

CHAPTER-1

Introduction

Introduction:

Liquid crystalline materials are generally organic compounds having physical properties intermediate between crystalline solids and isotropic liquids. The liquid crystalline phase was first observed in 1888 by F. Reinitzer [1] and O. Lehmann [2]. Friedel [3,4] suggested the term "mesomorphic phase" or "mesophase" to the liquid crystalline matter. At present several thousands of organic compounds are known to exhibit mesophases [5,6]. Few organo-metallic compounds [7,8] as well as some inorganic compounds [9] are also found to exhibit liquid crystalline properties.

Liquid crystals are fluids in which there occur a certain order in the arrangement of the molecules. As a result there is anisotropy in the mechanical, electrical, magnetic and optical properties. Although liquid crystals combine certain properties of a solid and an isotropic liquid, they exhibit very specific electro-optical magneto-optical phenomena. The molecules of the compound that shows mesophases are geometrically highly anisotropic in shape, like a rod or a disc. In the crystalline solid the centre of mass of the molecules are located on a three dimensional lattice while in the liquid state the three dimensional translational symmetry disappears and there only remains some short range order between the centres of mass of the molecules. In the liquid crystalline state the three dimensional translational symmetry of the centres of mass of the molecules is partially or fully absent but some degree of orientational order of the molecules is still present. Some of the books and review articles on liquid crystals which give details regarding molecular structure and physical properties of the compound exhibiting mesophases are listed in the references [5, 6, 8, 13-20]. Recent developments in the field of liquid

crystals and applications are also available in the recent publications [21-25].

1. Classification of Liquid Crystals:

Liquid crystals are broadly classified into two types, viz. 'Lyotropic' and 'Thermotropic'.

1.1 Lyotropic mesophase :

Lyotropic liquid crystals are solutions of rod like molecules in a normally isotropic solvent [26-29]. In such mesophase the amount of the solvent is the most important variable. Soap solution in water is a common example of lyotropic mesophase and its behaviour appears as a function of either concentration or temperature. The lyotropic mesophase is also exhibited by solution of deoxyribonucleic acid ; certain viruses in appropriate solvent (usually water) in suitable concentration.

Although lyotropic liquid crystals play an important role in living systems and are of great biological interest [22], the present work is restricted to the study of the thermotropic liquid crystals only.

1.2 Thermotropic mesophase:

Thermotropic liquid crystals are those where mesomorphic behaviour are exhibited due to the change of temperature. Thermotropic liquid crystals in which the mesophases are stable at temperatures above the melting point, both during heating and during cooling are called enantiotropic. In certain cases the liquid crystalline state is stable only at temperatures below the melting point and can be obtained only during cooling of the compound, phases of this kind are called monotropic. Friedel

[30], from his detailed optical and X-ray studies subdivided the thermotropic liquid crystals into three types, viz. nematic, cholesteric and smectic. The thermotropic liquid crystals can also be classified according to the shape of the constituent molecules. Calamitic liquid crystals have rod like molecules, where as discotic liquid crystals have disc shaped molecules. I shall confine myself to calamitic liquid crystals in the rest of this section 1.2.

1.2a Nematic mesophase :

The word nematic comes from the Greek word νημα which means thread. When a thin layer of nematic liquid crystal is observed between crossed polarisers under a polarising microscope then a characteristic pattern known as texture, is observed. The textures of nematic liquid crystals are generally thread - like, hence the name nematic. Nematic liquid crystals are characterised by long-range orientational order of the molecules but they do not have long range translational order, thereby possessing fluid like behaviour. Although there is no long range correlation between the centres of mass of the molecules, but still it differs from isotropic liquid in that the molecules are, on an average, aligned with their long axes parallel to each other. Thus, in nematic liquid crystals a preferred direction known as the director denoted by \mathbf{n} is defined whose direction in space is in general arbitrary. The molecules in the nematic phase rotate about their long axes very fast ($\sim 10^{-11}$ sec) and hence the nematic phase can be assumed to be uniaxial. The axis of uniaxial symmetry has no polarity, i.e., \mathbf{n} and $-\mathbf{n}$ are equivalent. Fig 1.1 shows the schematic diagram of molecular order of nematic and isotropic phase. Another characteristic of nematic phase is that the constituent molecules are identical to its mirror

