1 INTRODUCTION TO LIQUID CRYSTALS

1.1 GENERAL INTRODUCTION TO LIQUID CRYSTALS

There are three states of matter namely; solid, liquid and gas. There are situations in which more than just these three phases exist. For now, consider the large class of organic molecules which do not show a single transition from solid to liquid, but rather a series (more than one) of transitions between the solid and the normal (isotropic) liquid as their temperature is raised. These new phases have mechanical, optical and structural properties between those of the crystalline solid and the corresponding isotropic liquid. For this reason, these phases are referred to as a liquid crystalline phases, and the materials which form them upon a change in phase are often referred as thermo tropic liquid crystals. A more proper name is Mesomorphic (intermediate) phases.

Liquid crystalline properties are exhibited by several different types of system. In addition to certain classes of organic molecules, micellar solutions of surfactants, main and side change polymers, and a large number of biological systems are known to be liquid crystalline. Several text books [1-4] on liquid crystals have discussed these topics to varying degree. A number of publications which emphasize and review specific topics in significant detail are available in the literature (5-10).

Following De Gennes and Prost [1], liquid crystals are defined as an intermediate phase which (i) has liquid-like order in at least in one direction, and (ii) possess a degree of anisotropy, which is characteristics of some sort of
order. The latter requirement is typically met if the molecules which from liquid crystals are anisotropic, either rod-like (prolate) or disk like (oblate). However, that while all liquid crystalline phases are formed by anisotropic objects not all anisotropic molecules form liquid crystalline phases [11, 12].

1.2 ORDERING OF ANISOTROPIC OBJECTS

Objects which have shapes other than spherical may possess three types of order giving rise to different liquid crystalline phases. The types of order that are necessary to discuss the phases involved are described in the following text.

The simplest of these is orientational order (00). This is possible when the symmetry axes of the ordering objects are on average parallel to a well defined spatial direction, n, known as the director. The degree of order, denoted by the orientational order parameter, S, is the thermal average \( <\frac{3}{2} \cos^2 \theta - \frac{1}{2}> \), where \( \theta \) is the angle between molecules and the director. The orientational order parameter, S, is typically a function of temperature.

The second type of order is positional or translational order (PO). When PO is present, the system remains invariant under translation vectors. The arrangement of the basic units (e.g. molecules) and the mass density (and, consequently, the electron density) exhibit periodicity. In the simplest case, this periodicity is one dimensional, and may be conveniently represented by a density function of the form

\[
\rho (r) = \langle \rho \rangle + \text{Re} \left[ \psi \exp (ikr) \right],
\]
where \(<\rho>\) is the average electron density, Re means real part of \(\psi\), which is the complex amplitude and \(k\) is the wave vector. It is important to note that a liquid crystal system does not have to possess translational order in all three directions.

In particular, for the fluid smectic (A and C) phases, which possess positional order only in one dimension, the smectic order parameter representing the density variation is written as

\[ |\Psi(r)| = \text{Re}[\rho_1 \exp(i2\pi z/d)] \]

where 'd' is the thickness of smectic layers which are assumed to be perpendicular to the \(z\) directions [1].

A third type of order is bond orientational order (BOO) [13]. A bond is a line in spacing joining two adjacent molecules. If these orientations of these bonds preserved over along range, then a system possesses BOO. It is encountered in a category of smectic phases called the “hexatic smectic”. In these phases, the molecules within a smectic plane possess BOO and, since the molecules can best pack.
Figure 1.1 Schematic representation of the three basic types of order:

Figure 1.1 (a) Orientation order parallel to the direction $n$,

Figure 1.1 (b) Positional order in two dimensions with lattice vectors $a$, $b$

Figure 1.1 (c) Bond orientational order. In the last case, translation from one lattice site along the arrow by an integer multiple of lattice spacing shows a lack of translation symmetry.

