

CHAPTER 1

Introduction

1.1. Liquid crystals

Liquid crystals (LCs) or mesophases are fascinating state of matter, existing in between the three-dimensionally ordered crystals and completely disordered isotropic liquid [1,2]. Several compounds formed by organic molecules do not exhibit a direct transition from solid to liquid; rather it passes through a single or series of fluid like phases in between, known as the liquid crystalline phases. The self assembly of the molecules in LC compounds provides both the orientational order as in liquids as well as the positional order as in crystalline solids which may be of one or two dimensional. The combination of both these ordering promote the LC material to reveal the properties of both the crystalline (*i.e.*, anisotropy in optical, electrical and magnetic properties, periodic arrangement of molecules in one spatial direction etc.) and the liquid (*i.e.*, fluidity, viscosity, inability to support shear) states [3]. The main criterion for organic molecules to exhibit mesomorphic behavior is shape-anisotropy [1,2]. LCs are made up of molecules in various shapes such as the rod-like, bent-shaped or disc-like etc. In addition to this, the presence of flexible terminal chain in such molecules produces some molecular disorder, which also decides the type and temperature stability of the mesophases. It is interesting to investigate their physical properties systematically for better understanding about the nature of the mesophases which requires different tools and techniques. Moreover, due to the presence of optical and dielectric anisotropy in LCs, along with many other applications they are widely used in display technology. Therefore, a complete understanding of different LC systems can be helpful in modifying and improving their applications in display technology [4,5].

An Austrian botanist Friedrich Reinitzer was the first to discover the liquid crystalline phase in 1888 while working on Cholesteryl benzoate ($C_6H_5COOC_{27}H_{45}$) [6]. During the heating cycle, he observed that Cholesteryl benzoate formed a cloudy fluid state in between 145.4 °C and 178.5 °C which

then completely turned into the isotropic liquid. Further confirmation was made by a German physicist Otto Lehmann [7] when investigating such type of material in polarizing optical microscope and he named it as “flüssige kristalle” (meaning liquid crystals) in 1890. Furthermore, in 1922, George Friedel [8,9], renamed “mesophase” to such a fascinating class of matter. Since then a number of different phases have been identified as liquid crystalline mesophases. In both theoretical and experimental research, with the focus of complete understanding and continuous development of these mesophases, lots of works have been devoted. Various researchers have been successful in accomplishing the structural modification by considering intermolecular interactions of the LC molecules which emphasized the liquid crystal material for the applications in liquid crystal display, optical switch, phase modulator, beam steering, holography, laser projection, temperature sensor etc. [10-19].

1.2. Classification of liquid crystals

Based on the structural property of liquid crystal molecules, transition to different mesophases occurs mainly due to two distinct ways: one by purely thermal process and other under the influence of solvents. In the former process, the phase transitions among the intermediate phases occur by varying the temperature of the compound and are known as thermotropic liquid crystal. If the phase transition among the different mesophases are brought about by the change in concentration of solvent (influence of solvent) then such compounds are called as lyotropic liquid crystal. A brief introduction for both type of liquid crystals are discussed below.

1.2.1. Lyotropic liquid crystals

Lyotropic liquid crystals are associated with the amphiphilic molecules (surfactant), which comprises a polar head that is attracted towards water or polar substances (hydrophilic) and also non-polar flexible terminal tails (hydrophobic) [20-23]. In an anisotropic solution of such molecules with an

appropriate solvent, small aggregates are formed with a particular shape in which hydrophobic tails are protected by polar head and these small aggregates are called micelles. Generally, micelles are spherical in shape; they may be lamellar, cubic and hexagonal in structure. It has been observed that by increasing the surfactant concentration, molecular ordering also increases. Most general example of a lyotropic liquid crystal is soap solution, although it is most familiar in biological system like in certain proteins, lipid, cell membrane etc. [24].

1.2.2. Thermotropic liquid crystals

In case of thermotropic liquid crystal, the transition between different mesophases is caused by varying the temperature externally. The organic molecules associated with these types of compounds have a specific architecture with a rigid core or aromatic ring in addition to flexible terminal chain linked with it. Depending upon such molecular structure, liquid crystal compounds are further classified as rod-like or calamitic liquid crystal, disc-shaped or discotic liquid crystal, banana-like or bent-core liquid crystal as depicted in Fig. 1.1. Based on the position of bent angle, the bent-core liquid crystals are also of several types: hockey stick-shaped, T-shaped, star-shaped, pyramid-shaped etc. A limited description of the LC compounds composed of

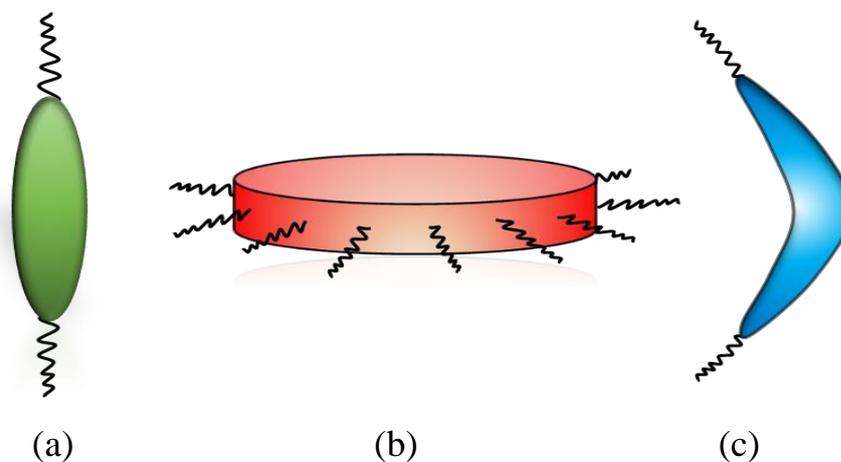


Figure 1.1. Schematic diagram of three different types of thermotropic liquid crystals: (a) calamitic, (b) discotic, and (c) bent-core.

calamitic and bent-core molecules has been demonstrated in the following sections which are relevant to the thesis work.

1.2.3. Calamitic liquid crystals

In general, the term “calamitic” or “rod-like” simply defines the macroscopic view of the structural unit. More precisely it can be stated that the molecules are constructed by a rigid straight aromatic core of phenyl rings, attached with one or more terminal alkyl or alkoxy chains at its end. Depending upon the chain length and number of phenyl rings in central core unit, such liquid crystal compounds possess distinct mesophase behavior and unusual mesomorphic properties, which are described in details further.

