CHAPTER-1

Introduction

1.1. Liquid crystals

Liquid crystals (LCs) are partially ordered anisotropic fluids, thermodynamically located between the three dimensionally ordered solid state crystals and the isotropic liquids [1-2]. They are very important [3] materials with many interesting properties and are uniquely identified for their applications in display devices [4,5]. The coexistence of fluid like and the crystalline properties [6] utilize them in many applications [7-8] like electro-optic display devices, thermography, medical diagnostic tools and so on. This peculiar phase of matter was originally discovered by an Australian botanist Reintzer [9] in the year 1888 and after that, named as liquid crystals by Otto Lehmann [10]. The presence of dual characteristics profoundly influences on both the physical properties as well as on the phase transitions and hence, they can response in a subtle and complex manner [11] by the application of external stimuli such as optical, thermal, electrical, magnetic, mechanical *etc*. This behavior of LCs renders to be surprising as well as very much usable [12,13] in the construction of flat panel displays.

In the year 1922, long time after the discovery of LCs, it had been pointed out on the basis of temperature variation of microscopic textures [14] that LCs can form different types of phases namely nematic, smectic, cholesteric *etc*. Many efforts have been made to investigate their structure, systematic classification of phases and their physical properties both theoretically and experimentally by means of various studies such as texture study, Differential Scanning Calorimetry (DSC), optical study, electrical study, X-Ray diffraction, Nuclear Magnetic Resonance (NMR) *etc*. [15-18]. The research works in the field of liquid crystalline phase transitions have been devoted [19] first few decades for better understanding of the phenomenon of critical fluctuations [20] associated with the phase transitions. The research activity in this field have found a new direction after the starting of its use in electro-optic displays since the year 1970 [21,22]. The synthesis of liquid crystalline materials has become most efficient and versatile field in both fundamental as well as applied aspects in soft condensed matter physics. Since then, physicists, chemists, biologists and technologists work together to exploit the fascinating science hide behind the LCs. However, in present times the field of liquid crystal provides a good platform for the researchers to investigate different types of phenomena such as phase transitions, collective motions [23-27], self-organized [28,29] criticality as well as physical properties associated with various liquid crystalline materials.

It has been found that [30] depending on certain geometrical and configurational constraints with respect to molecular structure and design, the LC materials exhibit their liquid crystallinity over a certain temperature range. The melting of crystal occurs by the disturbance of the center of mass of the molecules to some extent with enhancement of the temperature. The diffused X-ray pattern indicates the existence of some sort of short-range orderings that is the change of symmetry. These types of investigations strongly suggested the appearance of short-range positional order in addition to the long range orientational order that the various LC phases have. However, the substances loss these orders by heating into the liquid state. The state of the polarization of emergent light can be changed by some optically active solids such as calcite, quartz crystal *etc*. [30]. It has been found that some crystalline substances exhibit a strong birefringence behaviour after its change of state into turbid liquid crystalline state through melting when observation takes place between two polarizers crossed with one another. A clear liquid state reach from the turbid fluid at the clearing point on further heating the sample. The temperature range between the melting point and the clearing point of this turbid phase [10] is the 'liquid crystalline phase' or mesophase which is thermodynamically stable over a certain temperature range. The phase transitions among the various mesophases take place by two types of nature, one is the first order, in which an abrupt jump of physical parameters such as latent heat, density, birefringence or spontaneous polarization take place and the other is second order in which changes of those physical parameters occur in a continuous manner. The research involving the nature of phase transitions between different mesophases is one of the most important area in the field of soft condensed matter physics. Figure-1.1 shows the formation of liquid crystalline phases with the variation of temperature.

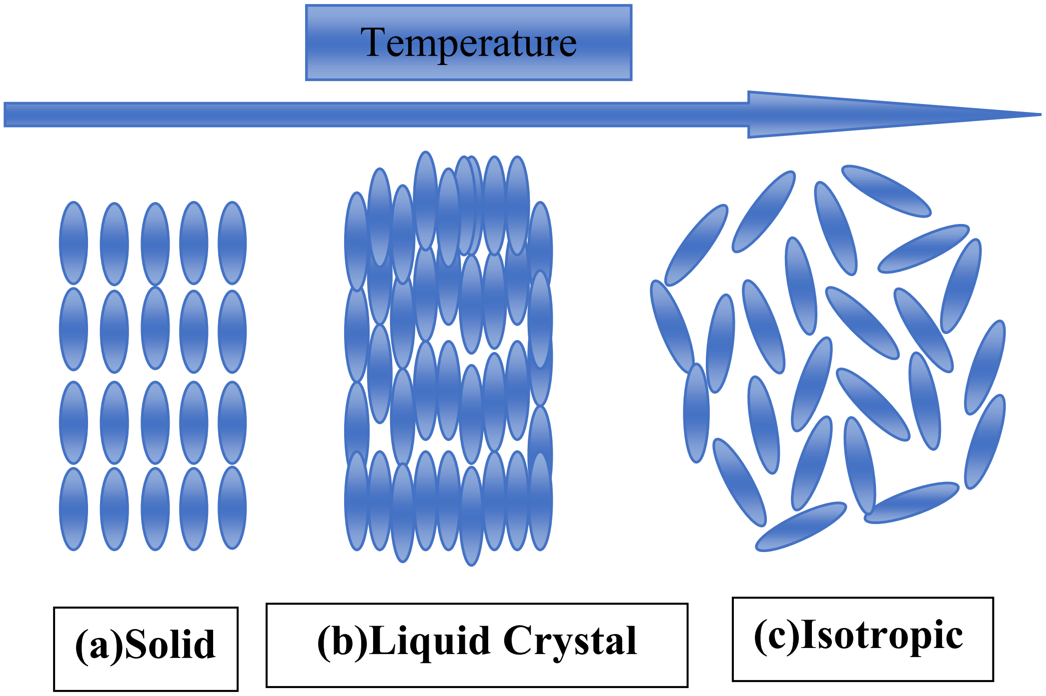


Figure-1.1: Schematic representation of molecular packing in the **(a)** crystalline solid **(b)** liquid crystal and **(c)** isotropic liquid state.

Due to the presence of inherent tunable birefringence and anisotropy, LCs have been gradually attracted in the field of electro-optic display devices [31,32]. The advancement of ferroelectricity in the tilted smectic phase [33] (SmC^*) with surface stabilized geometry gives a startling momentum on the research activity involving the ferroelectric liquid crystals. The fast response time [34] of the order of sub-micro second regime in surface stabilized ferroelectric liquid crystals (SSFLCs) [35-38] or nano-second orders in electroclinic effect [39-41], in comparison with the conventional nematics operated at milli-second speed, established a milestone achievement in the field of LC research. In the present days, the technology of LC display devices [42-44] competes with others due to their attractive features such as low power consumption, compactness, large birefringence, large viewing angles, high contrast ratios and reliable bistability. The anisotropy in some physical parameters and tunable birefringence are the most effective properties of LC systems.

In this thesis various liquid crystalline systems including achiral and chiral compounds have been chosen in order to investigate the phase transitions of different mesophases and simultaneously some physical properties have also been studied for few chiral ferroelectric liquid crystalline compounds. The main focus has been made on critical behaviour and to determine the nature of the phase transitions in order to check their universality class by preparing suitable liquid crystalline bi-component mixtures.

1.2. Classification of liquid crystals

Liquid crystals are generally classified on the basis of some factors such as (i) external controlling factors and (ii) shape of the molecules.

1.2.1. External controlling factors

Depending on the external controlling factors, for example concentration of solvent in a solution or by the thermal agitation, the transition between different liquid crystalline phases can occur [30]. On the basis of this point of view, liquid crystals are uniquely classified into two types, namely ‘lyotropic liquid crystal’ and ‘thermotropic liquid crystal’.

1.2.1.1. Lyotropic liquid crystal

In the lyotropic liquid crystals the stability of these LC phases is strongly determined by concentration of some solvent in the solution [1]. In the year 1850 during the observation of birefringent textures of a system made up of myelin collected from nerve cells (from protector sleeve that protects nerve cells) and water under polarizing optical microscopy, lyotropic liquid crystals were said to be discovered. The isotropic solution of solute particles having molecules with hydrophilic and hydrophobic end groups in the solvents such as water, alcohols *etc*., represent lyotropic liquid crystalline phases [45-49]. The presence of a polar ionic head group (such as water like solvents) and non-polar hydrocarbon chains associated with the molecules gives rise to the amphiphilic nature of the lyotropic LC phases.

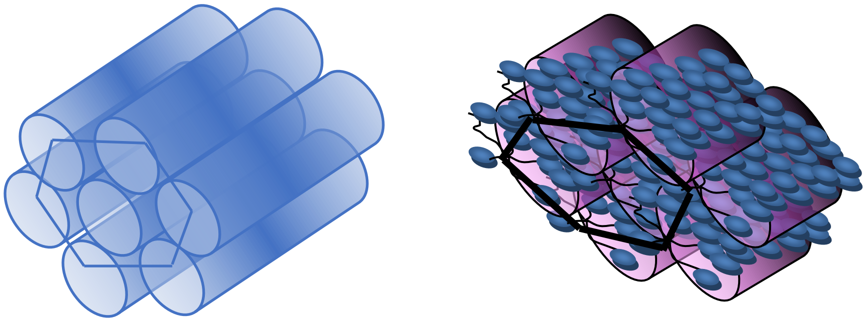


Figure-1.2: Shape of columnar liquid crystals

Although concentration of the material in the solvent is a crucial factor on determining the structure of lyotropic phases [50], temperature can also affect on the change of structures in certain systems. Figure-1.2 shows the schematic representation for columnar liquid crystals. There exist mainly three types of lyotropic liquid crystals [51-53], which are named as lamellar, hexagonal and cubic phases. The helical structures also present in the chiral lyotropic LC's [54].

1.2.1.1.1. Colloidal lyotropic phases

Colloidal lyotropic liquid crystal can be formed by the solution of biomolecules such as proteins, DNA type biomolecules and surfactants solution with high concentration. The variation of concentration can easily change the phases. These mesophases [1,55] were first observed by Onsagar [56] and Flory [57]. Precipited metal oxide, synthetic polypeptides and rigid polymers in appropriate solvents are some examples of these type of LCs. Extensive studies have been performed on the solution of DNA molecules, on some proteins and viruses to observe their liquid crystalline properties. Some analogous phases of nematic and smectic mesophases of thermotropic liquid crystals have been observed in the tobacco mosaic virus (TMV).

1.2.1.1.2. Self-assembled structures

In addition to small molecules, polymer liquid crystals, solution of DNA and viruses also shows liquid crystalline behaviour. These self-assembled structures are formed by some class of materials which consists of amphiphilic molecules in a solvent. Lyotropic micellar systems have formed spontaneously by these types of lyotropic LCs. The soap solution in water is an example of such system which consists of a polar head group and one or more hydrocarbon tails. When in a solvent, enough number of such molecules are dissolved, the occurrence of shielding from the polar water environment by the segregation of hydrocarbon tails take place which accounts for the lowest free energy state leading to the formation of aggregates of molecules.

Such aggregations of molecules are termed as micelles which are not covalently bonded and can exhibit several different geometries depending on the chemical nature of the molecules as well as thermodynamic conditions. The aggregates may be rod like or disc like with the presence of orientational and /or positional orderings to show a wide range of liquid crystalline phases including isotropic, nematic, lamellar, hexagonal and cubic phases [1,11]. Figure-1.3 shows the schematic diagram of lyotropic liquid crystals.

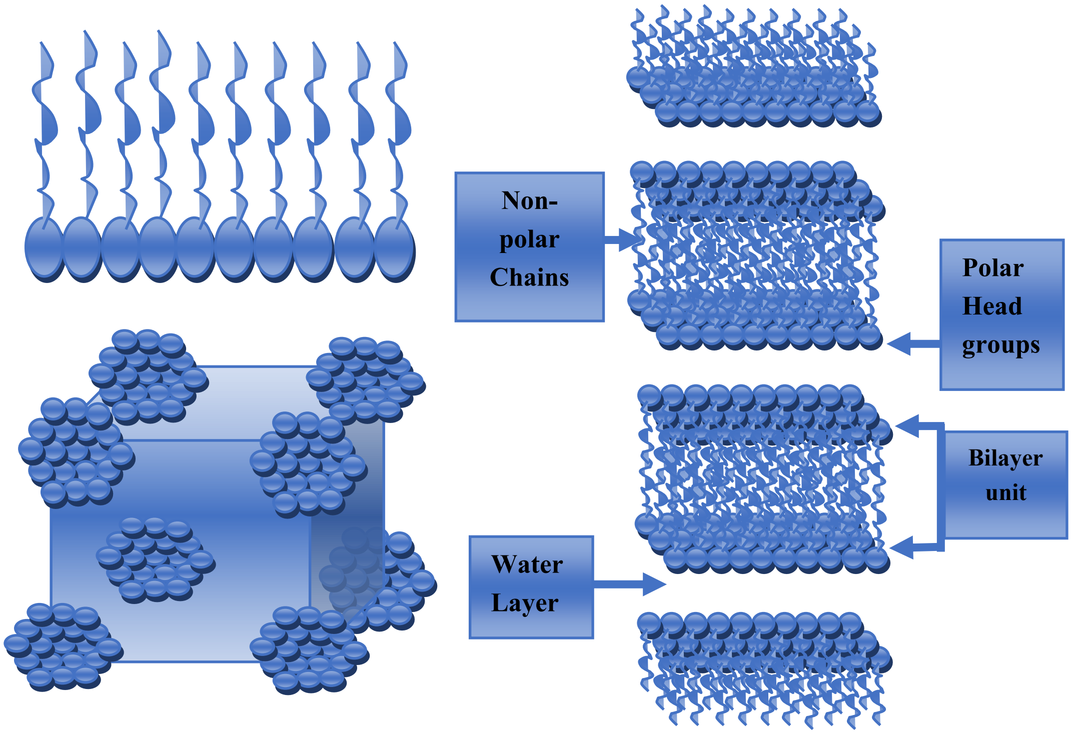


Figure-1.3: Schematic diagram of lyotropic liquid crystals (structure of the lamellar lyotropic liquid crystal).

1.2.1.2. Thermotropic liquid crystals

Thermotropic liquid crystals are such kind of materials in which the stability of structures [30,58,59] and the occurrence of different mesophases have strong dependence on temperature. The isotropic liquid state with the simultaneous disappearance of the long range positional and orientational orderings obtained from most of the crystals on heating. The presence of certain amount of shape anisotropy in the molecules, may cause the disappearance of long-range translational periodicity (in one, two or three dimensions) in the crystal preceding the collapse of the long-range orientational order. Such type of compounds without showing a single transition on entering from solid to liquid state, exhibits a cascade of transitions involving liquid crystalline phases having properties (mechanical and symmetry) intermediate between those of liquid and crystal. The transformation of a crystal into mesophase occurs at certain temperature which is known as melting point while the temperature at which the mesophase transforms into the isotropic state is called clearing point. The thermotropic LC property exhibited by most of the compounds consists of organic molecules. Although there are numerous numbers of organic compounds exist but only a small fraction shows LC properties. Such type of compounds that exhibits the behaviour usually consists of two parts one is hard or rigid part and the other is soft flexible part. The core region (aromatic or non-aromatic) accounts for the rigid part while end alkyl chains give the soft regions of the molecules. However, the specific combination of these two distinct parts give rise to a particular anisotropic shape of the molecules.

