

General Observation about Liquid Crystals: A Review

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ABSTRACT:

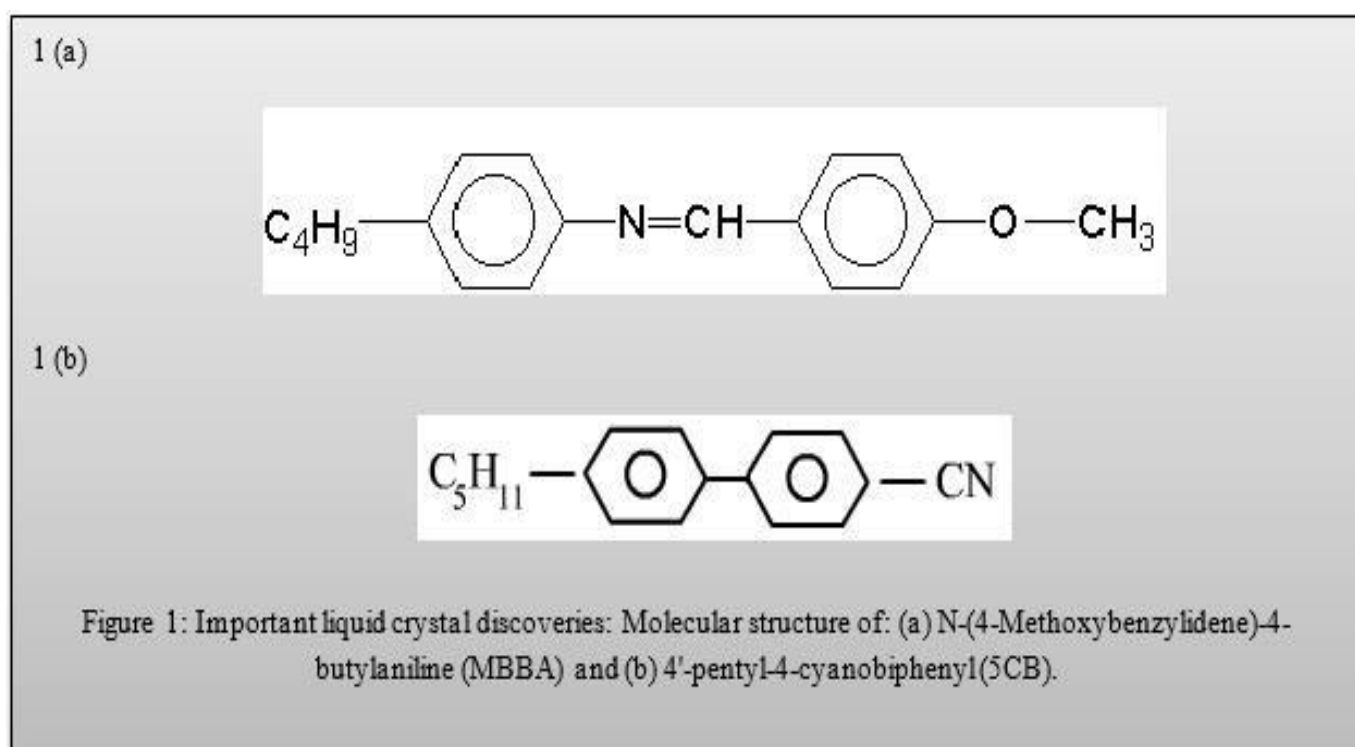
In this review article a literature overview of various aspects of liquid crystal science is deliberated. The review article deals with wide variety of liquid crystals, molecular structures, liquid crystalline phases, classification of liquid crystalline phases by chemical point of view and molecular ordering, phase sequences, chirality in liquid crystals and frustrated chiral phases.

Keywords: Liquid Crystals (LCs), Brief Description of the LCs Phases, Molecular Structures and Classification by Ordering and Frustrated Chiral Phases.

Liquid Crystals: Materials in nature can be divided into different phases, also called states of matter, depending on the mobility of the individual atoms or molecules. The obvious states of the matter are the solid, the fluid and the gaseous state. In the solid state, intermolecular forces keep the molecules close together at a fixed position and orientation, so the material remains in a definite shape. In the fluid state, the molecules are still packed closely together, but they are able to move around. Hence a fluid does not have a rigid shape, but adapts to the contours of the container that holds it. Like a liquid a gas has no fixed shape, but it has little resistance to compression because there is enough empty space for the molecules to move closer. Whereas a liquid placed in a container will form a puddle at the bottom of the container, a gas will expand to fill the container. Although the three categories seem very well defined, the borders between the different states are not always clear. Apart from the three familiar states, there exist a large number of other intermediate phases. A simple example is a gel. A gel is not quite solid, neither it is a liquid. **Liquid Crystals (LCs)** are another important intermediate phase which exhibits features from both the solid and the fluid state. LCs are neither quite liquid nor quite solid. Physically, they are observed to flow like liquids, but they have some properties of crystalline solids. LCs can be considered to be crystals which have lost some or all of their positional order, while maintaining full orientational order. Under certain circumstances, LCs phases have a liquid-like behavior and during others they have the opposite behavior. They represent thermodynamically stable phases existing between isotropic liquid and crystalline solid phases. There are many different types of LC phases, which can be distinguished based on their different optical properties (such as birefringence). When viewed under polarized light microscope, different LC phases will appear to have a distinct texture. The contrasting areas in the texture each correspond to a domain where the LC molecules are oriented in a different direction. Within a domain, however, the molecules are well ordered. LC materials may not always be in an LC phase (just as water is not always in the liquid phase: it may also be found in the solid and gaseous phase).

Historical Perspective: In 1888, Austrian botanical physiologist Friedrich Reinitzer (1858–1927), working at the Charles University of Prague, was extracting Cholesterol from carrots to establish its chemical formula. Reinitzer examined the physico-chemical properties of various derivatives of the Cholesterol. Other researchers had observed distinct color effects on cooling Cholesterol derivatives just above the solidification temperature. Reinitzer himself found the same phenomenon in Cholesteryl Benzoate [1], but

the colors near the solidification of Cholesteryl Benzoate were not the most peculiar feature. Reinitzer found that Cholesteryl Benzoate does not melt like other compounds, but had two melting points. At 145.5°C, it melted into a cloudy liquid, and at 178.5°C, it melted again and the cloudy liquid became clear. The phenomenon was found to be reversible. In 1890 the German physicist Otto Lehman [2] with his self-constructed polarized light microscope coupled with hot stage, observed the optical properties of other materials that also showed some anomalous melting characteristics. Lehman suggested the name "Liquid Crystals" because of the crystal-like molecular structure of these liquids. The name 'Liquid Crystals' originates from the fact that the phases are both liquid-like such as they flow and the shape is usually determined by the container it fills, and crystal-like, such as there is a degree of orientational ordering of the molecules. There are some materials like N-(4-Methoxybenzylidene)-4-butylaniline (MBBA) and 4'-pentyl-4-cyanobiphenyl (5CB) (see **Figure 1**) which when heated from their crystalline phase, completely lose their positional ordering but have some sort of the orientational ordering in the sense that their molecules are slightly oriented in a preferable direction as compared to the other directions.



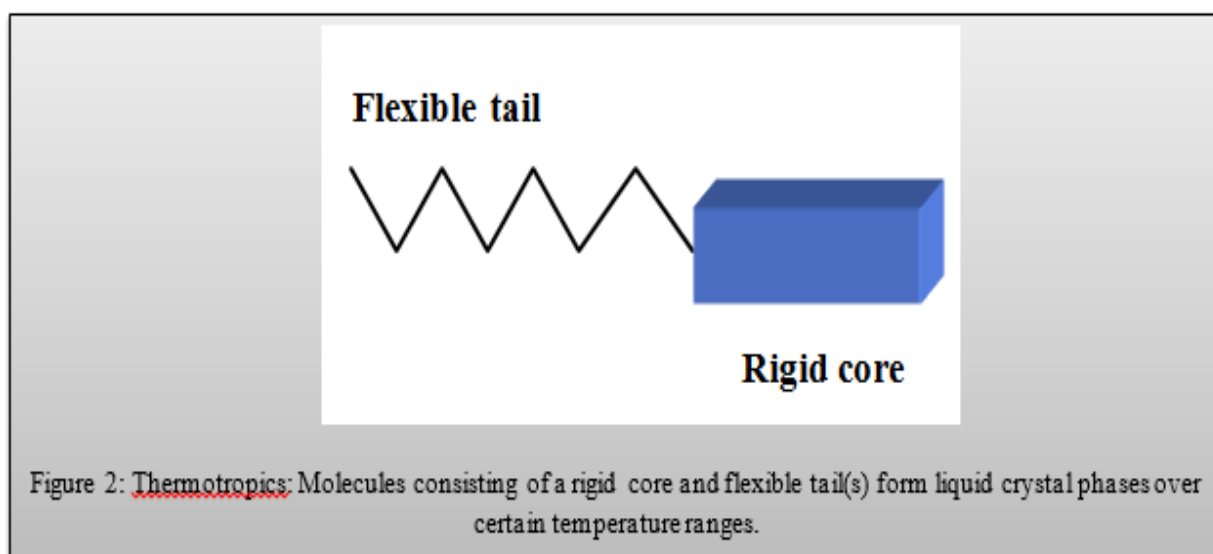
The LC phases are also known as the crystalline liquids, mesophases or mesomorphic phases. Subsequently, Daniel Vorlander [3] began a systematic synthetic study to find correlations between molecular structure and the occurrence of the liquid crystalline state. In 1906, he discovered the phenomenon of polymorphism in LCs, i.e. a given compound can exhibit more than one liquid crystalline phase. He also established the rule that liquid crystallinity occurs most frequently with a rod-like shape. LCs were not popular among scientists in the early 20th century and the material remained a pure scientific curiosity for about 80 years. In 1969, Hans Kelker succeeded in synthesizing a substance that has a nematic phase at room temperature, MBBA, the well-known "fruit-fly" of liquid crystal research [4]. The invention of the twisted nematic cell by Schadt and Helfrich in 1971 [5], led to the development of liquid crystal display (LCD) technology and since then number of studies on liquid crystalline state increased considerably, due to applications of LC material in electro-optical (EO) switching devices. Now, there are thousands of compounds, both naturally occurring and synthesized, that exhibit one or more LC phases. In 1991, when LCDs were already well established in our everyday life, Pierre-Gilles de Gennes (1932-2007) received the Nobel Prize in Physics for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to LCs and polymers.

