})^2 + \frac{1}{2}k_{22}(\vec{n} \cdot \nabla \times \vec{n})^2 + \frac{1}{2}k_{33}[(\vec{n} \cdot \nabla)\vec{n}]^2 \\
 & - \frac{1}{2}(k_{22} + k_{24})[(\nabla \cdot \vec{n})^2 + (\vec{n} \cdot \nabla \times \vec{n})^2 - \nabla n : \nabla n]
 \end{aligned}
 \tag{1.3}$$

where $\nabla n : \nabla n = \sum a_n^2$.

[Note: Nehring and Saupe (1971) argued that the second derivatives of \vec{n} make contributions to the elastic free energy comparable to the square of the ^{first} derivative. When this is taken into account the elastic free energy density expression has the form

$$\begin{aligned}
 w_e = & \frac{1}{2}k'_{11}(\nabla \cdot \vec{n})^2 + \frac{1}{2}k_{22}(\vec{n} \cdot \nabla \times \vec{n})^2 + \frac{1}{2}k'_{33}[(\vec{n} \cdot \nabla)\vec{n}]^2 \\
 & + k_{13} \nabla \cdot (\vec{n} \nabla \cdot \vec{n}) - \frac{1}{2}(k_{22} + k_{24})[(\nabla \cdot \vec{n})^2 \\
 & + (\vec{n} \cdot \nabla \times \vec{n})^2 - \nabla n : \nabla n]
 \end{aligned}
 \tag{1.3a}$$

where

$$\begin{aligned}
 k'_{11} &= k_{11} - 2k_{13} \quad , \\
 k'_{33} &= k_{33} + 2k_{13} \quad .
 \end{aligned}$$

The values of splay and bend constants experimentally determined are actually k'_{11} and k'_{33} . However there is no method of determining k_{13} separately. Hence for the sake of simplicity we shall hereafter take $k'_{11} = k_{11}$ and $k'_{33} = k_{33}$ and use Frank's expression for W_e to derive expressions for the critical magnetic field H_e .]

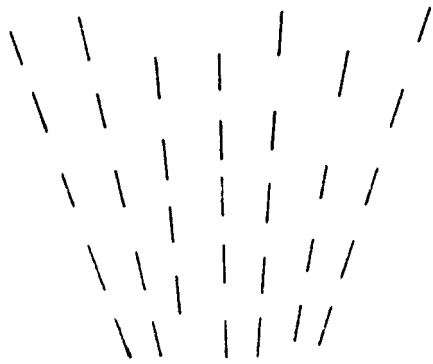
Ericksen (1962) has shown that $(\nabla \cdot \vec{n})^2 + (\vec{n} \cdot \nabla \times \vec{n})^2 - \nabla n : \nabla n$ identically satisfies the Euler-Lagrange equation and hence k_{24} does not contribute anything to the equations of equilibrium. k_{24} involves surface forces and torques which we need not consider if the director is strongly anchored at the surfaces. Hence the last term in the equation (1.3) is ignored. Then the elastic free energy density is

$$W_e = \frac{1}{2}k_{11}(\nabla \cdot \vec{n})^2 + \frac{1}{2}k_{22}(\vec{n} \cdot \nabla \times \vec{n})^2 + \frac{1}{2}k_{33}[(\vec{n} \cdot \nabla)\vec{n}]^2 \quad (1.4)$$

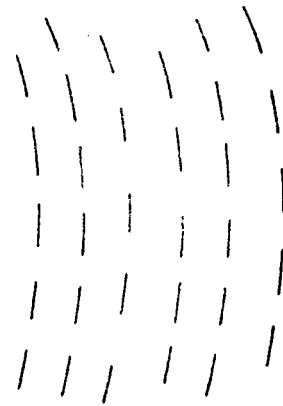
Hence a nematic liquid crystal has three independent elastic constants denoted by k_{11} , k_{33} and k_{22} corresponding to splay (fig. 1.2a), bend (fig. 1.2b) and twist (fig. 1.2c) distortions respectively.