The flexible end chains of the molecules provide the mobility of the LC systems. The parallel alignment of anisometric molecules (having two unequal axes) give rise to the orientational order while the positional order comes into play due to the specific attractive forces and amphiphilicity. The efficacy of these type of molecular interactions are strongly determined by the existence and magnitude of permanent dipole moments as well as anisotropy in molecular polarizability. Thus, the shape anisotropy in molecules plays a crucial role in determining the formation and type of the liquid crystalline mesophases. Figure-1.4 shows the different mesophases arises with the variation of temperature.

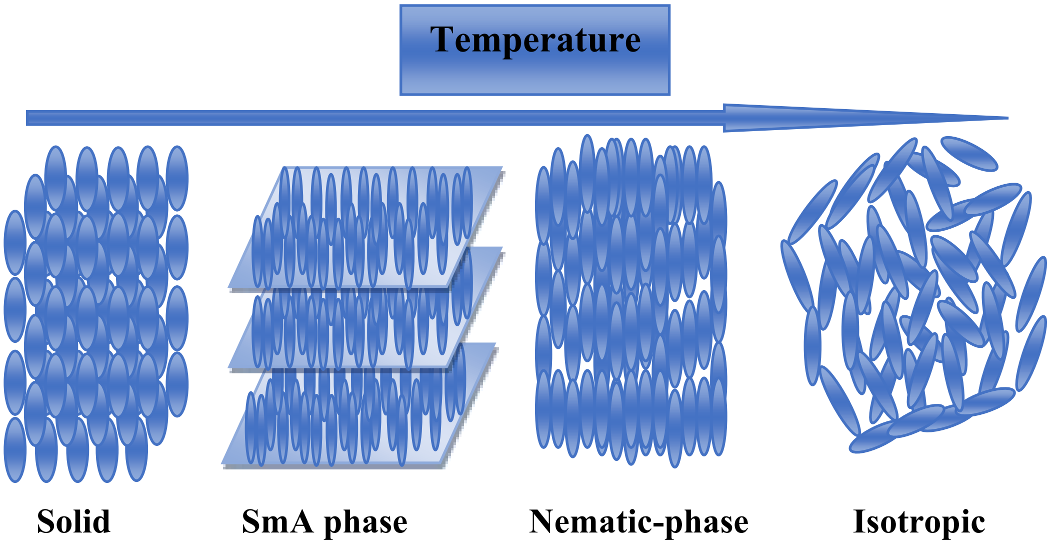


Figure-1.4: Different liquid crystalline phases with the variation of temperature.

1.2.2. Liquid crystals formed by the shape of the molecules

1.2.2.1. Calamitic liquid crystals

Calamitic liquid crystals are mainly consists of the rod like molecules [60]. After many years of research on liquid crystals, a general conclusion drawn by the researchers is that, liquid crystalline properties exhibited by the compounds must have certain requirements on their structures. The elongated shape of the molecules where its length should be more than its width is the first requirement of the compounds that possess the LC behaviour. An attractive force which is very strong in nature must associated with the elongated molecules. The probability of collision of molecules among themselves is very small because of their tendency to point in the same direction which gives the stable structure of the whole LC compounds. Besides that, the rigidity of the core structure and the flexibility of the end chains associated with the molecules also helps in the formation of the stable structure. The flexibility of the molecules helps them to situate among the cluster of molecules when move around. In order to show the liquid crystalline properties [61] both flexibility and rigidity of the molecules must be in balance with each other. The general structure of a calamitic LC molecule is shown in Figure-1.5. Where ‘C’ denotes the core group which is generally an aromatic ring such as benzene rings and some other available aromatics are saturated cyclohexane, biphenyl, terphenyl, unsaturated phenyl in various combinations.

Most of the liquid crystals are benzene derivatives [62] and there is a structural similarity between heterocyclic liquid crystals and benzene derivatives, with the replacement of one or more benzene rings by a pyridine, pyrimidine or other similar groups. ‘R’ represents the terminal group; few examples of end chain and terminal groups are alkyl (C_nH_{2n+1}), alkoxy ($C_nH_{2n+1}O$) and others such as alkylcarbonate, alcyloxyl, alkoxycarbonyl, nitro as well as cyano groups *etc*. The bridging or linking groups are denoted by ‘B’ and ‘L’, these are simple bonds or groups such as ester (-COO-), Schiff base (-CH=N-), stilbene (-CH=CH-), azoxy (-N=N-), acetylene (-C≡C-) and diacetylene (-C≡C-C≡C-) *etc*. The name of liquid crystalline compounds is often known by their nature of linkage group such as Schiff-based liquid crystal. ‘X’ denotes the substitution in the lateral position on the core groups which may be hydroxyl, halogen, methyl *etc*. Again, derivatives of cholesterol can form chemical compounds which exhibit the cholesteric or chiral liquid crystalline phases.

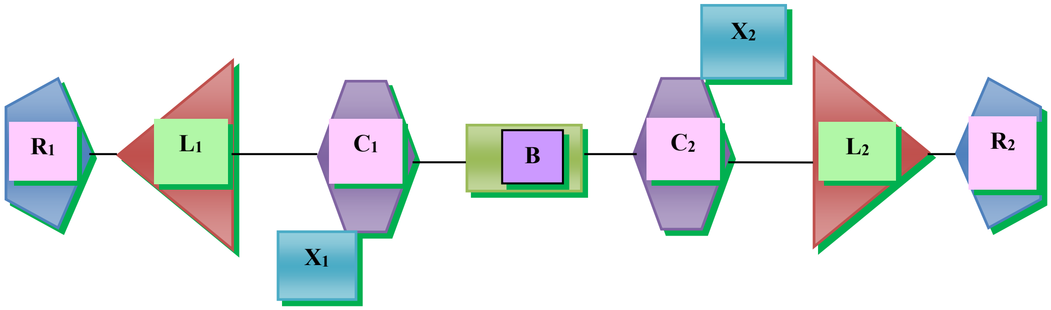
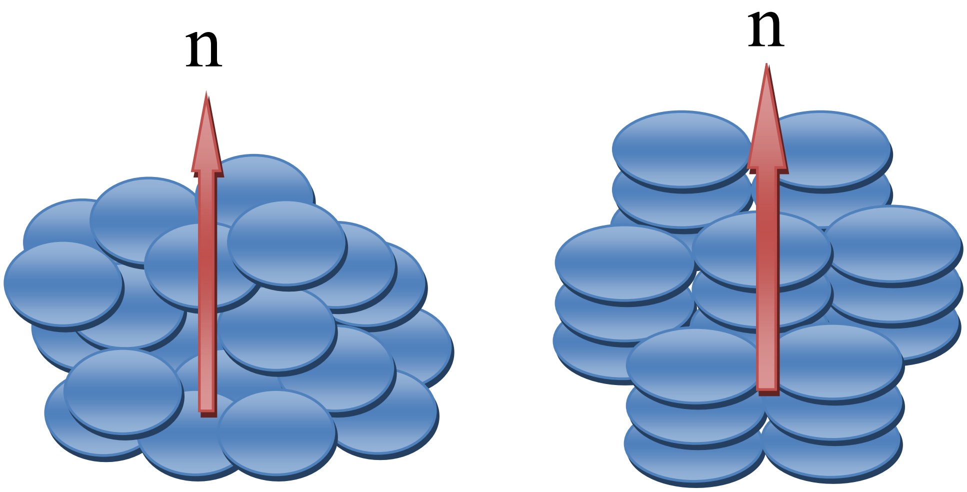


Figure-1.5: General structure of calamitic liquid crystal.

1.2.2.2. Discotic liquid crystals

In this type of liquid crystals, the phases consist of columnar structures in which columns are formed by the parallel alignment of the molecules having disc shape [63]. These molecules are capable to form self-assembled structures due to their disc or flat shape and remain packed in different forms. Some specific discotic LC phases also formed by the packing of disc like molecules, one over the other, such as in columns (hexagonal). There is a conspicuous irregular spacing between the discs within each of the columns. This type of structure has two directional translational periodicity and in the third dimension the liquid like disorder prevails in order to impart their identity among the liquid crystals. The designation of this phase of matter is ‘disc-like mesophase’.



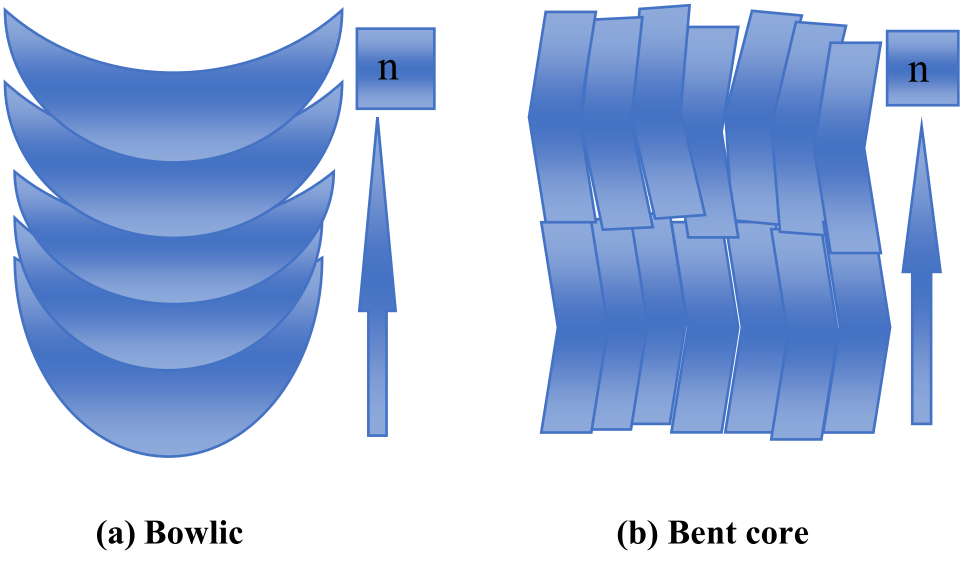
(a)Discotic Nematic **(b)Discotic Columnar**

Figure-1.6: Shape of discotic liquid crystals.

A nematic phase can also form [63] by the discotic LCs with the presence of long range orientational order, without any long-range positional order (with a director parallel to the disc normal). This type of phase is denoted as N_D phase, the discotic nematic can exhibits a twisted structure among the chiral LC compounds. Figure-1.6 (a-b) shows the shape of the discotic nematic and discotic columnar phases.

1.2.2.3. Bowlic liquid crystals

Lim [64] first proposed about these types of LCs formed by pyramidal or cone shaped molecules also look like bowl in three dimensional aggregates. They can also show mesophases which are similar to those of the one-dimensional rod like as well as two-dimensional disc like compounds. Figure-1.7(a) shows the shape of the bowlic liquid crystal.



(a) Bowlic

(b) Bent core

Figure-1.7: Shape of bowlic and bent core liquid crystals.

1.2.2.4. Bent liquid crystals

The bent or banana shaped molecules [65] form bent liquid crystals (BLCs). This type of liquid crystal exhibits both nematic and smectic like orderings. Further, there is conclusive establishment of the structural classification of these molecules. Figure-1.7(b) shows the shape of a bent core liquid crystal. So far, the different mesophases in bent core liquid crystals are identified [66] as B1, B2…… B7, B8. Various bending angles of these type of liquid crystalline compounds are confirmed by nuclear magnetic resonance (NMR) studies [65-68]. Nematic like textures are observed in the compounds which have lower angles, while different phases are formed by higher angle compounds. The presence of ferroelectricity and anti-ferroelectricity in bent core liquid crystalline phases, in spite of the absence of a chiral center is the most peculiar behavior of these supra molecular BLCs.

1.2.2.5. Polymeric liquid crystals

This type of structure mainly consists of some mesogenic subunits (may be either rod like or disc like) connecting together with flexible rings known as the main chain polymer liquid crystals (PLCs). Alternatively, if the mesogenic subunits is attached as side groups to the polymer chains are known as the side chain PLCs. The nature of the phases formed by this type of liquid crystalline compounds strongly depends on the spacers, backbone, flexible links *etc*. [69,70]. A schematic representation of these LCs has shown in Figure-1.8. These can be classified [68] into different classes (Figure-1.8) based on the type of flexible alkyl chains attached to the main core.