In a hexagonal fashion, the orientation of bonds possesses six fold symmetry. Complex order parameter $\psi_6$, similar to the smectic density wave has been used to account for BOO;

$$\psi_6 = \text{Re} \left[ I_6 \exp(6i\Phi) \right]$$

where $I_6$ is a complex amplitude, and $\Phi$ is the azimuthally angle with respect to the layer normal systems can posses long range BOO without long range positional order PO, but the reverse is not true. It is possible for PO to became short range due to the presence of dislocations and declinations which can leave the BOO unperturbed. The three types of order discussed above are shown in two dimensions in figure 1.1.
1.3 THE CONCEPT AND USE OF SYMMETRY IN LIQUID CRYSTALS

One of the strongest guiding principles in liquid crystal science has been symmetry i.e., physical properties of a liquid crystalline phase depend on the symmetry of the liquid crystal phase. Thus, the least order phase is the most symmetric isotropic (I) phase which exhibits isotropic behavior similar to regular liquids such as water. There is, a plethora of mesophases of lower symmetry than the I phase before the least symmetry crystalline phases belonging to the 230 space groups [14] which characterize crystals are encountered. This progression may be described by in terms of three types of order described above.

Consider imposing the simplest, i.e. orientation order of a collection of molecules. The resulting structure is known as Nematic (N) phase. Such as phase is described by the director and the orientational order parameter, S, defined above, if the molecules are on average parallel to director, n, the value of orientational order parameter, S, is positive and ranges between 0 and 1.

On the other hand, if the 00 is such that molecules, on average are perpendicular to n, then S is negative and its values range from 0 to \(-\frac{1}{2}\). Evidently, a Landau-Ginzburg type expressions for its free energy must not be invariant with respect to a change in the sign of S as its positive and negative values represent physically different system. This is usually ensured by including a cubic term in the free energy. A consequence of this symmetry requirement is that the transition from I to an orientational ordered state, or the N phase, must be the first order. Indeed, the I-N (Isotropic to Nematic) transition is always found to be first order with a large enthalpy of transition.
The physical property of a Nematic is described by a symmetric second rank tensor.

The presence of PO in one direction leads to the Smectic A (Sm. A) phase. However, there can be no long range order in one dimension [15], so this is really a quasi long range order (QLR). Transitions between the isotropic liquid and Sm A phase are first order while the transitions between the Nematic and the Sm A phase may be either first order or second order depending upon the coupling between the 00 and PO, which in turn depends on the width of the Nematic phase. A liquid crystal with a wide Nematic phase is more likely to exhibit a second order Nematic to Sm A transition.

A smectic phase has at least two unique directions, the director and layer normal. In the Sm A phase, these two directions are collinear. But there are phases in which the director makes an angle with the layer normal as in the Smectic C (Sm C) phase. In the chiral smectic (Sm C') phase, the director maintains a constant angle with respect to the layer normal. While describing a helical path as the sample is traversed along the direction normal to the smectic planes. The chiral phases invariably are ferroelectric in nature.
### Table 1.1 Illustration of possible phase progression

<table>
<thead>
<tr>
<th>PHASE</th>
<th>TYPE OF ORDER</th>
<th>OBSERVATION</th>
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<tbody>
<tr>
<td>Isotropic</td>
<td></td>
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<td></td>
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<tr>
<td>Nematic</td>
<td>00</td>
<td>N</td>
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<td></td>
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<tr>
<td>Smectic A</td>
<td>PO: n perpendicular to layers</td>
<td>Sm A</td>
</tr>
<tr>
<td></td>
<td>In-plane LR BOO, SR-PO</td>
<td>Hex B</td>
</tr>
<tr>
<td>Hexatic-B</td>
<td>In-plane: LR-P&amp;BOO</td>
<td></td>
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<tr>
<td></td>
<td>(Molecular rotations allowed)</td>
<td></td>
</tr>
<tr>
<td>Smectic B</td>
<td>In-plane: LR-PO&amp;BOO</td>
<td>Sm B</td>
</tr>
<tr>
<td></td>
<td>(Molecular rotations restricted)</td>
<td></td>
</tr>
<tr>
<td>Smectic E</td>
<td>In-plane: LR-PO&amp;BOO</td>
<td>Sm E</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Various smectic phases have BOO and PO to varying degree within a smectic plane and it is convenient to consider the extent of order that separates a smectic phase from the rest as illustrated in Table 1.1.