1.2.3.1. Nematic (*N*) phase

Nematic phase is the simplest and least ordered phase with the highest symmetry among all the mesophases of thermotropic liquid crystal. In case of a nematic phase, there exists a high degree of long-range orientational ordering without any positional ordering of the molecules, *i.e.*, the organic molecules are on the average preferred to align their long axis along a particular direction, though the molecular center of mass is arbitrarily oriented within a finite volume [25-27]. Hence, the compound possesses a high degree of mobility as like as isotropic liquid. The preferred aligned direction is called the nematic director or simply director and symbolized as \hat{n} (See Fig. 1.2). The directional distribution is symmetric in case of nematic molecules due to the presence of molecular head-tail symmetry [3], *i.e.*, there is an indistinguishable property between \hat{n} and $-\hat{n}$ with respect to the molecule. The preferred direction of molecules usually varied from point to point in the medium, but a homogeneously aligned domain is optically uniaxial and strongly birefringent. However, the biaxial nematic phase also exist [28-34], in which a second director \hat{m} is present and directed along molecular short axis, orthogonal to \hat{n} as illustrated in Fig. 1.2. The biaxial nematic phase is often found in case of

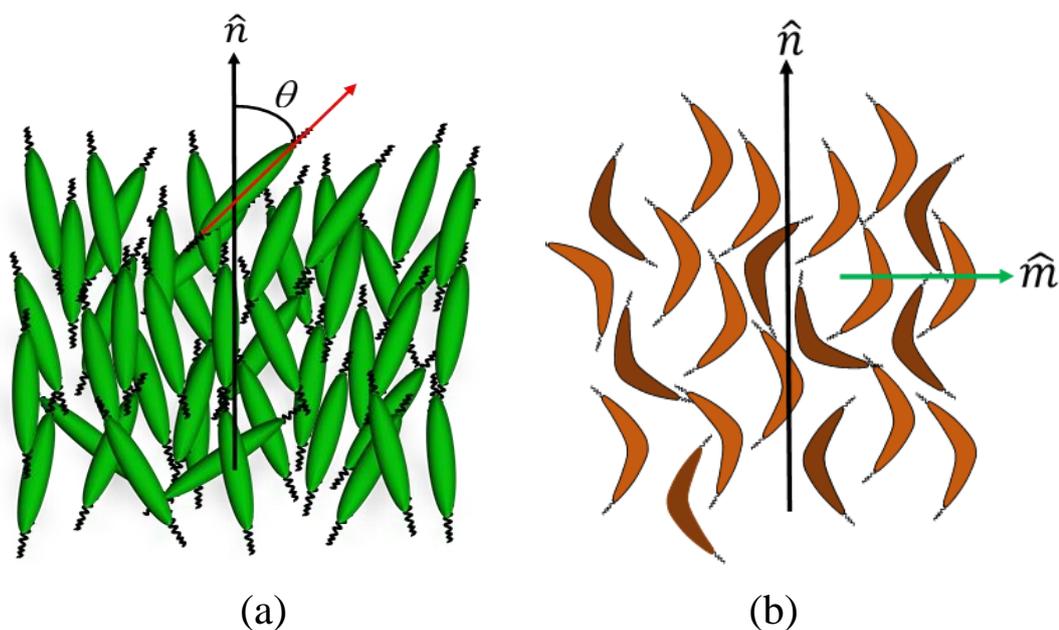


Figure 1.2. General representation of molecular ordering in (a) uniaxial and (b) biaxial nematic phase.

bent-core compounds. However, another type of nematic phase is also discovered, in which molecules are oriented in layers, called the cybotactic nematic phase [35-44]. Furthermore, due to the presence of polarity of the molecule, deformation of uniaxiality or biaxiality in nematic phase is also possible by the influence of the external field (electrical, magnetic or mechanical perturbation), which affects the optical and dielectric properties of the compound. This mechanism is most useful in display technological application.

The long-range orientational order of the molecules in the uniaxial nematic phase is defined by a scalar order parameter S and expressed as:

$$S = \langle P_2(\cos \theta) \rangle = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \quad (1.1)$$

where, θ is the angle between the molecular long axis and the nematic director \mathbf{n} , the bracket $\langle \dots \rangle$ indicates an ensemble average over all the molecules. However, the value of S is equal to 0 in case of isotropic liquid, as because of random orientation of the molecules. Moreover, well within the nematic phase or a perfectly order phase, θ is equal to 0, provides $\langle \cos^2 \theta \rangle = 1$ and hence $S =$

1. On other hand, if the molecules are oriented randomly in a plane perpendicular to the director, having the same director axis on the average, then θ is equal to $\pi/2$, and $\langle \cos^2\theta \rangle = 0$ which presented a value $S = -1/2$. Therefore, the theoretical prediction of this order parameter value varies from $-1/2$ to $+1$, whereas experimental value provides a range between 0.3 and 0.8 well within the nematic phase.

In the planar geometrical arrangement of the nematic LC sample, a schlieren textures with curved four and two dark brushes and often thread like or marble texture are observed under polarizing optical microscope [45].

1.2.3.2. Smectic (Sm) phase

In addition to orientational ordering, molecules have some degrees of positional ordering within the smectic phase which is generally appeared at lower temperature than nematic phase. This phase is more ordered than the nematic phase, *i.e.*, the smectic phase is more “solid-like” than the usual nematic phase. In this phase, the centers of mass of the molecules are on the average arranged within equidistant layers with a well-defined interlayer separation. The molecular director in each layer is aligned either orthogonal or tilted relative to the layer normal. Moreover, due to lack of interlayer attraction, individual layers of smectic phase can slide over one another as like fluid phase even though with a viscosity much higher compared to that in the nematic phase. Although, smectic phases have one-dimensional long-range positional order as like one-dimensional crystal, some other smectic phases have three-dimensional long-range Bond-Orientational Order (BOO), but without any long-range positional ordering as in case of hexatic phases. Depending on the orientation and ordering of molecules within the layer, smectic phases can be classified into different sub-phases which are designated in accordance with increasing order: Smectic *A*, Smectic *B*, Smectic *C*, Smectic *E*, Smectic *G*, Smectic *H*, Smectic *I*, Smectic *F* and so on. In the following section, brief introductions to some of those smectic phases have been presented.