Measurement of elastic constants

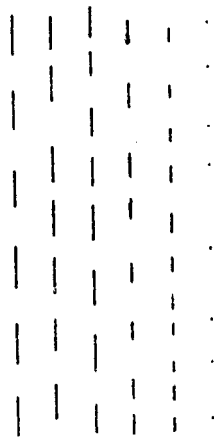
For an experimental determination of elastic



(a)
SPLAY



(b)
BEND



(c)
TWIST

Figure 1.2: The three types of distortions in a nematic liquid crystal

constants, it is convenient to induce the distortions by means of external fields such as magnetic and electric fields.

Nematogenic compounds are diamagnetic, with a strong anisotropy which arises from the aromatic part of the molecules. If χ_{\parallel} is the diamagnetic susceptibility along the long axis of the molecule and χ_{\perp} is that perpendicular to it, then the anisotropy of diamagnetic susceptibility $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ is positive ($\sim 10^7$ c.g.s. ^{units} ~~units~~). Because of this anisotropy, under the influence of a magnetic field, the molecules tend to be parallel to the field.

In the experimental set up, the sample is sandwiched between two plane glass plates. The molecules can be made to lie parallel to the glass plates unidirectionally (homogeneous alignment) or perpendicular to the glass plates (homeotropic alignment) by proper treatment of the surfaces.

When a magnetic field is applied, the magnetic torque

$$\vec{\tau}_m = \Delta\chi (\vec{n} \cdot \vec{H}) \vec{n} \times \vec{H} \quad (1.5)$$

and the magnetic energy density

$$w_m = -\frac{1}{2} \Delta\chi (\vec{H} \cdot \vec{n})^2 \quad (1.6)$$

where Δ^{χ} is the anisotropy of diamagnetic susceptibility per unit volume. It can be noticed that if \vec{H} is normal or parallel to the undistorted \vec{n} , then $w_m = 0$ while w_m is negative when \vec{H} is parallel to \vec{n} . The distortion of the director in the sample is determined by balancing the magnetic torque against the elastic torque. As we shall see below, there is no distortion in the sample upto a 'critical field' H_c . At H_c the medium undergoes a 'transition' to the distorted state, known as 'Fredericksz transition'. (Fredericksz and Rejzewska 1927). Above H_c the distortion in the sample increases with increasing H .

The presence of a critical field can be shown analytically as follows:

Expression for critical fields

For a uniformly oriented director in the undistorted state, there are three possible geometries in which the Fredericksz transition can be studied. In all the cases we assume that there is strong anchoring at the surfaces holding the sample.

Geometry I (Twist): We shall consider a homogeneously aligned sample contained between two plane glass plates and choose the coordinate system such that the magnetic field is applied along Y axis

and the undistorted director is along Z. (fig. 1.3a). x_0 is the sample thickness. In the distorted state, let $\varphi(x)$ be the angle between local director $\vec{n}(x)$ and Z axis. The distortion is a pure twist. Hence the equation (1.4) reduces to

$$W_0 = \frac{1}{2} k_{22} (\vec{n} \cdot \nabla \times \vec{n})^2 \quad (1.7)$$

$\vec{H} = (0, H, 0)$, $\vec{n} = (0, \sin \varphi, \cos \varphi)$. φ varies only along X. Therefore

$$\nabla = \left(\frac{d}{dx}, 0, 0 \right)$$

$$(\vec{n} \cdot \nabla \times \vec{n}) = \frac{d\varphi}{dx} .$$

The magnetic energy/unit volume $W_m = -\frac{1}{2} \Delta \chi (\vec{H} \cdot \vec{n})^2$. Therefore the total energy/unit vol

$$W = \frac{1}{2} k_{22} \left(\frac{d\varphi}{dx} \right)^2 - \frac{1}{2} \Delta \chi \cdot H^2 \sin^2 \varphi \quad (1.8)$$

The free energy per unit area across the sample thickness is $\int W dx$.

For equilibrium this energy should be a minimum. The Euler-Lagrange equation is

$$\frac{d}{dx} \left(\frac{\partial W}{\partial \left(\frac{d\varphi}{dx} \right)} \right) - \frac{\partial W}{\partial \varphi} = 0 \quad (1.9)$$

Therefore

$$k_{22} \frac{d^2 \varphi}{dx^2} + \Delta \chi H^2 \cos \varphi \cdot \sin \varphi = 0 .$$

Multiplying by $2 \frac{d\varphi}{dx}$ and rewriting,

$$\frac{d}{dx} [k_{22} (\frac{d\varphi}{dx})^2 + \Delta \chi H^2 \sin^2 \varphi] = C$$

where C is a constant.