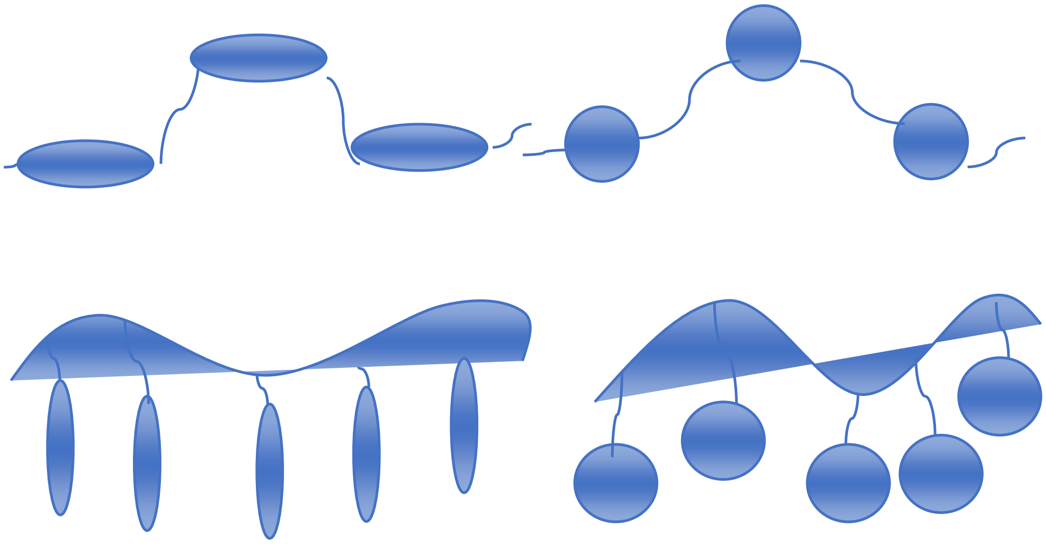
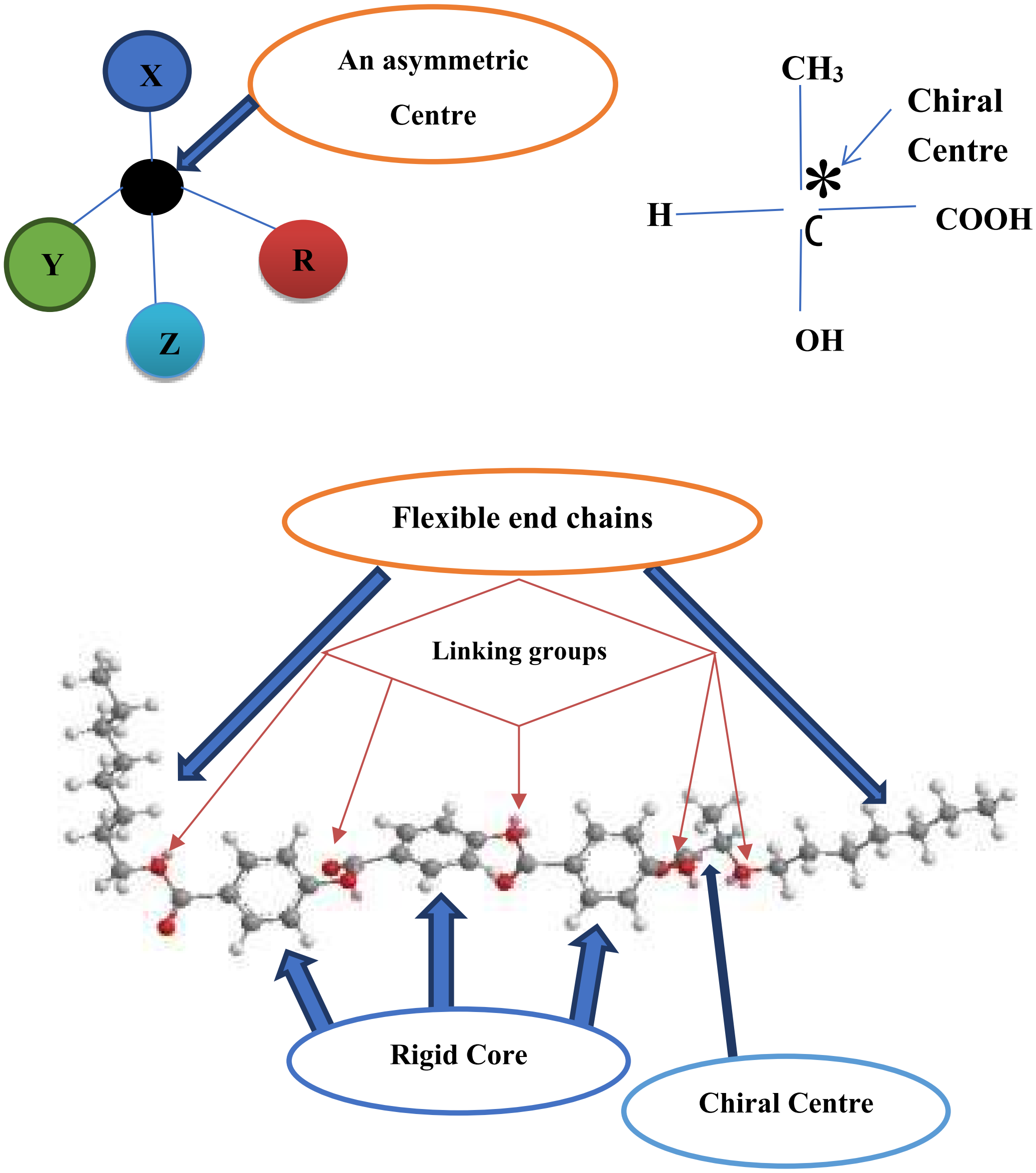


Figure-1.8: Schematic shape of polymeric liquid crystals.

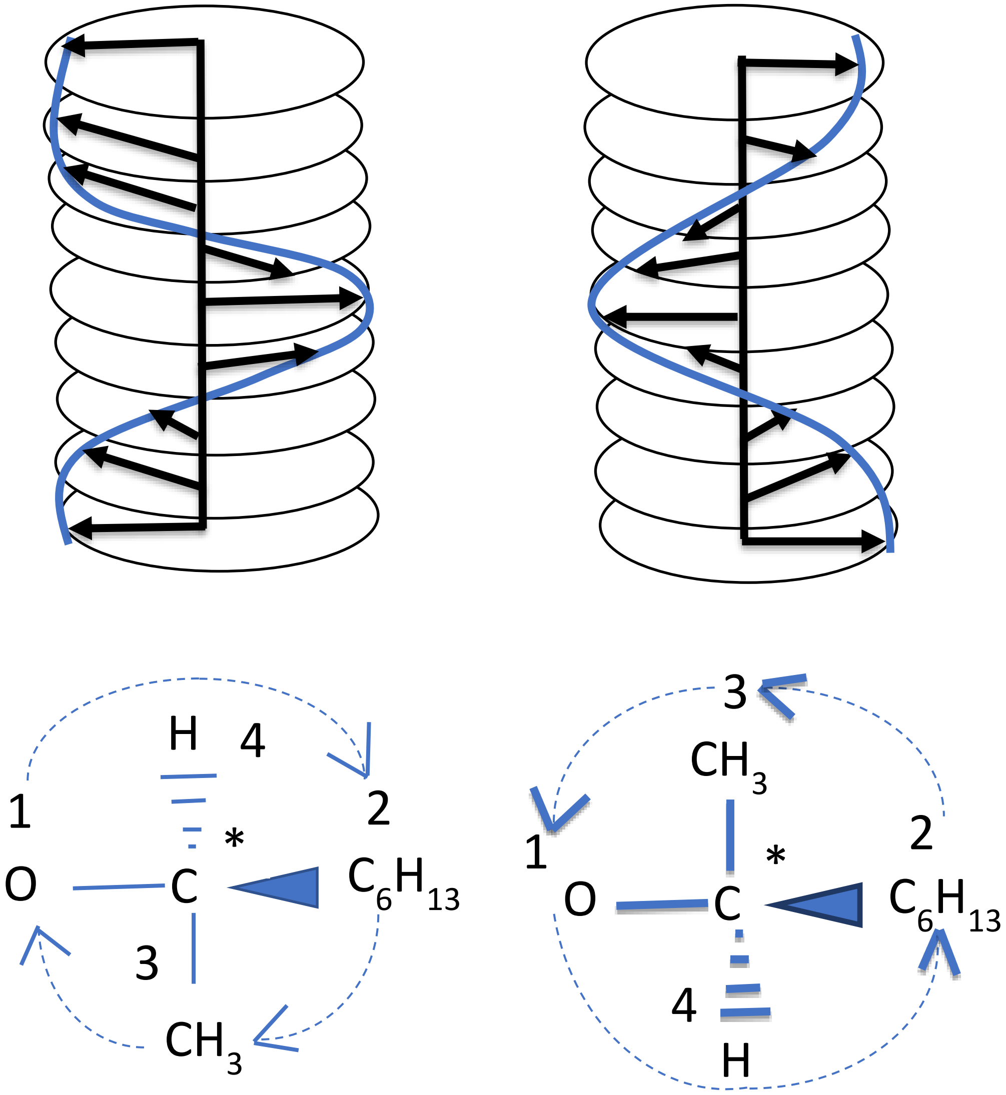
1.2.2.6. Chiral liquid crystals

Liquid crystalline compounds can also made up with chiral (lack of mirror symmetry) molecules [54]. The chirality on LCs can be induced mainly by two ways (i) asymmetrical substitution of the carbon atoms surrounded by four different ligands can include chirality within the molecule (ii) by preparing mixtures of chiral compounds as a guest with the existing non-chiral liquid crystals as a host with varying concentration and it has been observed that chirality effect increases linearly with the dopant concentration. It has been found that different physical properties are strongly affected by the introduction of chirality to some systems; for instance, the helical superstructures, in which the director shows a spirality along a certain specific direction in space, is the main characteristic features of chiral nematic or cholesteric phases.



Molecular conformation of Chiral FLC compound E8/7

Figure-1.9: Structure of a chiral molecule.



Clock wise rotation

R-enantiomer

Anti-Clock wise rotation

S-enantiomer

Figure-1.10: Schematic diagram of R and S-enantiomers.

The helical pitch accounts for the reflection of circular polarized light [71], that may be used in several LC applications. Also, the helical structure is associated with the chiral smectic-C* phase [72], which exhibits the properties of ferroelectricity such as spontaneous polarization. The spontaneous polarization is compensated locally by the formation of the helical superstructure. Besides the chiral phases some novel, frustrated phases have also been observed in the chiral materials known as blue phases [73] (BPs) and the twist grain boundary phases (TGBs) [54,74]. Blue phases (BPs) have novel and superior display effects over nematics. So far, numerous chirality related effects have been observed, which can be exploited in various novel displays, polarization modulators, light shutters, lasers and other photonic devices, like sensors, LC thermometers *etc*. The molecular optical activity is one of the most obvious effect which has been observed both for liquid as well as non-liquid crystalline materials. Again, the structural optical activity arises due to the helical superstructures with a pitch lies in the visible range of the optical spectrum and electric effects (the occurrence of ferroelectricity and antiferroelectricity) as well as the effect similar to the piezoelectric effect associated with the solid-state materials known as the electroclinic effect. Due to the presence of chiral center the enantiomeric effect has also been observed in the liquid crystalline compounds made up of chiral molecules. One is known as the R-enantiomer with the rotation of the helix in clockwise direction and another is the L-enantiomer with the helical rotation in anti-clockwise direction. Figure-1.9 shows the molecular conformation of a chiral liquid crystalline compound and Figure-1.10 represents the molecular conformation of R and S-enantiomers.

1.3. Types of orderings present in the anisotropic liquid crystalline phases

1.3.1. Order parameters

In typical liquid crystals depending upon the temperature the order parameter values [75,76] lie in between 0.2 to 0.9. The value of unity refers perfect order while an isotropic state corresponds to an order parameter value equal to zero. Figure-1.11 shows the schematic representations of the three order parameters (orientational, translational and bond orientational).

1.3.2. Orientational order

The tendency of the molecules to align along a preferred direction called the director on a long-range basis can be described by the orientational order. For example, in a nematic liquid crystal, their exists an average orientational distribution function $f(\theta)$, where θ is the angle between the molecular long axis and the director. A series of Legendre polynomials can well describe the distribution function as,

$$f(\theta) = S_0P_2\,(\cos\theta) + S_2P_2\,(\cos\theta) + S_4P_4(\cos\theta) + S_6P_6\,(\cos\theta) + \cdots \tag{1.1}$$

The Legendre polynomials are denoted by $P_n\,(\cos\theta)$ and S_n represents the co-efficients associated with the orientational distribution function. As the director can have only two opposite directions, $+\mathbf{n}$ or $-\mathbf{n}$ only even powers of the Legendre polynomials are retained. After proper normalization the dominant parameter S_2 can be used as the orientational order parameter.

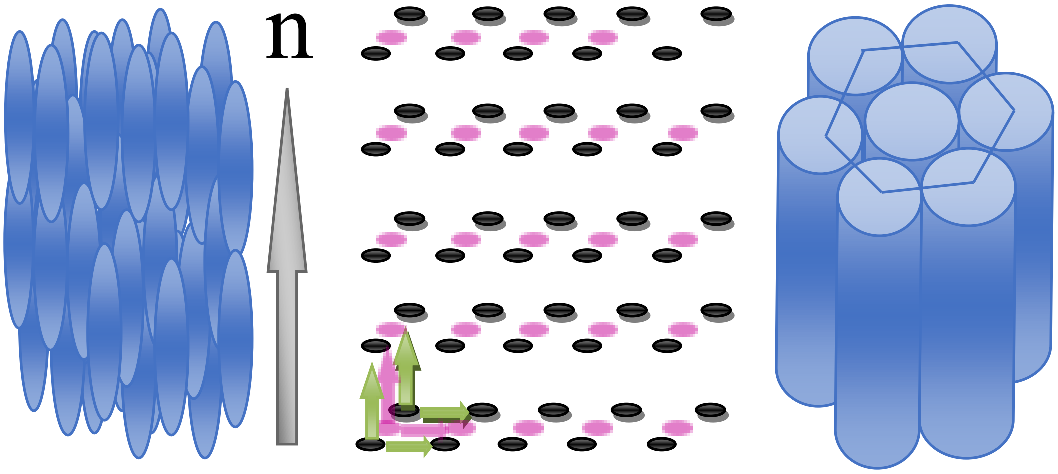
$$S_2 = \frac{1}{2}\langle 3cos^2\theta - 1\rangle \tag{1.2}$$

1.3.3. Translational order

The positional extent of the translational symmetry of an average molecule or group of molecules can be well described by the positional order. For example, the tendency of the molecules to form a layered structure can be described by an average density of the centers of mass $\rho(z)$, which varies along the normal to the layers in a sinusoidal fashion. The amount of positional order may be described by the amplitude of the sinusoidal part Ψ and may be represented as an order parameter:

$$\rho(z) = \rho_0\left[1 + \Psi\cos\left(\frac{2\pi z}{d}\right)\right] \tag{1.3}$$

where ρ_0 represents the average density and 'd' denotes the spacing between two adjacent layers.



(a) (b) (c)

Figure-1.11: Schematic representation of order parameters **(a)** Orientational order parameter **(b)** Translational order parameter **(c)** Bond orientational order parameter.

1.3.4. Bond orientational order

The bond orientational order parameter describes a line that joins the nearest neighbour molecular centers. Thus, a long range as well as short range positional order with respect to the line of centers become possible. This order parameter plays a vital role in the phase transitions related to the hexatic phases. Mathematically, the bond angle variation can be expressed as,

$$\Psi_6 = I_6 e^{6i\varphi} \tag{1.4}$$

where, φ is the azimuthal angle and I_6 represents the complex order parameter.

On the basis of these order parameters and other properties, the liquid crystals are broadly classified into the various intermediate phases.

1.4. Liquid crystalline phases

1.4.1. Liquid crystalline phases formed by thermotropic calamitic liquid crystals

1.4.1.1. Non-tilted phases

1.4.1.1.1. Nematic (N) phase

Nematic phase is the simplest among the known LC phases and it appears just below the isotropic state having viscosity which is comparable to those of the isotropic liquids. Thus, it is generally the least viscous phase among all the mesophases.

The nematic phase is characterized only by the presence of the orientational order or lack of the positional order, in that sense, this is the least ordered, more symmetric liquid crystalline phase. In this phase the molecular long axes of all the molecules are most likely to point in a specific direction, called the director, denoted by '**n**'. That means, in the nematic phase the molecular center of mass of each molecule arranged in a disordered manner similar to liquid phase but there is a statistical parallel orientation [77,78] of the long axes of the molecules along the director (**n**) leading to the long range orientational order. However, the director (**n**) can possess any arbitrary direction. Although, there is a variation of molecular direction from point to point inside the medium, a sample aligned uniformly is optically uniaxial and birefringent. The nematic phase with homogeneous alignment exhibits schlieren brushes [79], threaded marble and pseudo isotropic textures [29] when viewed under polarizing optical microscope.

