C H A P T E R   I

I N T R O D U C T I O N

1.1   LIQUID CRYSTALS

The term liquid crystal describes a state of matter that exists between the anisotropic crystal and the isotropic liquid. The liquid crystalline or mesomorphic substances exhibit strong anisotropy in certain properties, yet maintain a certain extent of fluidity. Liquid crystals were discovered by Reinitzer (1888), but the first detailed observations characerising these phases were made by Lehmann (1890).

A highly anisotropic shape of the molecules is necessary for mesomorphism, like for example the long and narrow rod-like or disc-like shape. The transition to the mesophase can take place either due to purely thermal processes (thermotropic mesomorphism) or due to the influence of solvents (lyotropic mesomorphism). This thesis deals with the study of only thermotropic mesophases.

1.2   THERMOTROPIC LIQUID CRYSTALS

The thermotropic liquid crystals composed of rod-like molecules have been known for a long time. However liquid crystals composed of disc-shaped molecules were only recently discovered (Chandrasekhar et al. 1977). Liquid crystals made up of rod-like molecules can be classified broadly into three types of phases, viz., nematic, cholesteric and smectic (Fig. 1.1).

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The nematic phase (Fig. 1.1a) is characterised by a long range orientational order of the molecules but without any translational order. The long axes of the molecules are aligned approximately parallel to one another. A vector $\vec{n}$, called the director, defines the average direction of orientation of these long axes. The director is found to be apolar, i.e., $+\vec{n}$ and $-\vec{n}$ are equivalent. The mesophase is optically positive and uniaxial.

The cholesteric mesophase is basically a nematic type, with a screw axis superimposed normal to the preferred molecular direction (Fig. 1.1b). It consists of orientationally ordered optically active anisotropic molecules, the director twisting about an axis orthogonal to the director. The distance between layers in which the director has turned through an angle of 2π defines the pitch 'p'. Over a certain spectral range cholesteric phases show a selective reflection of circularly polarized light. The cholesteric phase is optically negative.

The smectic phase has a layered structure. Within each of these layers various molecular arrangements are possible. The simplest types are smectic A and C. In the smectic A phase (Fig. 1.1c) the molecules are approximately parallel to one another and are arranged in layers, with the long-axes perpendicular to the layer. Within the layer the centres of gravity of the molecules are situated at random and the molecules have a relatively high degree of mobility. The structure of the smectic C phase (Fig. 1.1d) is related to that of the smectic A phase, i.e., it consists of essentially
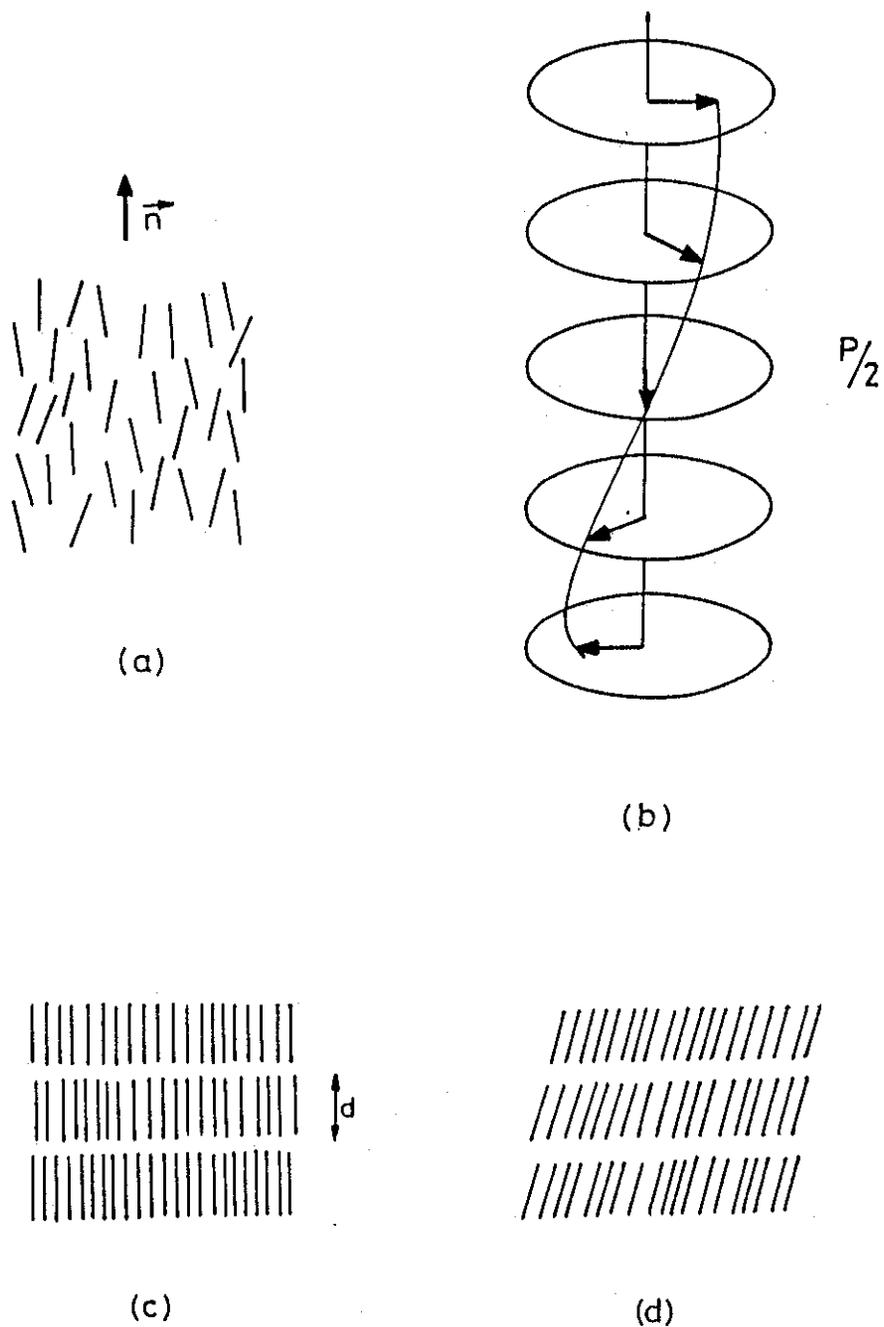
Figure 1.1

Schematic representation of the molecular arrangement in different liquid crystalline phases. (a) Nematic, (b) Cholesteric, (c) Smectic A, and (d) Smectic C.

parallel molecules in the layers, but these are tilted in a particular direction with respect to the layer normal. There are various other types of smectics, smectics B, D, E, F, G, H and I which are more ordered than A and C.

Examples of two typical 'rod-like' molecules and the phases exhibited by them are given in Fig. 1.2.

In some systems the nematic phase reappears on cooling from the smectic phase. This lower temperature nematic phase is called the reentrant nematic phase.

Discotic Liquid Crystals

As mentioned before, thermotropic mesomorphism is found to occur in compounds made up of disc-shaped molecules also. In these systems the director is parallel' to the short axes of the molecules. The different kinds of mesomorphic phases formed with disc-like compounds are:

1   the columnar phases (D) (Chandrasekhar et al., 1977; Tinh et al., 1978; Levelut et al. 1979)

2   the nematic phase (N_D) (Tinh et al. 1979), and

3   the twisted nematic phase (N_D^*) (Destrade et al., 1980).