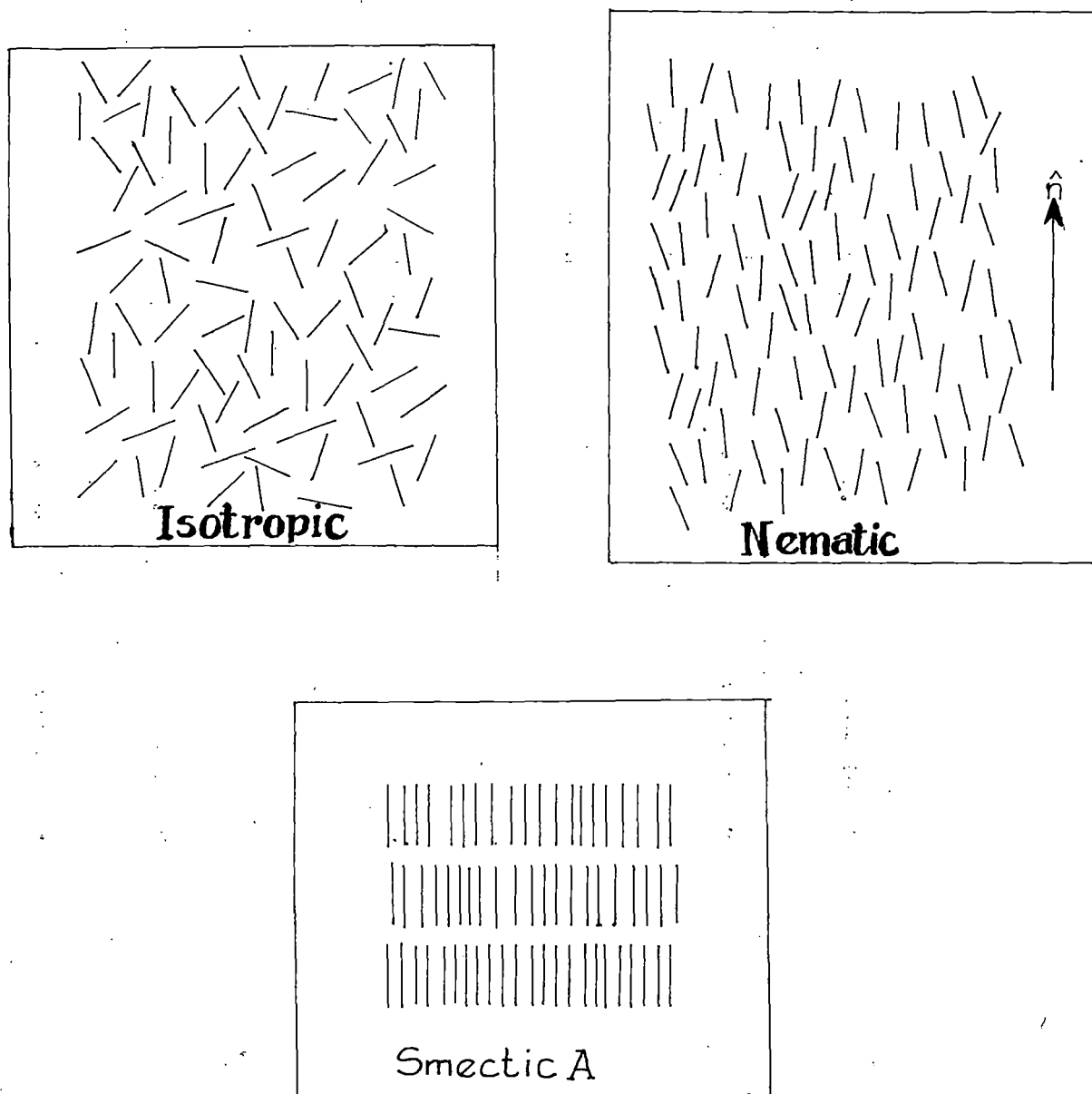


Figure 1.1. Schematic representation of molecular order in the isotropic, nematic and smectic phase.

image (achiral) or the system may be considered as a racemic mixture of left- and right-handed species. X-ray studies [32,38,39] indicates that some nematics consists of clusters of molecules, called the cybotactic groups. In each cluster the molecular long axes are parallel to each other and the molecular centres are arranged in more or less well defined layers: When the molecular long axes is normal to the layer then the phase is known as normal cybotactic nematic phase and if it is tilted with respect to the layer then the phase is known as skewed cybotactic nematic phase. The so called cybotactic groups may be thought of as smectic fluctuation in the nematic phase. Another type of nematic phase call the fibre type nematic [33] is also identified in some of the liquid crystalline compounds. In this type of mesophase there is one dimensional correlation of molecules along the director, \mathbf{n} , thus leading to the existence of strings of molecules or fibres in the nematics. Furthermore, a biaxial modification of the nematic liquid crystals has been discovered in certain polymeric liquid crystals [34] and lyotropic systems [35]. Figure 1.2 shows the schematic diagram of molecular order in different types of nematic liquid crystals.