a. Smectic A (Sm-A) phase

In case of smectic A (Sm-A) phase, molecules are aligned on average to a direction parallel to the layer normal (\hat{k}) with their centre of mass oriented arbitrarily as depicted in Fig. 1.3. Such a configuration can be described by considering a one-dimensional mass density wave along the layer normal. However, this one dimensional ordering is not truly long-range rather it can be said as quasi long-range. Furthermore, as this phase is optically uniaxial with respect to optic axis, the homeotropically aligned optical texture is appeared to be black where a fan-shaped or focal conic type textures are visible for planar aligned sample. On the basis of the relation between the molecular length and the layer spacing, the Sm-A phase can be subdivided into several distinct phases, namely Smectic A_1 , Smectic A_2 and Smectic A_d . All have the same point group symmetry but differ by translational symmetry due to specific packing of the molecules within a layer. In smectic A_1 the layer thickness is equal to the molecular length, whereas in smectic A_2 phase, the layer thickness is equal to the twice of the molecular length and the smectic A_d phase has an intermediate

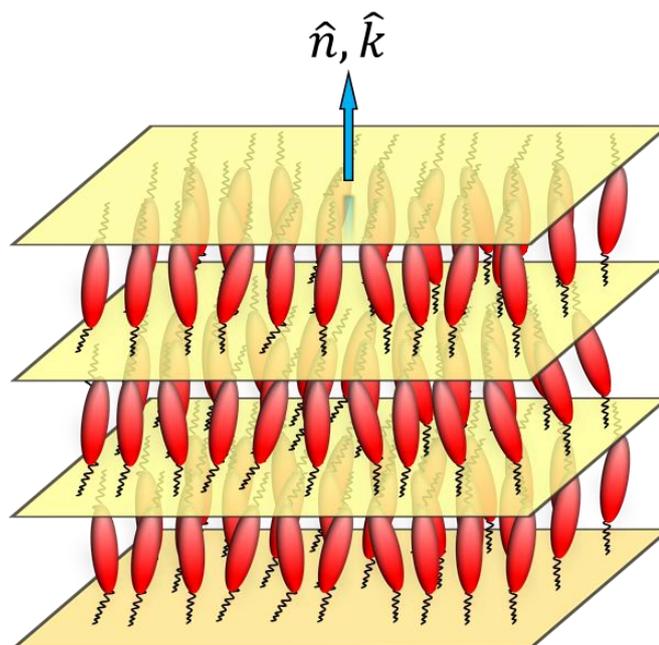


Figure 1.3. Structural representation of molecular ordering in smectic A phase. The director \hat{n} is parallel to the smectic layer normal (\hat{k}).

layer structure in-between smectic A_1 and smectic A_2 , *i.e.*, the layer thickness (l) is intermediate between the single molecular length (d) and twice of that ($2d$) [46-49].

b. Smectic C (Sm- C) phase

The molecular organization in the smectic C phase is quite similar to that of the smectic A phase, but the only difference is that the molecules are tilted by an angle θ (temperature dependent tilt angle) with respect to the layer normal (\hat{k}) as in Fig. 1.4. This tilt angle is more or less same for all molecules within a layer and also same for the adjacent layers. However, the smectic layers also have no positional correlation as like Sm- A phase, and hence exhibit fluid-like sliding features in one over another. In this case the molecules have the freedom to rotate about their tilt direction. Hence, due to the introduction of such tilt the rotational symmetry breaks about the layer normal [50,51]. Thus the Sm- C phase exhibits an optical biaxiality as well as a relatively greater

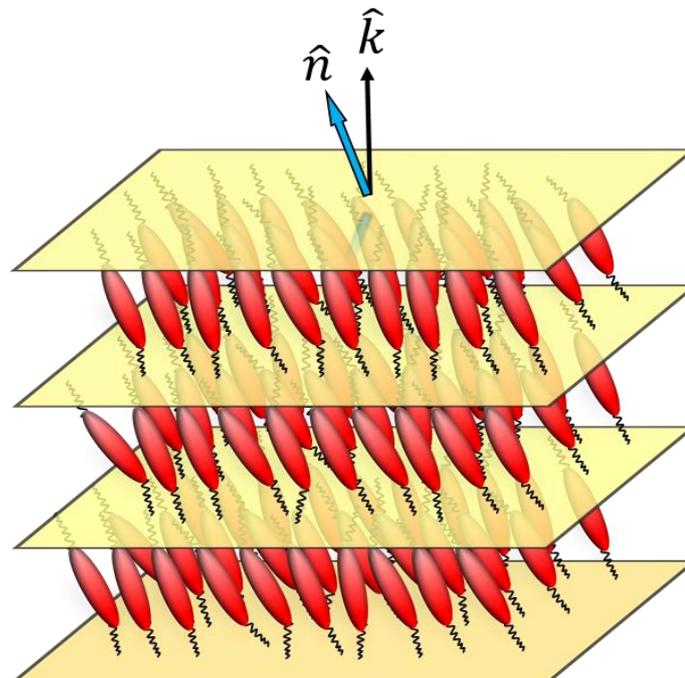


Figure 1.4. Structural representation of molecular ordering in layers for smectic C phase. The director \hat{n} is tilted with respect to the smectic layer normal \hat{k} by a certain angle.

viscosity than that of the Sm-A phase. Again, the Sm-C phase can also be subdivided into two distinct sub-phases, based on the relative tilt alignment of the molecules in adjacent layers – (a) the synclinic smectic C (Sm-C_s) phase, where the tilt direction is the same in adjacent smectic C layers and (b) the anticlinic smectic C (Sm-C_a) phase, where the tilt direction alternates in the adjacent smectic C layers. Moreover, the optical textures of the Sm-C phase can be visualized as fan-shaped and often as broken fan-shaped typed in planar alignment [45], while schlieren textures also visible in homeotropically aligned Sm-C_s and Sm-C_a phases [52].

c. Hexatic smectic (Sm-B, Sm-I, Sm-F) phases

Like other smectic phases discussed above, molecules are arranged in layers in hexatic phase, but the molecular centre of mass are arranged in a shape of hexagonal grid with long-range Bond-Orientational Order (BOO) of the hexagons. A short-range positional order of the molecules is also present in each smectic layer [53-56], whereas no positional correlation is present in between the adjacent layers [57]. Moreover, on the basis of molecular long axis direction, hexatic smectic phases are also classified into sub-phases- Sm-B, Sm-I, Sm-F etc. In Sm-B phase, the direction of molecular long axis is parallel to the smectic layer normal as in Fig. 1.5, which defines that Sm-B_{hex} is