The molecular arrangement in these phases is shown in Fig. 1.3. The columnar phases are formed of columns of stacked disc-like molecules. Four different types of columnar phases have been identified (Figs. 1.3a-1.3d). These have been classified taking into

$$C_4H_9 \!-\!\!\bigcirc\!\!-\!N = CH \!-\!\!\bigcirc\!\!-\!OCH_3$$
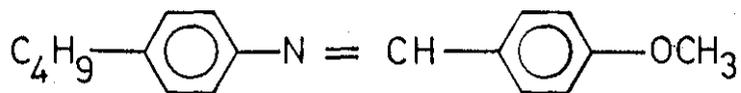
Crystal   23°C   Nematic   48°C   Isotropic

p–methoxy benzylidene – p′–butylaniline

(MBBA)

(a)

$$C_4H_9 \!-\!\!\bigcirc\!\!-\!N = HC \!-\!\!\bigcirc\!\!-\!CH = N\!-\!\!\bigcirc\!\!-\!C_4H_9$$
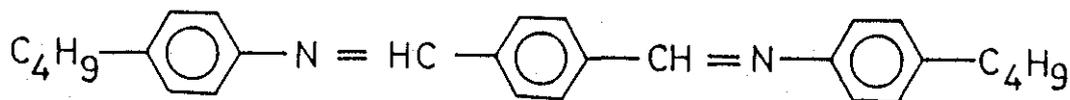
Crystal   113°C Smectic G 144.5°C   Smectic C 172°C

Smectic A 199°C Nematic   236.5°C   Isotropic

Terephthal – bis (–p–butylaniline)(TBBA)

(b)

Figure 1.2

Typical examples of compounds made up of rod-like molecules
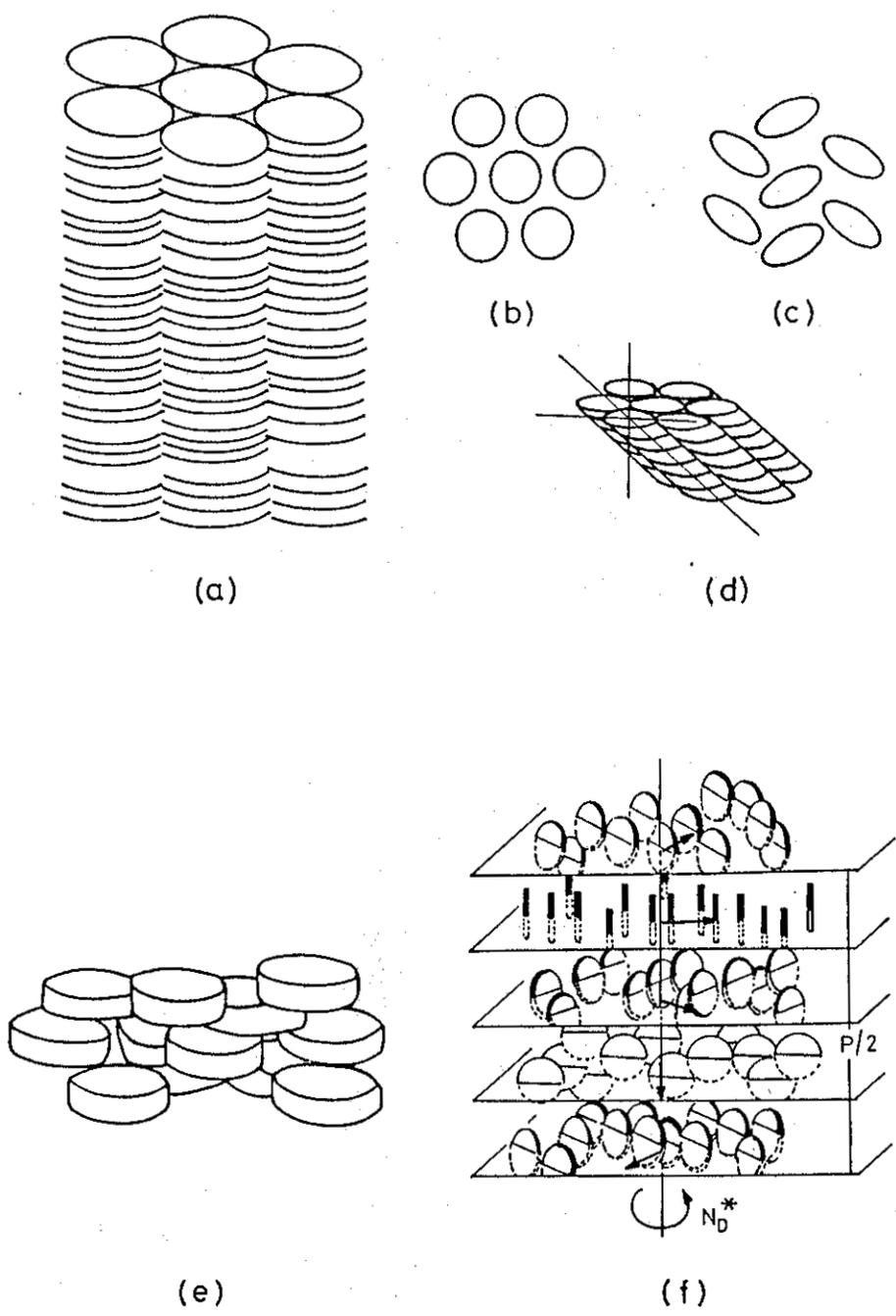which exhibit liquid crystalline phases

Figure 1.3

Schematic representation of the molecular arrangement in discotic liquid crystals. (a) Columnar phase, (b) hexagonal, and (c) rectangular modifications of the columnar structure. (d) tilted columnar phase, (e) N_d phase, (f) twisted nematic (N_D^*) phase.

account the regular (o) and irregular (d) stacking of the discs and considering the symmetry of the two dimensional lattice of columns, i.e., hexagonal (h) or rectangular (r). The different types of columnar phases thus obtained are D_{ho}, D_{hd}, D_{rd} and D_{ro}. A tilted phase where the discs appear to be tilted with respect to the column axis is also present and is called the D_t phase (Fig. 1.3d).

The N_D phase is an orientationally ordered arrangement of the discs with no long range translational order (Fig. 1.3e). In contrast to the classical nematic of rod-like molecules, the N_D phase is optically uniaxial and negative. The twisted nematic phase N_D^* is similar to the cholesteric phase (Fig. 1.3f). The N_D phase is quite fluid while the columnar phases are very viscous.

The reentrant phenomenon has also been observed in disc-like mesogens (Tinh et al. 1984). Both reentrant columnar phases and reentrant N_D phases have been obtained.

Examples of two typical discotic compounds is given in Fig. 1.4.

Most of the results in this thesis pertain to the nematic phase. Hence the properties of this phase will be described in detail in the following section.
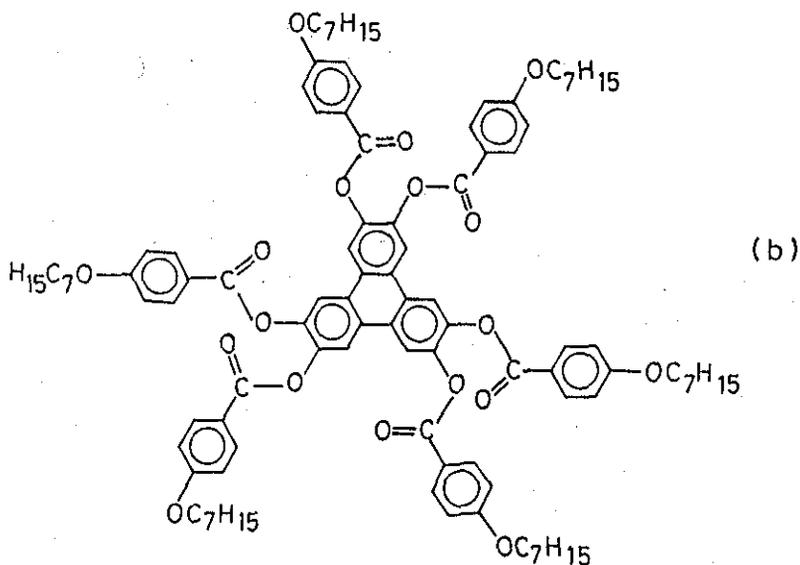
1.3 PROPERTIES OF THE NEMATIC PHASE

The nematic phase is more ordered than the isotropic phase

(a)
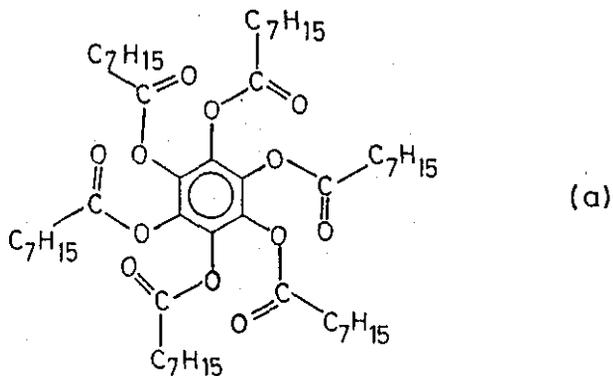
Crystal 80.2° C Mesophase 86.2°C Isotropic
83.6° C Mesophase

Benzene – hexa - n – heptanoate

(b)

Crystal 168° C Nematic D 251.5 °C Isotropic
Hexa Heptyloxy Benzoote of Triphenylene

Figure 1.4

Typical examples of compounds made up of disc-like mole-
cules which exhibit liquid crystalline phases.

and has a lower symmetry. We can therefore define an order para-
meter, **viz.**, the orientational order parameter which exists in
the nematic phase but vanishes in the isotropic phase.

