

CHAPTER I

INTRODUCTION

I.1 Historical Review

Previously, investigations and classifications of liquid crystalline phases were made principally by means of optical observation under a polarizing microscope. The optical appearance of thin layers of liquid crystals has been described in terms of microscopic "textures". As samples of different phases generally show different textures, the identification of liquid crystalline phases can thus conveniently be made. Moreover, the molecular arrangements can under suitable circumstances be determined from the optical properties.

To make an observation, the sample is usually enclosed between a glass slide and a cover slip. It has been suggested that the textures observed should be governed by surface effects. If the surface of the slide is smooth, the molecules will try to align themselves normal to the surface and the sample should then appear to be optically homogeneous. In general, however, the total alignment throughout the sample may not occur and inhomogeneous textures are often observed in practice. Under these conditions, Sackmann and Demus¹ classified the mesophases according to their microscopic textures as follows:

¹ H. Sackmann and D. Demus, The Polymorphism of Liquid Crystals, Mol.Cryst., 2, (1966) 81.

Thermotropic liquid crystals²

- a. Nematic textures.
 - i. Marbled texture
 - ii. Schlieren texture
 - iii. Pseudo-isotropic texture
- b. Smectic textures.
 - i. Focal conic (fan-shaped, polygonal) texture
 - ii. Schlieren texture
 - iii. Mosaic texture
- c. Cholesteric (or twisted nematic) textures.
 - i. Focal conic texture
 - ii. Plane texture



Recently, classification of liquid crystals has been made in terms of intermolecular arrangements, strata packing and other structural facts mainly by means of X-ray diffraction. At least seven different phases of smectic liquid crystals, have now been fairly well characterized by X-ray diffraction^{3,4}. These phases are different as regards their molecular arrangement in the strata. Smectic A, which shows

² G.H. Brown, Liquid Crystals and Their Roles in Inanimate and Animate Systems, American Scientist, 60, (1972)64.

³ G.H. Brown, J.W. Doane and V.D. Neff, A Review of the Structure and Physical Properties of Liquid Crystals, Butterworth & Co.(Publishers) Ltd., London, (1971) pp.18-19.

⁴ A Saupe, Recent Results in the Field of Liquid Crystals, Angew.Chem.Internat.Edit., 7, (1968) 97.

fan-shaped texture, has a random arrangement of the molecular centres within the strata. Smectic C⁵ has a tilted molecular orientation in the strata, while the molecules of smectic B exhibit the hexagonal-close-packed arrangement within each stratum. Under the polarizing microscope, smectic D behaves isotropically and their X-ray diffraction patterns indicate that these correspond to the cubic packing⁶. More recently, smectic H has been introduced by de Vries and Fishel⁷. This phase is a planar structure with the molecules making a characteristic tilt angle with respect to the planar normals and possessing order (probably hexagonal) among the centres of the molecules within each layer. In these polymorphic forms of smectic liquid crystals, smectic A has the highest degree of disorder. It has also been noted that, when a substance shows three smectic forms, the relationships of the phases with changing temperature is:

⁵ I.G. Chistyakov, L.S. Schabischev, R.I. Jarenov and L.A. Gusakova, The Polymorphism of the Smectic Liquid Crystal, in Liquid Crystals 2, Part II, G.H. Brown, ed., Gordon and Breach Science Publishers, Inc., New York, (1969) p.813.

⁶ G. Pelzl and H. Sackmann, Birefringence and Polymorphism of Liquid Crystals, in Symposia of the Faraday Society No.5: Liquid Crystals, 1971, (The Faraday Division, Chemical Society, London, 1972) p.68.

⁷ A. de Vries and D.L. Fishel, X-ray Photographic Studies of Liquid Crystals III, Structure Determination of Smectic Phase of 4-Butyloxybenzal-4'-Ethylaniline, Mol.Cryst. Liquid Cryst., 16, (1972) 311.