To determine the value of C, we can make use of the boundary condition,

$$\text{at } x = \frac{x_0}{2}, \quad \varphi = \varphi_m, \quad \frac{d\varphi_m}{dx} = 0 .$$

Therefore

$$C = \Delta \chi H^2 \sin^2 \varphi_m .$$

Therefore

$$k_{22} (\frac{d\varphi}{dx})^2 + \Delta \chi H^2 (\sin^2 \varphi - \sin^2 \varphi_m) = 0$$

i.e.,

$$\frac{d\varphi}{dx} = \left(\frac{\Delta \chi}{k_{22}} \right)^{\frac{1}{2}} \cdot (\sin^2 \varphi_m - \sin^2 \varphi)^{\frac{1}{2}}$$

Integrating

$$\int_0^{\varphi_m} \frac{d\varphi}{(\sin^2 \varphi_m - \sin^2 \varphi)^{\frac{1}{2}}} = \int_0^{\frac{x_0}{2}} \left(\frac{\Delta \chi}{k_{22}} \right)^{\frac{1}{2}} \cdot H dx = \left(\frac{\Delta \chi}{k_{22}} \right)^{\frac{1}{2}} \cdot \frac{H x_0}{2} \quad (1.10)$$

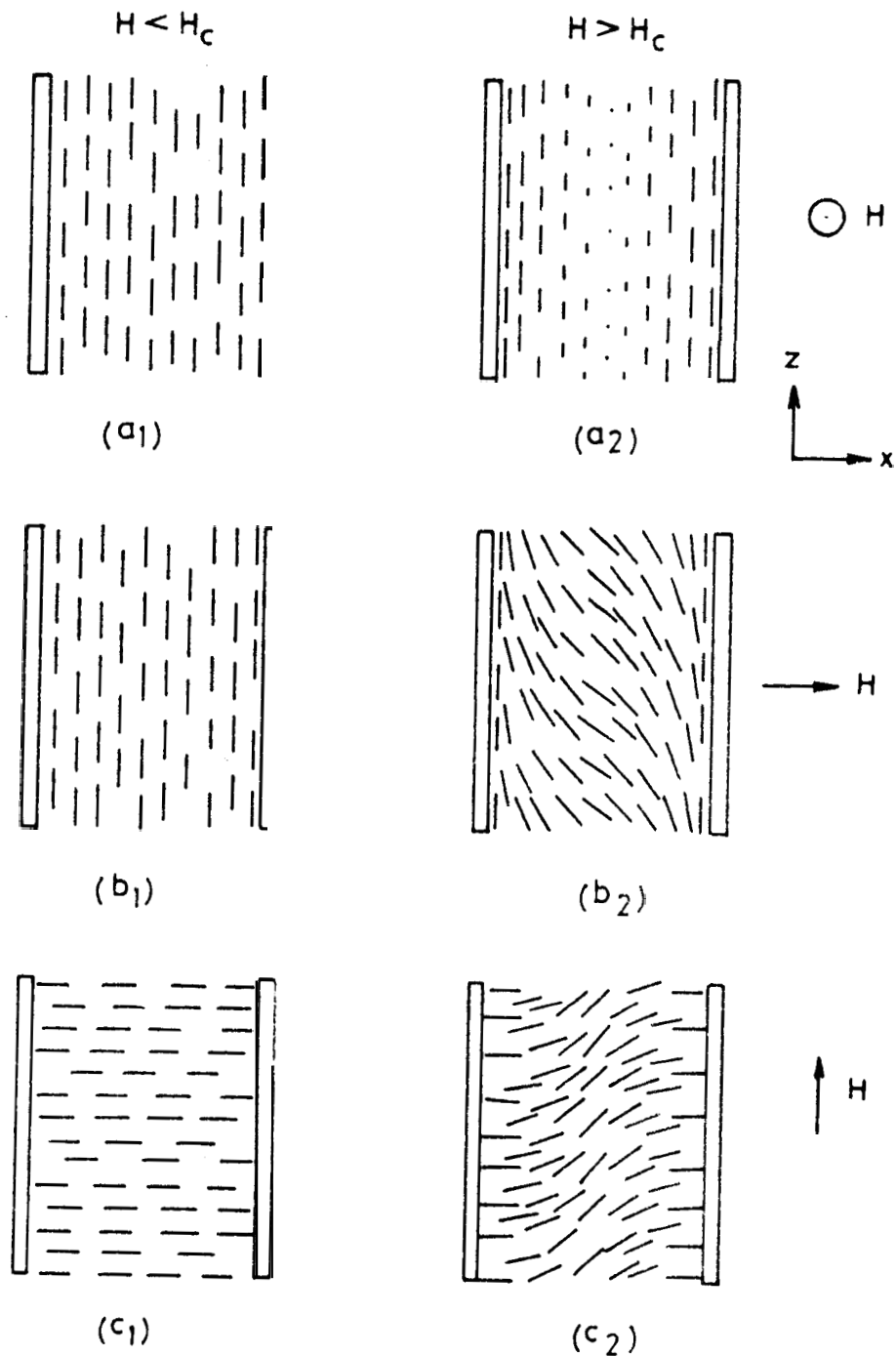


Figure 1.3:

The three principal geometries for studying the Fredericksz transition related to the (a) twist, (b) splay, (c) bend elastic constants. Molecular alignment (i) below H_c and (ii) above H_c are shown. In the usual experimental configuration, the light beam is incident normal to the glass plates.

Now putting $\sin \varphi = \sin \varphi_m \cdot \sin \psi$, equation (1.10) can be written or

$$\int_0^{\frac{\pi}{2}} \frac{d\psi}{(1 - \sin^2 \varphi_m \sin^2 \psi)^{\frac{1}{2}}} = \left(\frac{\Delta X}{k_{22}}\right)^{\frac{1}{2}} \cdot H \frac{x_0}{2} \quad (1.11)$$

To determine the critical field corresponding to Fredericks transition, $\varphi_m \rightarrow 0$.

Then the equation (1.1 I) reduces to

$$\int_0^{\pi/2} d\psi = \frac{\pi}{2} = \left(\frac{\Delta X}{k_{22}}\right)^{\frac{1}{2}} \cdot H_0 \frac{x_0}{2} .$$