A Brief Description of the Relevant Phases

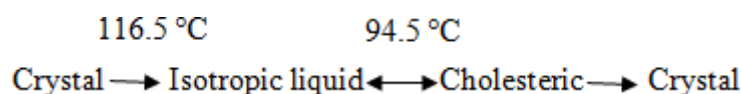
Classification by Chemical Point of View: LCs are divided into four classes: Thermotropic, Lyotropic, Amphotropic and Metallotropic. Thermotropic, lyotropic and amphotropic LCs consist of organic molecules, whereas metallotropic LCs can be based on low-melting inorganic materials.

Thermotropic Liquid Crystal: LCs, whose transitions between the phases are governed by temperature, are called THERMOTROPIC. Thermotropic LCs exist in both rod and disc shaped molecules. However, a vast majority of them are composed of rod-like molecules. These exhibit a variety of phases as temperature is varied. For instance a particular mesogen may exhibit various Smectic and nematic phases as temperature

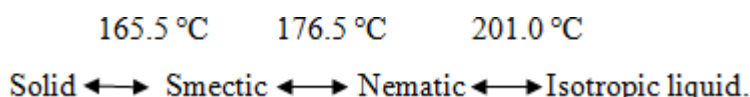
is increases. The mesophase(s) appear(s) at temperature between the melting point, below which the material exists as a crystalline solid, and above which the material exists as an isotropic liquid.



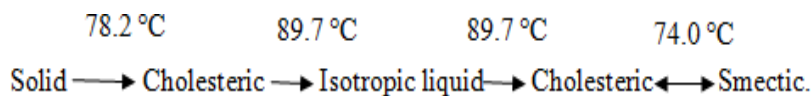
Thermotropics LCs are further classified into two categories; one is monotropics in which mesophase(s) observed in heating from solid to liquid state are not the same as in cooling from liquid to solid state; others are enantiotropics in which mesophase(s) observed in the heating cycle are exactly the same as that in the cooling cycle with the same transition temperatures. For example Cholesteryl Acetate [6] is monotropic with the following phase diagram:



The 5-chloro-6-n-heptyloxy-2-naphthoic acid [6] is an enantiotropic with the following phase diagram:

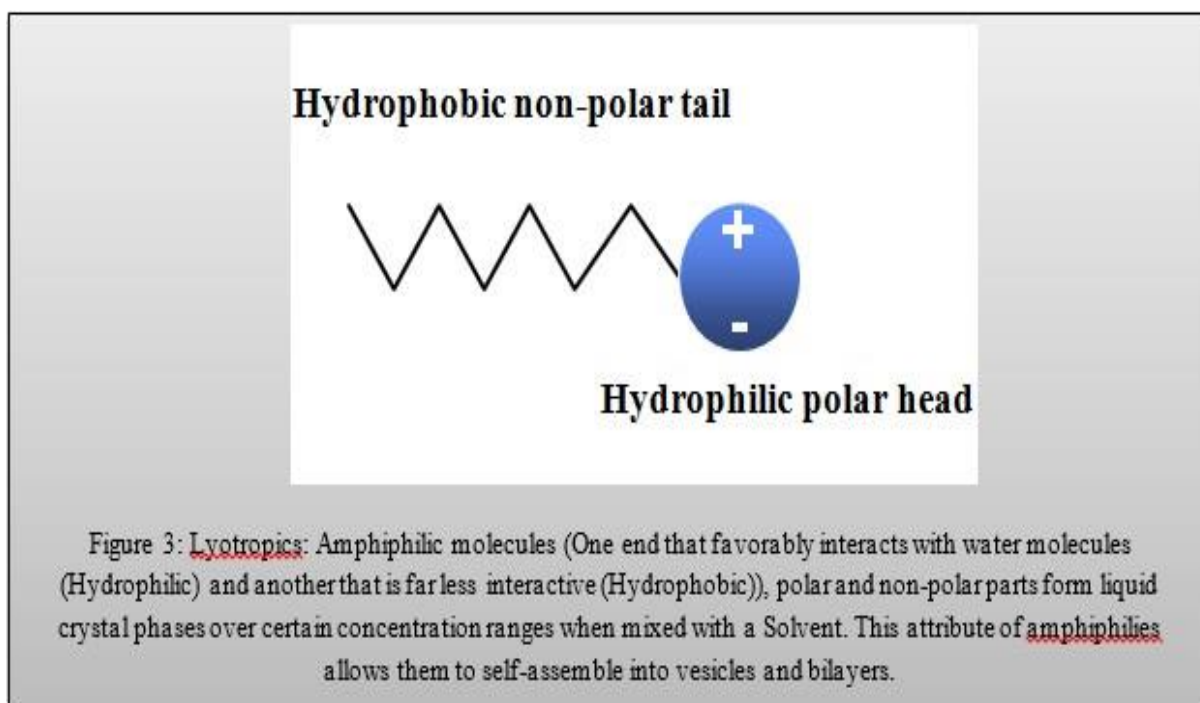


The mesophase(s) which are reversible in both heating and cooling cycles are called enantiotropic mesophase(s) and if a mesophase is not reversible it is called monotropic. Cholesteryl Pelargonate [7] has monotropic Smectic phase but enantiotropic cholesteric phase with the following phase diagram:



Lyotropic

Liquid Crystal: In blends of the different components, phase transitions may also depend on the concentration and these LCs are called LYOTROPIC. These lyotropic LCs are just as scientifically interesting and technologically important as thermotropic LCs.

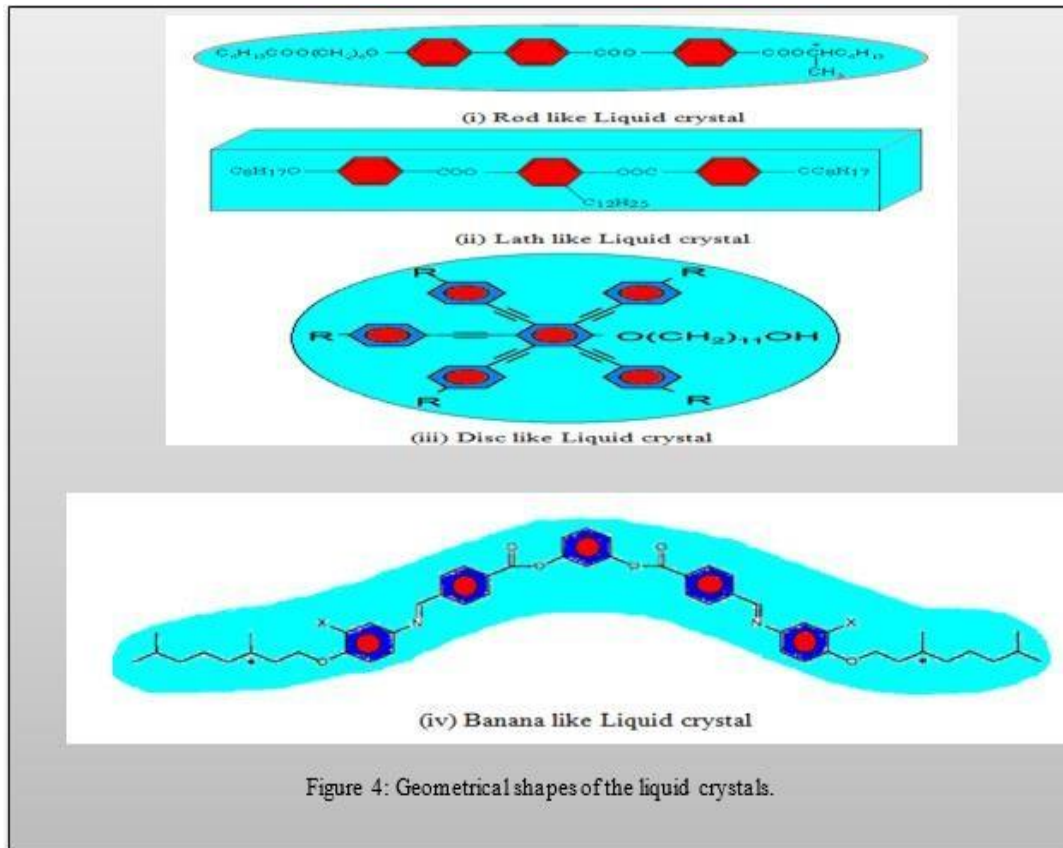


Lyotropic liquid crystalline phases are abundant in living systems, the study of which is referred to as polymorphism. Lyotropic liquid crystalline phases are abundant in living systems, the study of which is referred to as polymorphism. Accordingly, lyotropic LCs attract particular attention in the field of biomimetic chemistry. In particular, biological membranes and cell membranes are a form of LC [8]. Lyotropic LCs occurs when the stability of the phase is determined by the solvent concentration. Well known examples are mixture of the alkali nalkanoates (soaps) and water. Although temperature is still an important variable in determining the phase present, the concentration of one component with respect to the other is far more important here.

Amphotropic Liquid Crystal: AMPHOTROPIC LCs are those which exhibit the properties of thermotropic as well as lyotropic liquid crystalline states. Examples are the alkali salts of long chain aliphatic acids [9].

Metallotropic Liquid Crystal: LC phases can also be based on low-melting inorganic phases like $ZnCl_2$ that have a structure formed of the linked tetrahedra and easily form glasses. The addition of the long chain soap-like molecules leads to a series of new phases that show a variety of liquid crystalline behavior both as a function of the inorganic-organic composition ratio and of the temperature. This class of materials has been named Metallotropic [10].

Molecular Structures: Molecular structure of the LCs exists in various geometrical shapes as shown in Figure 4. These shapes could be: (i) Rod like, (ii) Lath like, (iii) Disc like and (iv) Banana like [9, 11].