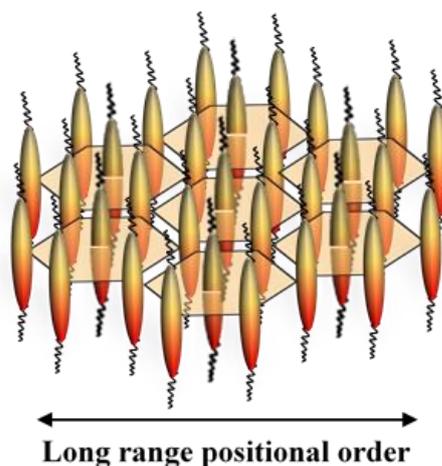


Figure 1.5. Structural representation of molecular ordering in each layer for hexatic smectic B phase.

uniaxial in nature as like Sm-A phase, while in case of Sm-*I* and Sm-*F* phases (Fig. 1.6) the molecular long axis is tilted with respect to layer normal. In case of Sm-*I* phase, tilt direction is perpendicular to the sides of hexagon, while the molecular tilt direction is towards the corner of hexagon for Sm-*F* phase [58].

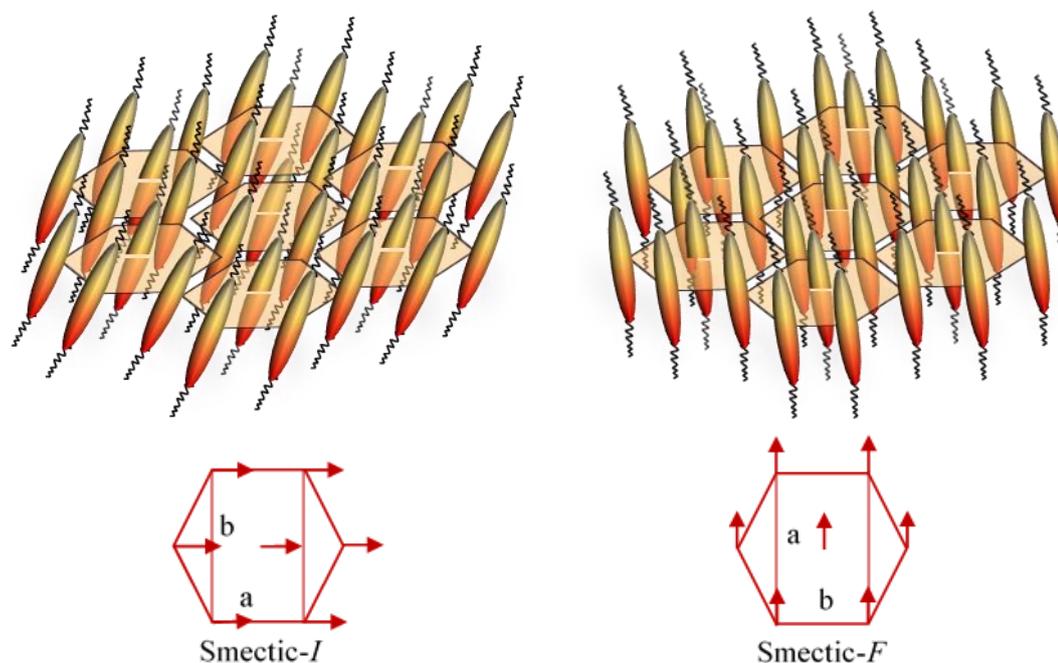


Figure 1.6. Structural representation of molecular ordering in each layer for smectic *I* and smectic *F* phases.

d. Soft crystal (*B*, *E*, *J*, *G*, *K*, *H*) phases

In case of soft crystal *B* phase, associated molecules are aligned perpendicular to the layers and having long-range translational order in the same way as like as hexatic Sm-*B* phase. However, in this case in addition to long-range bond orientational order, a long-range positional order is also present in three dimensions [57]. Alongside in crystal *E* phase, molecules are also arranged perpendicular to the smectic layers, but they have a tendency to arrange themselves in a herringbone pattern with orthorhombic symmetry in each layer [59] as illustrated in Fig. 1.7. This phase has no fluidity and supposed to form a most ordered crystal. Furthermore, there are some tilted soft crystal phases, such as crystal *J*, *G*, *K*, *H* etc. Soft crystal *J* and *G* are the three-dimensionally long-range ordered version of Sm-*I* and Sm-*F* phases

respectively [58,60,61]. The soft crystal H and K phases are tilted analogs of the crystal E phase. The molecules in the crystal H phase are tilted along the direction perpendicular to a side (towards a corner in case of crystal K phase) of the underlying hexagonal structure. In case of soft crystal B , J and G phases, the molecular rotation around the long axis is totally independent and they feel free to rotate, while in the crystal E , K and H phases the rotational hindrance is acting around the molecular long axes and such hindrance is so strong that only jumps between two favored positions are allowed [61,62]. All of the soft crystal phases exhibit mosaic type texture more or less similar to each other [45] under polarizing optical microscope.

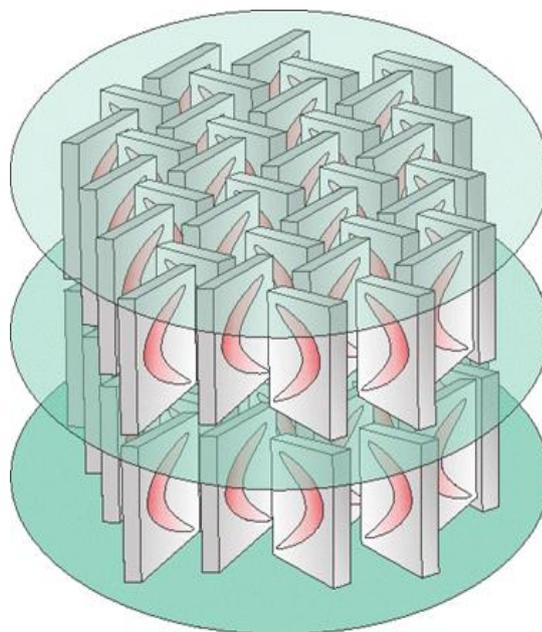


Figure 1.7. Molecular geometry of soft crystal E phase.