In principle a complete description of the nematic phase
requires a hierarchy of n-particle distributions to be specified.
But for simplicity only a singlet distribution is taken into account
in the mean field approximation. The state of alignment of the
molecules in the medium is then specified by an **orientational** distri-
bution function. If the molecules are considered to be cylindrically
symmetric, the medium is uniaxial and if θ is the angle made by
the long **axis** of the molecule with the director, the distribution
function can be written as $f(\cos\theta)$.

It is difficult to determine even the singlet distribution
function completely, but the first few coefficients of an expansion
in **Legendre** polynomials of the distribution function are accessible
by experiment. Only the even coefficients are non-zero because
of the apolar character of the director. $f(\cos\theta)$ can be expanded
as

$$f(\cos\theta) = \sum_{\ell=0}^{\infty} \frac{4\ell+1}{2} < P_{2\ell} > P_{2\ell}(\cos\theta) \qquad (1.1)$$

where the coefficients $< P_{2\ell} >$ are the order parameters. $< P_2 >$ can
be measured by various techniques like NMR, optical birefringence,
Infrared dichroism measurements, etc. This is often referred to

as 'the order parameter' and is denoted by S.

The measurement of $<P_4>$ is more complicated. Depolarized Raman scattering technique seems to be the most convenient (Jen et al. 1977). Not many measurements of $<P_4>$ are available.

If all the molecules are aligned along $\vec{n}$ such that $\theta = 0$, then $<\cos^2\theta> = 1$ and $S = 1$. If the molecules are randomly distributed in all directions as in the isotropic phase, all values of θ are equally probable and $<\cos^2\theta> = 1/3$ giving $S = 0$. The nematic-isotropic (N - I) transition is of first order.

1.4   MOLECULAR THEORIES

If a fluid of hard rods is considered with no forces between them, other than the one preventing their interpenetration, at low densities the rods can orient randomly and the fluid is isotropic. As the density is increased it is difficult for the rods to orient in all possible directions and the fluid undergoes a transition to the anisotropic phase. This transition was theoretically treated by Onsager (1949). The excess free energy relative to an ideal gas has to be evaluated using the orientational distribution function of the rods. Onsager made a virial expansion of the free energy and retained only the second virial coefficient. This approximation is valid only for very long rods with a length to breadth ratio $\simeq 100$. Zwanzig (1963) evaluated the higher virial coefficients by restricting the molecules to take up only 3 mutually perpendi-

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cular orientations. Flory (1956) and Flory and Ronca (1979) used a lattice model and made calculations at relatively high densities. But all these descriptions are valid for long polymeric molecules (Straley, 1973) and the predicted S at the nematic-isotropic transition is quite high (−0.85) leading to an abrupt transition from a strongly-ordered nematic to a completely disordered isotropic phase.

For relatively short rods (of length to bseadth ratio − 3-5) and high densities the scaled particle theory provides a convenient method for obtaining the excess free energy relative to an ideal gas. Cotter (1977) has obtained the most complete form of this theory as applied to nematic liquid crystals.

Another type of mean field theory was developed by Maier and Saupe (1959) according to which the anisotropic dispersion interactions between the molecules are responsible for the stability of the phase. Each molecule was assumed to be in an average orienting field due to its environment, but otherwise uncorrelated with its neighbours, i.e., the short range order was ignored. Assuming a cylindrical distribution about the preferred axis Maier and Saupe expressed the orientational potential energy of the molecule as

$$\epsilon(\cos\theta) \;=\; -\,AV^{-2}\,\frac{S(3\cos^2\theta-1)}{2}$$

where V is the molar volume and A is a constant depending on the molecular species. Cotter (1977) has shown that thermodynamic con-

sistency demands $\epsilon(\cos\theta)$ to be proportional to V^{-1}, rather than to V^{-2} as in the original Maier–Saupe model.

The normalized orientational distribution function

$$f(\cos\theta) = \frac{1}{Z}\exp[-\epsilon(\cos\theta)/kT] \qquad (1.3)$$

where k is the Boltzmann constant and T the absolute temperature, Z the partition function for a molecule which is given by

$$Z = \int_0^1 \exp[-\epsilon(\cos\theta)/kT]\,d(\cos\theta). \qquad (1.4)$$

The internal energy is given by

$$E = \frac{1}{2}N\int_0^1 \epsilon(\cos\theta)\,f(\cos\theta)\,d(\cos\theta) = -\frac{1}{2}NkTBS^2 \qquad (1.5)$$

where N is the Avagadro number and $B = A/VkT$.

The entropy in relation to that of the isotropic phase is given by

$$S = -Nk\langle\ln f\rangle = -Nk[\frac{1}{2}BS(2S+1) - \ln\int_0^1 \exp(\frac{3}{2}BS\cos^2\theta)\,d(\cos\theta)] \qquad (1.6)$$

and the Helmholtz free energy in relation to the isotropic phase is

$$F = E - TS = NkT[\frac{1}{2}BS(S+1) - \ln\int_0^1 \exp(\frac{3}{2}BS\cos^2\theta)\,d(\cos\theta)] \qquad (1.7)$$

The condition for equilibrium is $(\partial F/\partial S)_{V,T} = 0$, which leads

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to the following self consistency equation for S

$$S = \int_0^1 (\frac{3}{2}\cos^2\theta - 1)\ f(\cos\theta)\ d(\cos\theta) \qquad (1.8)$$

This theory leads to a first order nematic-isotropic transition with an S value of 0.42 at the transition point T_{NI}. Experimentally S at T_{NI} varies between 0.3 to 0.5 for different compounds. Higher order terms can be introduced in the potential to account for these differences (Chandrasekhar and Madhusudana 1971, Humphries et al. 1972). But the main drawback of the mean field theories is that they predict a heat of transition which is usually higher by a factor of 2 or 3. The theory can be improved by taking into account near neighbour correlations (Madhusudana and Chandrasekhar, 1973). However the shape anisotropy of the nematogenic compounds has not been taken into account in these theories.

A more realistic theory incorporates the attractive potential between the molecules as well as the hard rod features. Several hybrid models have been proposed. Among these Cotter (1977) has used the scaled particle theory to develop a hybrid model and has obtained the coefficient of the potential with a temperature dependent attractive part and an athermal part corresponding to the hard particle contribution. These theoretical results have been improved further by using the Andrew's (1975) model (Savithramma and Madhusudana 1980, Madhusudana 1981).

However in all these models the molecules have been taken

to be cylindrically symmetric. In reality most molecules deviate from this shape so that the transverse cross section deviates from a circular shape. Alben et al. (1972), Straley (1973), Luckhurst et al. (1975), Gelbart and Barboy (1979) have shown the importance of taking this deviation from cylindrical symmetry into account in the theoretical calculations.

Alben et al. (1972) have pointed out that one order parameter is not adequate to describe the uniaxial nematic phase made up of particles without rotational symmetry and that two order para-meters are reauired.

In general for a molecule of arbitrary shape the orientational order in the nematic phase can be characterised by the tensor

$$S_{ij}^{\alpha\beta} = \frac{1}{2} < 3i_\alpha j_\beta - \delta_{\alpha\beta}\delta_{ij} > \qquad (1.9)$$

where $\alpha, \beta = x, y, z$ refer to the laboratory fixed coordinate system and $i, j = \xi, \eta, \zeta$ refer to the frame linked to the molecule. The tensor $S_{ij}^{\alpha\beta}$ is real, symmetric and has zero trace. If the molecular coordinate system is chosen such that $S_{ij}^{\alpha\beta}$ is diagonal two indepen-dent order parameters which are denoted by S and D result.

This will be discussed in more detail in Chapter 3 where we also present some experimental results on the determination of the order parameter S, utilising the Infra red dichroism method.

As the deviation from cylindrical symmetry of the molecules

increases and the molecules become more and more biaxial, one can expect that the medium itself becomes biaxial. Freiser (1970) has generalised the interaction employed in the Maier-Saupe (MS) theory , of the nematic state in a manner consistent with the assymmetry of the molecules. Such an interaction leads to a first order transition from the isotropic phase to a uniaxial phase followed by a second order transition to a biaxial phase at lower temperatures.