Table 1.1 an illustration of a possible phase progression in a liquid crystal. The most symmetric and least ordered phase is at the top, and the most ordered and least symmetric phase is at the bottom.

Short range (SR) as is observed in liquids or long range (LR) as observed in crystals. Thus three distinct possibilities exist.
1) Both the BOO and PO are short range such smectic can be considered as fluids smectics, examples being Sm A, Sm C and Sm C' etc.

2) Long range BOO but short range PO these are referred to as the hexatic smectic phases. Smectic I, F and smectic Hex B are some examples.

3) Long ranges BOO and PO- such phases are very close to being crystalline phases except that molecules undergo rotational diffusion. They used to be known as smectic B, E, etc, but now a days they are referred to as the crystal B, crystal E, G, etc. phases.

Various (untitled) smectic phases, with the director parallel to the layer normal, are given different names as summarized in table 1.2 [8]. The use of symmetry goes beyond noting which phase is more symmetric than another and helping one discern the symmetry of physical properties of the corresponding phase. It also allows one to make analogies to phase transition in other non-liquid crystalline systems. For example as De Gennes [1, 16] has observed, the introduction of the smectic order parameter allows one to draw a strong analogy between the Sm A phase and the super conducting phase.

The tiled Sm C phase has been compared [17] with super fluid helium, and the Sm A to Sm C transition predicted to exhibit critical behavior similar to that of helium or XY model. Similarly, the transition between Sm A and hexatic B is described by a two dimensional order parameter and may similarly be described by the super fluid analogy. Suffice is to state that symmetry has been a crucial and indispensable tool in our understanding of the physics of liquid crystalline phases. At the same time, the flied of liquid crystals has been used
as a testing ground of theoretical ideals that are not manifest in other systems with such elegance and simplicity.

1.4 PHASES FORMED BY ROD LIKE MOLECULES

The liquid crystalline phases formed by simple entities organic molecules which can be viewed as short rigid rods of a length to diameter ratio of roughly 3-8. Such molecules exhibit various mesophases at different temperatures and hence are generically referred to as thermo tropic liquid crystals. A common feature of all molecules of this type is that they all comprise a central rigid core connected to a flexible alkyl chain at one or both ends. In understanding some of the physical properties of these phases one should note that the size of a typical molecule which forms a thermo tropic liquid crystal is such that X-rays work as an ideal and direct probe of the structure of these materials. Thus, a particularly good starting point X-ray scattering [8].

1.4.1 UNTILTED PHASES

This is a sub-class of thermo tropic liquid crystalline phases which are free form chirality’s and molecular tilt. However, these phases differ from each other in the type and extent of order and the symmetry they possess.

➤ THE NEMATIC PHASE

The simplest liquid crystalline phase is the Nematic phase. These are several types of Nematic phases but all of them can, to a first approximation, simply be thought of as liquids which have long range
orientational order, but lack of PO and BOO. An example of a Nematic made of rod like molecules is shown in fig1.1 (a). The various types of Nematic have slightly different properties based on the details of their molecular structure and chemical behavior. The two primary types of Nematic are uniaxial and biaxial.

The uniaxial Nematic is characteristic by the following features [2]:

(a) no PO, so no BOO

(b) OO parallel to the direction \(n\)

(c) The direction of \(n\) in space is arbitrary and typically imposed by outside forces such as electric/magnetic filed

(d) \(n\) and \(-n\) are equivalent

(e) Molecules which form Nematic are either archiral (identical to their mirror images or racemic contain equal number left and right handed molecules)

The biaxial Nematic phase is also characterized by the above properties. However, this liquid crystalline phase does not possess cylindrical symmetry about \(n\). This phase possess two unique directions perpendicular to \(n\) rendering it biaxial. It should be pointed out that, despite some reports, there are no known thermo tropic biaxial Nematic phases [18]. The existence of biaxial phases has been confirmed in lyotropic liquid crystals.
THE SMECTIC A PHASE

The name ‘smectic’ was coined by G. Friedel to describe certain mesophases that feel slippery like soap when touched and was originally associated with what is now known as the smectic A phase. The important feature which distinguishes smectic phases is that they have a layered structure. In fact, as mentioned above, PO and BOO have all been observed among molecules lying in a smectic plane resulting in over 20 smectic liquid crystalline phases.