1.2.3.3. Chiral phases

a. Cholesteric or chiral nematic (N^*) phase

Cholesteric or chiral nematic phase is more complex mesophase than usual nematic phase where the constituent molecules have chiral property, *i.e.*, the mirror symmetry is absent for the molecular structure. These chiral (optically active) molecules are similar to ordinary LC molecules, except one

or more chiral center which are generally introduced by substituting one or more carbon atoms asymmetrically as the linkage between aromatic core and associated terminal alkyl chain by four different ligands. The intermolecular interaction or force between the molecules precisely affected their effective orientations in such a way that they are separated by a very small angle with each other. Moreover, this orientation leads to the formation of a superstructure that can be visualized as a stack of two-dimensional very thin virtual layers without any positional ordering of the molecules within the layers. Additionally, the director axis of each layer rotated periodically about a perpendicular axis called helix axis [63]. Therefore, as a whole macroscopic helical superstructure is formed as like Fig. 1.8(a). In this molecular superstructure, the perpendicular distance for which the layer director rotates a full turn in helical axis is called pitch length (P). During cooling or heating, several types of cholesteric textures are observed in planar aligned sample (see

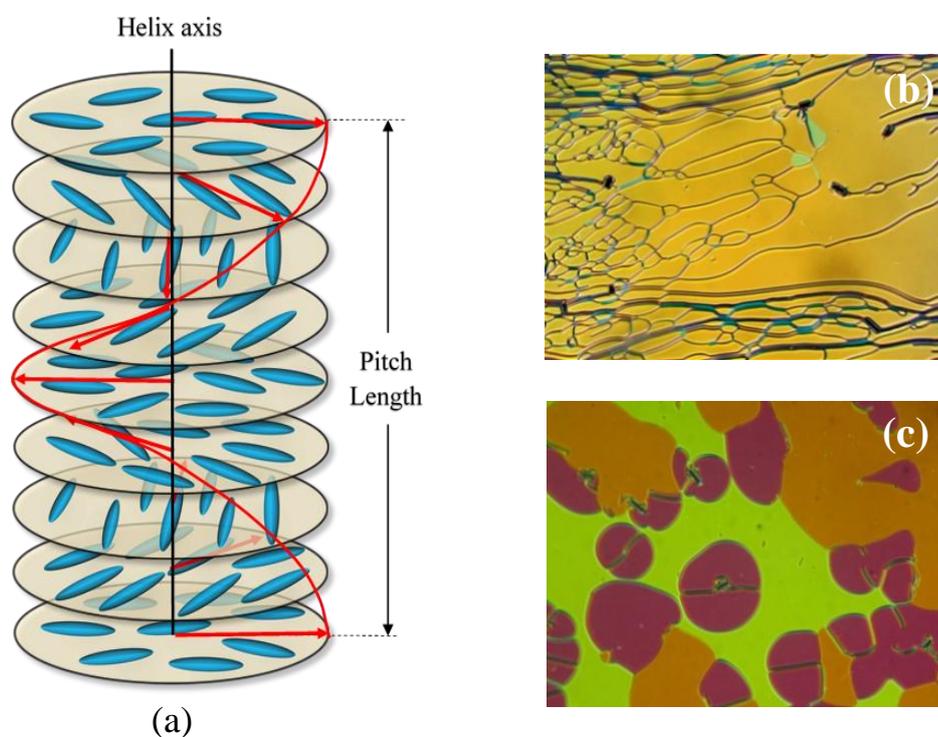


Figure 1.8. (a) Molecular representation of cholesteric or chiral nematic phase, (b-c) Optical textures appeared in cholesteric phase at two different temperatures.

Fig. 1.8(b-c)) as because the pitch length of helical rotation is temperature dependent. Hence, the cholesteric phase is nearly identical to usual nematic phase but having finite pitch length. Moreover, the advantages of this helical superstructure are - high optical rotatory power, reflection of lights (Bragg reflection) for wavelength equal to pitch length of the sample [64,65] etc. which are desirable for some electro-optic applications.

b. Chiral Smectic A (Sm-A*) phase

Chiral smectic A (Sm-A*) phase is the chiral analogue of Sm-A phase, where the molecules are aligned orthogonally in layers and at the same time they also rotate in a liquid-like fashion around their long axis [66-68]. However, the symmetry of this phase is further reduced than that of the Sm-A phase. Due to the absence of symmetrical correlation among the molecules in the smectic layer, the net transverse polarization vanishes, *i.e.*, the Sm-A* phase exhibits paraelectric behavior. Hence, in spite of being made up by chiral molecules, the Sm-A* is apolar in nature. Furthermore, by applying external electric field, molecular tilt angle and hence an effective polarization can be induced with respect to smectic layer normal, which is an interesting feature in technological applications.

c. Chiral Smectic-C (Sm-C*) phase

Similar to the Sm-A* phase, Sm-C* phase is chiral analogue of the Sm-C phase, without any mirror symmetry. As the molecules are tilted in-layer, a precession of molecular tilt direction around the layer normal is present in a macroscopic helical form [69,70]. However, due to existence of molecular tilt in smectic layers, only the two-fold rotational symmetry along C_2 axis is active in this phase and hence a non-zero polarization or ferroelectricity can be visualized in each layer directed perpendicular to the tilt plane of the Sm-C* phase [71]. However, as the azimuthal tilt direction is rotating by small amount from layer to layer around the helix axis, the overall polarization cancels out

for a complete rotational cycle of tilt director (See Fig. 1.9(a)). Hence, this phase can be named as “helielectric”, rather than “ferroelectric” [72]. Although, a non-zero finite macroscopic polarization can be induced in a specific geometries if the helix of Sm-C* phase unwinds by applying an external electric field or via elastic interactions with surface [73-76].