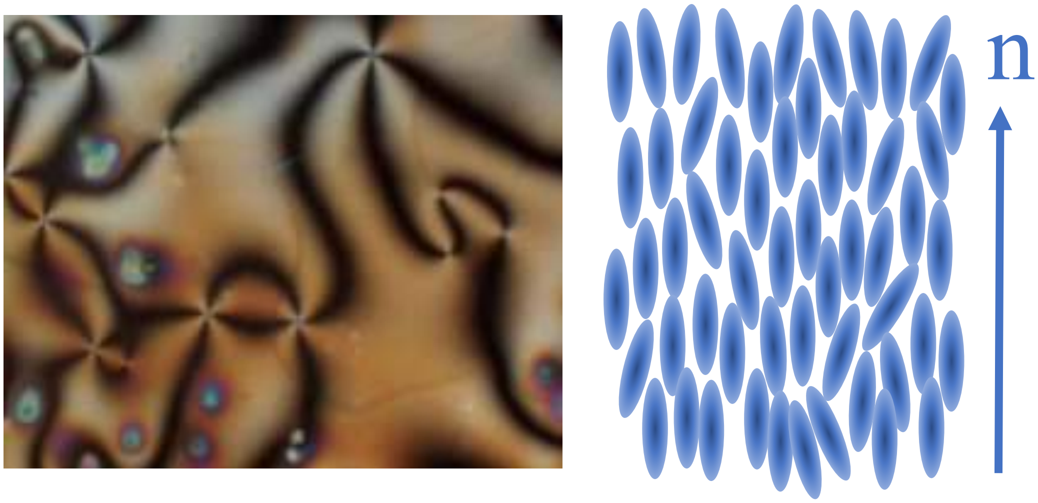


Figure-1.12: Texture and molecular arrangement of typical nematic liquid crystalline phase.

The homeotropic alignment of the nematic phase shows uniaxial cross under conoscopy. A biaxial nematic liquid crystal has been observed in organo metallic LC complexes by Chandrasekhar *et al.* [78] in the year 1987. Another type of nematic has also been observed which termed as cybotactic nematic in which short-range smectic-like ordering is present with the long-range orientational order. These are mainly two types one is skewed cybotactic nematic in which the layered structure of the molecules not only possess smectic like order but also significantly tilt with respect to the layer normal and the other is normal cybotactic nematic in which there is a parallel alignment of the molecules with respect to the normal of the layer of smectic like groups. The application of an electric field can switch the molecular orientation and in the two possible orientations the different optical properties make them very much useful in display devices. Because of the alignment of the molecules parallel with their long axes, they can display anisotropic physical properties. Figure-1.12 represents the characteristic texture and the molecular arrangement of a typical nematic liquid crystal.

1.4.1.1.2. Smectic (Sm) mesophases

In the smectic mesophases the arrangement of the center of mass of molecules on an average takes place in equidistant planes, which gives rise the simultaneous presence of both the orientational order, as well as positional order leading to the so-called layered structure. From the Greek word soap the name smectic is derived, different arrangements of molecules within the layer and their correlations from layer to layer gives rise to various types of smectic mesophases [1,6,14,60,75,77,80-82].

So far, about fifteen smectic modifications have been discovered historically which are designated as SmA, SmB, SmC, SmD, SmE, SmF, SmG, SmH, SmI, SmJ, SmK, SmM, SmO, SmQ and SmX according to their detection chronologically. The subtle nature of [14,76,77,83-85] the smectic polymorphism in comparison with the nematic polymorphism is due to the presence of both long-range orientational order, as well as a density wave [86-89]. The nematic phase always appears on higher temperature side than the smectic phases of a compound exhibiting both the two phases. There is no single compound reported till date, which exhibits all the smectic phases. All smectic phases have an essential characteristic of layer fluidity but there is a restriction of molecular motions within these planes. On the tilting of the constituent molecules with respect to the layer normal these smectic LC phases can be divided into two categories. The SmA and SmB phases belong to the orthogonal or non-tilted phases whereas SmC, SmF and SmI are tilted phases.

1.4.1.1.2.1. Smectic-A (SmA) phase

In this phase the molecules are arranged themselves parallelly with their ends in line forming layers in which the long axes of the molecules tend to be orthogonal to the layer planes. Molecules can freely rotate within the layers but there is no long-range packing of the molecular center of mass in the planes of the smectic layers exhibiting liquid like nature. The diffusion of molecules *i.e.*, the molecular movement from one layer to another, is quite free and the layers can freely slide over each other. The director lies along the layer normal in the smectic-A phase. Thus, there is a liquid-like packing of the molecules within the layers and long-range positional correlation is absent. Likewise, in successive layers there is no correlation between the lateral positions of the molecules. The layers are not well defined due to the disorderness of the molecules within the layers and that is why a one-dimensional mass density wave [86-89] is necessary to describe the SmA phase. If a liquid crystalline compound has SmA as well as other smectic phases, the SmA phase is always found to be at the higher end of the temperature range. Different sub-phases of SmA phase like SmA$_2$ (a bilayer phase), SmA$_d$ (a partially-bilayer phase) and Sm$\tilde{A}$ (a modulated phase) has also observed. The characteristic textures of the SmA phase [14] is either homeotropic black appearance or the homogeneous focal conic or fan shaped. On cooling from the isotropic liquid, the fan shaped textures are separates in the form of batonnets and polygon. The characteristic texture and the molecular arrangement of typical SmA liquid crystalline phase are shown in the Figure-1.13.

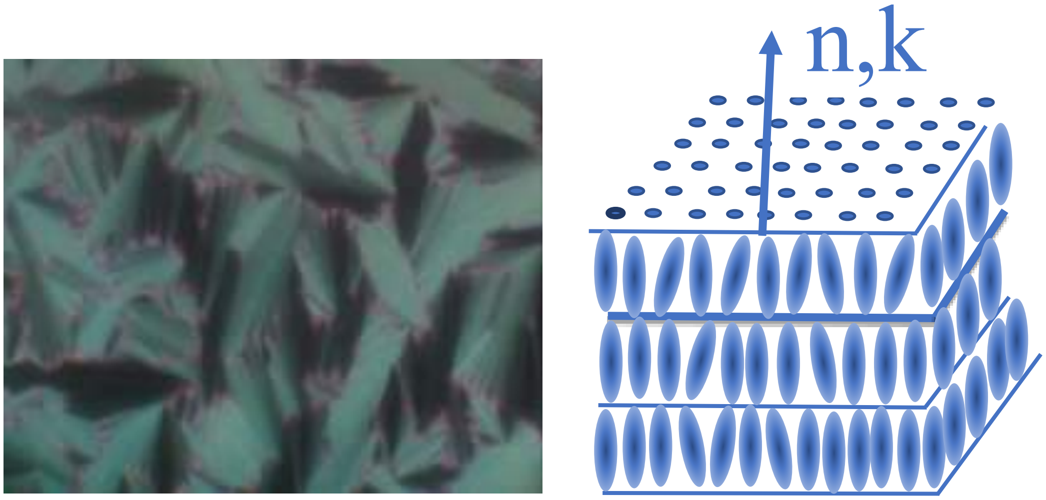


Figure-1.13: Texture and molecular arrangement of typical smectic-A liquid crystalline phase.

1.4.1.1.2.2. Smectic-B (SmB) phase

In the smectic-B (SmB) phase the molecules are arranged within the smectic layers [14] in hexagonally closed packed structure with the molecular long axis orthogonal to the layer planes. The SmB phase generally exists at a lower temperature than SmA phase. The SmB phase has highly structured layers in comparison with SmA phase. A hexagonal network is formed by the molecules and the rotation of the molecules about their long axes is nearly free. However, the hexagonal network dimensions are small, in comparison to the molecular size, so that the rotation of the molecules can hardly be regarded as free, but is probably co- operative in nature [90]. The molecules in SmB phase can be stacked in three different ways reported so far [91], namely AAA... (monolayer), ABAB...(bilayer), which is also the most common one and ABCABC...(trilayer).

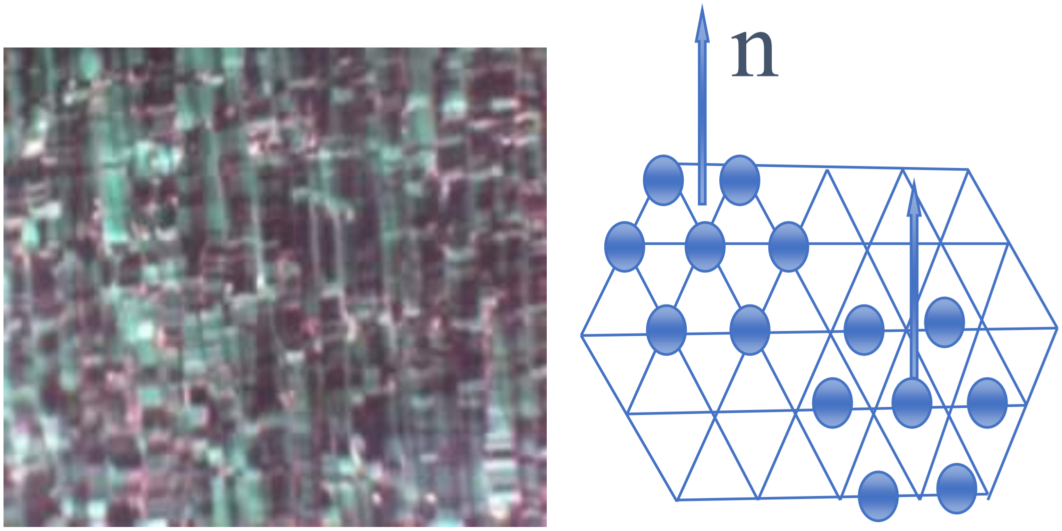


Figure-1.14: Texture and molecular arrangement of typical smectic-B liquid crystalline phase.

Hexatic SmB phase (SmB_{Hex}) different from the crystal SmB phase has been experimentally observed in some compounds [92]. In crystal SmB phase (B_{Cry}) [93] there is an orthogonal arrangement of the molecules with respect to the layer planes and the distance between the two layers is equal to the molecular length. The order of the molecules associated with the layers are relatively more than those in SmA phase. In hexatic SmB phase, the molecules possess both short range in plane positional as well as long-range bond-orientational order in and over the layers. The SmB phase adopts all the characteristic textures showed by the SmA phase with some modifications (paramorphosis) when it appears directly from SmA phase during cooling. Two natural textures are exhibited by the SmB phase (i) mosaic and (ii) paramorphotic focal conic or fan shaped textures. The appearance of transient transition bars across the focal conic or fan texture indicates the paramorphotic change during the SmA-SmB transition. Although this phase is more viscous than the SmA phase, but still exhibits shear flow. Figure-1.14 shows the characteristic texture and the molecular arrangement of typical SmB phase.

1.4.1.2. Tilted phases

1.4.1.2.1. Smectic-C (SmC) phase

In the SmC phase the molecular director (**n**) is tilted with respect to the layer normal at an angle ($\boldsymbol{\theta}$) which is known as tilt angle [94]. Further, molecular packing within the layers gives rise to liquid like nature. The SmA phase is generally optically uniaxial, whereas the SmC phase is optically biaxial in nature [14,57]. In the SmC phase the molecules associated with the layers are free to slide over one another *i.e.*, there is lack of long-range correlation except in the direction of tilt, that is why this phase is known as the tilted analogue of the SmA phase. The tilt angle varies from compound to compound which can be either temperature dependent [95] or independent [96] and in this phase increases monotonically with the reduction of the temperature. From the X-ray diffraction studies it has been found that the thickness of the layer in this phase is less than the length of the molecule. The characteristic texture of the SmC phase is generally either broken focal conic or fan shaped. The SmC phase can also exhibits the schlieren textures. Figure-1.15 shows the characteristic texture and the molecular arrangement of a typical SmC phase.

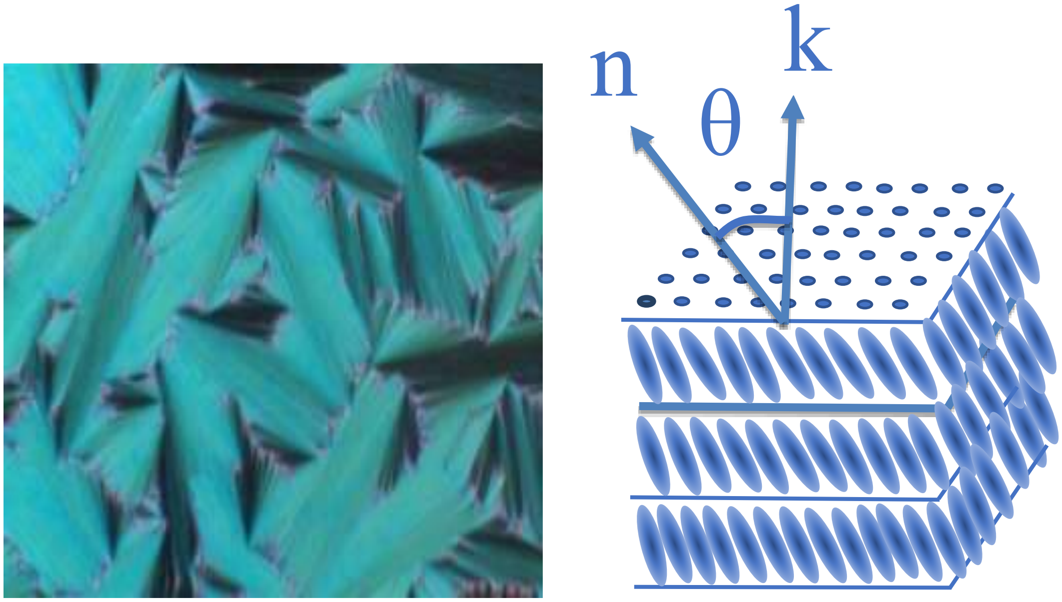


Figure-1.15: Texture and molecular arrangement of typical smectic-C liquid crystalline phase.

1.4.1.2.2. Smectic-D (SmD) phase

SmD phase is exhibited only by very few compounds [97,98] and the common sequence observed are I-SmD-SmC or I-SmA-SmD-SmC. A structural model for this phase was proposed by Diele *et al.* [98] with a close packing cubical shape of the spherical units involving several molecules. There is no characteristic texture associated with SmD phase, as this phase is found to be optically isotropic in nature. However, in the compound 4-hexyloxy-3-nitrobiphenyl-4-carboxylic acid, SmD phase exists in between SmA and SmC phases. In this particular compound a mosaic texture has observed initially which later transforms spontaneously into an isotropic texture.

1.4.1.2.3. Smectic-E (SmE) phase

A high degree of molecular ordering in smectic layers with distinct non-hexagonal lattice gives rise to the smectic-E (SmE) phase [14,20]. This phase is characterized by the herringbone structure.