Another possibility of obtaining the bi'axiality has been theoretically investigated. These theories are concerned with mixtures of nematogens composed of rod-like and plate-like molecules. When two nematogens made up of rod-like molecules are mixed together usually a continuous miscibility in the nematic phase is obtained. The Schroder-Van-laar (Schroder 1893, Van-Laar 1908) equation permits the calculation of the eutectic temperature and composition of the crystal to nematic transition. A typical phase diagram of mixtures of two nematogens is shown in Fig. 1.5. This kind of behavior is true for most nematic mixtures.

If one of the components of the mixture is non-mesomorphic, the nematic-isotropic transition temperature of the nematogen is depressed. Further the nematic and isotropic phases coexist over a considerable range (Fig. 1.6) (Martire 1979). We have found that special types of defects (the high strength defects) occur in certain mixtures of this type. The studies on these defects will be discussed in Chapter 6.

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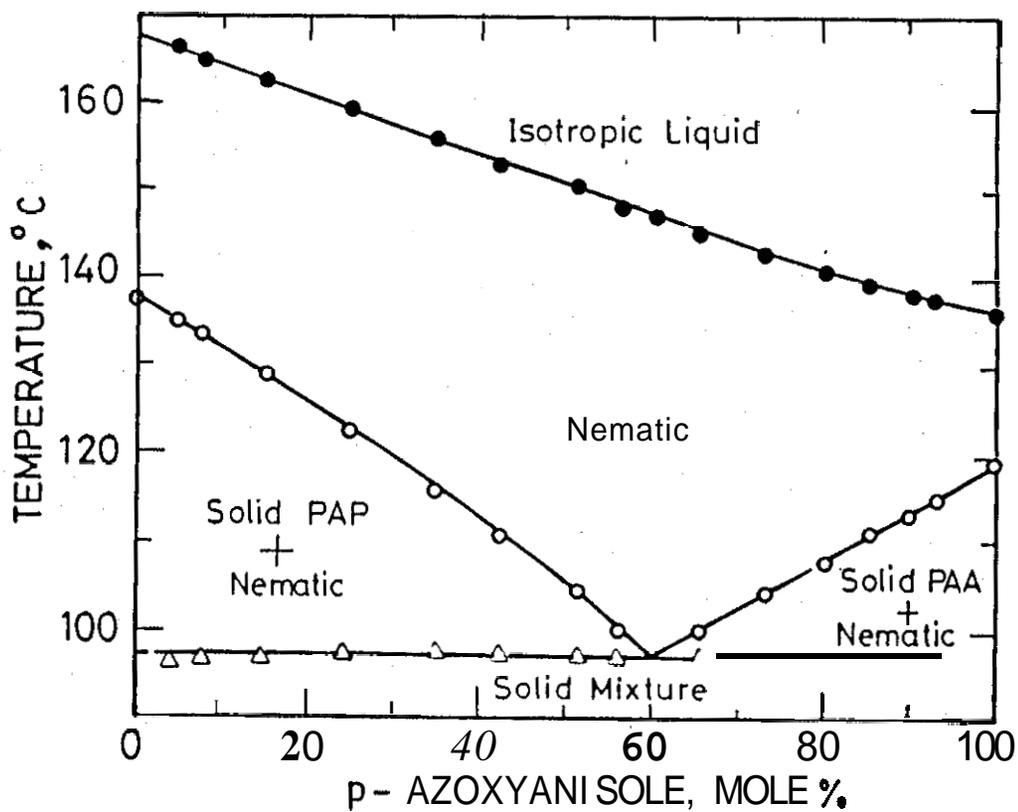
Figure 1.5

Typical phase diagram of mixtures of two rod-likenematogens
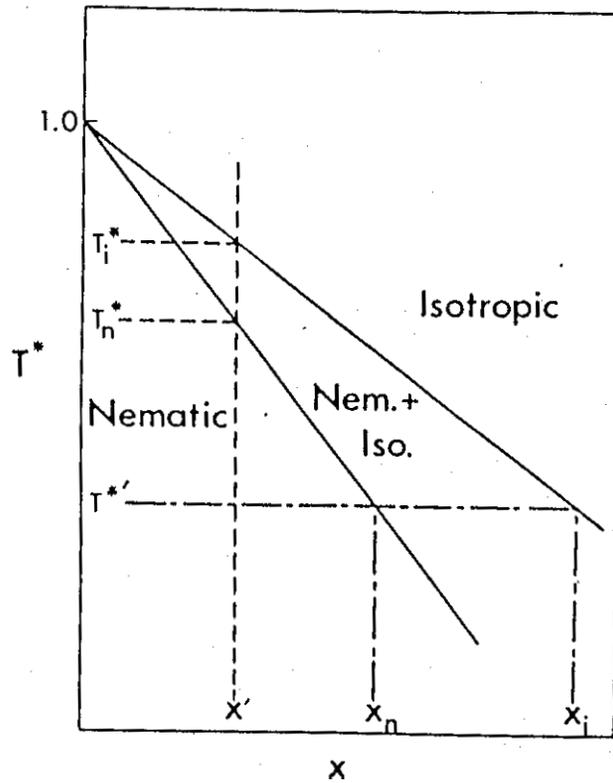(From Hsu and Johnson, 1973)

Figure 1.6

Coexistence of nematic and isotropic phases
in mixtures of mesomorphic compounds with
non-mesomorphic solutes. (From Martire 1979).

Often when terminal polar and terminal non-polar compounds, both of which exhibit only a nematic phase in the pure state, are mixed together a smectic phase results in the mixed state (e.g., Fig. 1.7) (For example, Dave et al. 1966, Schroeder and Schroeder 1968, Heppke and Richter 1978, Engelen et al. 1978). There is evidence that the occurrence of this 'induced smectic phase[1] in some mixtures can be attributed to charge transfer complexing. However an induced smectic A phase has been found in a system in which neither of the components has an appreciably strong polar end group (Suresh 1983).

One of our studies is on binary phase diagrams of two nematogens having rod-like and plate-like molecules. Alben (1973) theoretically studied such mixtures based on a lattice model and predicted the occurrence of a biaxial phase (Fig. 1.8). Later Rabin et al (1982) arrived at similar conclusions. The theories of Chen and Deutch (1984) using a Van der Walls type of theory and that of Caflisch et al. (1984) also using a lattice model, gave essentially the same type of results. The first experimental evidence for this biaxiality was observed in a lyotropic system (Yu and Saupe 1980) in a concentration and temperature range separating two uniaxial phases, one composed of disc-shaped micelles and the other of rod-shaped micelles.

However, when two thermotropic nematogens, one of them having rod-like molecules and the other having disc-like molecules, are
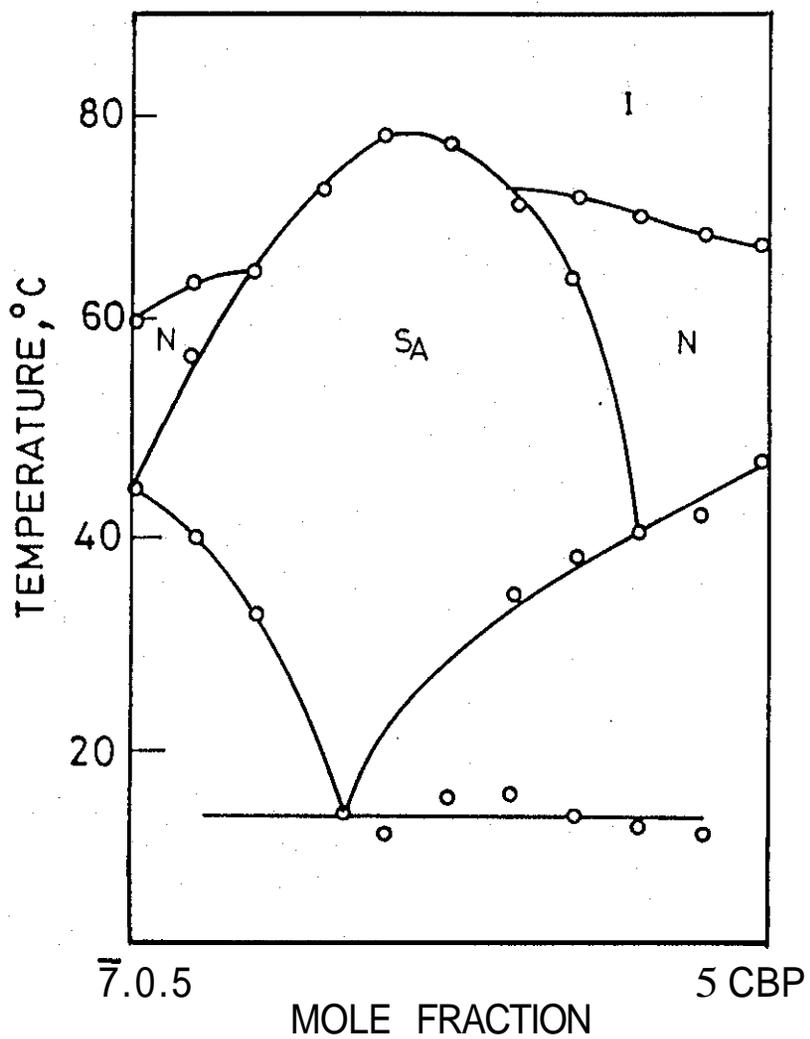
Figure 1.7