Isotropic \longrightarrow Smectic A \longrightarrow Smectic C \longrightarrow Smectic B.
 $\xrightarrow{\hspace{10em}}$
 Decreasing Temperature

It has been suggested by de Vries⁸ that there are three types of nematic phases, viz., cybotactic phase, skewed cybotactic phase and classical nematic phase. Cybotactic phase results from the molecular arrangement into groups in which the centres of the molecules lie in the same plane. This group is called a "cybotactic group". The mean direction of the molecules in each cybotactic group may be normal to the plane that contains the molecular centres, or may be inclined at some angle to the normal to this plane. The former arrangement is called "normal cybotactic" and the latter "skewed cybotactic". These phases are evidenced by X-ray diffraction patterns and also by their textures. The normal cybotactic group has a high tendency to exhibit the pseudo-isotropic texture, because in this case the molecules are aligned normal to the surface. The skewed cybotactic, on the other hand, can not show pseudo-isotropy at all, while the classical nematic phase, in which no regular arrangement between neighbouring molecules exists, may or may not show pseudo-isotropy. There is no sharp distinction between these three groups, since either cybotactic type will approach the classical type as the number of molecules in each group approaches 1; and the skewed cybotactic type will

⁸ A. de Vries, Evidence for the Existence of More than One Type of Nematic Phase, Mol.Cryst.Liquid Cryst., 10, (1970)31.

approach the normal cybotactic type when its angle approaches 0° .

The molecular orientation of the marbled texture is relatively simple. What is particularly interesting is the molecular alignment near the threads in the texture. Since threads sometimes transform into brushes of the schlieren texture, it is widely believed that the molecular orientation around these threads is not so different from that in the schlieren texture.

The schlieren texture, that appears as black brushes spreading throughout the nematic area, has been observed near the nematic-isotropic transition point. As the polarizer is rotated, the brushes rotate around point singularities. The term "disclination" has been named as an analogue of the crystal dislocation by Frank⁹. Because of the lack of a truly three-dimensional crystal structure, line singularities are possible in nematic liquid crystals.

Recently, investigation of the schlieren texture has been made in some details¹⁰. It was observed that as the polarizer was rotated, some brushes rotated in the direction

⁹ F.C. Frank, On the Theory of Liquid Crystals, Disc.Faraday Soc., 25, (1958) 19.

¹⁰ J. Nehring and A. Saupe, On the Schlieren Texture in Nematic and Smectic Liquid Crystals, J.Chem.Soc.Faraday Trans.II, 68, (1972) 1.

of the polarizer, whereas some rotated in the opposite direction. The brushes of the singularities with four brushes rotated with the same velocity as the polarizer, while the velocity of those with two brushes was twice. Thus, the singularities have been characterized by Nehring and Saupe¹⁰ by means of the index

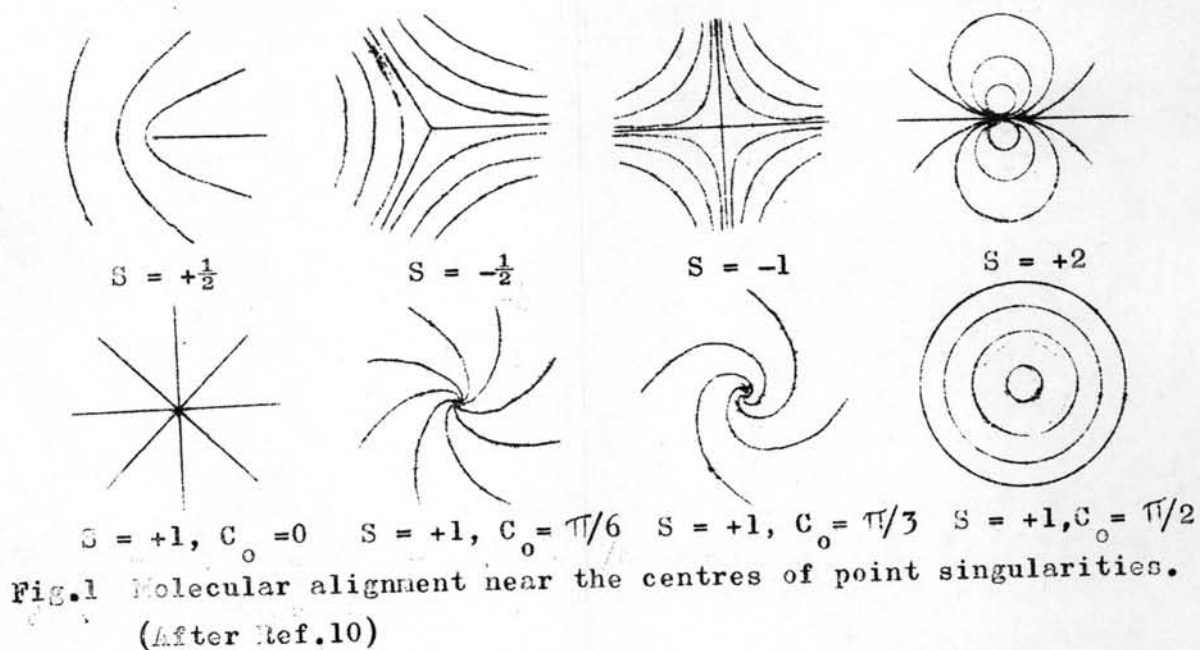
$$|S| = \frac{\text{number of brushes}}{4}$$