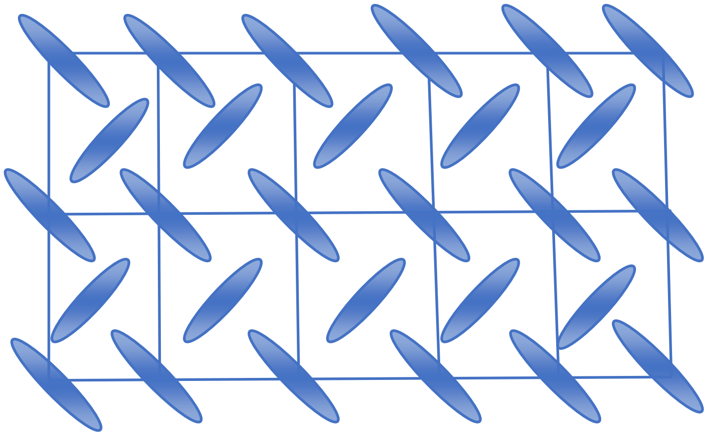


Figure-1.16: Molecular arrangement of typical smectic-E phase.

The unit cell in this phase is orthorhombic. This phase [14] is usually appears on cooling from SmA or SmB phases. It is generally observed [99] in the phase sequence of N-SmA-SmB-SmE with diminishing temperature. The X-ray diffraction studies indicate that (i) in this smectic layer there is a high degree of order with the existence of distinctly non-hexagonal lattice and (ii) the dimension of which is three. The optical biaxial nature in some of the SmE modifications have also been observed [100]. Optically uniaxial nature has been reported by Goodby [101]. This phase mainly exhibits the mosaic and the paramorphotic focal conic or fan shaped textures with concentric curves across the fans. The molecular arrangement of typical SmE phase has shown in Figure-1.16.

1.4.1.2.4. Smectic-F (SmF) phase

A closed packed quasi two-dimensional hexagonal structure exhibited by the SmF phase which occurs [14,102] at a temperature below the SmC phase. This phase is mainly observed in the homologues of pyridene derivatives [102], higher homologues of terepthalydene bis-p-n-alkylaniline (TBAA) series [101], Schiff base liquid crystalline dimers [103] and in few N (p-n-alkoxy benzylidene) p-n-alkylaniline (nO.m) compounds [104]. Similar to the SmC phase, SmF phase has also the long-range order in the tilting direction with a quasi-two-dimensional structure, but there is no correlation of molecular positions between the layers. The molecules arranged themselves in hexagonal layers having tilting of their long molecular axes with respect to the planes of the layers.

However, the hexagonal symmetry is preserved apparently through the bulk sample and the layers are free to slide over, but not free to rotate relative to one another, *i.e.*, the phase has an extensive three-dimensional bond orientational ordering. On viewing under the polarizing optical microscope SmF phase can exhibits stripped or chequered fan shaped or schlieren textures and the mosaic schlieren texture [14]. The characteristic texture and the molecular arrangement of typical SmF phase have been shown in Figure-1.17.

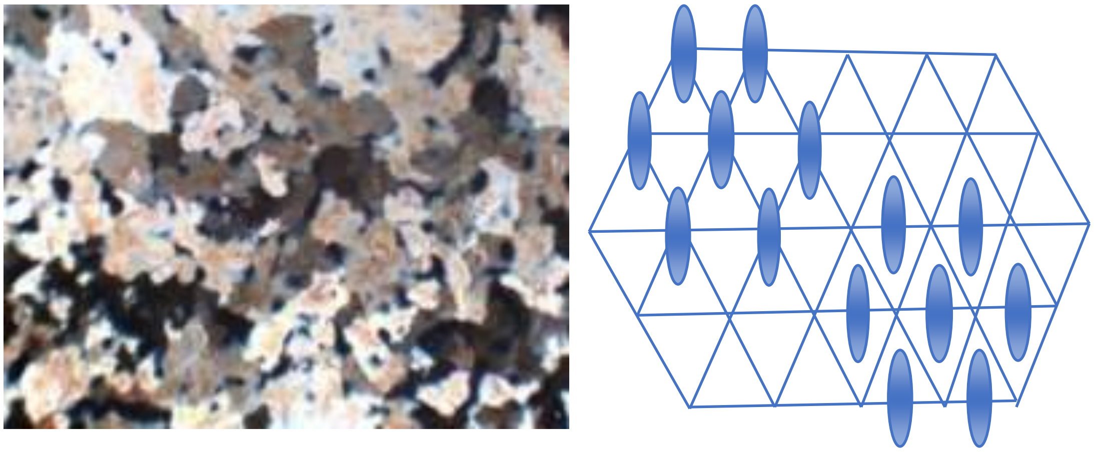


Figure-1.17: Texture and molecular arrangement of typical smectic-F liquid crystalline phase.

1.4.1.2.5. Smectic-G (SmG) phase

Highly ordered structure of smectic-G (SmG) phase similar to that of the SmE phase has been observed by an X-ray diffraction [105] study. A monoclinic cell is associated with the SmG phase in which the molecules are closely packed in a pseudo hexagonal structure within the smectic planes aligned at right angles to the direction of tilt.

The arrangement of close packing is of hexagonal type and the correlation of the layers gives rise to [14] a 3-D structure. There exists a dynamical molecular disorder with a considerable amount in SmG phase. The local structure associated with this phase is chevron packing (or herringbone) in which the molecules have co-operative oscillatory movement about their long axes. The SmG phase usually appears at the low temperature in the compounds N (p-n-alkoxy benzylidene) p-n-alkylaniline (nO.m).

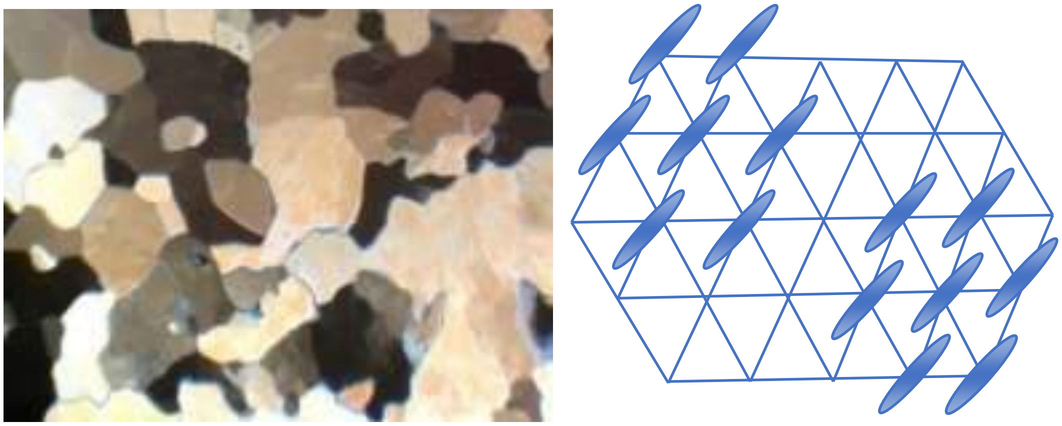


Figure-1.18: Texture and molecular arrangement of typical smectic-G liquid crystalline phase.

The magnitude of the tilt in the SmG phase is equal to that of the SmF phase as there is no discontinuous change of the layer thickness at the SmF-SmG phase transition. Generally, the SmG phase exhibits natural mosaic texture with an elongated platelet area that have an almost rectangular shape. Again, the paramorphotic textures of the SmG phase formed on cooling from $\mathrm{SmB_{Cryst}}$ phase are arced broken focal conic or fan shaped, mosaic with small poorly defined platelets weakly coloured textures. But the broken fan shaped texture with a patch work appearing like checkered board occurs by the SmG phase as it grown from SmC or SmF phases. The characteristic texture and the molecular arrangement of typical SmG phase are shown in the Figure-1.18.

1.4.1.2.6. Smectic-H (SmH) phase

The SmH phase have been first observed by Sakagami *et al.* [106] in the well-known compound terepthalylidene bis-p-n-butylaniline (TBBA) as well as its higher homologues. The SmH phase, is characterized by the highly structured layers analogous to the SmE phase with a tilting of the molecules. This phase does not exhibit [14] any distinct textures. A clear but strained focal conic or fan shaped texture has exhibited by the SmH phase obtained from SmC phase. On the other hand, SmH phase shows broken focal conic or fan shaped texture when obtained from the SmA phase. So, the characteristic textures of the SmH phase are mosaic and paramorphotic focal conic or fan shaped.

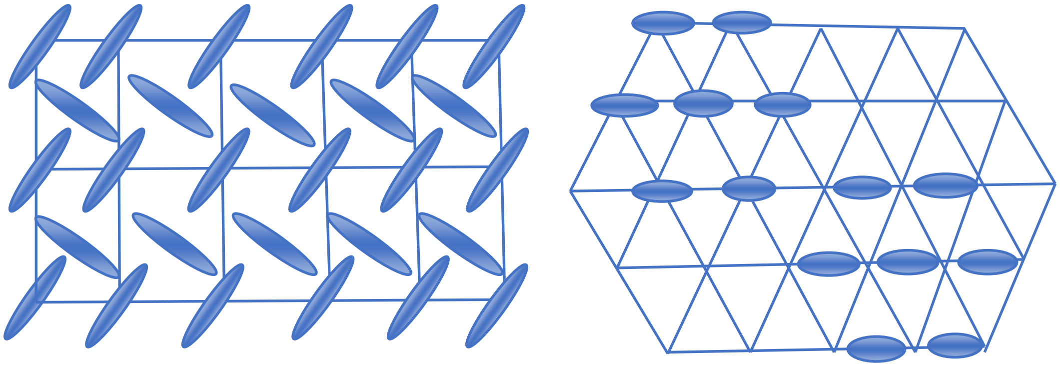


Figure-1.19: Molecular arrangements of typical smectic-H and smectic-I liquid crystalline phases.

1.4.1.2.7. Smectic-I (SmI) phase

SmI phase has the molecular structure which is nearly similar [14] to that of the SmF phase. The presence of in-plane long range positional ordering in the SmI phase is only difference from the SmF phase which has in-plane short-range positional ordering. However, there is a difference in the direction of molecular tilt relative to the hexagonal packing of the molecular long axes between these two phases. The tilt of the hexagon in SmF phase is towards an edge, while for SmI phase, the tilt is towards an apex of the hexagon. SmI phase has greater in-plane correlation length than in SmF phase. On cooling, the characteristic textures of this phase are formed from the homeotropic texture or the schlieren texture of the preceding SmA or SmC phases. Some compounds which show SmI phase are higher homologues of the TBAA series (alkyl = nonyl, decyl, dodecyl) [107], Esters like 4-(2′-methylbutyl) phenyl 4′-n-octyloxybiphenyl-4′-carboxylate (8OSI) and Amines, like N, N′-bis-(4′-n-heptyloxy benzylidene)-1, 4-phenylenediamine (7OBPD). In general, broken fan shaped, mosaic and schlieren textures are the characteristic textures of the SmI phase. The SmI phase can also exhibits bubbled texture which changes their size, with temperature and flow. Figure-1.19 depicts the molecular arrangements of typical SmH and SmI phases.

1.4.1.2.8. Smectic-J (SmJ) and smectic-K (SmK) phases

The SmJ and SmK phases have first observed by Gane *et al.* [108] in the compound bis-(4′-heptyloxy benzylidene)-1,4′-phenylenediamine (HEPTOBPD) and confirmed that these phases were analogous to SmG and SmH phases except for the tilting direction. Both the phases have monoclinic symmetry and the molecules packed in pseudo-hexagonal structure with the tilting towards the apex of the hexagon.

Again, the existence of the SmJ phase in the compound 4-n-hexylphenyl-4-n-pentylphenyl-4-n-decyloxybenzothiolate has confirmed by Leadbetter *et al.* [109]. Figure-1.20 shows the molecular arrangements of typical SmJ and SmK phases.

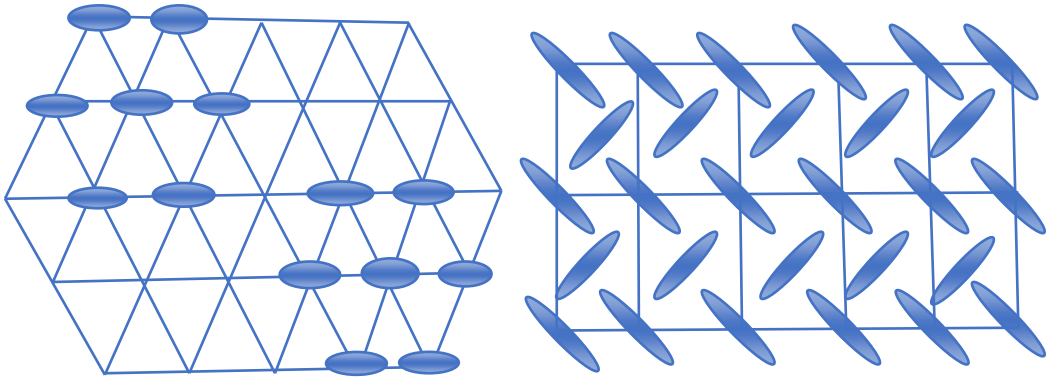


Figure-1.20: Molecular arrangements of typical smectic-J and smectic-K liquid crystalline phases.

1.4.1.2.9. Smectic-M (SmM) and smectic-O (SmO) phases

The existence of smectic-M (SmM) phase first reported by Heppke [110] *et al.* in the year 1992. This phase having short range positional order may belongs to the group of tilted smectic phases.

Levlut *et al.* established [110-113] the existence of the smectic-O phase in chiral and the racemic form of 1-methylheptyl-terphathalylidene-bis-aminocinnamate (MHTAC). By X-ray measurements it has been observed that this phase has a structure of tilted smectic with no positional order within the layers.

1.4.1.2.10. Smectic-Q (SmQ) and smectic-X (SmX) phases

Another type of liquid crystalline phase has discovered [111] by Levlut *et al.* which occurs in chiral, but not in racemic mixture of 1-methylheptyl-terphathalylidene-bis-aminocinnamate (MHTAC). This smectic phase is called smectic-Q phase which was also the source [114] of first SmO phase. Many compounds exhibit this type of phase.

Brand and Cladis [115] have observed SmX phase which exhibits a finite spontaneous polarization. It has been found that there is a similarity of the in-plane structure of this phase with that of the non-helicoidal SmG or SmK phases. Unlike the uniaxial helical chiral smectic phases, SmX phase is biaxial in nature.

1.4.2. Liquid crystalline meso-phases formed by thermotropic chiral liquid crystals

The chiral LC compounds have an asymmetric center (chiral center) [34,116,117] due to which chirality is imposed. These chiral LCs exhibits nematic as well as different kinds of smectic polymorphism with more or less similar structures and properties to those exhibited by non-chiral compounds and the asteric symbol ‘*’ indicates chirality of the phases. These phases are chiral nematic (N^*), chiral smectic-C^* (SmC^*) characterized by the helix, optical activity, selective reflection; SmI^* is tilted to side with no layer correlation, short range in-plane position; SmF^* is tilted to apex, having helix structure, optical activity, selective reflection; SmJ^* is tilted to apex with long range layer correlation and long range in-plane orderings; SmG^* is tilted to side positional order with no helix structure; this phase has pseudo hexagonal structure. On the other hand, SmK* is tilted to side with long range layer correlation as well as long range in-plane ordering; SmH* is tilted to apex having positional ordering without the helical structure; the molecular packing of these phases has herring-bone type. The twisted arrangement of layers arises due to the projection of tilt into the layer plane turns from one layer to the next. In chiral phases, there is a rotational hindrance on the mobility of the molecules about the long axes and ferroelectric properties are associated with these phases. However, the ferroelectric properties are found to be very promising for their utilization in switching and display devices.