1.2b Cholesteric or Chiral nematic phase :

The cholesteric liquid crystals are so called because many derivatives of cholesterol belong to this class of mesophase. The cholesteric mesophase is also a nematic type of liquid crystal except that it is composed of optically active molecules. As such they are also termed as chiral nematics [36-38]. The molecules of this class of mesophase have long range orientational order together with the spatial variation of the director leading to a helical structure. The helical structure (Fig 1.3) can be described by an intrinsic non-constant director.

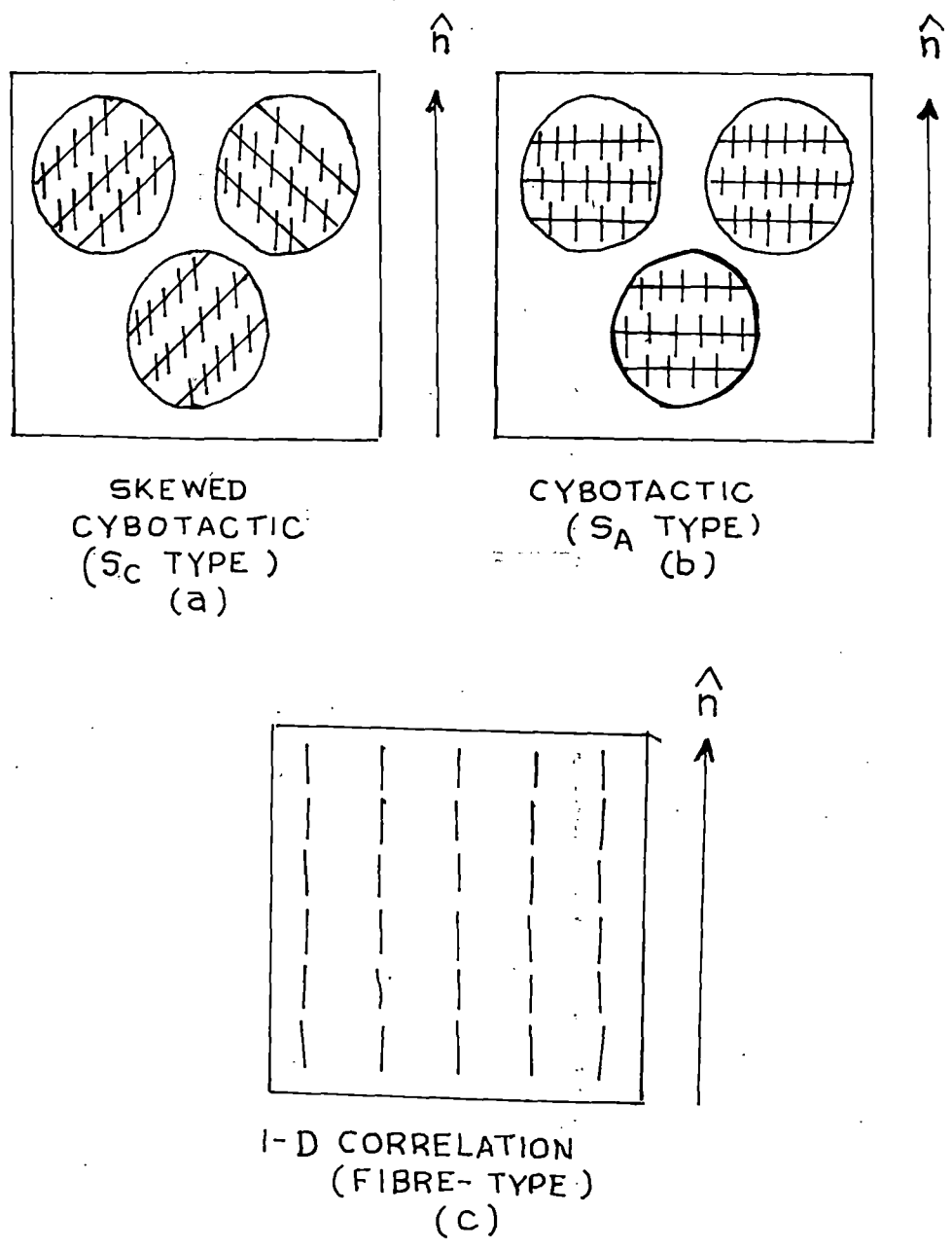


Figure. 1.2. Schematic representation showing molecular arrangements in nematics having three types of short range order.

$$n_x = \cos (q_0 z + c)$$

$$n_y = \sin (q_0 z + c)$$

$$n_z = 0$$

c being a constant

The helix axis is taken parallel to the z-axis. The pitch of the helix may be defined as the linear distance along the helix axis in which the full rotation of the director \mathbf{n} is completed. The pitch (p) is given by :

$$p = 2\pi / |q_0|$$

However, \mathbf{n} and $-\mathbf{n}$ are equivalent, the pitch in chiral nematics is given by :

$$p = \pi / |q_0|$$

The sign of q_0 distinguishes between left-handed and right-handed chiral nematics. When $q_0 = 0$, then the pitch is infinite and it corresponds to normal nematic phase. No liquid crystalline compounds are known to have phase transition from nematic to chiral nematic phase, however the application of electric or magnetic field may cause phase transition from chiral to nematic. Moreover the addition of small amount of chiral compound to nematic compound changes a nematic phase into a long pitch chiral nematic phase.