According to this classification, the types of singularities which have been observed are $\pm\frac{1}{2}$, ± 1 , where a positive sign indicates the positive direction of rotation with respect to the polarizer and a negative sign is for those that rotate in the opposite direction. Singularities of opposite signs always form dipoles, and annihilation of these can take place at higher temperatures.

The theoretical treatment of the molecular alignment near the singularities has been based primarily upon the continuum theory. Oseen¹¹ and Frank⁹ determined the structure with a molecular orientation perpendicular to the normal of the layer. Following this treatment Nehring and Saupe¹⁰ have derived the general condition for the alignment of singularities, obtained by minimizing the elastic energy density¹²

¹¹ C.W. Oseen, *The Theory of Liquid Crystals*, Trans. Faraday Soc., 29, (1933) 883.

¹² J. Nehring and A. Saupe, *On the Elastic Theory of Uniaxial Liquid Crystals*, J.Chem.Phys., 54, (1971) 337.



with the assumption that the preferred direction of the molecules is the same throughout the bulk. The solution that corresponds to a nematic phase without twist is

$$\Psi = S\alpha + C_0$$

$$S = \pm 1, \pm 2, \pm 3, \dots \quad \text{if } \theta \neq \frac{\pi}{2}$$

$$\text{or } S = \pm \frac{1}{2}, \pm 1, \pm \frac{3}{2} \quad \text{if } \theta = \frac{\pi}{2}$$

C_0 being a constant, and α the angle in cylindrical co-ordinates.

It is obvious that half-numbered singularities can not be observed in smectic liquid crystals, since it is required that the molecular alignment be parallel to the surface.

A schematic plot of the projection of molecular orientation in (x_1, x_2) -plane around the point singularities is shown in Fig.1 for a few values of S . When $S \neq 1$ the structure of the singularity is independent of C_0 . A change takes place for $S=1$ at different values of C_0 .

An investigation of these alignments can be made optically. By rotating the polarizer and the analyzer simultaneously, the transmitted light propagates as pure ordinary or pure extraordinary waves, where the optical axis is parallel to either the polarizer or the analyzer. Thus the molecular alignment can effectively be mapped (see Fig.2). The angle of a whole-numbered singularity changes by 2π in going around the singularity, while that of a half-numbered one changes by π .

The optical properties of a liquid crystal with one of its surfaces bounded by the isotropic liquid of the same compound have been studied recently by Meyer¹³. He stated that the molecules of half-numbered singularities should be aligned parallel to the surface. If the molecules are aligned at an acute angle to the surface, then there will be a misfit at the surface where the molecules of opposite tilts are present. Since no surface disclination has been observed, the molecules must be aligned parallel to the surface.

The interaction energy between disclinations has been determined by Nehring and Saupe¹⁰, and more recently by Imura and Okano¹⁴, under the assumption that $k_{11} = k_{33} = K$. They

¹³ R.B. Meyer, Point Disclinations at a Nematic-Isotropic Liquid Interface, Mol.Cryst.Liquid Cryst., 16, (1972)335.

¹⁴ H. Imura and K. Okano, Interaction between Disclinations in Nematic Liquid Crystals, Phys.Lett., 42A, (1973)405.