Therefore, the critical field

$$H_0 = \left(\frac{k_{22}}{\Delta X}\right)^{\frac{1}{2}} \cdot \frac{\pi}{x_0} \quad (1.12)$$

Now, the L.H.S. of eqn. (1.11) is an elliptic integral of the first kind. Using equation (1.12) we can write

$$\frac{H}{H_0} = \frac{2}{\pi} \int_0^{\frac{\pi}{2}} \frac{d\psi}{(1 - \sin^2 \varphi_m \sin^2 \psi)^{\frac{1}{2}}}$$

If $(H - H_0)$ is small, φ_m is small. Then

$$\frac{H}{H_c} = \left(1 + \frac{1}{4} \varphi_m^2 + \frac{11}{196} \varphi_m^4 + \dots \right) \quad (1.13)$$

For any value of A above H_c , the deformation at the mid-plane of the sample is given by this equation. (see e.g., Gruler et al. 1972).

Geometry II (splay and bend): Consider a homogeneously aligned sample between two plane glass plates. The geometry in this case is given in figure (1.3b). The magnetic field is applied along X axis. The undistorted director is along Z axis. Let $\varphi(x)$ be the angle between the local director and Z axis. Then

$$\vec{n} = (\sin \varphi, 0, \cos \varphi), \quad \vec{H} = (H, 0, 0).$$

In general the distortion is a combination of splay and bend. \vec{n} varies along X only, Therefore

$$\nabla = \left(\frac{d}{dx}, 0, 0 \right).$$

Prom equation (1.4), the elastic energy/unit volume is

$$\begin{aligned} w_e &= \frac{1}{2} k_{11} (\nabla \cdot \vec{n})^2 + \frac{1}{2} k_{33} [(\vec{n} \cdot \nabla) \vec{n}]^2 \\ &= \frac{1}{2} (k_{11} \cos^2 \varphi + k_{33} \sin^2 \varphi) \left(\frac{d\varphi}{dx} \right)^2. \end{aligned}$$

The magnetic energy/unit volume $w_m = -\frac{1}{2} \Delta\chi H^2 \sin^2 \varphi$.