1.4.2.1. Cholesteric (N*) or chiral nematic mesophase

Cholesteric mesophase is the chiral analogue of the nematic mesophase and therefore it is also called chiral nematic phase. A system composed of chiral molecules can exhibit chiral N phase [54]. The doping of the nematic LC on optically active molecules also gives rise the said mesophase. This phase was first observed in esters of cholesterols namely cholesteryl benzoate for which this phase is known as [118] cholesteric phase. As, this nematic phase is formed in an optically active material, the preferred direction of the long molecular axis in a uniformly oriented sample *i.e.*, in a monodomain does not remain constant over the whole sample, but shows a continuous twist on traversing through the sample along the optic axis and forms a helical structure having finite pitch. For this reason, this phase is also known as ‘twisted nematic’ or ‘spontaneously twisted nematic’.

The weak tendency of the neighboring molecules to align at different angles with one another accounts for the formation of helix of the local director in space with a well-defined pitch having much longer compared to a single molecule. The molecular conformation leads the handedness of the helical twist. The left and right-handed helices have distinguished by the sign of chirality which is attributed due to the presence of asymmetric center in the molecule. The unique optical properties namely selective reflection [119-120] occurs due to the helical arrangement of this phase. The interaction of the plane-polarized light and the chiral macroscopic structure gives rise to the rotation of the plane of polarization along the helix direction. When the pitch of the helix matches to a wavelength of the visible spectrum (~400-800 nm) a color effect appears on the chiral mesophase which is used in thermometric purpose. Most importantly, the helical pitch as well as the reflected wavelength is temperature dependent in nature. The unwinding of the helical structures can be done by the application of an electric field, which reorients the axis of the molecules along the direction of the applied field. There is an important role of the position of chiral center for the phase formation. In many cases, chiral center is associated with the flexible end chain leading to the depression of clearing point. So, the target material should possess reasonably high clearing point when doped with chiral molecule, in order to accommodate the steric effect of chiral moiety. However, the stability of the liquid crystalline phase reduces by the branched chiral chain with increasing viscosity. Another chiral frustrated phase termed as ‘Blue Phase’ [121-122] may appear in between the isotropic and the N^* phase.

The addition of a small quantity of chiral dopant into the nematic compounds may generate the chiral nematic phase. This cholesteric liquid crystalline phase is uniaxial in nature may either be positive or negative.

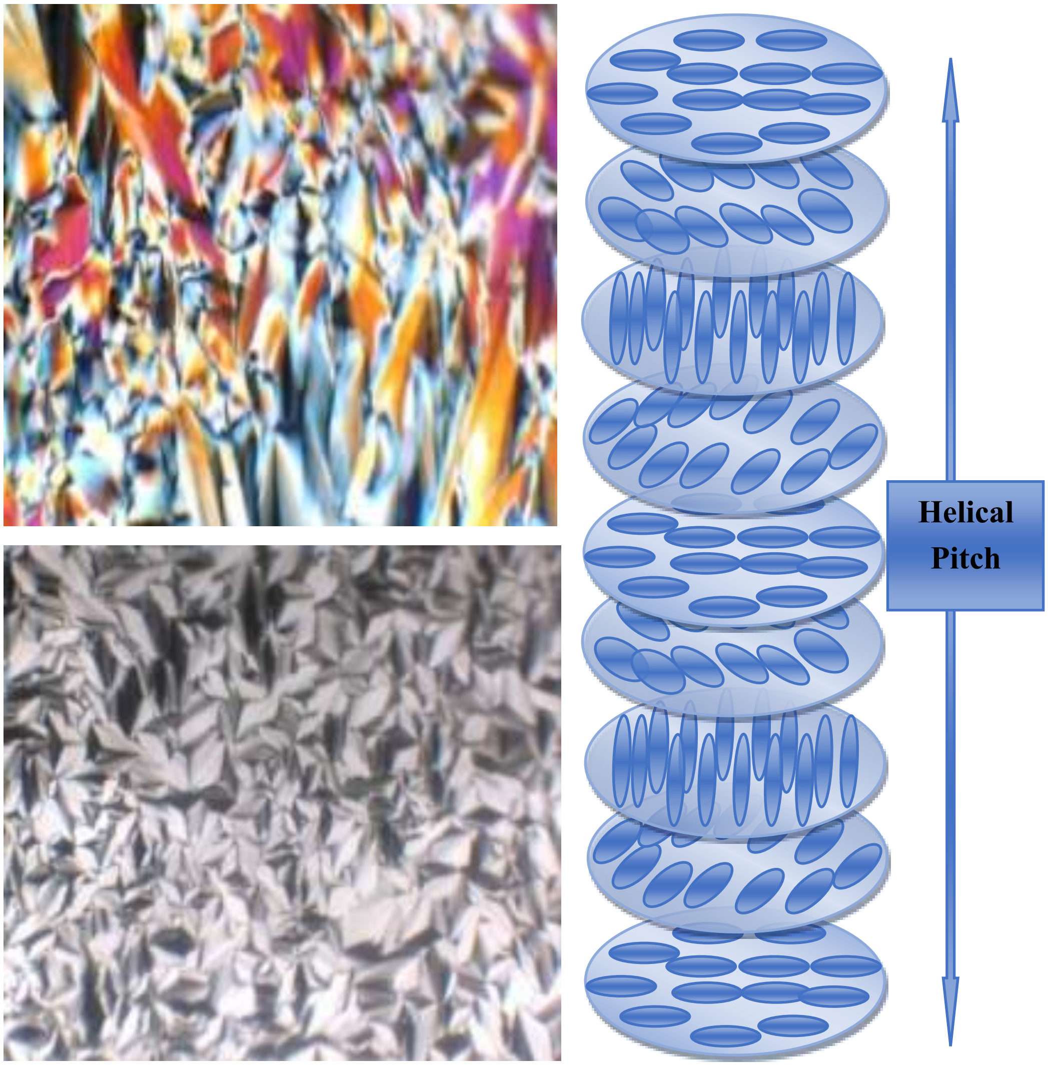


Figure-1.21: Textures and molecular arrangement of typical cholesteric or chiral nematic (N^*) liquid crystalline phase.

On viewing under the crossed polarizers, the textures of N^* phase may be focal conic, homogeneous and pseudo isotropic in nature. Moreover, non-planar polygonal textures [123,124] are also exhibited by this chiral nematic. Figure-1.21 shows the characteristic textures and the molecular arrangement of the cholesteric liquid crystalline phase (N^* phase) which is typically composed of nematic mesogenic molecules having a chiral center producing intermolecular forces that favour alignment among the molecules at a slight angle to one another. This leads to the visualized structure of very thin 2-dimensional nematic-like layers stacked with each other and there is a twisting of the director in each layer with respect to those above and below. The molecules represent many chiral nematogens which lie in the slabs having infinitesimal thickness with the orientational distribution about the director.

1.4.2.2. Chiral smectic-A^* (SmA^*) phase

The chiral smectic-A^* (SmA^*) phase which is composed of optically active molecules belongs to the same structure as that of the achiral SmA phase, with a reduction of symmetry due to the presence of molecular chirality. The packing of the molecules in each layer of this phase is formed in such a way that, the molecular long axis and layer normal are being parallel to each other with the simultaneous liquid-like rotation around the layer normal [125-127]. Due to the lack of correlation among the molecules in a smectic layer, there is no net transverse polarization and that is why the SmA^* phase is non-polar in nature. As a consequence, when an external electric field is applied in the SmA^* phase directed orthogonal to the layer normal there will be a coupling between the electroclinic susceptibility and the field. For relatively low applied fields the long molecular axes tilt with respect to the layer planes and the tilt angle varies linearly with the field. This linear electro-optic phenomenon is termed as electroclinic effect [128]. The characteristic texture of the chiral SmA* phase is focal conic in planar orientation and a dark field of view for homeotropic orientation. Figure-1.22 shows the characteristic texture and the schematic representation of the SmA* phase formed by the chiral rod-like molecules.

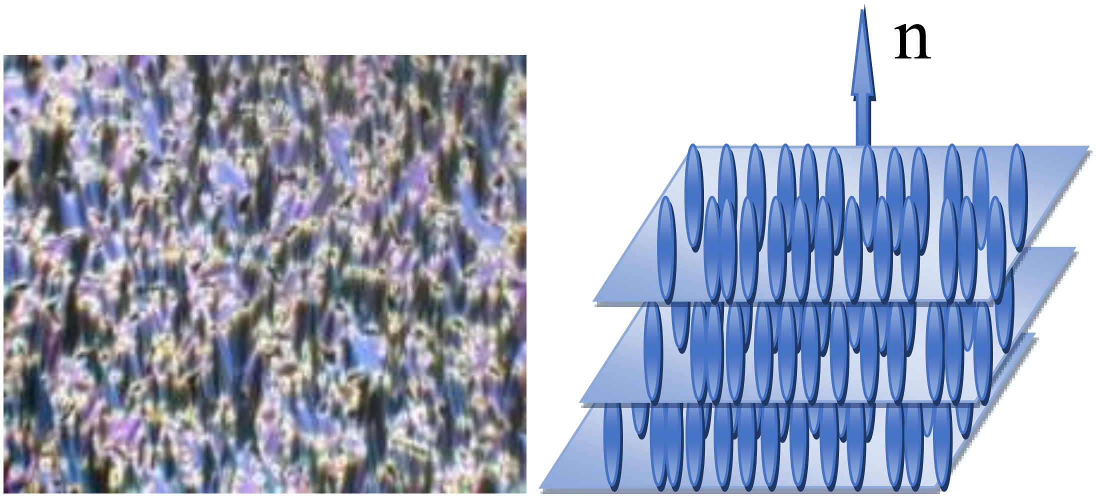


Figure-1.22: Texture and molecular arrangement of typical chiral smectic-A* (SmA*) liquid crystalline phase.

1.4.2.3. Chiral ferroelectric smectic-C* (SmC*) phase

The chiral smectic-C* (SmC*) phase, mainly composed of optically active molecules in which the helicoidal structure [129-133] is formed due to the precession of molecular tilt direction from one layer to another about the layer normal with a relatively large pitch of the helix. This helical deformation is relatively greater in comparison to the interlayer spacing. The suppression of symmetry occurs due to the presence of chirality. Spontaneous polarization is one of the most recognized property of a ferroelectric liquid crystal which exhibits polarization without an external electric field. In the year 1921 Valasek [134] first observed the ferroelectric effect in Rochelle salt which is the sodium potassium salt of tartaric acid recognized as the first solid which shows ferroelectric properties. The separation between the center of positive and negative charges give rise to the development of spontaneous polarization [135] in ferroelectric materials. There exists a certain temperature above which the spontaneous polarization vanishes known as the Curie temperature. The ferroelectricity in liquid crystal was first observed by an American Physicist R. B. Meyer [129] in the year 1975 by considering symmetry arguments and by observing the existence of non-zero spontaneous polarization ($\widehat{P_s}$) for each layer of the smectic-C* phase with a direction perpendicular to both the tilt plane and the layer normal. Meyer suggested that the LC smectic phases which are tilted with respect to the layer normal and composed of chiral molecules exhibit ferroelectricity [136]. The ferroelectric liquid crystal shows very similar behaviour like the ferroelectric solids in some aspects, as both exhibits spontaneous polarization and both have a Curie temperature at which the polarization vanishes macroscopically. However, the net polarization in the chiral smectic-C* phase is zero macroscopically because of the helical structure of this phase. A non-zero macroscopic polarization can only be obtained when somehow the unwinding of the helix can be made by applying external factors such as electric field, surface interactions [32,35,43,137] *etc*. Various sub-phases of the SmC* phase have also been found due to the presence of different molecular orderings into the adjacent layers which are denoted by SmC$_\alpha^*$, SmC$_\gamma^*$ and SmC$_\beta^*$ in order of appearance with decreasing temperature [138-141]. The fast response of the ferroelectric liquid crystals has opened a new avenue in the field of display technology and makes them commercially important in the applications of the flat panel displays especially micro-displays. Figure-1.23 shows the characteristic texture and schematic representation of the SmC* phase.

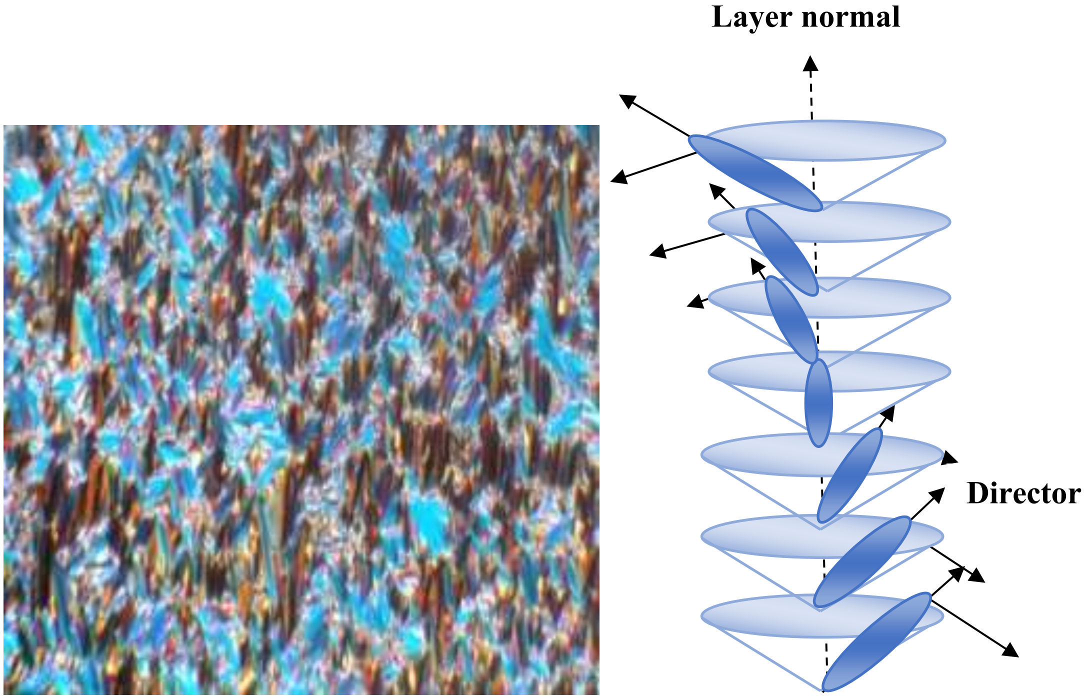


Figure-1.23: Texture and molecular arrangement of typical chiral smectic-C* (SmC*) liquid crystalline phase.