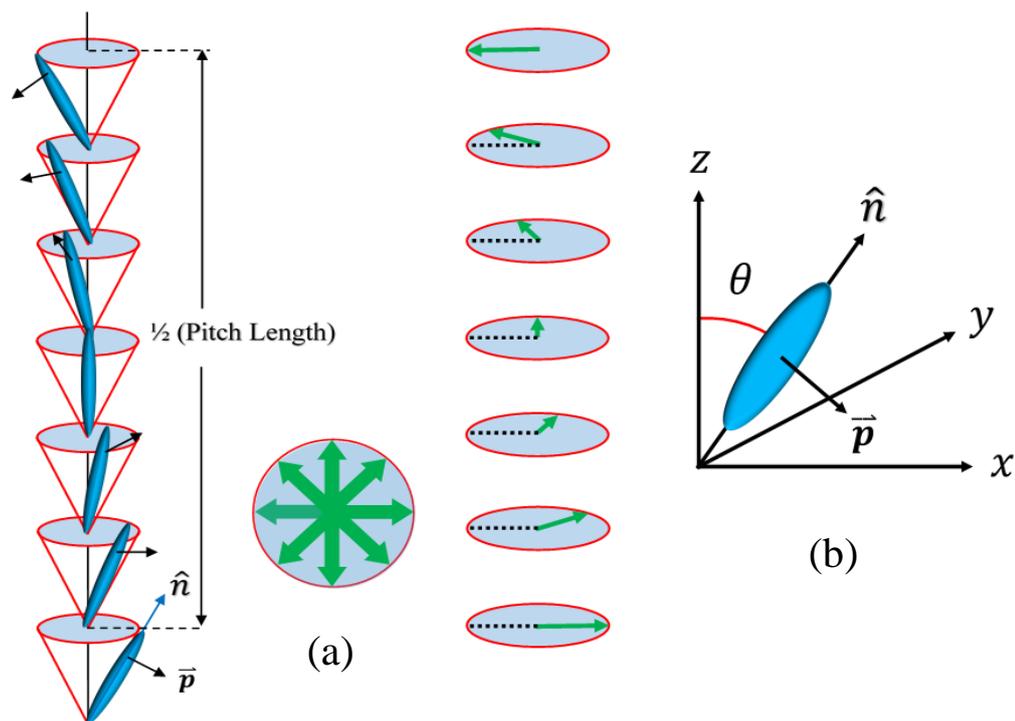


Figure 1.9. (a) Helical superstructure of the chiral smectic C (Sm- C^*) phase with the helix axis parallel to the smectic layer normal \hat{k} , (b) Orientation of a single molecule in each layer. The polarization vector \vec{P}_s is always perpendicular to the director \hat{n} and the tilt plane.

In contrast to this, an anti-ferroelectric chiral smectic C phase (Sm- C_A^*) has also been discovered, where the molecular orientations are same as like as Sm- C^* phase but the direction of tilt alternates in adjacent layers and hence, the direction of polarization also alternates from one layer to the next, canceling out the total polarization [77-80]. The polarization can be aligned uniformly between the layers on applying a strong external field. However, the tri-state switching characteristic of anti-ferroelectric Sm- C^* phase is potentially effective to achieve easy grayscale switching in display devices. Also the wide

viewing angle with a relatively large contrast ratio, inherent DC compensation and fast response time make anti-ferroelectric liquid crystals superior to ferroelectric liquid crystals. Nowadays high tilted or orthoconic anti-ferroelectric liquid crystals are used to remove its initial linear response and high-quality alignment problems [77-80].

1.2.3.4. Liquid crystalline frustrated phases

Chirality is the self-assemble property of chiral molecules. However, in this case, the molecular symmetry significantly reduced than achiral molecules. Again due to existence of temperature variant tilt angle and the pitch length, it drastically modifies the mesomorphic behavior of the sample. Sometimes it is not so compatible for the chiral molecules to hold both layer structure and twisted helical orientation simultaneously due to molecular constraints. Such type of disturbance leads to the formation of some defected and quite complex type of frustrated phases [81,82]. Blue phase (BP) and twist grain boundary (TGB) phases are the examples of such superstructure frustrated phases, which are briefly described in the following sections.

a. Blue phases

A thermodynamically distinct mesophase, called blue phase (BP) generally appeared in between isotropic phase and the cholesteric (N^*) phase for a narrow temperature scale in some highly chiral LC compounds. This type of frustrated phases can be regarded as self-assembled three-dimensional counterparts of the cholesteric phase, exhibiting cubic lattices (lattice period of several hundred nanometer) without any long-range positional order [81]. The blue phase is a cubic phase with regular lattice defect, *i.e.*, it consist of two double twist cylinders (Fig. 1.10(a)), arranged in two mutually perpendicular directions to form a continuous director field and a third double twist cylinder is placed mutually perpendicular with them to create a defect. Blue phases are the optically isotropic LC material which exhibit optical activity with a small

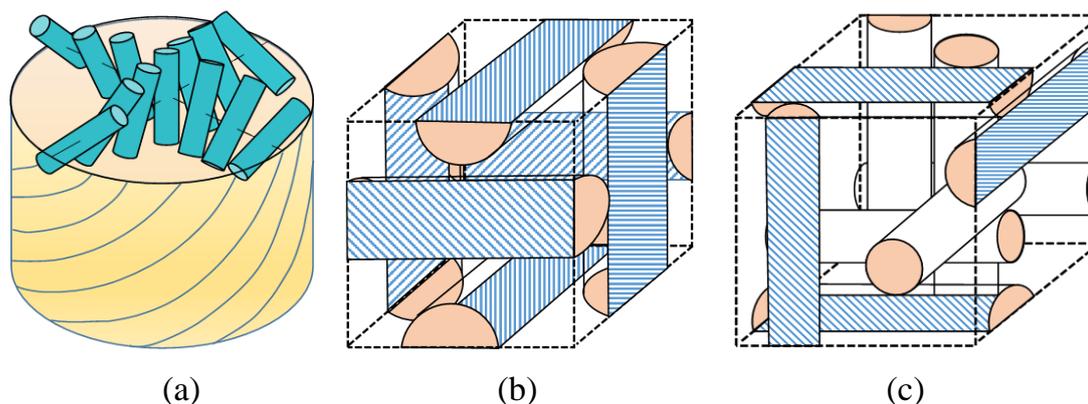


Figure 1.10. (a) Molecular representation in a double twist cylinder. Relative orientation of the double twist cylinders in case of the (b) BPII* and (c) BPI* phase.

value of birefringence. However, the naming of these phases as blue is due to their Bragg reflections in the blue wavelengths. Furthermore, blue phases have three distinct sub-phases – BPIII*, BPII* and BPI* that emerges in order of decreasing temperature from isotropic phase [83]. BPIII* (observed at highest temperature and appears foggy) is amorphous in nature and it has a local cubic lattice structure defect in the director field. Besides in BPII* phase has a unit cell (simple cubic) of lattice defects and in BPI* phase has a three-dimensional periodic structure in the director field with body-centered cubic symmetry which are shown in Figure 1.10(b-c). Due to presence of several advantageous property such as very fast switching times, non-zero elastic shear modulus etc., blue phases are potentially attractive for LCD devices and photonic applications.