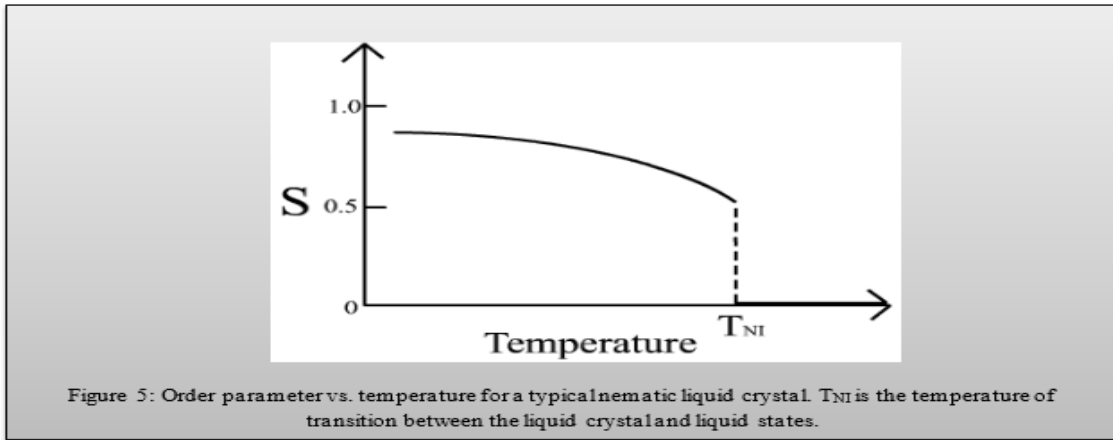


Classification by Ordering: In 1922, George Friedel [12] proposed a classification of LCs based upon the different molecular ordering of each substance. What makes a LC different from the ordinary liquid phase is the tendency of the molecules to point along a common axis. Even if the molecules positions are random, their orientations can be aligned with one another in a regular pattern and that's what creates the ordered structure of a LC. The characteristic orientational order of the LC state is between the traditional solid and liquid phases and this is the origin of the term mesogenic state, used synonymously with LC state.

Orientalional Order: The molecules of the liquid crystal tend to align themselves along a common direction, known as the director (\mathbf{n}). The order parameter, S , defined as

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$$

(1) Where the rod shaped molecules makes an average angle $\bar{\theta}$ with the long axis of the molecule, quantified the degree of the orientational ordering. The brackets denote an average over all of the molecules in the material. In an isotropic liquid, the average of the cosine terms is zero, and therefore the order parameter is equal to zero. For a perfect crystal, the order parameter evaluates to one. Typical values for the order parameter of a LC range between 0.3 and 0.9, with the exact value a function of temperature, as a result of the kinetic molecular motion. The tendency of the LC molecules to point along the director leads to a condition known as anisotropy. This term means that the properties of a material depend on the direction in which they are measured. The anisotropic nature of LCs is responsible for the unique optical properties exploited by scientists and engineers in a variety of applications.



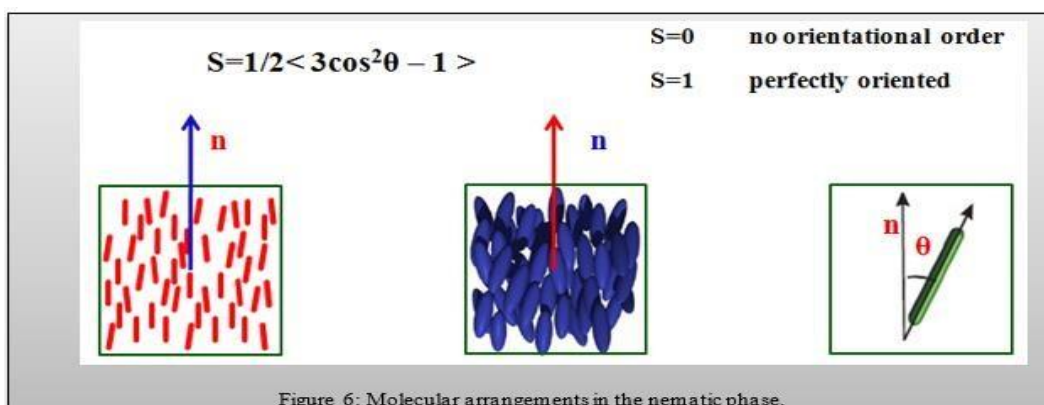
Positional Order: In addition to the orientational ordering, it is also possible for LC phases to form a degree of the positional ordering of the molecules. These phases are classed as Smectic (Sm). The molecules are arranged approximately into layers, forming two dimensional liquids. Different types of the Smectic ordering can be distinguish according to whether there is tilt, twist and long range translational ordering of the molecules into the layers. The least ordered Smectic phases are Smectic A (SmA) and C (SmC) shows positional order in one dimension only. In some cases, a plot of the density of the centers of mass versus distance along an axis z normal to the layers follows the sinusoidal relation:

$$\rho(Z) = \rho_0 \left[1 + \phi \sin \left(\frac{2\pi z}{d_0} \right) \right] \quad (2)$$

where ρ_0 the mean density and d_0 is layer spacing. The layer spacing in general is typically a few nanometers. ϕ the Smectic order parameter, which is the ratio of the amplitude of the oscillation to the mean layer density and hence expresses the extent to which the material is layered, typically $\phi < 1$.

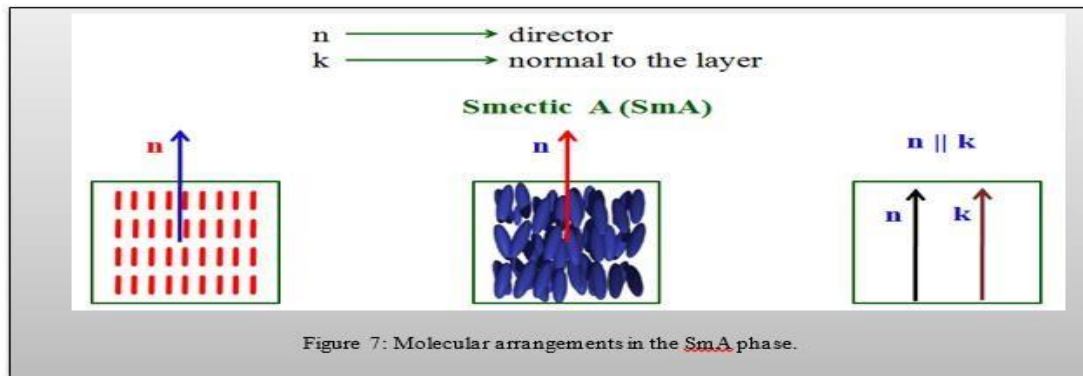
Liquid Crystals Phases:

Nematic Phase: NEMATIC is the most common and simplest LC phase. The word “nematic” is derived from the Greek word for “Thread” as thread like textures were observed under the polarized light microscope [13]. In this phase, the molecules maintain a preferred orientational direction as they diffuse throughout the material, but there is no translational order as shown in **Figure 6**. Flory and Ronca, in 1979 [14] theoretically shows that, for rod shaped molecules, if the ratio of the molecular length to its width is greater than 6.4, then the forces of the interaction that cause orientational order in solid phases are larger than those cause positional ordering and cause a nematic phase to exist in a temperature range intermediate between the crystalline solid and the isotropic liquid. At much lower temperature, the thermal agitation energy (kT , k is the Boltzmann constant and T is absolute temperature) is comparable to the positional ordering. As the temperature is increased from the solid phase, two distinct phase transitions are observed. At first, the positional order and then the orientational order are lost. This is a rather simplified explanation for the liquid crystal phase possesses orientational order only. There are more complex interactions involved in the formation of the other LC phases.

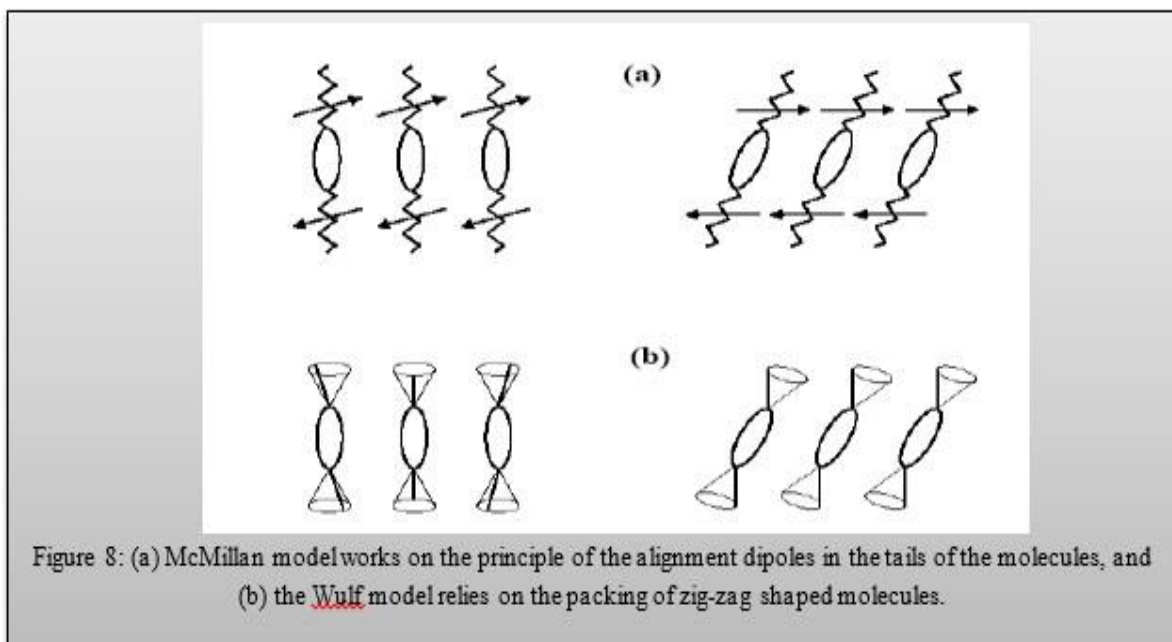


Smectic Phase: The word SMECTIC is derived from the Greek word for “soap”. This seemingly ambiguous origin is explained by the fact that the thick, slippery substance often found at the bottom of a soap dish is actually a type of the Smectic LC [13, 15]. Molecules in this phase show additional degrees of the translational order not present in the nematic phase. In this Smectic phase, the molecules maintain the general orientational order of nematics, but also tend to align themselves in layers; with a well-defined interlayer spacing, which can be measured by X-ray diffraction [16]. The inter layer attractions are weak compared to the lateral forces between the molecules, and the layers are able to slide over one another relatively easily. This gives rise to fluidity to the system with higher viscosity than nematics.