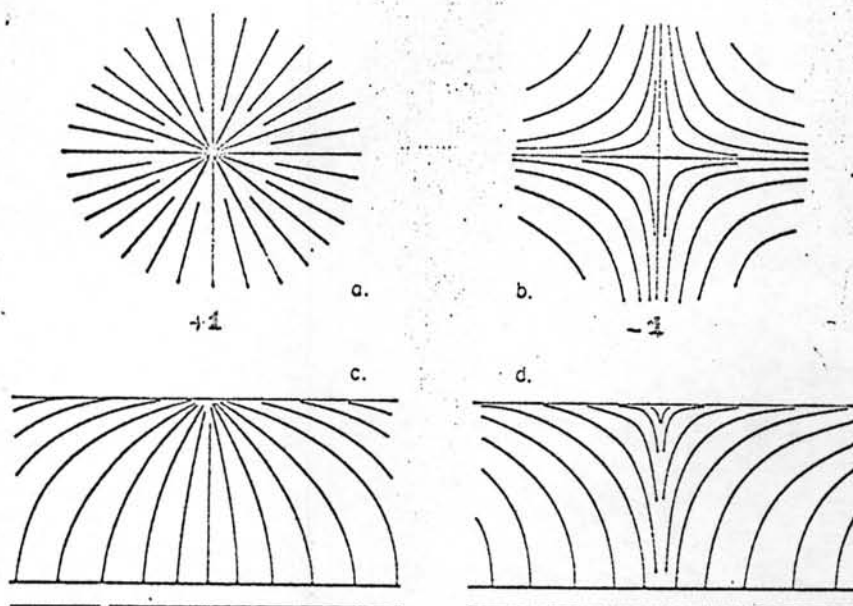


Figure 2. Elements of the structures of point disclinations: a. and b. The orientation patterns in the nematic-isotropic interface around $+1$ and -1 points respectively. c. and d. Structures in the nematic layer below the disclination points. For a $+1$ point, the structure can be like either c. or d., and is symmetrical about a vertical line through the point. For a -1 point, a vertical section through one principal axis of b. would look like c., and through the other principal axis would look like d.

(After Ref.13)

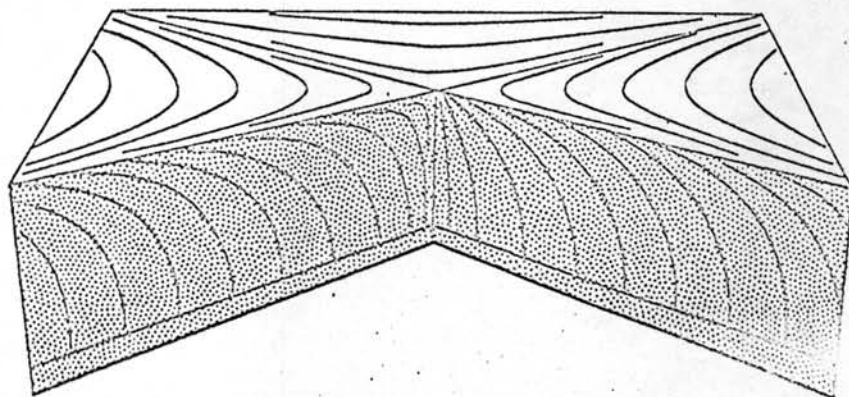


Figure 3. A three-dimensional view of the structure around a -1 point. The shaded areas are vertical sections.

(After Ref.13)

formulated the force of interaction between the two disclinations with the assumption that $r_0 \ll a \ll L$, which leads to

$$F = \frac{\pi K S_1 S_2}{2a}$$

where a = distance between the disclinations

S_1, S_2 = indices of two disclinations

r_0 = core radius of the disclination

L = characteristic dimension of the system.



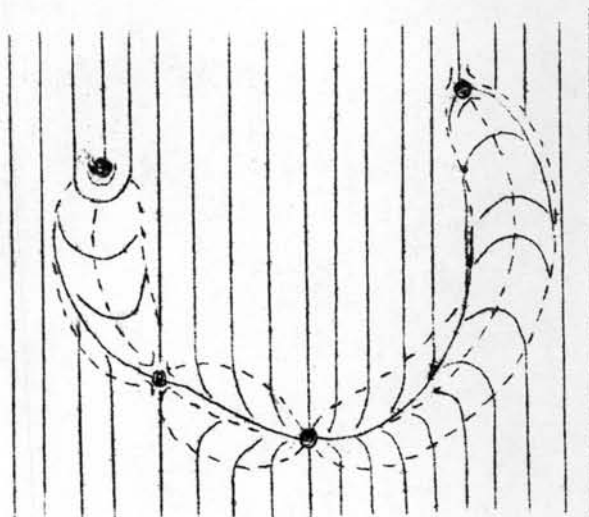
It is obvious that the force is attractive when S_1 and S_2 are of different signs and repulsive when they are of the same signs.

The formulation is analogous to that for the force of interaction between two screw dislocations. Near the boundary, the interaction between the wall and the disclination is equal to that between the disclination and its image reflected by the wall. The force is always repulsive.

Electric fields can also induce singularity pairs in the sample. Hundreds of point singularities are usually observed; they recombine rapidly, leaving only a few points.