Therefore the total energy per unit volume is

$$W = \frac{1}{2} [(k_{11} \cos^2 \varphi + k_{33} \sin^2 \varphi) \left(\frac{d\varphi}{dx}\right)^2 - \Delta\chi H^2 \sin^2 \varphi] \quad (1.14)$$

Using Euler-Lagrange equation and simplifying as in the previous case, the deformation at the mid-plane of the sample can be calculated using the relation

$$\int_0^{\varphi_m} \left(\frac{k_{11} \cos^2 \varphi + k_{33} \sin^2 \varphi}{\sin^2 \varphi_m - \sin^2 \varphi} \right)^{\frac{1}{2}} d\varphi = \frac{x_0}{2} (\Delta\chi)^{\frac{1}{2}} \quad (1.15)$$

Putting $\sin \varphi = \sin \varphi_m \sin \psi$ and simplifying,

$$\int_0^{\pi/2} \left[\frac{1 - A \sin^2 \varphi_m \sin^2 \psi}{1 - \sin^2 \varphi_m \sin^2 \psi} \right]^{\frac{1}{2}} d\psi = x_0 \left(\frac{\Delta\chi}{k_{11}} \right)^{\frac{1}{2}} \quad (1.16)$$

where

$$A = \frac{k_{11} - k_{33}}{k_{11}} .$$

The critical field is given by letting $\varphi_m \rightarrow 0$ in equation (1.16) yielding,

$$H_0 = \frac{\pi}{x_0} \left(\frac{k_{11}}{\Delta\chi} \right)^{\frac{1}{2}} \quad (1.17)$$

Using this equation k_{11} can be calculated. Now equation (9.16) can be written as

$$\frac{H}{H_0} = \frac{2}{\pi} \int_0^{\pi/2} \left[\frac{1 - A \sin^2 \varphi_m \sin^2 \psi}{1 - \sin^2 \varphi_m \sin^2 \psi} \right]^{\frac{1}{2}} d\psi$$

The distortion φ_m at the mid plane of the sample at any field H above H_0 can be obtained from this equation. The integral is an elliptic integral of the second kind. For small values of φ_m ,

$$\begin{aligned} \frac{H}{H_0} &= 1 + \frac{1}{4}(1 - A)\varphi_m^2 + \dots \\ &= 1 + \frac{1}{4} \frac{k_{33}}{k_{11}} \varphi_m^2 + \dots \end{aligned} \quad (1.18)$$

The equation involves both k_{11} and k_{33} . Hence by studying the distortions above H_0 , k_{33} can also be determined. (see Gruler et al. 1972).

Geometry III (bend and splay): Consider a homeotropically aligned sample between two plane glass plates. The geometry for this case is shown in figure (1.3c). The director in the undistorted sample is along X axis. \vec{H} is along Z axis. If $\varphi(x)$ is the

angle made by the local director with X axis

$$\vec{n} = (\cos \varphi, 0, \sin \varphi) \quad \vec{H} = (0, 0, H)$$

\vec{n} varies along X only. Therefore

$$\nabla = \left(\frac{d}{dx}, 0, 0 \right)$$

In general, the distortion is a combination of bend and splay.

The elastic energy per unit volume from equation (1.4) is

$$W_e = \frac{1}{2} k_{11} (\nabla \cdot \vec{n})^2 + \frac{1}{2} k_{33} [(\vec{n} \cdot \nabla) \vec{n}]^2$$

In this case, the equation of equilibrium is obtained by merely interchanging k_{11} and k_{33} in the equation of equilibrium of the previous section. Hence we get

$$\int_0^{\pi/2} \left[\frac{1 - A \sin^2 \varphi_m \sin^2 \psi}{1 - \sin^2 \varphi_m \sin^2 \psi} \right]^{\frac{1}{2}} d\psi = \left(\frac{\Delta x}{k_{33}} \right)^{\frac{1}{2}} H \frac{x_0}{2} \quad (1.19)$$

where

$$A = \frac{k_{33} - k_{11}}{k_{33}} .$$

The critical field

$$H_c = \frac{\pi}{x_0} \left(\frac{k_{33}}{\Delta\chi} \right)^{\frac{1}{2}} \quad (1.20)$$

For small value of φ_m ,

$$\frac{H}{H_c} = 1 + \frac{1}{4}(k_{11}/k_{33})\varphi_m^2 + \dots \quad (1.21)$$

which equation involves both k_{33} and k_{11} (see Gruler et al. 1972).