1.2c Smectic mesophase :

Smectic liquid crystals have stratified structures and variety of molecular arrangement are possible within each stratification. Within the layer, the long axes of the molecules are parallel to each other thereby exhibit orientational order as in the nematic phase. In addition to this the centre of the molecules are, on the average, arranged in equidistant planes showing one degree of translational order. In most smectic phases, the molecules are mobile in two directions and can rotate about one axis. The

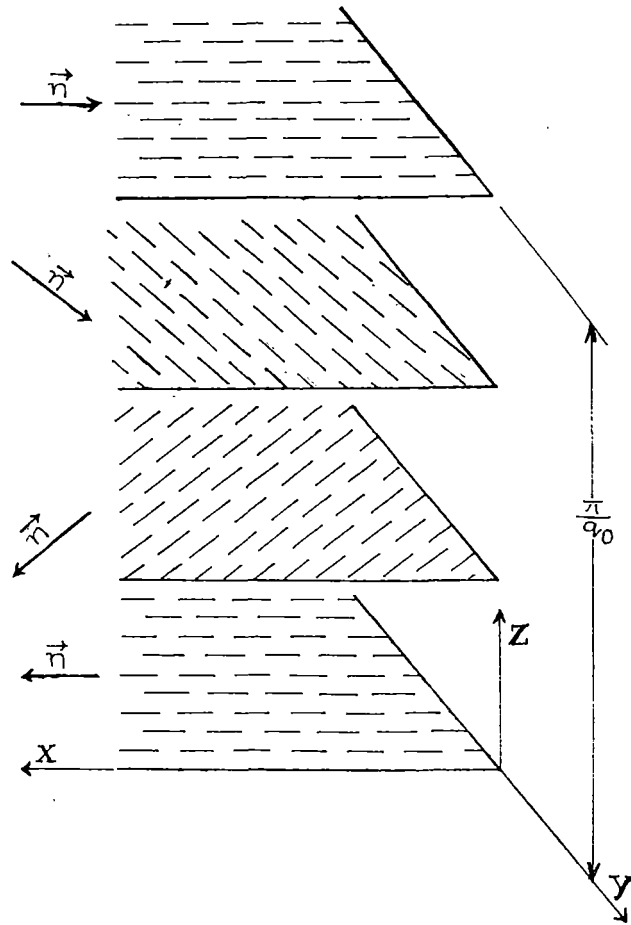


Figure 1.3. Schematic representation of the helical structure of the cholesteric liquid crystals.

inter-layer attractions are weak compared with the lateral forces between the molecules, and the layers are able to slide over one another relatively easily. Consequently, the smectic phase have fluid properties, but are much more viscous than the nematic phase. Smectics are much more ordered than the nematics and consistent with their higher order, the smectic phases always occur at temperatures below the nematic domain. Classification of the smectic mesophases are generally done by three different methods, viz. ; miscibility, texture, and x-ray diffraction studies. The various types of smectic mesophases that have been identified [40-49] are designated as follows [50] :

$S_A, S_B, S_C, S_E, S_F, S_G, S_H, S_k, S_l, \text{etc.}$ -----

Since the present work deals mostly with smectic A phase and smectic A_d phase, only these phases are discussed.