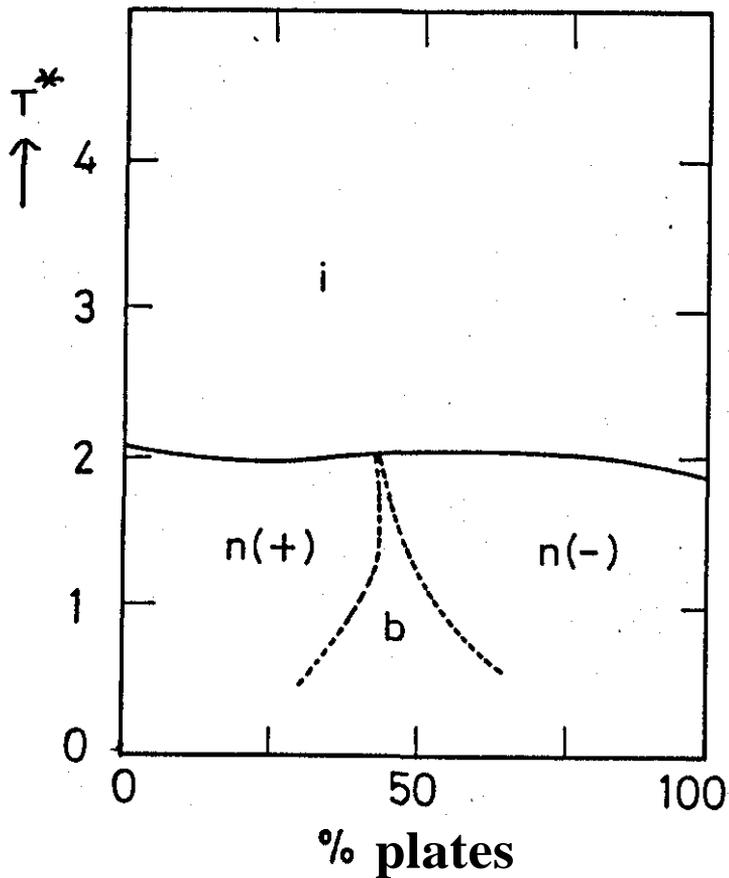Phase diagram of two pure nematogens exhibiting an induced smectic phase. (From Engelen et al., 1978).

Figure 1.8

Theoretical phase diagram of mixtures of rods and plates indicating the occurrence of a biaxial phase. i : isotropic, n(+) : positive uniaxial, n - : negative uniaxial, b : biaxial phase, T* : effective temperature. (From Alben 1973).

mixed together, instead of getting a biaxial nematic phase, we found a coexistence of two nematic phases. This result will be discussed in Chapter 2.

1.5   CONTINUUM THEORY OF NEMATIC LIQUID CRYSTALS

Since nematic liquid crystals are characterised by an orientational order, any deformation of the director field is opposed by a restoring torque. The deformations are described by the continuum theory. Oseen (1933) and Zocher (1933) initiated the continuum model which was reexamined by Frank (1958).

These deformations cost elastic energy. Oseen assumed that the intermolecular forces are additive and have short range. The deformation dependent part of the energy density was expressed by him as a linear combination of ten terms whose coefficients define a total of eight elastic constants. Five of these terms and three of the elastic constants do not enter the Euler–Lagrange equation which determines the possible equilibrium structures of the liquid crystal. They were thus omitted by Oseen (1933). Frank derived the theory in a phenomenological approach and some of the terms dropped by Oseen were reintroduced by him.

Following the formalism of Frank an expression for the elastic free energy density can be obtained as follows. Let $\vec{n}(r)$ represent the preferred orientation at any point r. It is assumed to vary slowly with position and is defined at other points by continuity.

At any point **r** a right handed Cartesian coordinate system x,y,z with z-axis along $\vec{n}$ is introduced. The x-axis is arbitrarily chosen but is taken to be perpendicular to z and y-axes. The six components of curvature (see Fig. 1.9) are given by:

$$S_1 = \frac{\partial n_x}{\partial x} \quad , \quad S_2 = \frac{\partial n_y}{\partial y} \quad ,$$

$$t_1 = -\frac{\partial n_y}{\partial x} \quad , \quad t_2 = \frac{\partial n_x}{\partial y} \quad ,$$

$$b_1 = \frac{\partial n_x}{\partial z} \quad , \quad b_2 = \frac{\partial n_y}{\partial z} \quad , \tag{1.10}$$

where S, t and b denote splay, twist and bend deformations respectively. Considering the symmetry of the uniaxial nematic phase Frank (1958) has shown that the free energy density F_d is given by

$$F_d = \frac{1}{2}[K_{11}(S_1 + S_2)^2 + K_{22}(t_1 + t_2)^2 + K_{33}(b_1^2 + b_2^2)]$$

$$- (K_{22} + K_{24})(S_1 S_2 + t_1 t_2) \tag{1.11}$$

where K_{11}, K_{22} and K_{33} are the splay, twist and bend elastic constants associated with the three independent bulk distortions of the nematic (Fig. 1.9). The equilibrium structure of the liquid crystal can be determined by minimising the volume integral of the free energy density. A necessary condition for a structure to have an energy minimum is that $\vec{n}$ is a solution of the Euler-
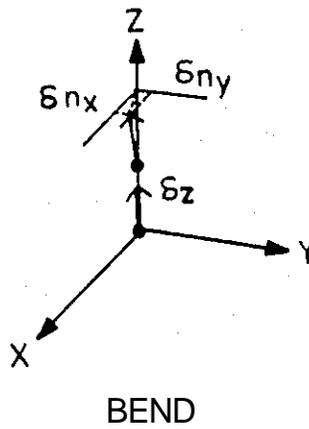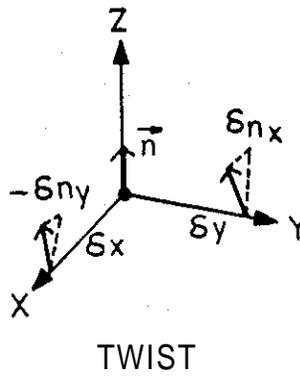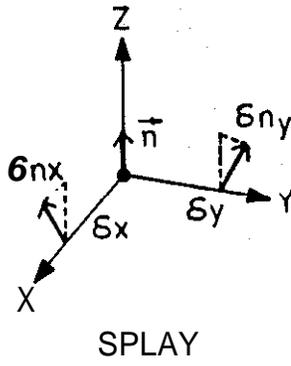
SPLAY

TWIST

BEND

Figure 1.9

The three types of deformation in a nematic liquid
crystal (From Frank 1958).