The simplest is the Sm A phase made of non chiral and non polar molecules and characterized by a one dimensional layered structure (or PO), in which each layer is essentially a two dimensional liquid as shown in figure 1.3(a). However, arguments [15] show that one dimensional liquid cannot exhibit long range PO nevertheless, PO almost does exists, and this system is said to exhibit quasi long range order or have Landau –Peierls’ instability. This phase is uniaxial, the layers are essentially in compressible, and the long axes of molecules with in the layer, on the average, are perpendicular to the layers. The Sm A phase is characterized by short range PO and short range BOO in the layers and quasi long range PO perpendicular to the planes. It may be thought of, some what crudely, as a stack of two dimensional fluid layers. Some liquid crystal phase formed by untitled rod like molecules are shown in figure 1.2.
Figure 1.2 Liquid crystal phases of untilted rod-like molecules

Figure 1.2 (a) The smectic A phase: there is quasi long range PO normal to the layers, 00 with the mean orientation of the molecules perpendicular to the layers and short range PO and BOO with in the layers.

Figure 1.2 (b) A view of the short range hexagonal PO of the molecules with in a layer of a Hex B phase. The molecules are perpendicular to the smectic phase as indicated by the circles.

Figure 1.2 (c) The local herringbone arrangement of molecules in a layer of the crystal E-phase. The ellipses represent a view of the rigid benzene rings in the molecules. The lattice has a rectangular unit cell.

> THE HEXATIC B OR HEXATIC SMECTIC B PHASE

These two names for the same phase, abbreviated as Hex B, describe a phase which is characterized by a layered structure, just like the Sm A
phase, and long range BOO within the layers. BOO is the essential property of a hexatic phase. This is a very special class of smectic characterized by quasi long range PO in the direction perpendicular to the layers. Short range PO within the smectic layers (although typically longer than in the Sm A), and most importantly BOO. In the Hex B phase, the molecules are locally hexagonally packed, and the resulting six fold BOO is maintained for macroscopic distances. The Hex B is a uniaxial phase. In three dimensions, the transition from Sm A to Hex B phase is expected to be in the same universality class as super fluid helium. However, this is not the case. The explanation is that there is a strong coupling between the mass density and the hexatic order parameter, and fluctuation in the order parameter influences its behavior near the transition \cite{2}. A schematic of the BOO of a hexatic phase is shown in figure 1.2 (c). A top view of the molecules with in a smectic plane, which indicates that the molecules are perpendicular to the planes shown in figure 1.2 (b).

The hexatic phases have been studied quite extensively in two dimensional freely suspended films. In these studies liquid crystal film were drawn over a hole in a metal or glass plate. These films have smectic layers aligned almost perfectly parallel to their physical surface rendering the data interpretation easier than in bulk samples. The transition between Sm A and Hex B (in two dimensions) can be second order. The Halperin-Nelson Young theory \cite{19} has been applied to describe this transition. This theory predicts that in two dimensional dislocations destroy PO but not BOO. This is indeed the case.
THE CRYSTAL B PHASE

There are several crystalline smectic phase; that is, smectic which are very close to there dimensional crystals. They differ from true crystal phase in one important aspect. The molecules in them have freedom of rotation about their long axis that is their thermal motion is not completely frozen out. Such phases, in which the position of the molecules is fixed but their motion is not arrested, should more correctly be classified as plastic crystalline phases [8]. The common feature of these phases is that the average molecular orientation is normal to smectic layers and within each layer the molecules are ordered in a triangular lattice and possess long range PO and, of course, BOO. The stacking of these triangular arrays varies from material to material and restacking transitions have been observed.