1.4.2.4. Chiral anti-ferroelectric SmC_A^* phase

Anti-ferroelectric liquid crystalline materials, mainly composed of chiral molecules with polar substituents at their chiral center with the presence of rigid core. In the anti-ferroelectric smectic phases, local dipoles are arranged antiparallelly in the adjacent layers. These phases are called anti-ferroelectric liquid crystalline phases by taking analogy with magnets. There is an anti-ferroelectric version of the chiral smectic-C^* phase, denoted by SmC_A^* phase and appears at a temperature lower than that of the ferroelectric SmC^* phase. The anti-ferroelectric phase is characterized by alternating the directions of the spontaneous polarization and molecular tilt alternates in the adjacent layers thus the average value of the spontaneous polarization becomes zero. However, the anti-ferroelectric phase can be switched to the ferroelectric phase by applying a sufficiently strong electric field. It is worth to note that every rotation of π about the layer normal can repeats the helicity of the anti-ferroelectric whereas in ferroelectric phase this rotation is 2π. The applications of these anti-ferroelectric liquid crystals are so potentially immense that it opens a new branch of material science and technology.

1.4.2.5. Chiral ferrielectric SmC_γ^* phase

In the ferrielectric phases the presence of an uneven number of layers in which the molecules have two opposite directions giving rise to a lower resultant spontaneous polarization. There is a ferrielectric version of the chiral smectic-C^* phase which is denoted by SmC_γ^*.

Figure-1.24 (a-b) shows the schematic representations of the anti-ferroelectric and ferrielectric liquid crystalline phases.

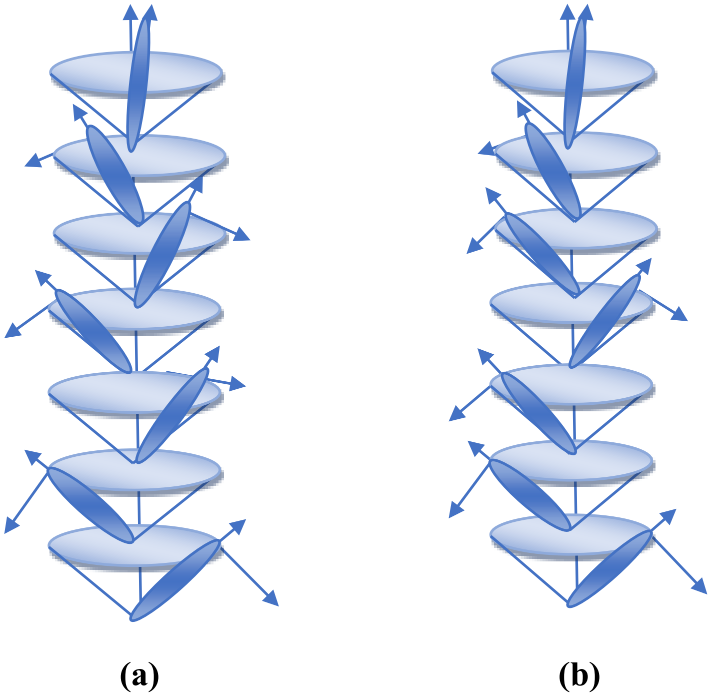

(a) **(b)**

Figure-1.24 (a-b): Molecular arrangements of typical **(a)** Anti-ferroelectric and **(b)** Ferrielectric liquid crystalline phases.

1.5. Sequence rule and re-entrant behaviour in calamitic liquid crystals

A rich variety of polymorphism exhibited by the mesogenic compounds in which one mesophase can transfer into another one, having different order by changing the symmetry of the system under the influence of some external factors such as temperature, pressure, concentration *etc*. The molecular ordering destructed progressively by the increase in the temperature and as a result the high temperature liquid crystalline (LC) phases are more disordered than the low temperature one. Many intermediate mesophases may appear in a thermotropic LC in between the anisotropic crystal and the isotropic liquid states with increasing temperature of the LC material. If the LC material have two or more phases, then it is called poly-mesomorphic and the process is known as poly-mesomorphism. A rule for a general phase sequence were derived [29,142-145] by observing systematically the appearance of various phases in polymorphic compounds. According to which nematic phase occurs at higher temperatures than that of the smectic phases. Considering all possible structures in calamitic LCs a sequence has been derived: Isotopic (I) - N - SmA - SmC - SmB - SmI - SmF - Crystal B -SmJ - SmG - SmE - SmK - SmH- Crystal for achiral materials and I - BP- N^*- SmA^* - SmC^* - SmI^* -SmF^* for chiral LCs on cooling. So far, there is no single compound found which shows all these mesophases. However, there exist many compounds which show real phase sequences that can be considered as parts of this theoretical phase sequence.

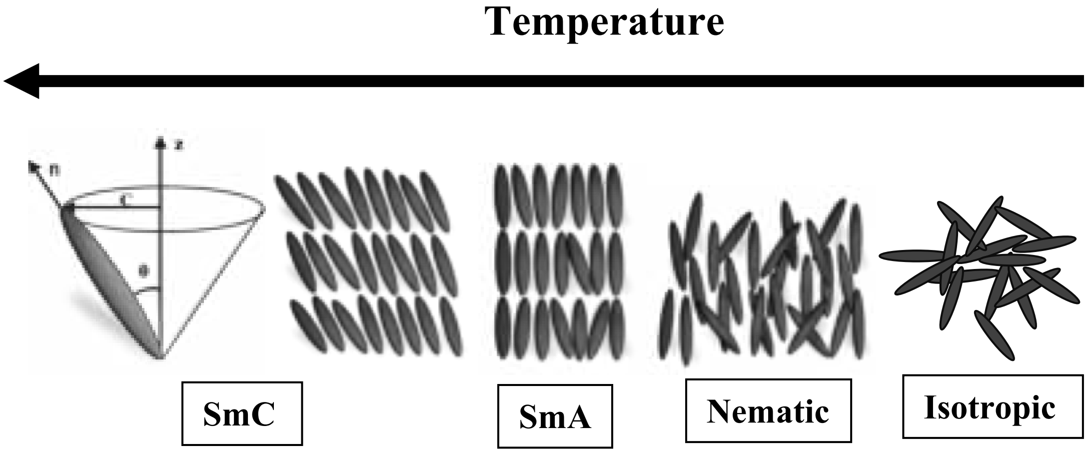


Figure-1.25: Normal mesophase sequence on cooling.

The normal mesophase sequence on cooling of a liquid crystalline compound in which the higher ordered phases appear in the low temperature region as shown in Figure-1.25. However remarkable exceptions to this normal phase sequence have been detected in re-entrant transitions [146]. The re-entrant phase transition occurs in a system, when the variation of any thermodynamic variable such as temperature or pressure results in two or sometimes more phase changes and finally attains a state which is macroscopically similar to the initial state, that is in some distinct cases less ordered mesophase re-appears in the low temperature region. This phenomenon is known as re-entrant polymorphism.

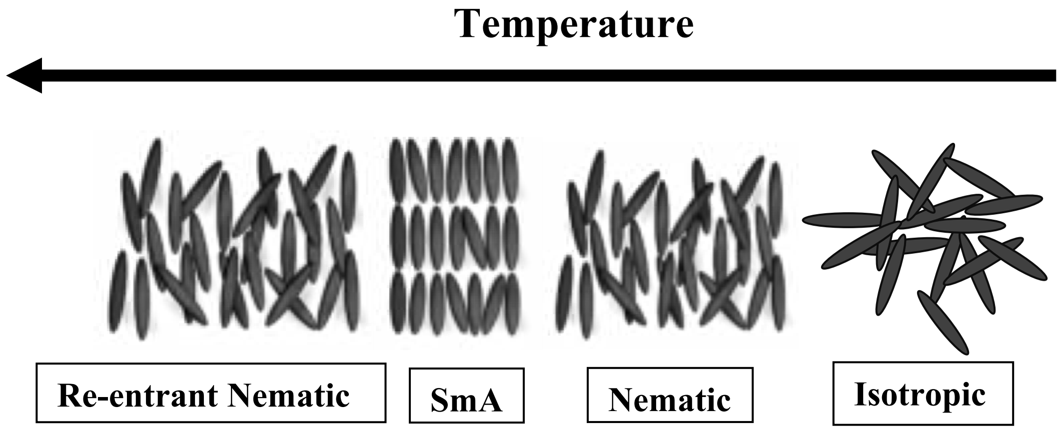


Figure-1.26: Re-entrant polymorphism on cooling.

In the year 1975 the re-entrant nematic phase was first discovered by P. E Cladis [147] in a bi-component mixture of two strongly polar liquid crystalline compounds namely cyanobenzilidene octyleoxyanniline (CBOOA) and hyxyleoxybenzilidine aminobenzonytryle (HBAB).

The re-entrant nematic phase appears at the low temperature than that of the smectic-A phase. At present, the re-entrant behavior is a well-established phenomenon observed in the mixtures and in pure compounds as well [148-150]. Additionally, re-entrant smectic phases and multiple re-entrant phases [151-154] have also been found by different groups in various systems; even quadruple re-entrance is possible with a compound having four or five benzene rings [155]. Figure-1.26 shows the re-entrant nematic phase sequence.

1.6. The concept and use of symmetry in liquid crystals

Many physical properties and phenomenon involving phase transition strongly related to the symmetry associated with the system which is one of the most important guiding principle in the science of liquid crystal. The symmetry and order of the phases are inversely related with each other, that means higher the symmetry least the order of the phase and vice-versa. The least ordered or most symmetric phase is the isotropic state which exhibits the liquid like behavior. On the other hand, the nematic structure is characterized by the presence of orientational order of the molecules. The positive value of the orientational order parameter S between 0 and 1 indicates the parallel arrangement of the molecules with respect to the director (**n**). On the other hand, the perpendicular arrangement of the molecules with respect to **n** gives rise the negative value of S in between 0 to -0.5. This symmetry requirement ensures that the transition from the isotropic to orientationally ordered nematic phase is associated with the first order nature which was also proved by large change in enthalpy. A quasi-long-range order is associated with the presence of short-range positional ordering and absence of long-range ordering in one dimension [156]. The direct transitions from the isotropic liquid to the SmA phase is first order while the coupling between the positional and orientational order directly depends on the range of the nematic phase. The range of the nematic phase accounts for the first order or second order nature of the N-SmA phase transition. A second order N-SmA phase transition occurs in LC compounds having relatively wide nematic range. The SmC phase is associated with the tilting of the director with respect to the layer normal. In the chiral SmC* phase, a constant angle is maintained by the director with respect to the normal of the layer describing a helical path when traversing along the direction normal to the smectic layer planes. Various combination of the long-range and short-range orderings of the positional order and bond orientational order give rise to different smectic structures. There are mainly three distinct possibilities exist

(i) The fluid like smectics such as SmA, SmC, SmC* phases appear with the presence of positional ordering (PO) but there is no bond orientational ordering (BOO).

(ii) Hexatic smectic phases such as SmI, SmF, SmB$_{\mathrm{Hex}}$ have the combination of long-range BOO and short-range PO.

(iii) The third possibility is that, the presence of both long-range BOO and PO gives rise the phases which are very close to the crystal structure except the molecular rotational diffusion. The examples are smectic B, E, G *etc*.

The concept of symmetry not only grows the idea about different structures and physical properties of the LC phases but also allows one to make analogy of phase transitions between liquid crystalline and non-liquid crystalline phases. For example, de Gennes [1,157] have found a strong analogy of the SmA phase with the superconducting phase by introducing the smectic order parameter, on the other hand, there has some analogy of tilted SmC phase and the superfluid helium [158]. The critical behavior of the SmA-SmC phase transition has been predicted to exhibit either heliumlike or the XY model. In the similar manner the SmA to SmB_{Hex} phase transition can be described by a two-dimensional order parameter such as superfluid analogy. Ultimately, one can say that, in order to understand the physics of liquid crystalline phases, symmetry becomes the crucial and indispensable tool. Finally, it can be remarked that the liquid crystalline field has been used as a testing ground of theoretical ideas with such elegant and simplicity that are not manifest in other systems.

1.7. Concept of phase transitions

After the discovery of liquid crystal, so far numerous experimental techniques have been developed in order to investigate this peculiar phase of matter. Some of the experimental techniques such as X-ray diffractometry [159,160], Dilatometric analysis [161,162], Electron Spin Resonance (ESR), Electron Paramagnetic Resonance (EPR) [163,164], Nuclear Magnetic Resonance (NMR) [165,166], Raman Spectroscopy [167,168], Fourier Transform Infrared Spectroscopy (FTIR) [169,170], Differential Scanning Calorimetry (DSC) [171-175], Optical birefringence method (OT) [176-180], Volumetric measurements [181-183] *etc*.

The experimental data obtained from these techniques, has been interpreted to understand the phase transitions in liquid crystalline systems as well as the changes associated with the various physical and the electro-optical properties. The anisotropy related to some physical properties such as the refractive index, dielectric permittivity *etc*. provide important information about the nature of liquid crystalline systems. There are mainly two principal refractive indices, n_o and n_e corresponding to the liquid crystalline systems. The first one, is associated with the ordinary ray, which is defined as the electric field of the light wave vibrating perpendicular to the optic axis. Another one is the extraordinary ray where the electric field associated with the linearly polarized light wave vibrates parallel to the optic axis. For a nematic or uniaxial smectic liquid crystal, the direction of the optic axis is along the director. The birefringence as well as the order parameter of liquid crystalline materials can be obtained by measuring the refractive indices.

The phase transitions associated with the liquid crystalline systems is one of the most important phenomena related to the information about the change of molecular ordering with the external influences. The change of thermodynamic variables of a system from one form to another by the application of external influences such as temperature, pressure, concentration, magnetic field, electric field *etc*. leads to a transformation of phase; which is most important macroscopic phenomenon in the research point of view in developing the idea about the phase transition in the field of soft condensed matter.

The simplest examples of the phase transitions in nature are melting of solid to liquid, freezing of liquid to solid, boiling of liquid to gas and condensation of gas to liquid which can be observed easily but in order to observe the mesophase transitions there is a need of experimental results which gives the information about the behavior of the liquid crystalline mesophase transitions. If the influencing factor is temperature, then the higher temperature phase is more symmetric than the lower temperature phase [184,185]. Phase transition is always involved with the change of symmetry which in turn associated with the ordering of different phases with decreasing temperature. The molecular ordering increases consequently leads to the decrease of symmetry with the progression of phase transition. The order parameter is one, which can be physically observable and the change of which at the transition point gives the idea about the nature of the phase transitions. Different types of physically observable order parameters belong to different systems such as magnetization, electrical polarization and pair wave function for ferromagnetic, ferroelectric and superconducting systems respectively. On the other hand, the order parameter for fluid and for the superfluid are the density difference and the ground state wave function respectively, while the most convenient order parameter is the degree of molecular ordering for the nematic liquid crystals.

There are mainly two types of phase transitions; first order and second order associated with the liquid crystalline systems. According to Paul Ehrenfest [186,187] the first order derivative of Gibb's free energy (G) that is the entropy is discontinuous while it becomes continuous in the second order phase transition.