Smectic A (SmA) Phase: In the Smectic A phase (SmA), molecules are oriented more or less parallel to each other and their position is ordered in layers, in which the layer spacing is approximately equal to the length of the molecules (see Figure 7).



It means that in addition to the orientational order, there exists a degree of the positional order, determined by the formation of so-called Smectic layers. The director in the SmA phase is normal to the Smectic layers and determines the optic axis of the system. Fluctuation of the electron cloud of one molecule induced a temporary dipole in the neighboring molecules. The existence of the layer structure of SmA phase is thought to be due to the interaction between the dipoles (Vander Waals forces) in two nearby molecules. When the molecules are lined up with each other positionally, the energy of interaction between the dipoles is lowest. So the layered structure forms.



Smectic C (SmC) Phase: The existence of the tilted Smectic phases is believed to be a combination of the two types of effects. The first one, the McMillan model [17], suggests that the tilt is caused by the alignment of the dipoles in the molecular tails. **Figure 8 (a)** illustrates this showing the SmA-SmC transition. Another one, the Wulf model [18] suggests that the zig-zag shape of the molecules encourages them to pack with their cores at an angle to the layer normal as shown in **Figure 8 (b)**. In reality, the formation of SmC phase will be a combination of both dipolar and the steric interactions.

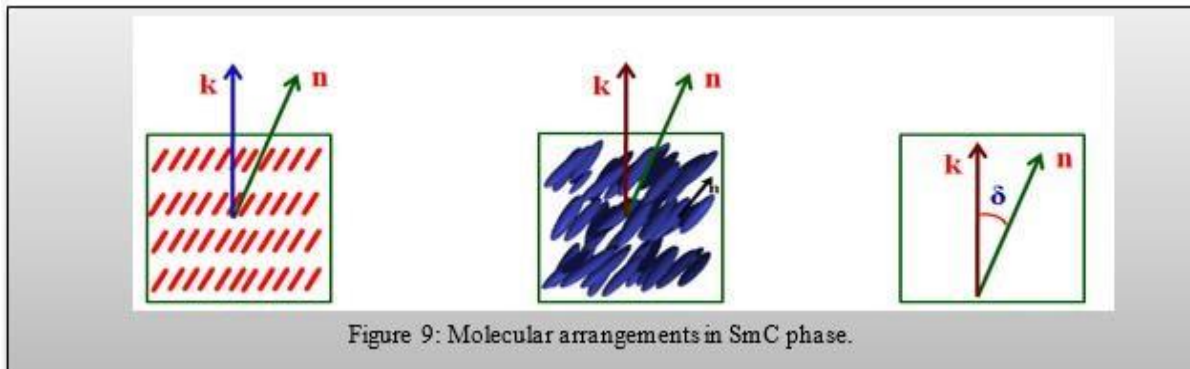


Figure 9: Molecular arrangements in SmC phase.

In Smectic C phase director 'n' is tilted with angle ' δ ' with respect to normal of the layer 'k' are as shown in **Figure 9**. The structural classifications of Smectic LCs are given in **Table 1**.

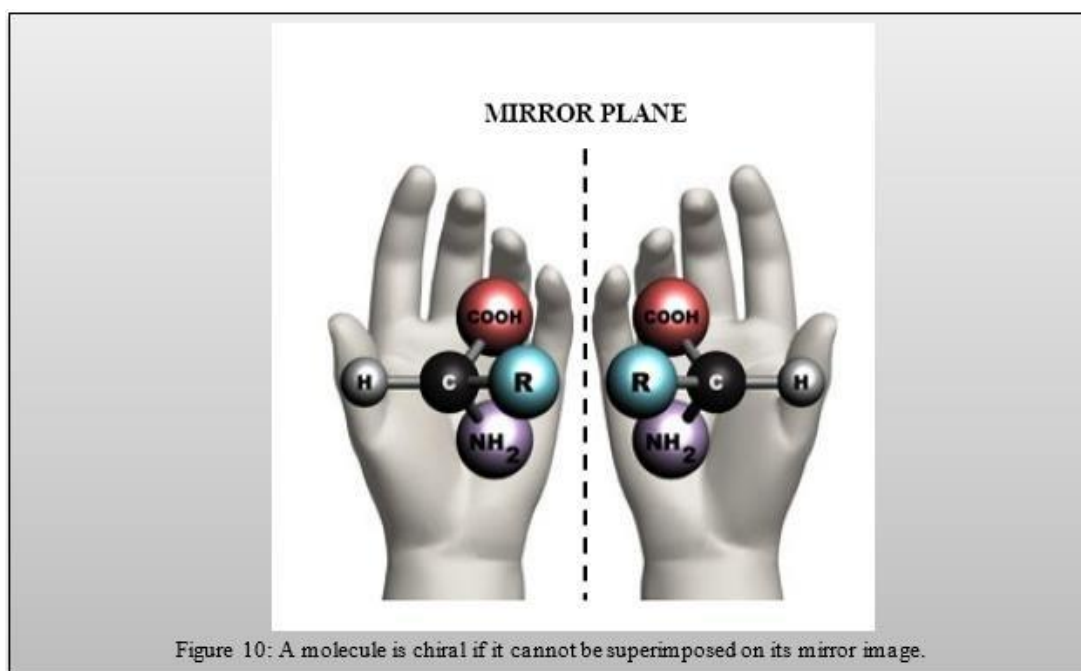
Phase Sequences: Liquid crystalline materials may not always be in a LC phase (just as water is not always in the liquid phase: it may also be found in the solid or gas phase), very often have more than one liquid crystal phase between liquid and solid phases. For example, a typical phase sequence might be detected simply by Differential Scanning Calorimeter and the following sequences could be observed.

Solid----- Smectic C----- Smectic A---- Nematic Isotropic Liquid

Symmetry and Chirality in Liquid Crystals: An object is chiral if its mirror image cannot be superimposed by any translations or rotations as shown in **Figure 10**. In LCs chirality can be introduced in two ways. One is by incorporation of chiral centers (carbon atoms) within the LC molecule, by which chirality can be directly introduced. Another way, the most popular one, is the addition of a small amount of chiral dopant molecules to an achiral host phase. The dopant itself may or may not have a liquid crystalline phase. The systems with dopants possess induced chirality. An asterisk '*' is usually used to labeled a chiral phase.

Table 1: Structural Classifications of Smectic Liquid Crystals.

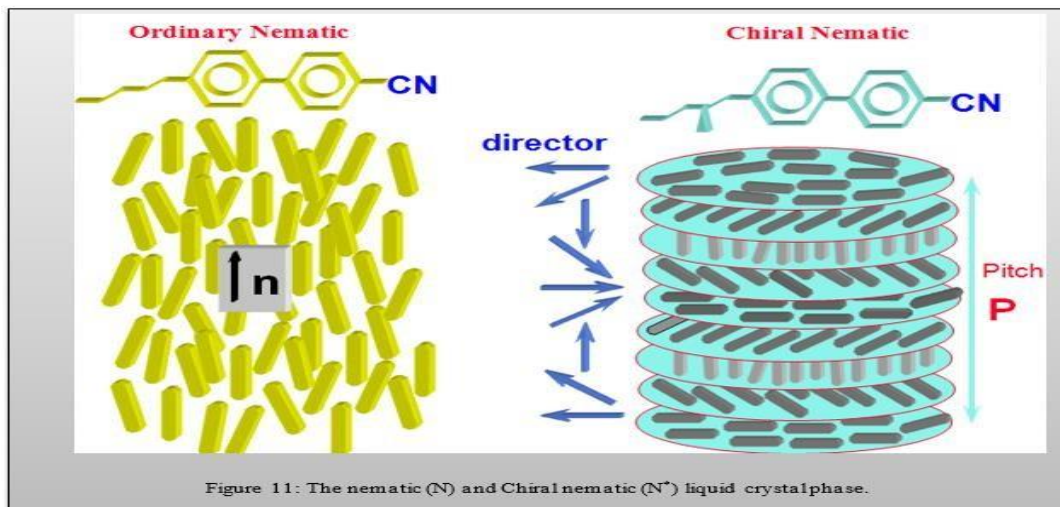
1. **Smectic A:** Liquid-like layers with molecules upright on the average. Negligible in plane and inter layer correlations. Thus, this phase can be classified as an orientationally ordered liquid on which a 1-D density wave in superimposed.
2. **Smectic B:** Basically similar to **SmA** phase but with higher in-plane ordering. Two distinct types of smectic had been identified, (a) **Crystal B**, 3-D crystal having hexagonal lattice and weak interlayer ordering. (b) **Hexatic B**, stack of interacting **hexatic** layers with short-range in plane ordering and 3-D six-fold bond orientational ordering.
3. **Smectic C:** Liquid-like layers as in **SmA**, but with the molecules inclined with respect to layer normal.
4. **Smectic C*:** Chiral Smectic C with twist axis normal to the layer.
5. **Smectic D:** Cubic lattice with micelle type molecular arrangement. This phase is usually observed between **SmA** and **SmC** or between **SmC** and Isotropic phase.
6. **Smectic E:** 3-D orthorhombic crystal with interlayer herringbone structure.
7. **Smectic F:** Tilted **hexatic** structure with C centered monoclinic ($a > b$) with in-plane short range positional correlation and weak or no interlayer positional correlation.
8. **Smectic G:** 3-D crystal with C-centered monoclinic ($a > b$).
9. **Smectic H:** 3-D crystal with C-centered monoclinic ($a > b$) and having herringbone structure.
10. **Smectic I:** Tilted **hexatic** C-centered monoclinic ($b > a$) with slightly greater in plane correlation than **SmF**.
11. **Smectic J:** 3-D crystal with C centered monoclinic ($b > a$) structure.
12. **Smectic K:** 3-D monoclinic ($b > a$) structure with herringbone.