Lagrange differential equation. As we have seen F_d is a function of $\vec{n}$ and its gradients.

$$g_{\alpha\beta} = \frac{\partial n_\beta}{\partial x_\alpha} \qquad \alpha, \beta = 1,2,3$$

where $x_1 = x$, $y_1 = y$, $z_1 = z$ and $n_I = n_x$, $n_2 = n_Y$ and $n_3 = n_z$. Imposing a small variation $\delta\vec{n}(r)$ at all points we have

$$\delta F_d = \int [\frac{\partial F_d}{\partial n_\beta} \delta n_\beta + \frac{\partial F_d}{\partial g_{\alpha\beta}} \frac{\partial}{\partial x_\alpha} (\delta n_\beta)] dV \qquad (1.12)$$

Integrating the second term by parts and neglecting the surface term, i.e., assuming that the anchoring at the boundaries is strong

$$\delta F_d = \int [\frac{\partial F_d}{\partial n_\beta} - \frac{\partial}{\partial x_\alpha}(\frac{\partial F_d}{\partial g_{\alpha\beta}})] \delta n_\beta \, dV \qquad (1.13)$$

This yields the Euler-Lagrange equilibrium equation

$$\frac{\partial F_d}{\partial n_\beta} - \frac{\partial}{\partial x_\alpha}(\frac{\partial F_d}{\partial g_{\alpha\beta}}) = 0 \qquad (1.14)$$

Terms of the form div $\vec{u}$, where $\vec{u}(r)$ is an arbitrary vector field, may be transformed to surface integrals using the Gauss theorem. These terms do not contribute to the equilibrium condition (1.14). For example the term associated with $(K_{22} + K_{24})$ introduced by Frank can be written as (Ericksen 1962)

$$\frac{\partial n_x}{\partial x} \frac{\partial n_y}{\partial y} - \frac{\partial n_y}{\partial x} \frac{\partial n_x}{\partial y} = \frac{\partial}{\partial x} (n_x \frac{\partial n_z}{\partial z} - n_y \frac{\partial n_x}{\partial y}) + \frac{\partial}{\partial y} (n_y \frac{\partial n_x}{\partial x} - n_z \frac{\partial n_y}{\partial z})$$

$$+ \frac{\partial}{\partial z} (n_z \frac{\partial n_y}{\partial y} - n_x \frac{\partial n_z}{\partial x}) \qquad (1.15)$$

and can thus be omitted. Finally in vector notation the free energy density of the nematic is usually written as

$$F_d = \frac{1}{2} [K_{11}(\text{div } \vec{n})^2 + K_{22}(\vec{n} . \text{curl } \vec{n})^2 + K_{33}(\vec{n} \times \text{curl } \vec{n})^2] \qquad (1.16)$$

The free energy density is a quadratic function of the curvature in the director fields, i.e., in the gradients on $\vec{n}$.

Nehring and Saupe (1971) argued that the terms linear in the second derivatives of $\vec{n}$ can make contributions of the same order of magnitude as the quadratic terms of the first derivatives. If this is taken into account a term of the form $\text{div}(\vec{n} \text{ div } \vec{n})$ connected with K_{13} should be included in F_d. Frank who considered terms of similar order associated with $(K_{22} + K_{24})$, ignored this term. However as in the case of the latter, the K_{13} term makes no contribution when there is strong anchoring at the boundaries. This problem will be dealt with in detail in Chapter 5 along with an experimental method of determination of the elastic constant K_{13}.

As mentioned earlier the nematic medium is characterised by an apolar director. Most of the nematic liquid crystals made up of rod-like molecules have a positive diamagnetic susceptibility. Therefore if a magnetic field is applied perpendicular to the origi-

nal direction of alignment of a nematic sample that is strongly
anchored at the boundaries, distortions in the uniform pattern
can be obtained (Fig. 1.10). However as the effect of the magnetic
field is opposed by the strong anchoring at the boundaries, these
distortions take place only at a field strength. greater than a
certain threshold value H_c. Distortions of this kind were first
studied by Freedericksz (1933).

At a given field the stable equilibrium state can be found
by minimising the free energy with respect to the variations in
the director profile. The expression for the critical field is

$$H_c = \frac{\pi}{d} (K_{ii}/\Delta\chi)^{1/2} \qquad \bullet \qquad (1.17)$$

Different geometries as shown in Fig. 1.10 can be used for
measuring the three elastic constants K_{11}, K_{22} and K_{33}, H_c is usually
measured by employing an optical technique for detecting the distor-
tion (see for e.g., de Gennes 1975, Chandrasekhar 1977).

Typically K_{ii} is of the order of 10^{-6} dynes. For example
the values of the three elastic constants for para-azoxyanisole
at 120°C are:

$$K_{11} = 0.7 \times 10^{-6} \text{ dynes}$$
$$K_{22} = 0.43 \times 10^{-6} \text{ dynes}$$
$$K_{33} = 1.7 \times 10^{-6} \text{ dynes.}$$

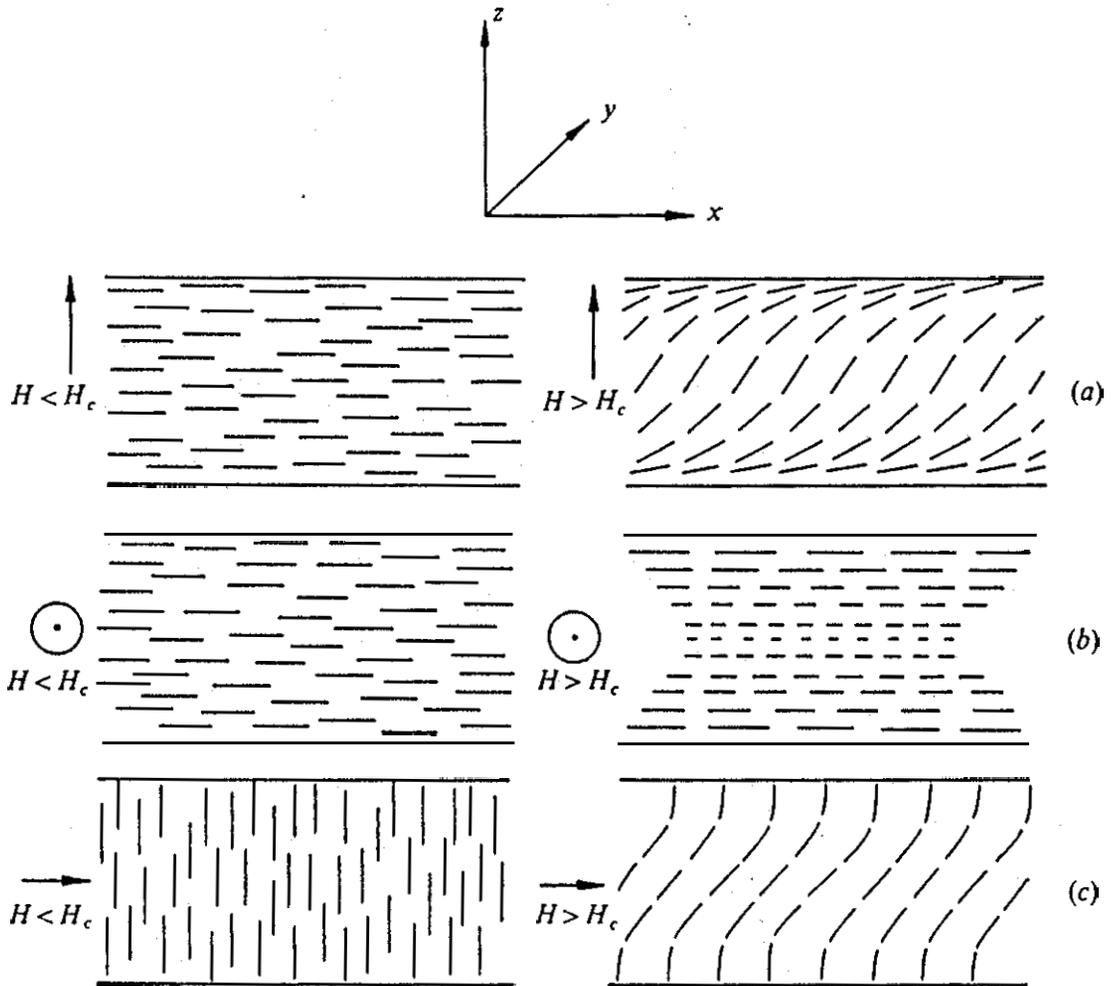The K_{ii} values decrease rather strongly when T increases. (They

Figure 1.10

The three geometries used in Freedericksz transition experiments (From Chandrasekhar 1977).

vary roughly like the square of the order parameter.) Since the three elastic constants are of the same order of magnitude, it is often very convenient to treat problems of curvature distortion if the three elastic constants K_{11}, K_{22} and K_{33} are taken to be equal (one constant approximation).

In Appendix I we present revised absolute values of the elastic constants K_{11}, K_{22} and K_{33} of several cyano biphenyls which were originally measured using experimental techniques mentioned above.

1.6   DEFECTS

In liquid crystals various defects are easily visible under the microscope even under low magnification. These defects are stabilised by boundary conditions. They also occur when there is a disturbance of the orientation caused by electric or magnetic fields, temperature gradients and mechanical stresses.

The term 'disclination' was suggested by Frank to describe defects caused by discontinuities in the director field $\vec{n}(r)$. There are two types of disclinations, line and point disclinations.