Detection of twist deformation

There has been considerable interest of later in the measurement of elastic constants of nematic liquid crystals since short range order in the medium has a profound influence on the magnitudes of some of these constants. In simple nematics the elastic constants can be related directly to the orientational order parameter S by using the mean field approximation (Saupe 1960). Ignoring the weak volume dependence $k_{ii} \propto S^2$. Hence the ratios of the elastic constants should then be essentially temperature independent. This is, in fact, found to be marly so for PAA and PAP (Gruler 1973).

A simple and direct method of determining elastic constants is to measure the critical field H_c

using an optical set up to detect the distortion. Optical detection of H_c has the advantage in that a small well aligned region in the sample can be chosen for observation. For splay and bend, the sample is taken between two plane glass plates. The light is allowed to fall on it normally. A pair of polarizers and a quarter wave plate are sufficient to detect H_c . However under normal conditions of observation wherein ^{the} light falls normally on the sample contained between two plane glass plates, this method is not suitable for determining the twist constant k_{22} for reasons which will be discussed now.

Let a homogeneously aligned sample be contained between two glass plates. We can think of the sample as made up of a number of thin sections (each of thickness $\sim 10^{-7}$ cm, say) parallel to the glass plates. Consider a case in which a magnetic field just above the critical field is applied normal to the undistorted director as in figure (1.3a) to produce a twist deformation. The director orientation within each section is taken to be constant. The mid-plane of the sample has the maximum deformation (φ_m) given by the equation (1.13)

$$\frac{H}{H_c} = 1 + \frac{1}{4}\varphi_m^2 + \frac{11}{192}\varphi_m^4 + \dots$$

If the applied field is 1% above H_0 , then $\varphi_m \sim 0.2$ radians. If the thickness of the medium $l \sim 20 \times 10^{-4}$ cm, then as a rough order of magnitude the average twist per layer $\beta \sim 2 \times 10^{-5}$ radians. If the birefringence of the nematic $l a \sim 0.2$, the phase retardation a between the ordinary and extraordinary rays per layer $\sim 2 \times 10^{-3}$ radians, so that $a/\beta \sim 10^2$. According to the 'adiabatic theorem' (Mauguin 1911) under such circumstances the normal waves are two linearly polarized waves (one parallel and the other perpendicular to the director) and hence these two directions of polarization rotate with the director. This conclusion can also be drawn from the optical theory of light propagation through such media. [For instance, see de Vries (1951), Chandrasekhar et al. (1973), Ranganath et al. (1973)]. As a result even when $H \nearrow H_0$ the emergent light has the same state of polarization as that in the undistorted sample. It is particularly simple to appreciate this result in terms of the 'Poincare sphere' (see Appendix I).

Let the incident light beam, represented by P (figure 1.4) be linearly polarized along the director axis of the first section. Each section of the sample is a retarder. If a magnetic field slightly above H_0 is applied the directors