Chiral Nematic Phase (N^*): When chiral molecules (dopants) are mixed with the achiral molecules in the nematic phase, a nematic phase with twisted structure known as CHIRAL NEMATIC (N^*) (or CHOLESTERIC) is formed (see **Figure 11**). The director in the N^* phase, instead of being uniformly oriented, rotates in space about an axis that is perpendicular to it. As in the nematic phase, the molecules have no longer positional order, and no layering. The distance, in which the director makes full 2π radians rotations along the helix axis, is called the helix pitch (P). The pitch varies typically between a few hundred nanometers (short pitch) to many micrometers (long pitch). Generally the pitch is much longer than the molecular length and strongly depends on the concentration of the dopant in the mixture. A unique aspect of the chiral nematic phase is the temperature dependence of the pitch. As the temperature increases, so does the length of the pitch. This changes the macroscopic properties of the bulk material. The cholesteric twist can be either right- or left-handed, depending on the configuration of the chiral elements within the molecule. Due to helical structure, this phase possesses special optical properties which make them useful for important application [19].

Chiral Smectic Phases: There are different type of the chiral Smectic liquid crystal phases viz. SmA^* , SmB^* , SmC^* and SmI^* etc. and crystal chiral smectic mesophases viz. SmJ^* , SmG^* and SmK^* etc. which could generate from chirality as a direct result of molecular chirality of the constituent molecules. The higher ordered chiral smectic mesophases (SmJ^* , SmG^* , SmK^* and SmH^*) have tilted structure and possesses three-dimensional long-range order and therefore are called crystal chiral smectic phases [20]. SmG^* and SmH^* have tilted chiral phase but no helix structure. The chiral smectic liquid crystal phases can be further divided into two categories viz. orthogonal chiral smectic phases (SmA^* and SmB^*) and tilted chiral smectic phases (SmC^* , SmC_A^* , SmC_γ^* and SmI^*). In the SmA phase of LC, molecules of all the Smectic layers are aligned in an average direction perpendicular to the plane of the Smectic layers of equal spacing and is denoted by unit vector \mathbf{n} , called director. However inside a layer molecules do not show any long range positional ordering and such layer behaves as two-dimensional liquid. The Smectic A phase built of chiral molecules are denoted as SmA^* phase, where $*$ indicates chirality of the constituent molecules only not helical structure in the phase [20, 21]. The SmB^* phase (chiral analog of SmB phase) is an orthogonal phase similar to SmA^* phase. The main difference between the SmB^* and SmA^* phases is that the centre of mass of molecules within each chiral Smectic layer exhibit a hexagonal order [20]. The SmB^* phase has two modification in literature as the hexatic SmB^* phase and the crystal SmB^* phase. The hexatic SmB^* phase is characterized by two-dimensional director order of the hexagonal nature within Smectic layer and the crystal SmB^* phase has an additional order due to correlation in molecular position between successive layer. Molecular ordering in the tilted LC Smectic phases due to optical active (chiral) substances imparts to them a new property; spontaneous polarization in the absence of external electric field [22]. All Smectic phases with tilted

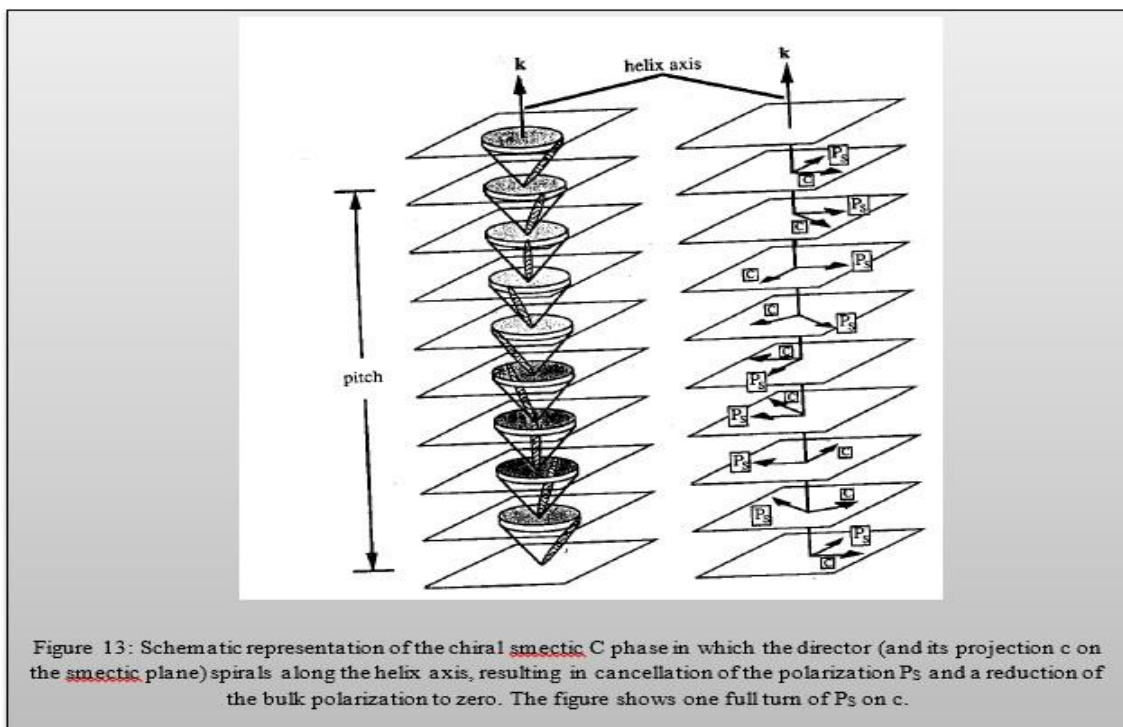
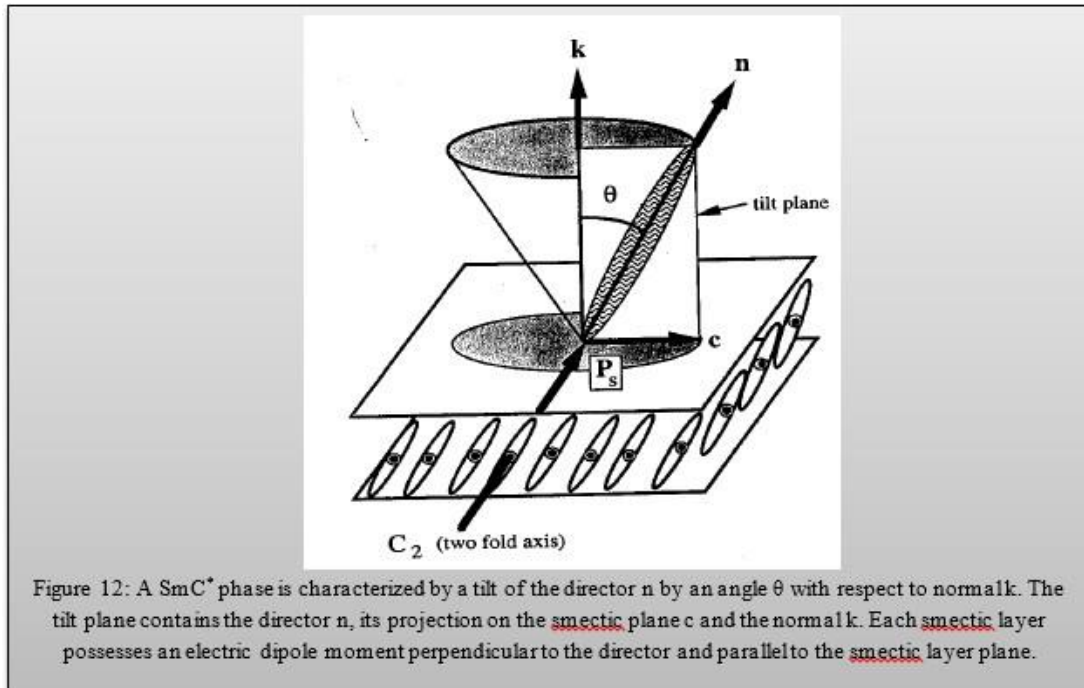
structure derived from the chiral molecules exhibits ferroelectric properties. The chiral Smectic C phase (SmC^*) is one of the most commonly exhibited phase of the tilted chiral Smectic phase. In the SmI^* phase molecules are oriented similar to SmC^* phase with short-range correlation in Smectic plane but no layer correlation. It possesses pseudo hexagonal structure. The study of SmC^* phase is important because of their electro-optical properties and their application as fast switching display devices [20]. Recently several new types of ferroelectric and antiferroelectric LC phases in the tilted Smectic have also been investigated in the optically pure material of high spontaneous polarization [23]. The antiferroelectric Smectic C* phase (SmC_A^*) is a new type of phase in which adjacent layers of the molecules are oppositely tilted to give an antiferroelectric arrangement [24]. A brief description of various chiral Smectic C phases is given below.



Ferroelectric Chiral Smectic C Phase: The chiral smectic C (SmC^*) phase is chiral analogue of SmC phase. The structure of SmC phase is lamellar and molecules within the layers are tilted at a temperature dependent angle (θ) from the layer normal. Let us consider one Smectic layer as schematically drawn in **Figure 12**. The non-chiral smectic C phase has a monoclinic symmetry and belongs to the point group C_{2h} . It has a mirror plane and a two-fold axis perpendicular to it. The mirror plane is given by the Smectic layer normal \mathbf{k} and the Smectic C director, i. e. the tilt plane (see **Figure 8**). If the constituent molecules are chiral, then the chirality will break the mirror symmetry and we are left with only one symmetry axis C_2 . The chirality, together with the piezo- and flexo-electric effects, induce slight precession from layer to layer in the tilting and hence in the in-plane spontaneous polarization. This leads to the formation of helicoidal structure (see **Figure 13**) with the axis parallel to the Smectic layer normal; the net spontaneous polarization of a material may then become zero [25]. In most of the ordinary liquid crystalline phases e.g. nematic, cholesteric, SmA and SmC that appear successively on lowering the temperature from isotropic liquid phase, the symmetry is so high that the free rotation around the molecular long axis and head-tail equivalence prevent the occurrence of ferroelectricity. In chiral smectic C phases, however symmetry is low enough to allow the existence of the chirality induced improper ferroelectricity, which does not result from the dipole-dipole interaction. The molecules in each Smectic layer still rotate around their long axis, but this rotation is now biased in a particular sense along the C_2 axis of the point group C_2 . In the other words, the low local symmetry forces the transverse dipole moments of the molecules, if there are any, to align in a sense of the direction perpendicular to the tilting plane, leading to a microscopic polarization within the Smectic layer given by

$$\mathbf{P} = P_0 \frac{\mathbf{k} \times \mathbf{n}}{|\mathbf{k} \times \mathbf{n}|} \quad (3)$$

Where \mathbf{k} is unit vector parallel to the layer normal and \mathbf{n} is the director; the sense of \mathbf{k} is chosen so that \mathbf{k} coincides with \mathbf{n} when the tilt angle θ becomes zero. The reversal of the tilting sense naturally results in a reversal of polarization sense [25-26].