Linear defects occur frequently in nematic liquid crystals. They can be visualised by using the Volterra process (Volterra 1907).

Volterra Process

A perfect medium is cut along an arbitrary surface S and the two lips S' and S" of the cut surface are displaced relative to each other by a symmetry permitted rotation around a certain axis. The void which now exists is filled with perfect material, or if there is an overlap of the two parts the excess of the material is removed and the medium is allowed to relax such that the director continuity is still maintained. This produces a line discontinuity along a line L (see for example fig. 1.11).

The most frequently occurring types of disclinations are those in which the rotation axis is parallel to the line L. These are called wedge disclinations. The Schlieren texture exhibited by nematics is due to these wedge disclinations. If the rotation is perpendicular to the singular line, we get a twist disclination. In this case the line of singularity is in the plane in which the molecules lie. These are often seen as loops separating regions of different twist.

Schlieren Textures

When a sufficiently thin (−20 μm) nematic sample is taken between glass surfaces that have not been treated to give any preferred alignment at the boundaries, one often sees a set of singular points. These correspond to discontinuities in the director orientation and are disclination lines viewed end on. When the sample is taken between crossed polarisers these points are seen to be
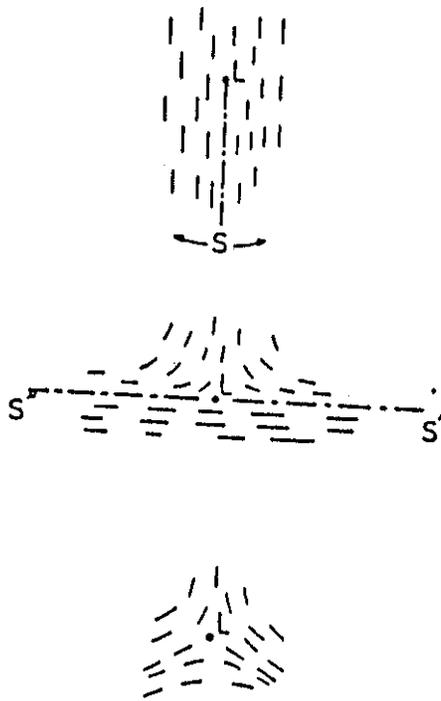
Figure 1.11

Generation of a disclination line by
Volterra process.

connected by black brushes. This texture is called the Schlieren texture. A typical example is shown in Fig. 1.12.

The brushes are regions where the director is either parallel or perpendicular to the plane of polarisation of the incident light. The polarisation is unchanged by the sample in these regions and the light is extinguished by the crossed analyser. Usually the points are associated either with four brushes or two brushes. If the polarisers are rotated simultaneously the brushes also rotate continuously showing that the orientation of the director changes continuously about the points, which themselves remain unchanged. The sense of rotation may be the same as that of the polarisers (positive disclinations) or opposite (negative disclinations). The rate of rotation is about equal to that of the polarisers when there are four brushes and twice as fast when there are only two brushes.

The different types of disclinations can be characterised by a number 's' called the 'strength' defined as 1/4 X (number of brushes). The sum of s of all disclinations in a sample tends to be zero. Disclinations with opposite values are always connected together. Often near the nematic–isotropic transition point, the disclinations merge together. If the sum of their s values equals zero they totally annihilate each other. If on the other hand the s values add up, a new disclination with an s value equal to the sum, results
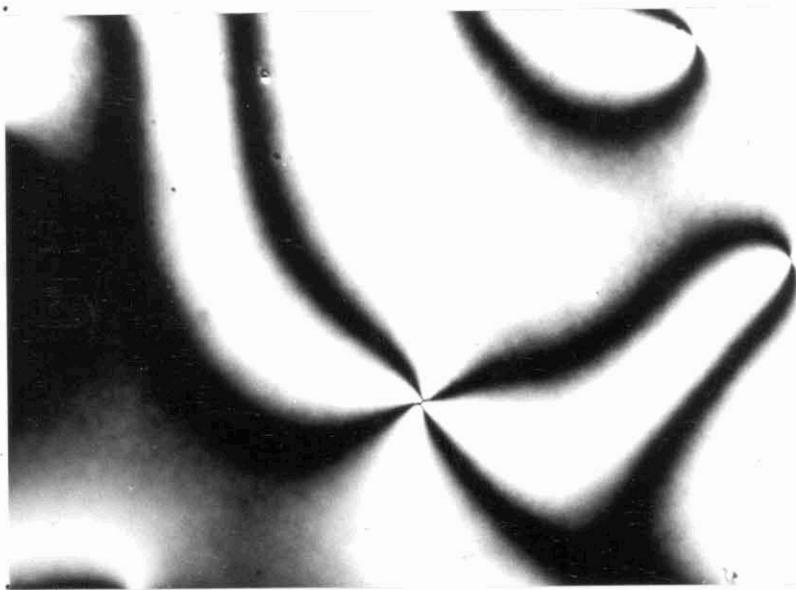
Figure 1.12. A typical Schlieren texture exhibited by nematic liquid crystals.

The significance of these textures was **first** understood by Lehmann (1890) and Friedel (1922), but a mathematical treatment of the actual configuration around the disclinations was given by Oseen (1933) and Frank (1958). A more thorough discussion of the Schlieren texture is due to Nehring and Saupe (1972). The continuum theory of elastic deformations forms the basis of such theoretical treatments. Assuming a one constant approximation, solutions to the director field around disclinations can easily be obtained. If ψ is the angle made by $\vec{n}$ with the x-axis, and a is the angle that the radius vector connecting the given point to the centre of the defect makes with the x-axis, and assuming that $\vec{n}$ is confined to the xy plane the solutions take the form

$$\psi = s\alpha + c \qquad (1.18)$$

where c is a constant. In this approximation ψ becomes multiple valued at the origin and hence leads to a singularity at that point. Assuming that a core region extends from the origin to r_c, the energy per unit length of an isolated disclination is given by (Nehring and Saupe 1972)

$$W = W_c + \pi K s^2 \ln R/r_c \qquad (1.19)$$

where W_c arises from the core region and R is the size of the sample. For a given R the elastic energy carried by a defect is thus seen to be proportional to s^2 which means that all defects with $|s| > 1/2$ should spontaneously break up to form defects with $|s| = 1/2$. However defects of strength ± 1 are frequently seen.

Cladis and Kleman (1972) and Meyer (1973) resolved this problem and showed that the energy of the disolination of strength $|s| = 1$ is reduced if the director is allowed to relax out of the plane perpendicular to the disclination line, such that it is along the z-axis at the origin. This solution has no singularity and the'line energy does not depend on R.

Often pairs of disclinations with opposite s values are seen. In the one constant approximation the solutions for the director pattern around a pair of defects with planar director field and of strength $\pm s$, can be written as

$$\psi = s(\alpha_1 - \alpha_2) + c \tag{1.20}$$

where α_1 and α_2 are the angles as defined earlier with respect to the two defects. The constant c determines the orientation of the director far away from the defects.

Until recently only defects of strength ± 1 and $\pm 1/2$ had been observed in nematic liquid crystals. In Chapter 6 we report the first observations of defects of strength $\pm 3/2$ and ± 2 in thermotropic nematic liquid crystals.