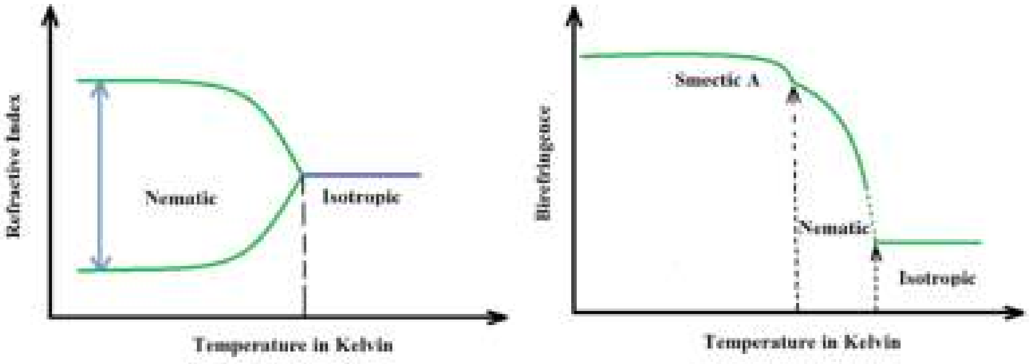
On the other hand, in view of the modern approach [188] the first order phase transitions are those which have the involvement of the latent heat and discontinuous variation of the thermodynamical parameters at the transition point while the second order transitions do not accompany by the involvement of the latent heat and continuous variation of the thermodynamic parameters occurs at the transition point. It is also worth to note that, the nature of the phase transition [189] depends on the change in the order parameters. The order parameter in the vicinity of the transition is discontinuous for the first order phase transition and continuous for the 2nd order phase transition. The rich polymorphism of LCs makes them a promising and most important candidate in the field of liquid crystalline research involving phase transition in order to develop both theoretical and practical aspects. Several peculiar behaviors such as the critical phenomena with the existence of true critical region, presence of tricritical point (TCP) as well as multicritical points, the occurrence of single and multiple re-entrant behavior *etc*. have been observed in liquid crystalline systems, for which this unique state of soft condensed matter is consider as most vital area of the physics of phase transitions. The LC phase transitions are generally weakly first order or second order in nature with the existence of critical phenomena [190,191] exhibiting an unusual behaviour in the vicinity of transition which is termed as critical points, for example increase in susceptibility, fluctuation of order parameter, the specific heat capacity anomaly *etc*. The diverse symmetries and the coupling of various order parameters associated with different LC phases is the key parameter of the crossover phenomenon from one critical behavior to other in the field of liquid crystals.

1.8. Physical properties of liquid crystalline materials

The structural arrangement of LC molecules is the basic building unit of the occurrence of different physical as well as chemical properties. The main features of these molecules forming liquid crystalline phases are (i) they should be elongated and anisotropic in shape (ii) the presence of flat segments of molecules such as benzene rings (iii) the molecular long axis is defined by the rigid backbone containing double bonds (iv) the presence of strong dipoles and easily polarizable groups associated with the molecules seems important. Such type of structures of these LC molecules make the liquid crystalline phases anisotropic in nature which consequently leads to the dependencies of some physical properties on the direction of measurements. Many physical properties can be changed with the external influences such as temperature, pressure, electric field or magnetic field *etc*. In short numerous practical applications in LC is based on the anisotropic nature and proper tuning of the various physical properties. Some of the important physical properties have been discussed below which are directly related to many useful liquid crystal applications [80,192].

1.8.1. Optical anisotropy (Birefringence)

The liquid state is isotropic in nature due to the free rotation of the molecules in liquids average out any asymmetry. Due to the presence of anisotropy related to shape and polarization, the mesogens are birefringent in nature and exhibits different properties of the electric vector associated with light propagating parallel and perpendicular to the director or optic axis. A plane polarized light is split into two components one is ordinary (O) and another is extraordinary (E) on entering through a liquid crystalline phase. As the electric field associated with the O-ray is perpendicular to the optic axis, so there is no dependency of the refractive index 'n_o' on the direction of propagation. On the other hand, the E-ray lies in a plane that contains the optic axis, so its refractive index '$n_e(\theta)$' varies with the angle made by the ray propagation direction with the optic axis. Thus, there is a dependency of the birefringence of the medium, on the propagation direction and the birefringence is defined as $\Delta n(\theta) = n_e(\theta) - n_o$. Most of the nematic liquid crystals have positive birefringence $(\Delta n > 0)$, indicates that the E-ray lagged behind the O-ray on passage through the LC phases [177,193]. Figure-1.27 (a-b) shows the temperature variation of refractive indices and birefringence.



(a) **(b)**

Figure-1.27 (a-b): (a) Refractive index and **(b)** birefringence as a function of temperature.

1.8.2. Dielectric anisotropy

The magnitude of the dielectric permittivity along ($\varepsilon_{\parallel}$) and perpendicular ($\varepsilon_{\perp}$) to the director and the dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$) *i.e.*, the difference between them indicates the interaction between the liquid crystalline molecules and an electric field. The ratio of the capacitance of a material (C_m) to that in vacuum (C_v) is termed as the dielectric permittivity (C_m/C_v) of that material. There is a dependency of dielectric constants on the frequency of the applied field up to transition to the isotropic liquid. Above the clearing point, $\Delta\varepsilon$ decreases to zero as the dielectric constants measured along all the three axes are equal because of the isotropic nature of liquids.

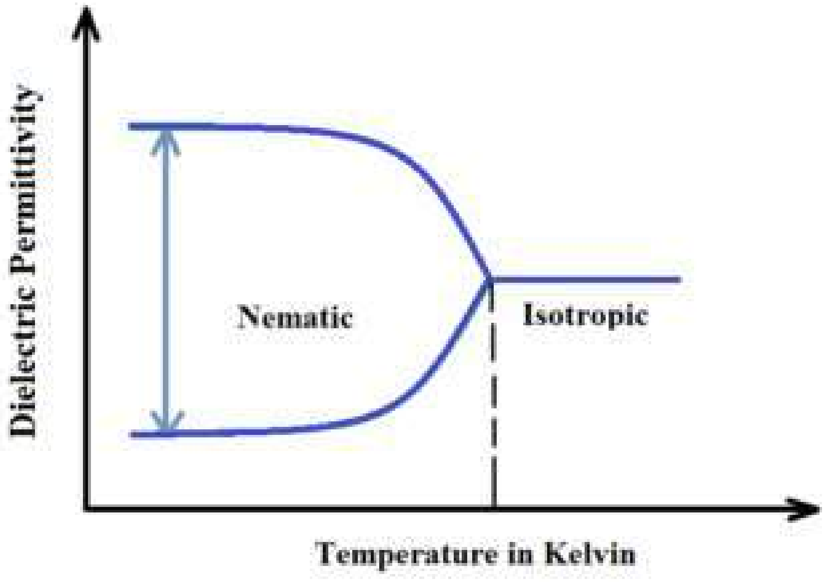
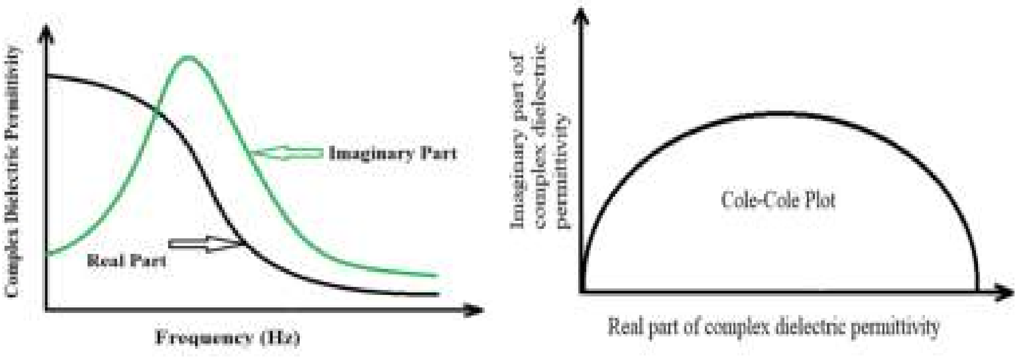


Figure-1.28: Dielectric permittivity as a function of temperature.

The resulting permanent dipole moments give rise to the sign and magnitude of the dielectric anisotropy ($\Delta\varepsilon$). Because of the presence of permanent and induced dipoles, LC molecules exhibit dielectric anisotropy. The components ($\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$) of the dielectric permittivity change as a function of temperature [194]. For the nematic liquid crystal, the variation of dielectric permittivity as a function of temperature has shown in Figure-1.28.

1.8.3. Dielectric spectroscopy

The dipole moments are induced on application of an electric field to a dielectric material. The weak electric field mainly have the distorting effect and breaks the symmetry of dipole distribution, as a result a macroscopic polarization is induced. There are mainly three types of contributions arising from electronic, ionic and dipolar interactions. The magnitude of the influence of the electric field on each process is described by the permittivity (ε). All processes with the presence of full contributions could be in phase with the applied field in the low-frequency regime.



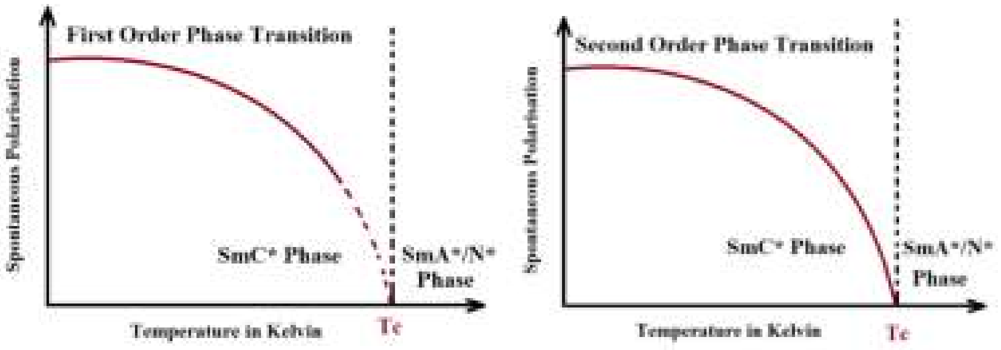
(a) **(b)**

Figure-1.29 (a-b): (a) Complex dielectric permittivity as a function of frequency and **(b)** Cole-Cole plot.

However, with the increase of frequency, slower processes cannot be able to follow the instantaneous field and consequently decrease their contribution to the permittivity (ε). The induced polarization becomes out of phase with the field and the corresponding difference in phase can be expressed by the imaginary part of a complex permittivity. There is some relaxation phenomenon related to different liquid crystalline phases [195]. The frequency variation of real as well as imaginary parts of the complex dielectric permittivity have shown in Figure-1.29 (a) and the nature of the variation of imaginary part with the real part of the complex dielectric permittivity the so-called Cole-Cole plot has shown in Figure-1.29 (b).

1.8.4. Spontaneous polarization

The existence of spontaneous polarization is one of the consequences of the presence of chirality in the SmC* phase, which arises due to the transverse components of molecular dipoles in each smectic layer. Thus, such a layer has ferroelectric in nature. The chemical structure of the molecules determines the direction of polarization. The variation of the polarization and the tilt angle values with temperature are such that; in the SmA* phase they possess zero value and gradually increase on cooling in the SmC* phase [194]. The growth may be discontinuous or continuous at the transition point depending on the nature of the phase transition. However, in the deeper inside of the SmC* phase the saturation of the spontaneous polarization is generally observed which has been shown in Figure-1.30 (a-b).



(a) **(b)**

Figure-1.30 (a-b): Spontaneous polarization (P_S) *versus* temperature (T) curve **(a)** Discontinuous for the first order phase transition **(b)** Continuous for the second order phase transition.

Due to the helix formation inside a bulk sample the net polarization is cancelled out. The dielectric properties associated with such structure is described with the term helielectric. As, in the absence of field the net polarization is zero, helielectrics are a sub-class of antiferroelectrics. In relatively thin samples like 'bookshelf geometry' the suppression of the helical structure occurs by the surface interactions and the molecules could be in one of the open tilt cone positions, characterized by the opposite (up and down) polarization directions and could be switched with the opposite electric fields. Thus, for such type of configuration the truly ferroelectric behavior can be observed. In the unwound state the optic axis which coincides with the director reorients in the plane of the surfaces during such in-plane switching. Clark and Lagerwall [35] were first introduced this type of structure and is termed as surface stabilized ferroelectric liquid crystals (SSFLCs) [196].

In the ferroelectric materials there exist a critical temperature T_C below which the electric polarization develops in absence of the external applied field *i.e.*, it becomes spontaneously polarized. Thus, a transition of phase occurs at T_C. Above the critical temperature T_C, the random orientation of the elementary dipoles gives rise to the paraelectric phase and below T_C, the dipole-dipole interaction generated an internal field, which oriented the dipoles in a certain direction, account for the appearance of the spontaneous polarization (P_S). With lowering [197] the temperature the gradual increase of spontaneous polarization takes place in accordance with the following equation [198,199]:

$$P_S = P_0(T_C - T)^\beta \tag{1.5}$$

where T_C is the critical temperature associated with the concerned phase transition, β is the critical exponent corresponding to the spontaneous polarization order parameter. The presence of lateral molecular dipole moments (p_i) is an essential reason for the existence of P_S and the natural way of enhancing P_S is to increase the value of p_i. One has to realize that a simple addition of p_i does not gives rise the P_S value in a given volume. This value decreases significantly by the rotation of LC molecules around their long axes and various intermolecular rotations. Therefore, by restricting the molecular rotations one can increases the value of P_S. Thus, one can see that the enhancement of spontaneous polarization closely related with the molecular configuration such as the presence of chiral center, number of asymmetric carbons and the nature of the bond between the chiral part and central linear rigid core.

Although, many compounds with large values of spontaneous polarization have synthesized so far, but the process of synthesizing and studying of the materials with high P_S is an active area of research. From the application point of view the value of the spontaneous polarization (P_S) associated with ferroelectric liquid crystal is one of the most crucial parameters for investigating their behaviors in the presence of an electric field and thus a careful optimization is required for certain electro-optical devices. However, the alignment of the LC materials in the E-O cells strongly depends on the kind of the existing mesophase (may be either the cholesteric N^* or the smectic-A^* phases) at temperatures just above the ferroelectric SmC^* phase.

1.8.5. Viscosity

The presence of molecular interactions inside the materials give rise to the collective property such as viscosity. In understanding the dynamical behavior of some chiral systems, the torsional viscosity (η) which arises due to the rotation of the molecules about the SmC^* cone plays a significant role. The torsional viscosity not only depends on the spontaneous polarization and the response time but also related to the molecular structure of the compounds. It has been observed that the torsional viscosity increases with decreasing temperature which implies the energy barrier for rotation increases significantly. The hindering of the molecular rotation for some chiral ferroelectric liquid crystalline systems (CFLCs) may also account for the bulky nature of the chiral unit and polar methoxy group substituted in the lateral position [194].

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