Antiferroelectric Chiral Smectic C Phase: Antiferroelectric liquid crystals (AFLCs) are new class of materials in which molecules are oriented similar to that of ordinary ferroelectric liquid crystals (FLCs) in each Smectic layers but the orientation correlation of the molecules in different layers is supposed to be quite different in two cases. The molecules in neighbouring layers are tilted in opposite direction with respect to the layer normal in the antiferroelectric states; hence, the net dipole moments of the two adjacent

layers are cancelled out which implies the lack of macroscopic spontaneous polarization [24]. The competition between adjacent Smectic layers to form anticlinic and synclinic structure causes an appearance of different new type of chiral smectic C subphases viz. SmC_{α}^* , SmC_{β}^* and SmC_{γ}^* in AFLC materials in addition to antiferroelectric phase (SmC_A^*) upon cooling from isotropic phase. The proposed structure of antiferroelectric chiral smectic C phase (SmC_A^*) is depicted in **Figure 14**. The SmC_A^* structure does not lose the periodicity of half the pitch, unlike the SmC^* structure, even in oblique view. The SmC^* structure is optically similar to the chiral nematic (cholesteric) structure, except that the local optical biaxiality is pronounced and the slowest axis is parallel to the helicoidal axis [27].

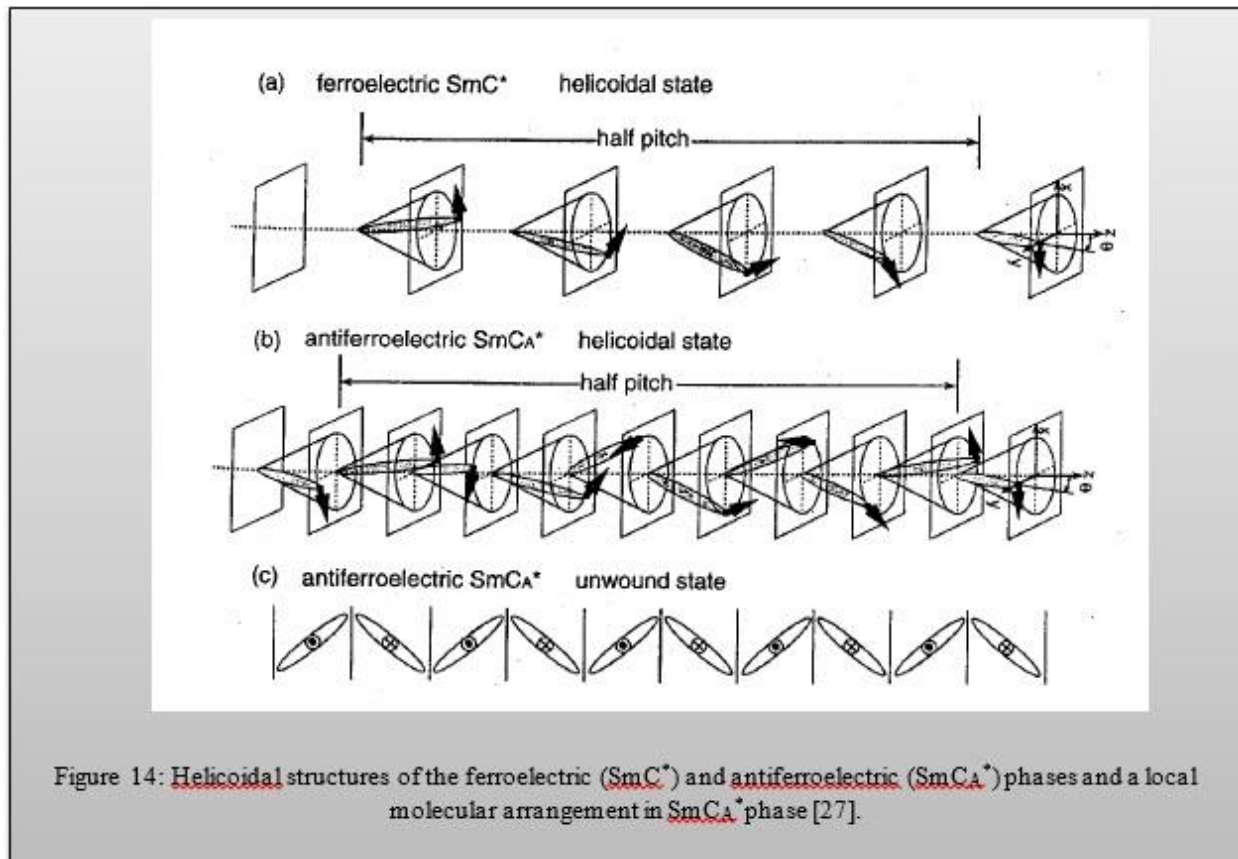


Figure 14: Helicoidal structures of the ferroelectric (SmC^*) and antiferroelectric (SmC_A^*) phases and a local molecular arrangement in SmC_A^* phase [27].

The molecules in the neighbouring layers tilt in almost the same direction but in the opposite sense; the spontaneous polarizations in the neighbouring layers point in the opposite sense of the direction perpendicular to the tilting plane, thereby cancelling each other. There is yet no net spontaneous polarization. Antiferroelectricity in chiral liquid crystal has been first time reported by Chandani et al. in MHPOBC [23] although its existence has predicted in a ferroelectric liquid crystal (FLC) mixture in 1982 [28]. The molecules that exhibit antiferroelectric phases have structures that contain central rigid cores composed of at least three aromatic or heterocyclic rings. Attached to the core is a terminal chiral group that has its chiral centre positioned adjacent to the core and on the peripheral side of the asymmetric atom there is a chain of at least six carbon atoms in length [29]. Thus, in effect, molecules with this form of the structural architecture would be expected to exhibit strong molecular chirality, which might be expected to affect the liquid crystalline properties of the material.

Other Antiferroelectric Chiral Smectic C Phase: SmC_{α}^* phase has been assigned to be biaxial Smectic phase first predicted to exist by Matsushita [30]. It appears in antiferroelectric materials below SmA^* phase. X-ray diffraction data shows that SmC_{α}^* phase is tilted Smectic. Recently Mach et al. [31] have shown that the SmC_{α}^* phase has incommensurate structure with a modulation period between five and eight Smectic layers on the basis of resonant X-ray. Switching characteristic indicate that it is antiferroelectric at least in the temperature region just below the phase transition from SmA^* to SmC_{α}^* and gradually changes in

ferrielectric structure with decrease in temperature [27]. Dielectric studies indicate that the SmC_α^* phase shows antiferroelectric like properties at higher temperatures and changes to ferroelectric like structure on cooling [32]. The cause of antiferroelectricity in SmC_α^* phase is different from those of SmC_A^* phase. The SmC_β^* phase has been first realized by Gorecka et al. in MHPOBC on the basis of conoscopy observation [33]. It has been observed between SmC_α^* and SmC_γ^* phases. In early days of its recognition it has been considered as ordinary ferroelectric SmC^* phase. Latter in a compound MHPBC [34] a phase between SmC_α^* and SmC_γ^* phases have been reported of antiferroelectric nature and denoted as AF phase. In some investigation [35] it has been reported as ferrielectric structure. Recently Gorecka and co-workers [36] have been able to solve the long known controversy of ferroelectric and ferrielectric nature of SmC_β^* (sometimes denoted as SmF_{12}^*) phase. They have shown that in the optically pure antiferroelectric liquid crystal MHPOBC, the SmC_β^* phase is neither ferrielectric nor ferroelectric phase but has antiferroelectric properties with four layer structured unit cell, which has been identified in several other AFLC compounds and denoted as AF phase [37-39].

Ferrielectric Chiral Smectic C Phase: One of the most striking features of AFLCs is the emergence of various subphases. The discovery of subphases was associated with the discovery of the antiferroelectric phase in MHPOBC. Gorecka et al. [33] in MHPOBC have reported the first ferrielectric phase on the basis of its unusual conoscopy behaviour. The ferrielectric chiral smectic C phase has an alternating tilted structure except that alternation is not symmetrical and more layers are tilted in one direction than the other. On the basis of the Ising model many structure of the ferrielectric phases have been predicted [22]. At least three ferrielectric subphases FI_L , SmC_γ^* and FI_H have been experimentally reported even though they are not always observable [39-40]. On the basis of conoscopy observation, Hiraoka et al. [41] have proposed a model for SmC_γ^* phase. According to which, it has ferrielectric nature and its periodic unit consist three Smectic layers, in two of which, the molecules tilt in the same direction whereas in the third layer molecules tilt in the opposite direction [42-43]. In 1998, Mach et al. [31] have succeeded to determine the macroscopic structure of SmC_γ^* phase on the basis of resonant X-ray experiment and they have confirmed same structure as proposed earlier. As in the three-layered ferrielectric phase, molecules in the two layers tilt in the same direction whereas in the third layer molecules tilt in the opposite direction [42-43], therefore effective value of spontaneous polarization in ferrielectric phase is equal to one third of spontaneous polarization of that exists in ferroelectric phase.

Frustrated Chiral Phases: In some cases reduction of the symmetry of a system causes some strange structural behaviour to occur. The molecules wants to pack in certain manner but such a structure cannot be adopted everywhere. Accordingly this leads to what are called frustrated phases. Chiral liquid crystals have the tendency to form a cholesteric like helical structure; however molecular interaction may favour a Smectic layer structure. It is impossible to realize a continuous structure that exhibits both a cholesteric director field and a Smectic layer structure at the same time. The competition between these two structural features can result in frustrated structure containing a regular lattice of grain boundaries, which in turn consist of a lattice of screw dislocations [44]. These frustrated phases are called twist grain boundary (TGB) phases. TGB phases usually appear in the temperature range between a cholesteric (N^*) phase with short pitch and a Smectic phase typically SmA/SmC^* . In particular they are expected to appear close to $N^*/\text{SmA}/\text{SmC}^*$ triple point [45]. Chirality of the system is an essential precondition for the occurrence of TGB phases. In mixture of chiral and non-chiral component, the concentration of the chiral component must exceed a critical value in order to lead TGB phases [46]. Till now a large variety of new frustrated phases such as TGBA, TGBC, TGBC^* , melted grain boundary (MGB) phases, a defect line liquid N_L^* , antiferroelectric twist grain boundary phase and Smectic blue phases (BPI, BPII and BPIII) have been experimentally observed in pure compound as well as in mixtures.