THE CRYSTAL E PHASE

As in the crystal B phase, the molecules within a smectic E plane are arranged on a triangular (or hexagonal) lattice and are perpendicular to the smectic layers. This phase differs from the crystal B phase in the rotational motion of molecules. In the crystal E phase, the thermal motion of molecules is reduced to the extent that they arrange themselves in a herringbone pattern with in a smectic layer. The interlayer molecular packing is shown in fig 1.3 (c). With this type of packing their continuous rotational freedom is hindered. NMR [20] studies have concluded that molecules can undergo correlated six-fold jump rotational diffusion motion.
1.4.2 TILTED PHASES

There is a complete set of smectic phases in which the long axis of molecules (or the director) is not perpendicular to the layer normal, but makes a relatively large angle. Just like the untitled phase discussed above, the various tilted phases possess different structures and order.

![Diagram of tilted phases](image)

**Figure 1.3 Schematic representations of tilted phases formed by rod like molecules.**

Figure 1.3 The Sm C phase; the layers are indicated by the lines and the molecules by ellipses short range order in hexatic smectic F and hexatic smectic I phase as shown in figure 1.3 (b) and figure 1.3 (c) respectively. Here the major axis of ellipse indicates the molecular tilt direction with respect to the hexagon axes.
THE SMECTIC C PHASE

The Smectic C phase is similar to the Sm A phase in that it is a layered structure and each layer may be thought of as a two dimensional liquid film with no BOO or PO. However in this case the molecules are on the average tilted with respect to the normal to the layers. i.e., n and smectic layer normal are not collinear, figure 1.3 (a) furthermore, the tilt angle $\alpha$, that the molecular axis makes with the layer normal, is a strong function of temperature. In the case of a transition from Sm A to Sm C phase at temperature $T_{AC}$, smectic layer spacing at a temperature $T$ below the transition $d(T) = d(T_{AC}) \cos(\alpha)$. The angle $\alpha$ which is an order parameter for this phase can range from zero to as high as 45-50° deep in the Sm C phase [21]. Most of the Sm A to Sm C transitions are second order but first order transitions in fluorinated compounds has recently been observed [22]. A consequence of the tilting of the molecules is that this phase exhibits biaxial optical and physical properties.

THE SMECTIC F AND SMECTIC I PHASES

Tilted phases with in plane hexatic order have also been observed. These may be thought of as tilted analogs of the Hex B phase. However, with hexagonal arrangement with in smectic planes, the molecules can tilt along two distinct directions with respect to hexagonal lattice. In the Hex F phase, the tilt is in a direction perpendicular to the sides of the hexagon. If molecules tilt towards corner, it is known as the Hex I phase. When both phases are formed by the same material, the Hex I is always the higher
temperature phase. The short range in-plane order of these three phases is shown figure 1.3(b) and figure 1.3 (c).

> **THE CRYSTAL G AND CRYSTAL J PHASES**

The crystal G and crystal J are the phases normally obtained at temperature lower than the Hex F and Hex I phases. The molecular arrangement within a smectic plane possesses long range PO and BOO. In both these phases and their higher temperature hexatic versions, the molecules are tilled with respect to the layer normal by approximately 25 to 30°. The local order is hexagonal which is distorted due to molecular tilt, with molecules having rotational freedom comparable to the untilted crystal B phase.

> **THE CRYSTAL H AND CRYSTAL K PHASES**

The smectic K and H phases are tilted versions of the crystal E phase. The molecules in the crystalline H or K phase are tilted in a manner similar to the smectic G or J and Hex F (Hex I) phases, i.e., along the direction perpendicular to a side (towards a corner) of the under lying hexagonal structure. The general sequence of tilted phase with decreasing temperature is shown in table 1.2. However, the actual order of phases varies from material to material.
Another class of liquid crystals that are extensively used in display applications [23-38] are ferroelectric liquid crystals. For the synthesis [39-42] of these materials a chiral carbon moiety is a prerequisite.