1.2 c1 Smectic A phase :

Smectic A is the simplest type of smectic phase. The smectic A mesophase is made up of layers which move freely with respect to each other. Within the layers, the long axes of the molecules lie almost parallel to one another, their mean direction being normal to the plane of the layer. The molecules are free to rotate about their long axes, and the distribution of the molecules within the layers are random [43,51,52]. Thus, within the layers the molecules have a low degree of translational order, each layer being a two - dimensional liquid. The molecular arrangement of smectic A phase is shown in Fig 1.1.

The smectic A phase has the highest temperature of the smectic phase and on heating it undergoes a transition to the nematic or cholesteric mesophase, or directly to the isotropic phase. At thermal equilibrium the

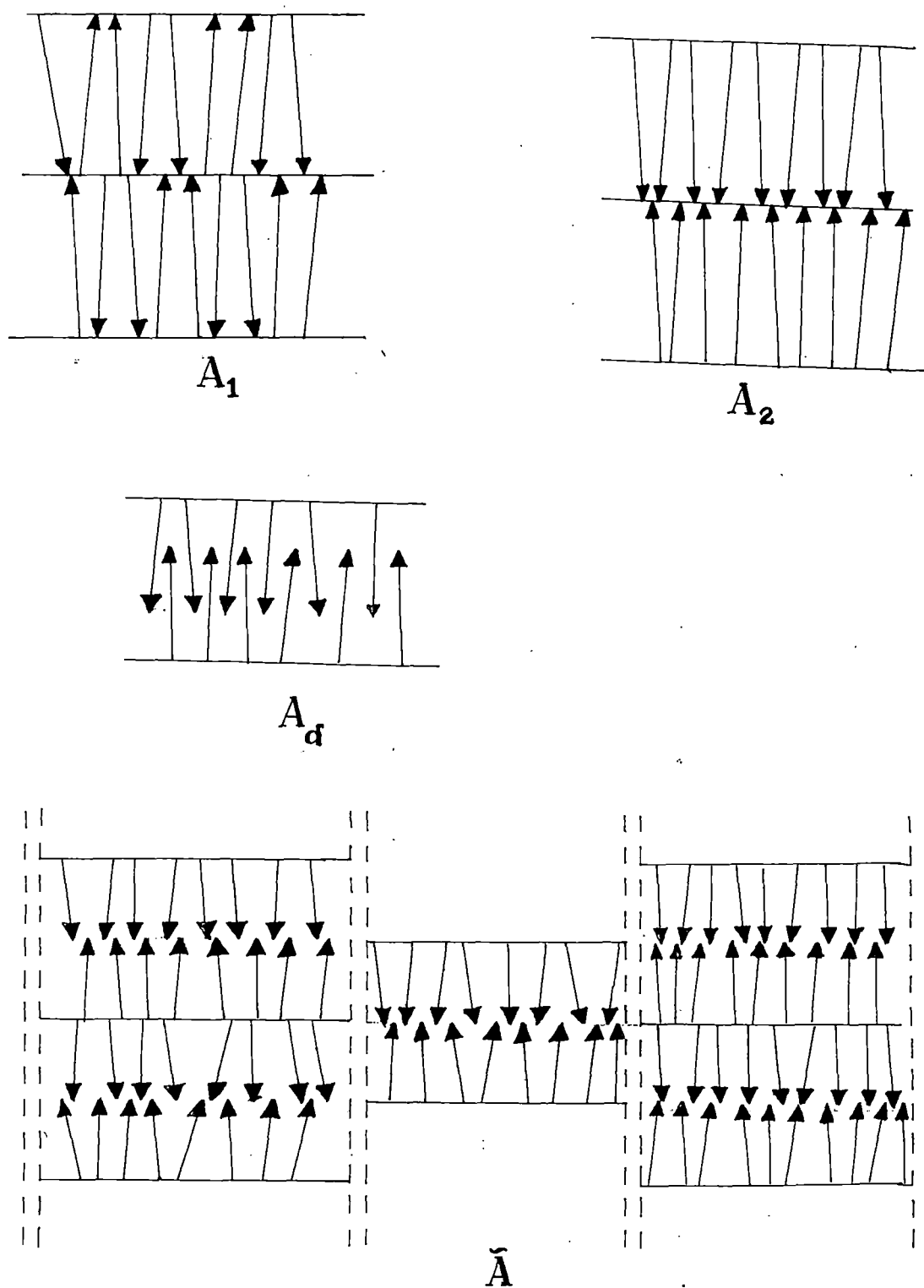


Figure 1.4. Schematic representation of the molecular arrangement in the different forms of smectic A phase composed of polar molecules; monolayer A_1 , bilayer A_2 , partially bilayer A_d and antiphase \tilde{A} .

smectic A phase is optically uniaxial [53] due to the infinite fold rotational symmetry about the axis parallel to the layer normal. Apart from the focal conic textures [54-60] smectic A also exist in homeotropic texture [54-60]. Smectic A phase can be further subdivided into several distinct phases [61-67] such as monolayer smectic A_1 , bilayer smectic A_2 , partially bilayer smectic A_d and smectic antiphase \tilde{A} . In the monolayer smectic A_1 phase the layer spacing (d) is approximately equal to the molecular length (l) whereas in the bilayer smectic A_2 phase the layer spacing (d) is approximately in between l and $2l$. The structures of these phases are represented schematically in Fig. 1.4. When the molecules, possess a dipole moment positioned at the end of the molecules, then the molecules can minimise their dipole interaction via antiparallel dipole correlation. Consequently smectic A_d phases can be formed with a layer thickness, that is approximately given by $d \approx a + 2b$, where a and b are the length of the aromatic head and the aliphatic tail, respectively. Typically this leads to $d \approx 1.4 l$ where $l = a + b$. The dipole - dipole interaction has a profound effect on many physical properties. The details regarding polymorphism in smectic A are discussed in references [68-75].

1.3 Some new liquid crystalline phases:

1.3a Discotic phase:

A new type of mesophase has been discovered [74] which cannot be classified either as a nematic or as a smectic. This phase is formed in materials with molecules which are approximately disc-shaped. The disc are packed together in columns, although their arrangement within an individual column can be either ordered or random. Such mesophase are called discotic liquid crystals and its structure may be classified into three