Twist Grain Boundary A Phase: The twist grain boundary phase (TGB) phase of a chiral liquid crystal combines a helical twist and Smectic layering. The TGBA phase was predicted theoretically by Renn and Lubensky [44]. They showed that a new phase (now named TGBA) can exist, which has regular spaced

grain boundaries of the screw dislocations that separate the material into Smectic-A blocks and each block is rotated about the pitch axis by a discrete angle relative to adjacent block. TGBA phase is an intermediate structure between SmA and cholesteric N*. It is an analog of the Abrikosov flux vertex lattice in a type -II superconductor in external magnetic field [47]. The first experimental realization and characterization of TGBA phase was done by Goodby et al. [44] in 1989 in a chiral compound nP1M7 (R and S-1-methylheptyl 4'-(4'-n-alkoxyphenyl) propionoyloxy]-biphenyl-4-carboxylates). TGBA phase was found to occur after normal Smectic phase while heating. Almost at the same time Lavrentovich et al. reported SmA*(TGBA) phase in mixture of Cholesteryl Pelargonate and Nonyloxy-Benzoic acid [48]. The TGBA phase can be considered as an intermediate state between two incompatible phases viz. cholesteric phase (which appears at higher temperatures) and SmA phase (that appears at lower temperatures). The molecular structure required to generate the TGBA phase is one, which has strong molecular chirality i.e. a very tight pitch and high enantiomeric excess. Additionally a weak layer ordering is thought to be required in order that the twisting is facilitated. The TGBA phase structure consist of the slabs of SmA phase, that are broken by screw dislocations which abruptly twist the molecular director of the neighbouring Smectic slabs with respect to each other through an small angle $\Delta\Psi$, thereby forming a helical structure (see **Figure 15**).

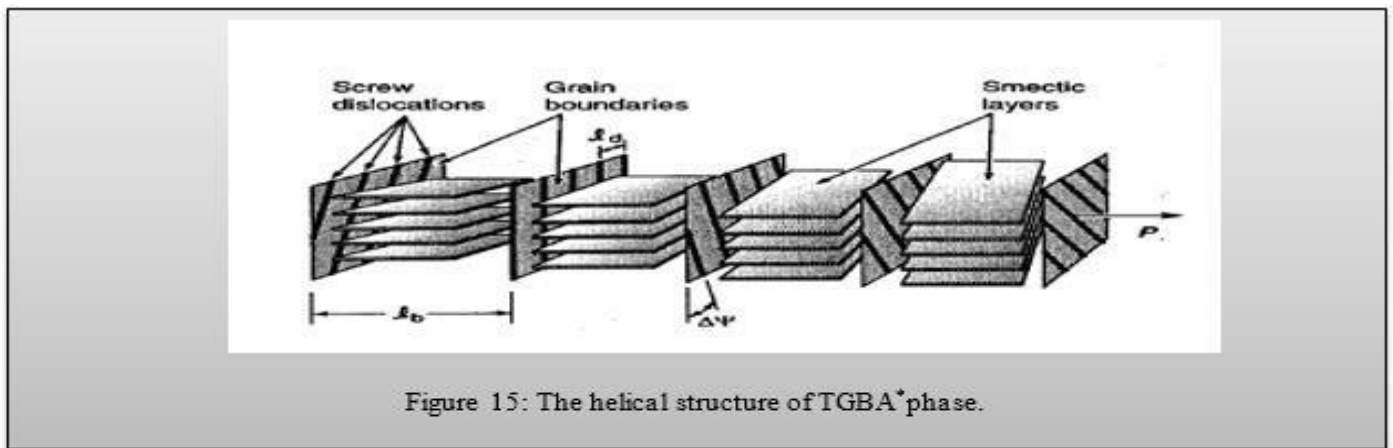


Figure 15: The helical structure of TGBA* phase.

The order within each slab is equivalent to the SmA phase. The molecules are uniaxially aligned along the local director \mathbf{n} and arranged in the layers. The layer normal \mathbf{Q} is parallel to \mathbf{n} . The layer spacing $d=2\pi/|\mathbf{Q}|$ is in the range of few nanometer (nm). The grain boundaries between the slabs are defect walls consisting of the parallel defect lines (twist dislocations). The distance l_d between defect lines are similar to the slab thickness l_b in the TGBA phase. The director \mathbf{n} forms a helical structure due to tilt between neighbouring slabs. The helix axis \mathbf{h} is perpendicular to the director and pitch is in the range of a few hundred nm to few μm . A length along helical axis corresponding to the twist of Smectic slabs (director) by angle 2π is the pitch of the TGB helix. Length of the Smectic slabs (l_b), distance between defect lines (l_d) and pitch (P) are related by equation:

$$\alpha = \frac{\Delta\chi}{2\pi} = \frac{l_b}{P} = \frac{1}{\pi} \tan^{-1} \left(\frac{d}{2l_d} \right) \approx \frac{1}{\pi} \sin^{-1} \left(\frac{d}{2l_d} \right) \quad (4)$$

Where d is the layer spacing and α is a number. If α is irrational, the structure is incommensurate i.e. there is no periodicity of the orientation of the slabs along the pitch axis however if α is rational, the system is commensurate and has an n -fold screw axis. Allen et al. [49] has carried out the first simulation of twist grain boundary phase in 1998, in which a twist is imposed on the direction of preferred orientation. On quenching the system from a twisted nematic phase to a state point within the Smectic A phase, they observe a structure which corresponds closely to that of TGBA* phase. The simulated structure is shown in **Figure 15** and in the qualitative agreement with the theoretical predictions. The typical smectic layers can be clearly seen in **Figure 16**. The molecules are colour coded by orientation to highlight the formation of distinct domains. The overall twist from the front to the back of the simulation cell is maintained by specially developed boundary conditions. Twist grain boundary phases exhibit three distinct structural features: (i) helical structure (ii) Smectic layers and (iii) a helical axis parallel to Smectic layer plane. Despite the fact

that TGBA phases are Smectic, their appearance in polarizing microscope observation shows strong similarities to the cholesteric phase.

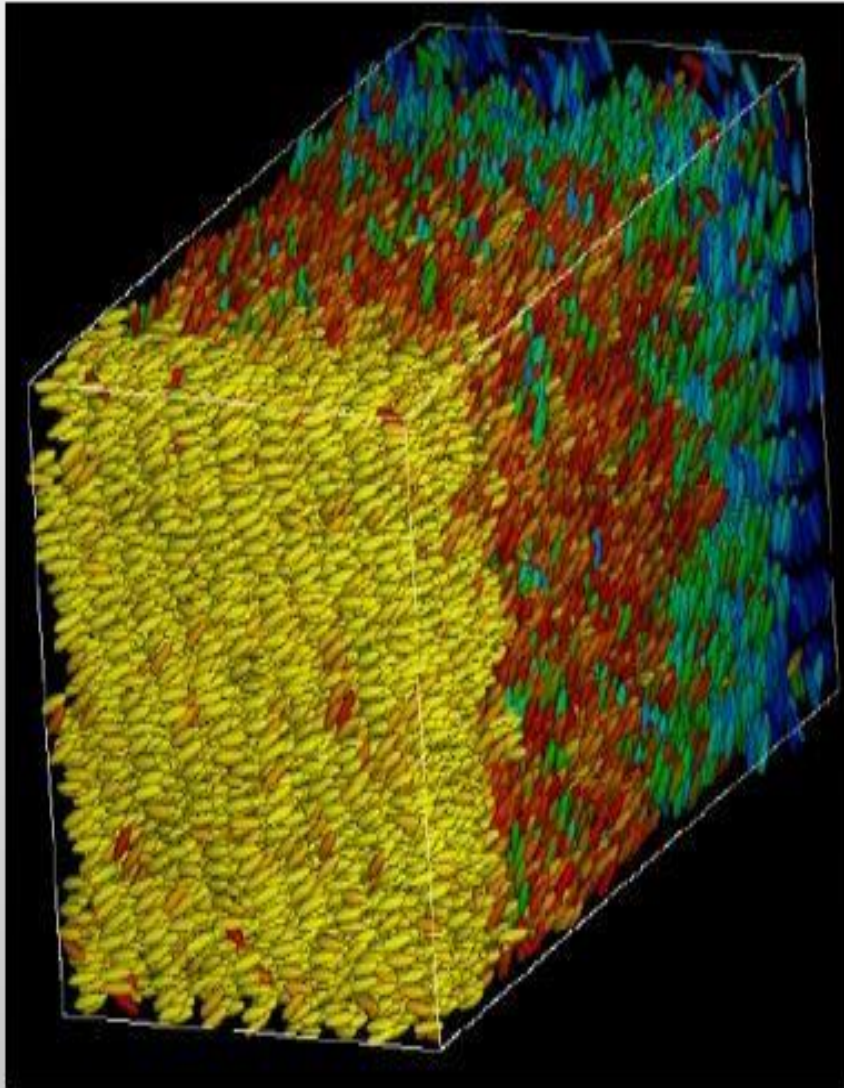
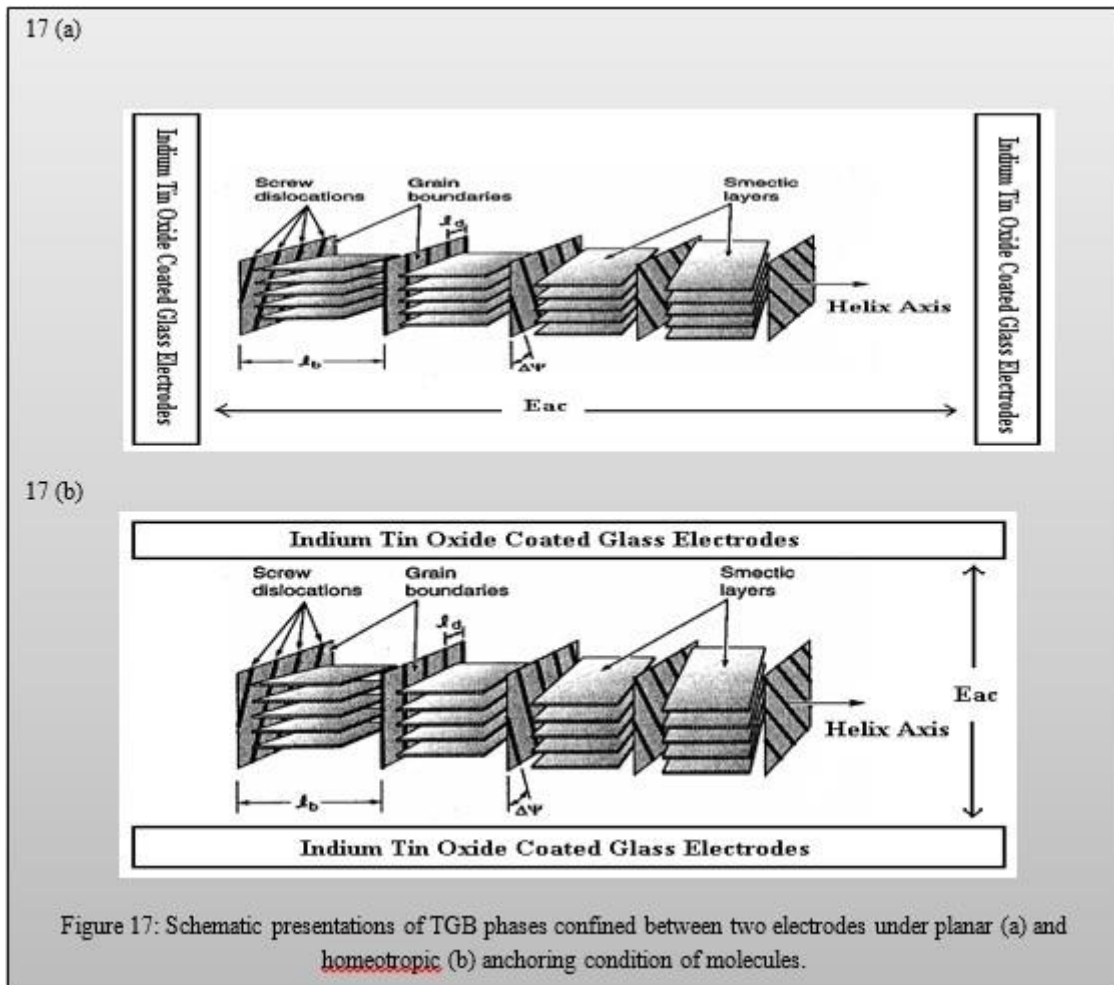