1.7 LIQUID CRYSTALS FORMED FROM DISK SHAPED MOLECULES

The liquid crystalline phases formed by disk shaped molecules are referred to as the discotic phases. They were first synthesized and identified in 1977 [2, 43]. Structurally they generally form either Nematic or columnar phases. The simplest columnar phase consists of a stacked disks forming a one dimensional liquid like structure the columns themselves form a two dimensional lattice, Hexagonal, rectangular and other lattice types have been identified. Tilted phases have also been reported [43]. The discotic Nematic phase is denoted by $N_D$ where the subscript D is to avoid confusion with the normal Nematic phase. This phase is characterized by the short axis of the molecule aligning parallel to the director. The $N_D$ phase is diamagnetically and
optically negative. This is in contrast with the rod like Nematic which are mostly optically and diamagnetically positive. Figure 1.4 illustrates the N$_D$ phase and the columnar phases.

The structure of the columnar phases merits some discussion. There is no PO along the columns. The columns themselves are arranged with PO and form a two dimensional array which is either a rectangular or a hexagonal lattice. There is orientational order (at least for the cores of these molecules) with in the columns. The rectangular or D$_r$ phase has columns which occupy a rectangular lattice. The molecules are oriented away from the column axis in this phase. The resulting tilt forms a herring bone pattern such as shown in figure 1.4 (c). The columns of the hexagonal D$_h$ phase are arranged in a hexagonal pattern. The molecules are tilted with in the columns, but there is no coordinated azimuthal orientation of the molecules in the columns.

**Figure 1.4 The structure of Nematic columnar phases**
Figure 1.4 the structure of the $N_D$ (a) and columnar (b) phases, in columnar phases there is PO in the columns. The rectangular columnar phase, $D_r$, is shown in (c) and the hexagonal column phase, $D_h$, is shown in (d). In these two parts of the figure the molecules are tilted. This is illustrated by drawing the disks as ellipses.

### 1.7 POLYMERIC LIQUID CRYSTALS

Another class of thermo tropic mesogens is polymer liquid crystals. These structure consists of mesogenic subunits (either rod like or disk like) which are connected together with flexible links forming what are known as the main chain polymer liquid crystals (PLC). Alternatively, the mesogenic subunits can be attached to the polymer chains as side groups or pendates. These are known as the side chain PLC. The nature of the liquid crystalline phases which form depends on the backbone, spacers, flexible links etc. these are reviewed in several reference [4, 44]. A schematic presentation of this PLCs is shown in fig 1.5.

![Schematic representation of polymeric liquid crystals.](image-url)
1.7 LYOTROPIC LIQUID CRYSTALS

1.7.1 COLLOIDAL LYOTROPIC PHASES

Solutions of bio molecules such as proteins and DNA and sufficiently concentrated solutions of surfactants can form another interesting class of liquid crystals. Since the phase behavior is most easily induced by changes in concentration (although temperature is still an important variable) these are referred to as lyotropic liquid crystals. These meso phases [1, 2] were first considered by Onsager [45] and Flory [46]. Representative examples are synthetic polypeptides, precipitated metal oxides, and rigid polymers in appropriate solvents. Typically these molecules achieve length to diameter ratios of 10-20. Liquid crystal properties of solutions of DNA molecules, some proteins, and viruses have also been extensively studied. Of particular interest is tobacco mosaic virus (TMV) which has a length of approximately 3000Å and a diameter of 200Å and is known to form phases analogous to the Nematic and smectic phases of thermo tropic liquid crystals.

1.7.2 SELF - ASSEMBLED STRUCTURES

In addition to small molecules, polymer liquid crystals and large chemically bonded objects such as viruses, another simple class of materials exhibits liquid crystalline phases. This class of materials consists of amphiphilic molecules in a solvent in which they spontaneously form lyotropic micellar systems. An example of such system is a solution of soap in water. A critical soap molecule consists of a polar head and one or more hydrocarbon tails. When a sufficient number of such molecules is dissolved in a solvent, the
lowest free energy state in which the hydrocarbon tails segregate to shield themselves from the polar water environment. This leads to the formation of aggregates of molecules. Molecules in such aggregates, called micelles, are not covalently bonded and can assume several different geometrics depending on the thermodynamic conditions and chemical nature of the molecules. These aggregates can be rod like or disk like which can be orientationally and or positional ordered to exhibit a wide range of liquid crystalline phases including isotropic, Nematic, lamellar, hexagonal and cubic phases [1, 5]. A typical surfactant and a few simple phases of amphiphilic materials are shown in fig 1.6.
Figure 1.6 (a) A cartoon of a typical amphiphilic molecule.