b. Twist grain boundary (TGB) phases

Another distinct and special type of frustrated mesophase, named Twist Grain Boundary (TGB) phase appears in between chiral nematic (N^*) and higher ordered smectic phases [84,85] at relatively lower temperature than the blue phase. In general the molecules in cholesteric phase possess a helical structure around the helix axis and on the other side in smectic phases, the

molecules have a tendency to align themselves in layer structure. Therefore, a direct transition from cholesteric phase to smectic phase is not always favorable to the orientation of molecules. Hence such incompatibility to hold both rigid structural features at a same time is responsible for this type of frustrated phase. In those defected superstructures, some locally ordered defected or smectic slabs are formed which are again separated by the grain boundaries which in turn consists of a lattice with screw dislocations [84,85]. However, the successive layers are relatively twisted by a constant small angle to give a helical structure with the helix axis orthogonal to the layer normal direction. This phase is equivalent to the Abrikosov flux lattice phase of a type-II superconductor in an external magnetic field [84,86,87]. Moreover, the TGB phases can be classified further into distinct sub-phases- TGBA, TGBC and

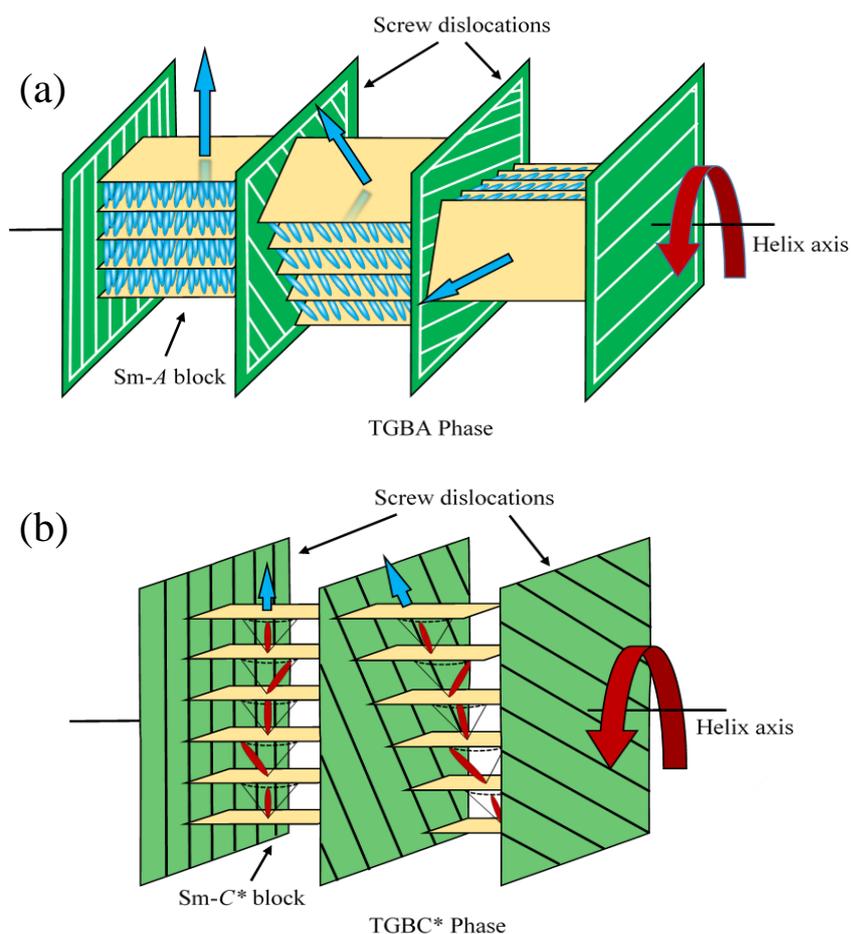


Figure 1.11. A structural representation of the molecular superstructure with screw dislocations for (a) TGBA and (b) TGBC* phases.

TGBC* phases, based on the layer structure within the slabs of TGB phase. If the molecules are aligned orthogonally with the layer plane, as like as Sm-A phase, modified phase is called TGBA phase (See Fig. 1.11(a)), whereas in case of TGBC phase, molecules are tilted within building blocks, as like as Sm-C phase [86-88]. Furthermore, if the smectic blocks are formed as helical Sm-C* type, the obtained phase is designated as TGBC* phase as illustrated in Fig. 1.11(b). TGBA phases are generally appears before the TGBC phase as being cooled from isotropic phase and also the pitch length is greater in TGBC phase. The planar oriented optical texture of TGBA phase exhibits a Grandjean type appearance with a temperature dependent pitch length, whereas the homeotropically aligned sample represents a fingerprint texture (equidistant line pattern) and often filament type textures, which is of the order of magnitude of the pitch length [45,89]. Besides in TGBC* phase, square grid type optical textures were observed which are described further in Chapter 7.

1.2.4. Bent-core liquid crystals

Apart from calamitic liquid crystals with rod-like molecular shape, various fascinating mesogenic properties have also been revealed in the compounds having other molecular geometries. Among them, the banana-shaped or bent-core molecules unveil a new branch in the field of thermotropic liquid crystal as they exhibit several striking properties in different mesophases due to the modification in the core unit. Earlier the bent-core molecules were thought of as inadequate molecules to form liquid crystal mesophases because they excluded a large volume under rotation about their long molecular axis, leading to a destabilization of the liquid crystalline phase [90]. In 1929, D. Vorländer and his group synthesized several bent-core LC compounds [91,92] and reported that they are not as stable as the calamitic molecules in temperature range. Furthermore, in 1991, Matsunaga *et al.* synthesized few series of the bent-core liquid crystals [93-96] and reported that the nonlinear molecular structure of the bent-core molecules is not necessarily incompatible

for the formation of LC mesophases. Again in 1996, Niori *et al.* first discovered the polar switching behavior in achiral bent-core compounds in one of the smectic phases [97]. More surprisingly, Link *et al.* [98] discovered the chirality in layers in bent-core mesogens composed of achiral molecules [99]. Sekine *et al.* also discovered the spontaneous chiral character in non-tilted mesophase [100,101]. Hence, the occurrence of unpredictable exciting mesomorphic behavior of different unique mesophases in the bent-core compounds brought them at the focus of scientific attention, unveiling a fascinating new domain in the branch of thermotropic liquid crystals.