groups, viz. the columnar, the nematic and the lamellar. Previously very similar disc-like mesogens have been observed in petroleum and coal tar [75,76]. At present remarkable progress have been achieved in the field of discotic liquid crystals [77-81].

1.3b Blue phases :

For chiral nematics with a relatively short pitch (less than 7000\AA), several different types of phases have been observed between the isotropic and the chiral nematic phase and these are known as the 'blue phases'. The temperature region in which these blue phases are stable is very small (approximately $0.1\text{ }^{\circ}\text{C}$). Compounds with relatively high pitch can display upto three different types of blue phases [82]. Blue phase shows optically isotropic structure with colours in reflected light. The structure of blue phase is not yet completely explained but it is clear that they exhibit cubic symmetry and the basic structure is related to cholesteric phase. The most probable model to explain the structure of the blue phase is in terms of the defect in a cubic array. Blue phases do not possess double refraction, however, they show optical activity and selective reflection of circularly polarised light.

1.3c Chiral tilted smectic phases :

Liquid crystalline compounds which exhibit optical activity can form a chiral smectic C mesophase in which each successive layer is rotated through a certain angle with respect to the tilt direction so that a twisted structure is formed. This structure has ferro-electric (FE) properties when positively oriented molecular dipoles are present. Ferri electric (FI) and anti-ferro electric (AF) phases are also observed. [83]. The ferroelectric

structures possess two fold-rotational axis of symmetry parallel to the smectic layer and perpendicular to the director \mathbf{n} . In the twisted form, the lateral dipole moments of the molecules are cancelled on average. If a lateral dipole moment is present, each smectic layer possess an electric polarisation parallel to the two fold axis of symmetry. Hence the director and the polarisation spiral together along the helix axis, leading to an overall zero bulk polarisation. By interaction with the walls or in electric or in magnetic fields, the twist can be unrolled and this form the phase can show ferroelectric properties which originates from a summation of many lateral molecular dipole moments. In the FI phase the local dipole moments are partially compensated whereas in the AF phase, the adjacent layers of the molecules are oppositely tilted. Recently both AF phase [84] and FI phase [85] have been observed in a substance MHPOBC. Ferroelectric liquid crystal has attracted much attention for fast switching electro-optical display devices.