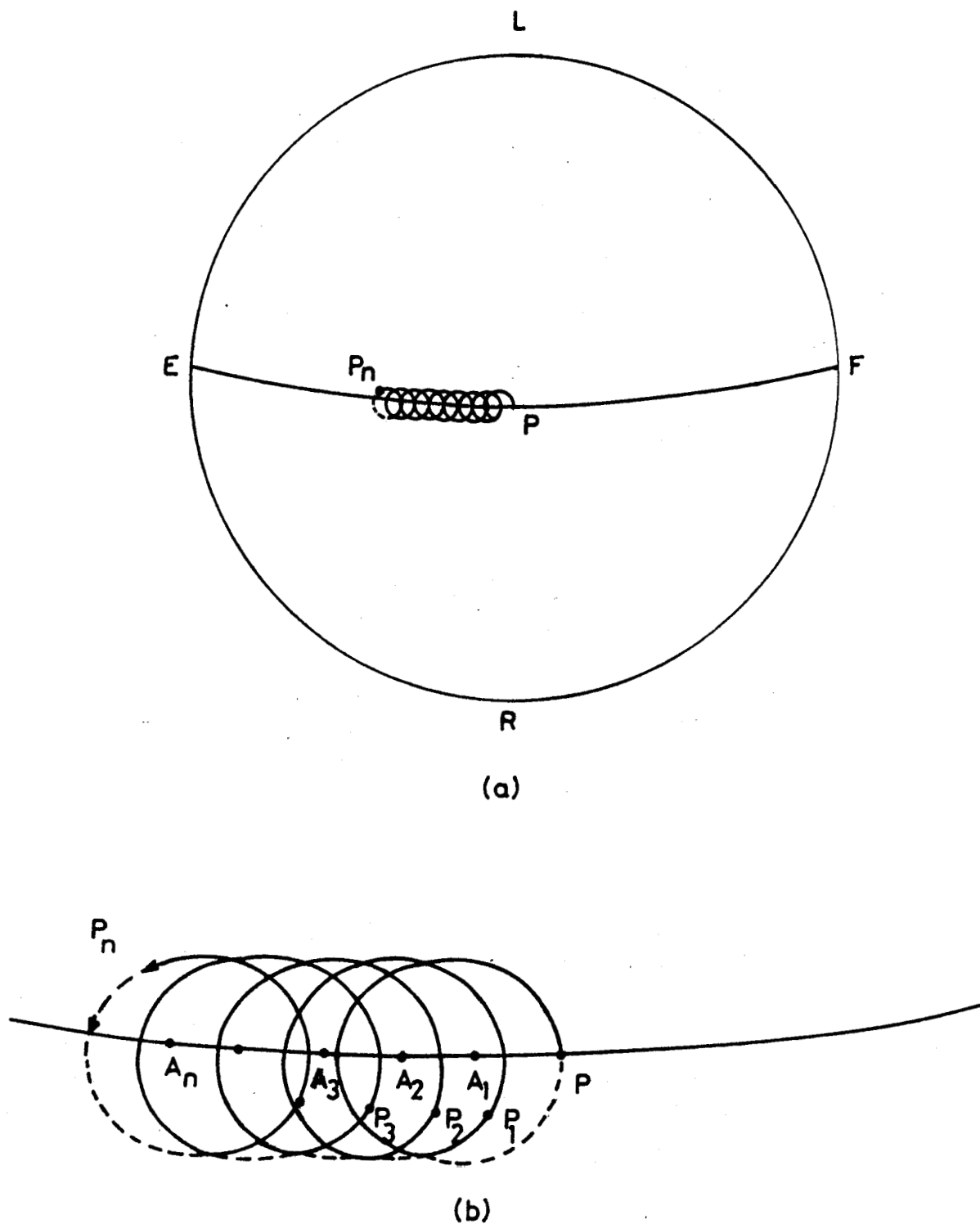


Figure 1.4

(a) The states of polarization of light beam which is incident normal to the plates, as it traverses a weakly distorted nematic in the conventional geometry shown in figure 1.3a. The details are shown in (b): see text.

in adjacent sections are, slightly tilted with respect to each *other*. The tilt is small compared to the retardation produced by each section. For example, PA_1 (figure 1.4b) is the rotation by the first section. With A_1 as centre, P is rotated on the sphere through an angle equal to the retardation due to the first section. P_1 represents the state of polarization when the light emerges, out of the first layer. Similar statements hold good for the points P_2, P_3 , etc. P_n represents the state of polarization when the light beam reaches the mid-section. As can be seen in the figure when $a \gg \beta$, as the light traverses a weakly deformed medium, the polarization is dragged along by the director. In the other half of the sample, the tilt of \vec{n} between adjacent sections is in the opposite direction while the retardation continues to be in the same *sense*. The dotted line shows ^{schematically} the polarization as the light traverses the medium beyond the mid plane. Therefore, as the light emerges out of the last section the polarization is practically at P. In other words, the director drags the ^{plane} ~~state~~ of polarization. An exactly similar argument can be used for the polarization perpendicular to the director. Thus with the experimental set up in which the director is anchored

to the walls, when light is incident normal to the sample film, the state of polarization of the emergent beam is practically the same as for the untwisted medium and the twist deformation cannot be detected optically. Because of this difficulty there have been very few attempts in the past to determine k_{22} .