Figure 1.6 (b) an example of a rod like micelle.

Figure 1.6 (c) A slice of a bilayer structure. This is an example for a lamellar phase.

Figure 1.6 (d) A cubic phase formed by spherical aggregates).

This area of liquid crystal research, in fact, precedes the age of thermotropic liquid crystals. Early work [47] demonstrated the existence of mesophases with PO in one (lamellar or smectic phases), two (hexagonal and rectangular phases) and three (cubic) dimensions. The observation of the Nematic phase came more recently [48,49]. It typically consists of a rod like or disk like micelles with their symmetry axis orientationaly ordered. This phase is observed between the isotropic phase and a smectic like phase called the lamellar phase of disk like micelles. For cylindrical micellar systems, it appears between the isotropic and the hexagonal phase. These phases can be observed
over a rather large concentration range typically from 0.1 to 0.5 weights precent as well as over a wide temperature range. The Onsager theory explains the isotropic to Nematic phase transition in these materials rather well. Finally, the nematic composed of rod like micelles is called the canonic [5] Nematic Nc. A review of research in this filed has been prepared by Boden [50].

1.8 N-(p-n- ALKOXY BENZYLIDENE) – p-n-ALKYL ANILINES (nO.m)

Phase transitions interest physicists, chemists and metallurgists. This inter disciplinary subject is also of technological relevance [51, 52]. The literature abounds in experimental and theoretical studies of phase transitions and many unifying concepts have emerged in the recent years [53, 54].

Liquid crystals are known for their anomalous physical properties near the phase transitions. They maintain orientational and positional order in a mesophase. The majority of mesogenic molecules are composed of an aromatic core with one or two flexible end alkyl chains [55]. Alkyl chains enhance the thermal range of the liquid crystal by lowering the melting point. The liquid crystal properties, mainly the clearing temperature and the entropy of transitions are influenced by the end chains [56-61].

The research on liquid crystals involves the design, synthesis and characterization of phase variants involving different techniques. The N- (p-n-alkoxybenzylidene) – p-n-alkylanlines, (nO.m), attracted much attention as they exhibit rich but subtle polymorphism [62-64]. The lower homologues exhibit [65,56] the Nematic and orthogonal smectic phase, while the higher ones exhibit [66] the interesting tilted smectic phases including smectic-F with the
quenching of the Nematic phase. However, the compounds with intermediate of chain lengths show [54,55] both the Nematic and smectic phases. The higher homologues with alkoxy carbon number greater than 10 are found [63-77] to be rich in the manifestation of a direct titled smectic-F phase from the isotropic melt.

The N-(p-n-alkoxybenzylidene)-p-n-alkylanilines, (nO.m), is well known Schiff base liquid crystals. The synthesis of these compounds, with variation of the alkoxy and alkyl chain numbers, has gained momentum since the synthesis of MBBA a well known room temperature nematogen, in 1969 [78]. Because of the ease in preparation and the convenient working temperature, these materials have become model systems for the study of 2D, 3D melting. The earlier studies on the lower homologues with alkoxy and alkyl chain lengths less than 7 have shown that these compounds exhibit mainly Nematic and orthogonal smectic phases with rare presence of titled phase such as smectic-C and smectic-G. An exception in 50.6 [79] which exhibits the phase sequences variant NACBFG.