Inversion Walls

Schlieren textures may also arise when the surfaces try to impose a uniform orientation on the sample, for example when the glass plates have been rubbed. The alignment is generally parallel
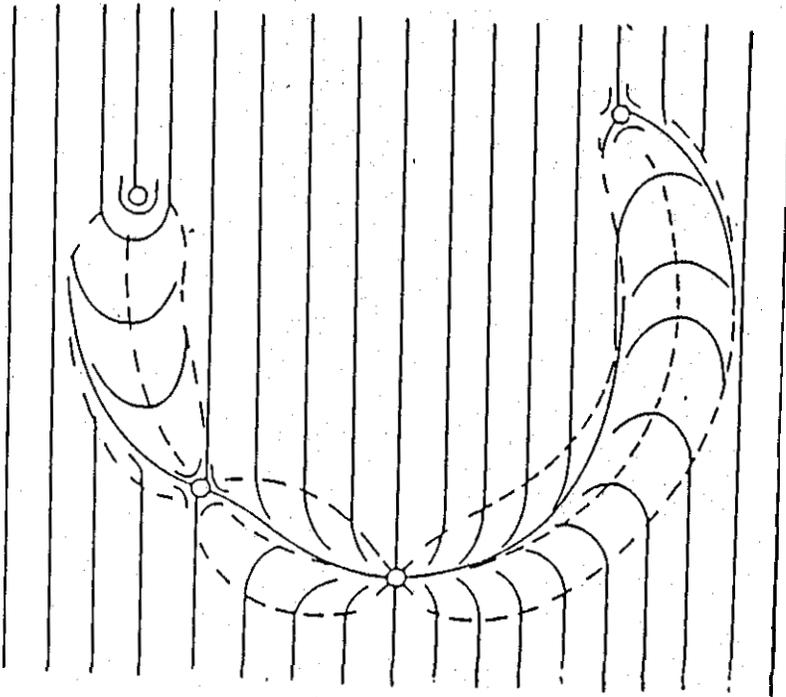
Figure 1.13

Molecular alignment in the vicinity of an
inversion wall of the first kind.
(From Nehring and Saupe 1972).

to the direction imposed by the surfaces except in the region of the wall (Fig. 1.13) (Nehring and Saupe 1972). In this region the alignment changes continuously with a change of $\pi/2$ at the centre. The total change in crossing the wall corresponds to a turn of the preferred orientation by n. Between crossed polarisers two black brushes appear one on either side of the central line ($\pi/2$ line). One brush of each pair is more diffuse than the other. These walls are called inversion walls of the **first** kind. Another type of inversion wall called inversion wall of the second kind occurs when molecules are tilted out of the plane of the bounding surface. These are inversion walls with respect to the **tilt** direction. Molecules on different sides of the wall are tilted in opposite directions and on going through the wall a continuous change in **tilt**, angle takes place, with the molecules aligned parallel to the surface in the centre of the wall (Nehring and Saupe 1972).

The inversion walls may form closed loops or start from disclinations of strength $\pm 1/2$, which may be connected to disclinations of strength ± 1. In Chapter 6, we report observations on inversion walls of the first kind associated with defects of strength $\pm 3/2$.

1.7 HYDRODYNAMICS OF NEMATICS AND CHOLESTERICS

The nematic liquid crystal flows but there is a close coupling between the flow and the orientation of the molecules. The flow can induce a change in orientation which in turn affects the motion, or a change in orientation can lead to flow which tends to counteract

or reinforce the change of alignment.

Dynamic problems of anisotropic liquids were first studied by Anzelius (1931) and Oseen (1933). The coupling between orientation and flow for nematic and cholesteric liquid crystals in particular was analysed by Ericksen (1966) and Leslie (1968, 1979). Quantitative studies on flow properties have been made by various groups (see de Gennes 1975; Chandrasekhar 1977).

As in conventional hydrodynamics the dynamical situation for a nematic liquid crystal is specified by a velocity field $\vec{v}(r)$ giving the flow of matter, and in the Leslie formulation (Leslie 1979), the director $\vec{n}(r)$ describing the local state of alignment is specified in addition. We first write an expression for the dissipation or the entropy source, due to all friction processes in the fluid. There are two types of dissipative losses, conventional viscosity effects and losses associated with a rotation of the director with respect to the background fluid. Following the notations of de Gennes (1975) the dissipation $T\dot{S}$ is given by

$$T\dot{S} = \int [A : \sigma^s - \vec{\Gamma} . \vec{\omega} + \vec{h} . \dot{\vec{n}}] d^3r \qquad (1.21)$$

where σ^s is the symmetric part of the stress tensor, A is the symmetric part of the velocity gradient tensor given by

$$A_{\alpha\beta} = \frac{1}{2}(\partial_\alpha v_\beta + \partial_\beta v_\alpha) ,$$

$\vec{\omega} = \frac{1}{2}$ curl $\vec{v}$, is the antisymmetric part of the velocity gradient

tensor, $\overset{\leftrightarrow}{\Gamma} = \vec{n} \times \vec{h}$ is the torque per unit volume exerted by the internal degrees of freedom. $\overset{\rightarrow}{\dot{n}}$ is the material derivative of $\vec{n}$, i.e., change of $\vec{n}$ per unit time as experienced by a moving molecule, $\vec{h}$ is the molecular field.

Eq. 1.21 can be written as

$$T\dot{S} = \int [A : \overset{\rightarrow}{\sigma}^{s} + \vec{h} . \vec{N}]d^3r \qquad (1.22)$$

where $\vec{N} = \overset{\rightarrow}{\dot{n}} - \overset{\leftrightarrow}{\omega} \times \vec{n}$. The vector $\vec{N}$ represents the rate of change of the director with reference to the background fluid. Eqn. (1.22) contains the two types of dissipative losses due to viscosity effects and rotation of the director.

In the Ericksen–Leslie model the hydrodynamic stress is assymmetric and has in general six viscosity coefficients.

The contribution to the entropy source is now expressed as a sum of products of fluxes and the conjugate forces (de Groot and Mazur 1962). Choosing as fluxes the components of the symmetric tensor $A_{\alpha\beta}$ and the components of the vector $\vec{N}_{\mu}$, a set of phenomenological equations expressing the forces in terms of the fluxes can be written. Usually one is concerned with very slow motions so that the fluid can be treated as incompressible. In the limit of slow motions the fluxes are linear functions of the thermodynamic forces. Cross effects between various phenomena exist, since each flux may in principle be a linear function of all thermodynamic forces. Spatial symmetries of the nematic reduces the number of

phenomenological coefficients. The Onsager reciprocity theorem gives rise to additional relationships amongst the phenomenological coefficients thus reducing the number of independent viscosity coefficients. Thus the following equations are obtained for the complete viscous stress $\sigma'_{\alpha\beta}$ and the hydrodynamic molecular field $\vec{h}$ (de Gennes 1975)

$$\sigma'_{\alpha\beta} = \alpha_1 n_\alpha n_\beta n_\mu n_\rho A_{\mu\rho} + \alpha_2 n_\alpha N_\beta + \alpha_3 n_\beta N_\alpha$$
$$+ \alpha_4 A_{\alpha\beta} + \alpha_5 n_\alpha n_\mu A_{\mu\beta} + \alpha_6 n_\beta n_\mu A_{\mu\alpha} \qquad (1.23)$$

and

$$h_\mu = \gamma_1 N_\mu + \gamma_2 n_\alpha A_{\alpha\mu} \qquad (1.24)$$

together with the relations

$$\gamma_1 = \alpha_3 - \alpha_2 \qquad (1.25)$$

$$\gamma_2 = \alpha_2 + \alpha_3 = \alpha_6 - \alpha_5 \qquad (1.26)$$

The six coefficients a_i are usually called the Leslie coefficients and have the dimensions of viscosity. Equation (1.26) was first derived by Parodi (1970) using the Onsager principle. This reduces the number of independent coefficients to five.

The cholesteric liquid crystal is a chiral system consisting of orientationally ordered optically active anisotropic molecules, with the director twisting about an orthogonal axis. In parity conserving systems the Curie (or Von Neumann) principle requires that the symmetry of physical effects must be contained

in the causes which give rise to them. But in chiral systems which lack mirror symmetry the principle predicts novel types of coupling between fluxes and forces.

Hence in cholesterics a possibility now exists of a coupling between thermal and mechanical effects. This type of thermomechanical effect was observed by Lehmann (1900) soon after the discovery of liquid crystals. He found that in small cholesteric drops taken between two glass surfaces a thermal gradient along the helical axis gives rise to a continuous rotation of the structure about that axis. The thermomechanical effect results in an angular momentum density of the director even though the applied force has the character of a polar vector. Leslie (1968) worked out a detailed hydrodynamic theory of the cholesteric state and obtained solutions corresponding to the Lehmann rotation phenomenon. Later Martin et al (1972) and Lubensky (1972) developed a hydrodynamic theory of layered systems and showed that the symmetry of such systems allows for a thermomechanihal effect which couples the phase of the layers with a temperature gradient.

To our knowledge the Lehmann experiment has never been reproduced. We have studied an analogous effect ⁻ the electromechanical coupling in a cholesteric, under the action of a DC electric field. These studies are reported in Chapter 4 in detail.
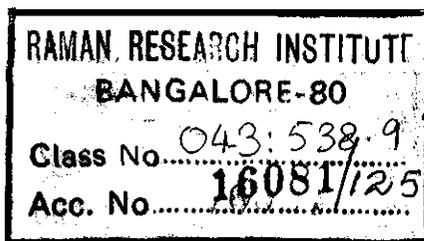
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