The schlieren texture can arise as a consequence of the imposition from the surface, e.g. when the cover slip has been rubbed. The inversion line appears as a sharp black line joining two point singularities of opposite signs. There are two possible kinds of inversion wall being formed, as proposed by Nehring and Saupe¹⁰. The "inversion wall of the first kind" always occurs when the molecules try to align themselves

Fig.4 Molecular alignment in an inversion wall of the first kind. Solid lines give the vector field of the projection of \vec{L} in the plane of the layer; broken lines are selected curves of equal alignment (i.e., curves along which projection of \vec{L} is constant). (After Ref.10)



parallel to the rubbing direction. The molecular orientation then changes continuously from one side of the wall to the other. At the centre of the wall the molecules are aligned normal to the remaining part. Thus the total change is equal to 180° on crossing the wall.

Another type of inversion wall, the "inversion wall of the second kind", has been observed when the molecules are tilted out of the plane of the layer. Either side of the inversion wall are tilted in the opposite directions, while the centre of the wall remains unchanged. However, it is still a continuous change across the wall, and there is a maximum birefringence in the centre of the wall.

In contrast to the case of point singularities without the inversion walls in which only point singularities of opposite signs can be annihilated, coalescence of singularities of the same sign can be observed when these are joined by the inversion walls¹⁰. The energy and interaction between

the singularities derived from the continuum elastic theory do not apply in this case, and the energy of the inversion walls has to be taken into account.

The inversion lines are different from threads in the nematic mesophase. Threads sometimes float freely, and sometimes their ends are fixed to the surface. Point singularities may be short threads that either ends are fixed when being viewed end on.

Nematic droplets.

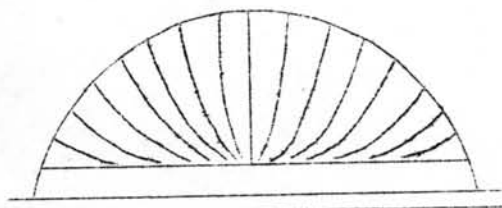


Fig. 6 The internal structure of a droplet sample. The curving lines indicate the direction of the optical axis in the nematic portion. (After Ref.13)

At the isotropic-nematic transition, spherical droplets are observed. At the isotropic-smectic transition on the other hand, rod-shaped textures or bâtonnets are formed. The formation and internal structure of the nematic droplets are still not very well understood. However, molecular orientations in the droplets with distinct crosses are mapped by

Meyer¹³ optically. The polarizer and analyzer are rotated together and the optical axes of the sample are plotted.

Meyer¹⁵ proposed that, in the absence of an external

¹⁵ R.B. Meyer, Piezoelectric Effects in Liquid Crystals, Phys.Rev.Lett., 22, (1969) 918.

perturbation, the polar molecules in the mesophase are arranged in such a way that the total structure is nonpolar. When an external stress is applied, the structure is distorted. Either splay or bending will polarize the sample. He stated that curvature would induce space charges and vice versa. The attraction between nematic droplets is considered to be an evidence that supports this conclusion.

II.2 Purpose of the Present Experiments

The principal purpose of the present investigation is to study the effects of molecular structure, their arrangements and interaction, impurities, mechanical constraints, and structural imperfections on the formation and optical properties of each type or nematic textures, especially near the mesomorphic-isotropic transition temperature. It is suggested that the formation of schlieren texture in the nematic phase is mainly influenced by the molecular structure, i.e., its dipole moment and the overall molecular geometry. A number of nematic liquid crystals will be investigated. Obviously, the stress field caused by structural imperfections and the presence of impurities must also play an important role on the formation and appearance of this texture. Nematic substances mixed with foreign particles and nematic-nematic mixtures will also be studied. It has previously been established that a pre-transition exists in the heat capacity curves of PAA and some other nematic liquid crystals. It is

suggested that this pre-transition may correspond to the change from marbled to schlieren texture in a thin layer of liquid crystal in the nematic phase.

On cooling slowly from the isotropic to the nematic phase, nematic droplets are formed. These droplets always combine to form the schlieren texture. It is reasonable to expect that the nucleation and growth mechanism of these droplets may be determined by the dislocations created by thermal fluctuation and the impurities present in the sample. The growth rate of these droplets are to be determined optically at constant temperature for some nematic compounds and for the mixture EPP-Hep/PAA.. An attempt will then be made to deduce some information concerning the growth mechanism from these data.