Figure 16: A snapshot from a molecular dynamics showing the molecular order in TGBA phases [49]. The molecules are colour coded by orientation to highlight the formation of distinct domains.

Preparation under planar boundary condition often results in Grandjean texture, while homeotropic alignment (director perpendicular to the substrate) generally shows the typical TGB filaments. Schematic diagrams of arrangement of the molecules in TGB phases in two measuring configurations i.e. planar and homeotropic are shown in **Figure 17**.

Twist Grain Boundary C and C* Phases: In 1992, Renn [45] predicted various types of TGB phases in the vicinity of A-N*-C* multicritical point within the framework of the chiral Chen-Lubensky model. He proposed the existence of two additional TGB phases on the SmC side of the phase diagram. Like the TGBA phase these additional TGB phases consist of a twisted array of two-dimensional Smectic slabs, stacked along pitch axis. The three phases are distinguished by the nature of the slabs: TGBA, TGBC, TGBC* consist of SmA, SmC and SmC* slabs respectively.



The first experimental realization of TGBC phase was done by Nguyen and co-workers [50] in 1992. TGBC phase is direct generalization of the TGBA phase, each Smectic block being like a small SmC material uniformly tilted in the same direction. The TGBC phase is reported to be a commensurate phase, with the ratio of the TGB helical pitch over the Smectic block thickness p/l_b , being an integer [51]. The structure and textures of the TGBA phase seems to be quite well understood. But to some extent the structure and texture of TGBC* phase is still a matter of discussion. Experimental evidence of existence of TGBC* was provided by Nguyen et al. soon after its prediction [50]. Owing to the local SmC* tilt of the molecules with respect to the Smectic layer normal and to the existence of a spontaneous polarization, several different structures may in principle occur in the TGBC* phase [45]. Generally, the SmC* phase exhibits a helical superstructure in bulk materials. For several possible TGBC* structures this twist is expelled into the twist grain boundaries. This means the local SmC* slabs exhibit a uniform tilted director configuration. Hence the TGBC* structure is more complicated and various TGBC* structures are possible. In this phase, the direction of the molecular tilt is twisted around the axis, perpendicular to the TGB helical axis and common to slabs of Smectic blocks. These superslabs or helislabs following Renn [45] are rotated from one another in the TGB axis direction, by an angle χ_1 consistent with the TGB helix. They give a second superimposed twist grain boundary structure to the TGBC* phase, where the defects are disclination lines. There are various models proposed to consider the configuration of TGBC* phase namely TGBc, TGBcp and TGBct [52]. A model proposed by Dozev et al. [53-54] for possible TGBC* structure, indicating a vanishing Smectic order parameter at the grain boundaries. Hence they called it melted grain boundary (MGB) phase and was named TGBct in reference [52]. Pramod et al. [55] have proposed a two dimensionally undulating to explain the double helix structure in TGBC* phase and called this the undulated twist grain boundary C* (UTGBC*) phase. The textures of TGBC* phase is analogous to those observed for TGBA: Grandjean textures for planar boundary conditions

and fingerprint/filament textures for homeotropic anchoring. There is however another variant of a TGBC* phase, which can easily be recognized and has become known as the square grid texture for planar anchoring conditions [56-57]. There seems to be good evidence that the square grid pattern is in fact due to TGBC* structure predicted by Renn [45]. In this case not only the occurrence of a helical superstructures due to the TGB helix is observed, but also the SmC* slabs exhibit the director helix of bulk SmC* phase, with the helix axis perpendicular to that of TGB twist. There are various models viz. TGBC₁*, TGBC₂*, UTGBC* etc. [52-55] proposed to explain the structure of TGBC* phase, but it cannot be conclusively decided, which model actually accounts for the occurrence of the square grid pattern. In any case, the TGBC* phase exhibiting the square grid texture must be three dimensionally modulated phase.

Blue Phases: An interesting phenomena in cholesteric materials is the observation of the so called blue phases between isotropic and cholesteric phase in a very narrow temperature range ~ 1 °C [58-59] but sometimes it may be super cooled in cholesteric phase [60] and may be observed for the temperature range of more than 10 °C [61]. Although blue phase was first observed by Reinitzer [1] in his very first paper of liquid crystal, but Lehmann [62] recognized it as a stable phase in 1906. Blue phases are characterized by short pitch [63-64]. Interestingly blue phase does not always have only blue colour and as temperature changes, colour of blue phase changes with a change in pitch. The temperature range of the blue phase is relatively narrow and is optically isotropic. The blue phase is further classified into three categories BPI, BPII and BPIII or gray phase occurring in the order of increasing temperature. All of them are optically active but isotropic. From observation of optical Bragg reflection [65] and other studies [61] it is found that BPI is body centered cubic lattice, BPII is a simple cubic lattice and BPIII is probably amorphous [66]. Some suggestions have been made that BPIII, called the blue fog, should be quasi-crystalline [67-68]. In 1991, a new BPIA phase have been discovered between BPI and cholesteric phase [69]. The presence of helical pitch causes equilibrium fluctuations of the director \mathbf{n} to be anisotropic and hence the phase becomes biaxial. It is found that the pitch induced phase biaxiality is very important in the vicinity of phase transition. As the blue phase is stable only in the neighbourhood of the isotropic phase, the phase biaxiality plays a dominant role in explaining the blue phases [70].

Chiral Line Liquid: The chiral line liquid (N_L^*) predicted by Kamien and Lubensky [71] is the analog of the flux line liquid occurring in type II superconductors with strong fluctuations. Instead of forming of regular array, the defects are rather disordered. However, the precise structure of the N_L^* phase is still unknown. Calorimetric studies [72] shows that an additional state occurs in liquid crystals between the TGBA phase and the usual cholesteric (N^*) phase. The transition from TGBA phase to this N_L^* phase is found to be first order transition [72-73] with very small latent heat. The N_L^* phase develops rather continuously into N^* phase on heating. The change from N_L^* to N^* phase is accompanied by a very broad peak of the heat capacity which extends over several K. The X-ray studies [74] have revealed a commensurate TGBA structure in presumed TGBA temperature range and an incommensurate TGBA-like structure with quasi long range Smectic order in presumed N_L^* temperature range.

Conclusions: In this review article various aspects of liquid crystal science has been summarized as following manner:

- Liquid Crystals and its Historical Perspective
- Brief Description of the Relevant Phases: Classification by Chemical Point of View
- Thermotropic Liquid Crystal
- Lyotropic Liquid Crystal
- Amphotropic Liquid Crystal
- Metallotropic Liquid Crystal
- Molecular Structures

- Classification by Ordering: Orientational Order and Positional Order
- Liquid Crystals Phases: Nematic Phase, Smectic Phase, Smectic A (SmA) Phase, and Smectic C (SmC) Phase.
- Phase Sequences of Liquid Crystalline Materials
- Symmetry and Chirality in Liquid Crystals
- Chiral Nematic Phase (N^{*})
- Chiral Smectic Phases
- Ferroelectric Chiral Smectic C Phase
- Antiferroelectric Chiral Smectic C Phase
- Other Antiferroelectric Chiral Smectic C Phase
- Ferrielectric Chiral Smectic C Phase
- Frustrated Chiral Phases: Twist Grain Boundary A Phase, Twist Grain Boundary C and C^{*} Phases, Blue Phases, and Chiral Line Liquid

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