1.3d Injected smectic phase :

By mixing two pure nematic liquid crystals it is possible for us to obtain the so called injected or induced smectic phase [90-91]. As such, the formation of injected smectic phase is accompanied by a marked deviation of the nematic isotropic transition temperature from a linear dependence on composition. Induced smectic phase can generally be formed in a binary mixture in which one of the constituent have a strong terminal polar group while the other have a non-polar terminal group [92-107]. In binary mixtures, dipole-induced dipole interaction is responsible for the phase stabilisation. However injected smectic phase has also been observed in a mixture of other type of molecules [108-110]. A quantitative theory of

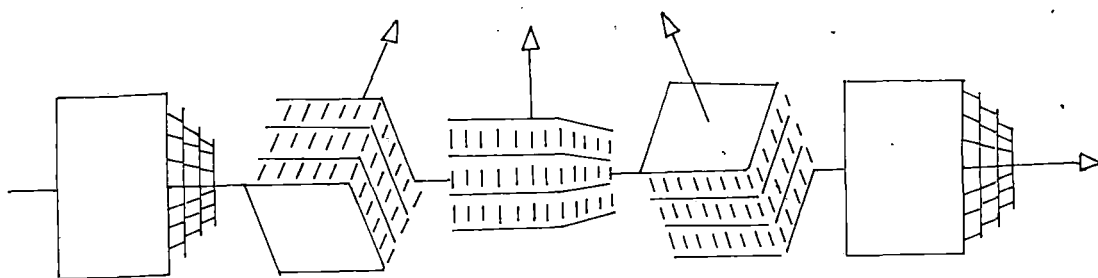


Figure 1.4a Schematic representation of the structure of smectic A* phase.

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formation of injected smectic phase is difficult as it would require the inclusion of position dependent attractive and repulsive interactions for both the components. A molecular model of the induced smectic phase has been discussed by de Jeu et al [111].

1.3e Smectic A* phase:

The term smectic A* phase was coined by Goodby et. al [134]. Smectic A* phase consists of regular array of dislocations which is being formed in the smectic A under an imposed twist or bend distortion. Smectic A* is composed of optically active molecules and its helical axis is parallel to the layers. For this reason smectic A* structure may be imagined as a series of smectic A blocks or grains separated by twist grain boundaries, the director being rotated by a constant angle on going from one grains to the next. The pitch of the helix axis is found to be about $1\mu\text{m}$ [135] and the grain size obtained from x-ray measurement [135] is about 180 \AA . Furthermore, Renn and Lubensky [136] termed this phase as the "twist grain boundary phase". The structure of the smectic A* phase is shown schematically in Figure (1.4a).

1.3f Re-entrant phase:

When a compound exhibits both smectic and nematic phase, then as a rule, the nematic phase occurs at the higher temperature. In 1975 Claudis [112] discovered exception to this rule in certain strongly polar materials, the so called phenomenon of re-entrant polymorphism. The nematic re-entrant phase was first observed on binary mixtures of two cyano compounds. The phase sequence of transition on cooling was as follows :-

Isotropic \rightarrow Nematic \rightarrow Smectic A_d \rightarrow Nematic re-entrant \rightarrow Crystal.

Claudis [114,115] reported the re-entrant nematic phase in pure terminal polar compounds (octyloxy cyano biphenyl) at elevated pressures. The re-entrant nematic phase has been observed in some pure compound at atmospheric pressure [116-123]. More complex example of multiple re-entrant polymorphism have been found in a pure substance [108]. The re-entrant phase have been found also in non-polar compounds [93-96].

From the molecular point of view, a simple model has been proposed by Cladis [129-131] which gives an approximate qualitative explanation of the re-entrant phenomenon. a more elaborate model, which take into account attractive forces and hard core repulsions, dipole-induced dipole interactions etc. have been proposed by Longa and de Jeu [111]. S. Chandrasekhar [133] has also discussed qualitatively the re-entrant phenomenon based on the molecular point of view.

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