The aim of the present work is to determine all the elastic constants of two homologous series of compounds (Chapters 3 and 4). We chose the Fredericksz transition technique as it is simple and yields good results. In the next Chapter we shall describe a simple and direct method to determine k_{22} by allowing light to enter the sample at an oblique angle thereby making α and β of comparable magnitude in the direction of observation.

In simple nematics the elastic constants are expected to follow the prediction of the mean field theory. However, in the case of a nematic liquid crystal which exhibits smectic A phase at lower temperatures, the short range order or the molecular distribution function is temperature sensitive. As the smectic A-nematic transition point (T_{AN}) is approached, smectic like short range order builds up in the nematic.

The smectic structure is layered. Bend and twist deformations which tend to alter the layer thickness, are forbidden in this phase. Therefore, as T_{AN} is approached, bend and twist deformations become difficult because of the smectic like domains building up in the nematic. As a result k_{22} and k_{33} diverge as T_{AN} is approached and tend to infinity if the transition is quasi second order (de Gennes 1972). The splay deformation does not alter the layer thickness and hence is allowed in the smectic phase. Hence k_{11} is not renormalized as T_{AN} is approached. This was experimentally verified for k_{33} by Cheung *et al.* (1973). We have made some measurements on k_{22} and k_{33} for some compounds which show smectic A and nematic phases. The results are discussed in Chapter 5.

In principle an electric field can be used instead of a magnetic field to deform a nematic liquid crystal (Zwetkoff 1937) and hence to determine its elastic constants. There is an exact analogy between the electric and magnetic fields as far as the threshold condition is concerned, but at higher fields the problem is more complex in the electric field case because of local field corrections: the electric field at any point in the sample is not *Pa* the same direction as the applied electric field. (Gruler and

Meier 1972, Deuling 1972).

Freedericksz transition under an electric field has been detected by optical method (Zwetkoff 1937, Gruler & Meier 1972). An important precaution to be taken in these Freedericksz transition measurements is that the sample has to be very pure to avoid conduction induced instabilities. Electrical conductance measurements (Greulich et al. 1975) and capacitance measurements (Gerritsma et al. 1971) have also been used to detect the critical field. However a slight disadvantage with the last two methods is that they need a sample which is well aligned in the entire area between the electrodes.

In general, when an electric field is used to deform the sample the dielectric alignment is frequency dependent (Gruler and Cheung 1975). When a component of the electric dipole along the long axis of the molecule exists, the rotation of the molecule about a short axis of the molecule becomes difficult as the frequency is increased (Meier and Saupe 1966). As a result, ϵ_{\parallel} (dielectric constant parallel to the director) relaxes at a fairly low frequency (\sim MHz) compared to ϵ_{\perp} (Maier & Meier 1961). Therefore the anisotropy of dielectric constant and hence the

critical field for a Fredericksz transition is frequency dependent. By studying the critical field as a function of frequency the dielectric relaxation can be studied. This will be discussed in detail in Chapter 7.

Usually a nematic liquid crystal is a good electric insulator. However, there are always some ionic impurities which give rise to electrical conduction in the sample. In simple nematics these ions move along \vec{n} more easily than normal to it. This causes an anisotropy in the electric conduction. $\sigma_{\parallel} > \sigma_{\perp}$ (Svedberg 1914) where σ_{\parallel} and σ_{\perp} are the conductivity along and normal to \vec{a} respectively. However, in compounds exhibiting both smectic and nematic phases, there is considerable smectic-like short range order in the medium slightly above T_{AN} . In such cases ions find themselves easier to move parallel to the layers than along \vec{a} , as a result of which $\sigma_{\parallel} < \sigma_{\perp}$ (Rondelez 1972).

When the anisotropies of dielectric constant and electric conductivity are of opposite sign, the aligning effect of one is opposed by the other, giving rise to electrohydrodynamic instability above a voltage threshold (Fredericksz and Zolina 1933).

Striations called 'Williams domains' (Williams 1963) are seen in the field of view in a 'sandwich' geometry with a nematic liquid crystal of negative dielectric anisotropy and positive conductivity anisotropy taken between two glass plates. Therefore, in critical field measurements the, frequency of the electric field and the compound should be properly chosen so that the effects due to dielectric relaxation and electrohydrodynamic instabilities can be neglected. We have made some new observations of electrohydrodynamic instability in one particular geometry which will be discussed in Chapter 8.

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