1.8.1 GROWTH OF SMECTIC F PHASE

Investigations on isotropic to liquid crystalline phase transitions, especially involving smectic phases, allow theoretical predictions [78] for the growth of 2D and 3D crystals from the isotropic liquid phase. The growth of a smectic-F phase from an isotropic liquid involves the formation of 2D structural order. In fact, very few compounds are reported that exhibit directly this transition [59, 54]. The smectic-F phase with monoclinic symmetry and
long-range tilt order, possessing a hexagonal molecular packing within the smectic layers (normal to the long axes of the molecules), has a quasi two-dimensional solid structure (i.e., poor correlation between layers). Materials exhibiting a 2D smectic ordering possessing a long-range bond orientational order with short-range tilted order [55] are important both in fundamental and applicational research, since piezoelectric response is reported [56, 79] for the chiral version of the smectic-F phase. The isotropic to smectic-F phase transition involves the growth of an ordered tilted smectic phase.

1.8.2 HIGHER HOMOLOGUES SERIES OF nO.m

The research on liquid crystals of N-(p-n-alkoxybenzylidene)-p-n-alkylanilines, (nO.m) series, involves the synthesis and characterization of phase variants in newly synthesized compounds using techniques like polarizing microscopy and differential scanning calorimetry.

The data available an n.O.m homologues [80-85] show that the homologues with alkoxy carbon number is greater than 7 and alkyl carbon number is from to 1 to 16 show mainly Nematic and orthogonal smectic phases, such as the smectic-A and smectic-B phase, with the rare exhibition of tilted phases, such as smectic-C,-F and -G. However, it has been observed [86-91] that the homologues with alkoxy carbon number is greater than 10 exhibit both orthogonal and tilted smectic phases with quenching of the Nematic phase for all values of m, i.e., from 1to 6. Further, it is interesting to note that with increase of alkyl carbon number, the orthogonal smectic phases also get quenched with the onset of tilted smectic-F and G phases.
As a part of systematic studies on the synthesis and characterization of n.O.m compounds of different n and m values, this thesis presents the results on three homologues series, viz.

N-(p-n-butyloxybenzylidene)-p-n-alkylanilines (40.m),
N-(p-n-octyloxybenzylidene)-p-n-alkylanilines (80.m) and
N-(p-n-pentadecyloxybenzylidene)-p-n-alkylanilines (150.m).

1.9 CRYSTALLIZATION KINETICS

The smectic orderings exhibited by the nO.m liquid crystals can be broadly classified as orthogonal and tilted phases. The molecules in the orthogonal smectic phases are parallel to each other with their long axes perpendicular to the layer plane, resulting in free rotation of the molecules around the long molecular axis [92]. Consequently, in the case of tilted phase the significant difference is the tilt of the molecular long axes with respect to the layer normal, leading to the hindered rotation of the molecule along the long axis. Furthermore, the layer thickness in a tilted mesophase is smaller than the molecular length while in the case of orthogonal ordering they are approximately equal. This degree of variation in the layer thickness, coupled with the molecular rotation, has a significant influence on the rate of crystallization. In fact, the distribution of heat transformation in both orderings, which has a direct impact on the rate of crystallization, is rather complicated process which may be elucidated structurally by detailed X-ray investigation. Alternatively, the study of crystallization kinetics [93, 94] is a
powerful tool to understand the various mechanisms involved in crystallization of liquid crystals.

The liquid crystalline materials belonging to the class of benzylidene aniline exhibits a fascinating mesomorphic behaviour associated with a distinct molecular ordering. The convenient working thermal range makes them suitable for systematic kinetic investigations. A detailed crystallization kinetic analysis of orthogonal and tilted smectogens of higher homologues of the benzylidene aniline nO.m series are studied.

A variety of techniques are used for the study of crystallization kinetics. The classical calorimetric and optical polarization techniques are predominantly used to understand the crystallization kinetics of various smectogens. For the first time in the history of liquid crystals a new technique has been devised and extensively used in the present nO.m study.

The theoretical background is derived from the Avrami equations and the experimental results are compared with the Avrami exponents. Further a quantitative approach has been made to understand the influence of the crystallization kinetics on the following

- chain length of the homologous nO.m series,
- tilted or orthogonal phase prior to the crystal formation referred as kineto phase and
- Avrami exponents