The structure of bent-core molecules can be described in general as a central bent-unit of aromatic rings comprising one or more alkyl or alkoxy terminal chains attached at both ends of the molecules. Bent-core molecules are also symmetric or asymmetric depending on the position of bending and terminal polar or non-polar chain length determining the basic mesogenic behavior of these compounds. Fig. 1.12(a-b) illustrates symmetrical and asymmetrical bent-core molecules. Due to the existence of kink shape in the molecular structure, each molecule has two distinct axis around which it can rotate, *i.e.*, the bent-core molecules have two different directors – (i) along the molecular long axis, as like as calamitic molecules (\hat{n}), and (ii) along the molecular short axis or the bow axis (\hat{m}). However, the bent-core molecules self-organize themselves in a number of exclusive ways due to their non-linear molecular conformation as well as the steric interaction between the molecular associations. They experience a periodic potential while translating through the neighboring molecules, causing a translational symmetry breaking of the molecules along the long axis. At the same time there also exists a rotational hindrance about the director \hat{n} to reduce the excluded volume effect. Consequently, the molecules organize themselves in a close packed smectic like layer structure with a common direction of molecular bow axis (\hat{m}). Moreover, as the molecules comprised of two segments at a certain angle to

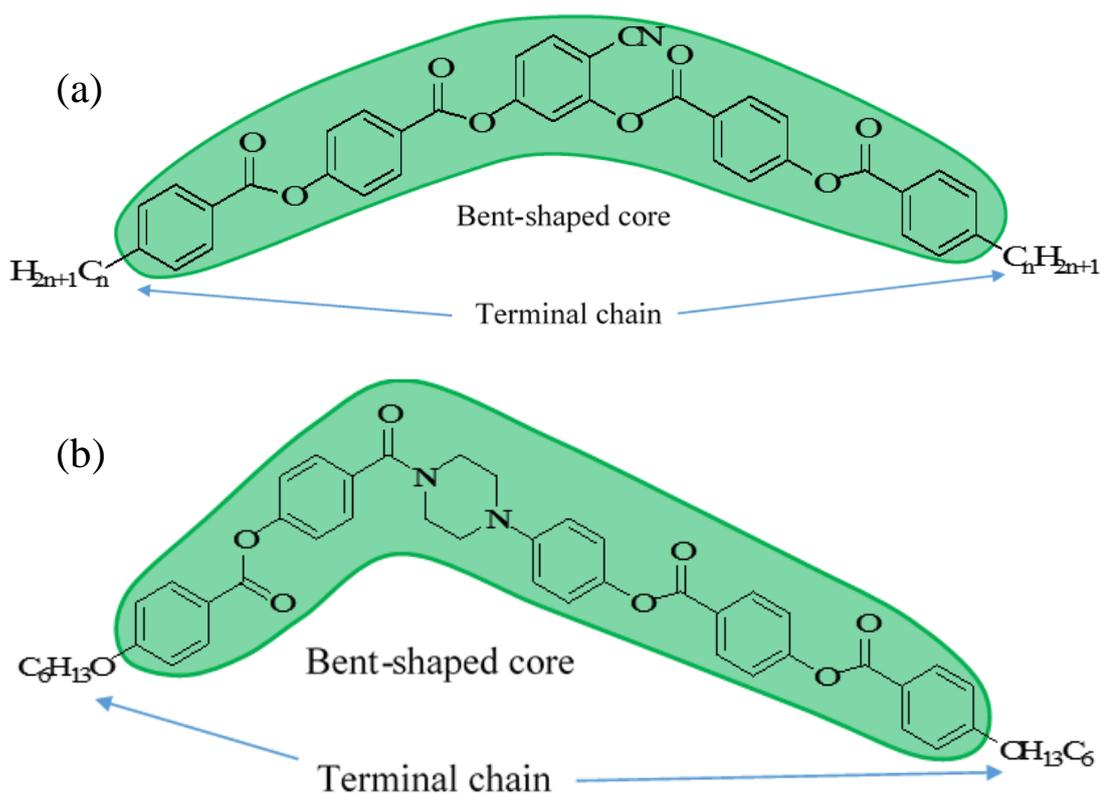


Figure 1.12. Molecular structures of (a) a symmetrical and (b) an asymmetrical bent-core compound.

each other and due to existence of polar linking groups, it produces a permanent dipole moment along the molecular transverse axis. The mutual correlations of those molecular dipoles packed in smectic-like layer structure reveals a small polar domain within the layer which can be switched by applying the external field. Hence, a macroscopic ferroelectric phase builds up within the system when the polarizations of adjacent layers are parallel [97] to each other and the anti-ferroelectric phase developed when they are aligned in anti-parallel way [102]. Furthermore, a combination of molecular tilt and polar vector produces the layer chirality effect, although the molecules are not optically active [90,98,99,103-105]. Thus the bent-core LC compounds represent a number of unusual modified smectic phases with ferroelectric, anti-ferroelectric nature as well as chirality in some mesophases.

Depending upon the mutual orientation of the molecules and associated mesophase behavior, the bent-core or banana-shaped compounds

can exhibit a group of columnar and smectic phases, named as B phases – the series B_1 to B_8 [90,99,106]. These types of phases have different mesomorphic characteristics than phases formed by usual calamitic mesogens. Moreover, the conventional mesophases such as Sm-A, Sm-C phases as well as nematic phases also been observed in some bent-core compounds, provided the bend angle is not too acute and the molecular length is sufficient to overcome the destructive nature of the bent-shape structure [32-34,38,107-116]. Conversely, some exotic mesophases with diverse molecular ordering like as dark conglomerate phase [117], polar Sm-A [118,119] and polar Sm-C phases with synclinic or anticlinic tilt ordering (Sm- C_s or Sm- C_a) along with ferroelectric or anti-ferroelectric polar ordering (Sm- CP_F or Sm- CP_A) and also biaxial nematic [34,97,98,120,121] phases has also been observed in several bent-core compounds. In the following section different mesophases formed by banana-shaped or bent-core compounds has been discussed.

1.2.4.1. Smectic phases of bent-core liquid crystals

a. B_1 phase

The B_1 phase is assigned to a columnar mesophase and it consist of two-dimensional lattice structure with rectangular form [122] which are generally observed in the bent-core compounds having short terminal alkyl chains. According to Watanabe *et al.* the B_1 phase is made up of columns formed by small fragments in layer structure [122]. However, the associated molecules in such fragments are oriented in parallel to each other to give rise a particular polarization direction in each layer, while the direction of polarization in adjacent layers are anti-parallel to each other [122] as shown in Fig. 1.13. However, the direction of polarization is orthogonal to the columnar axis. Hence, due to anti-parallel alignment of polarization vector in adjacent layers, the effective polarization in this phase vanishes. Again due to the mutual interactions between columnar boundaries, produces a steric hindrance for the rotational motion of the molecules which further restricts the field-induced

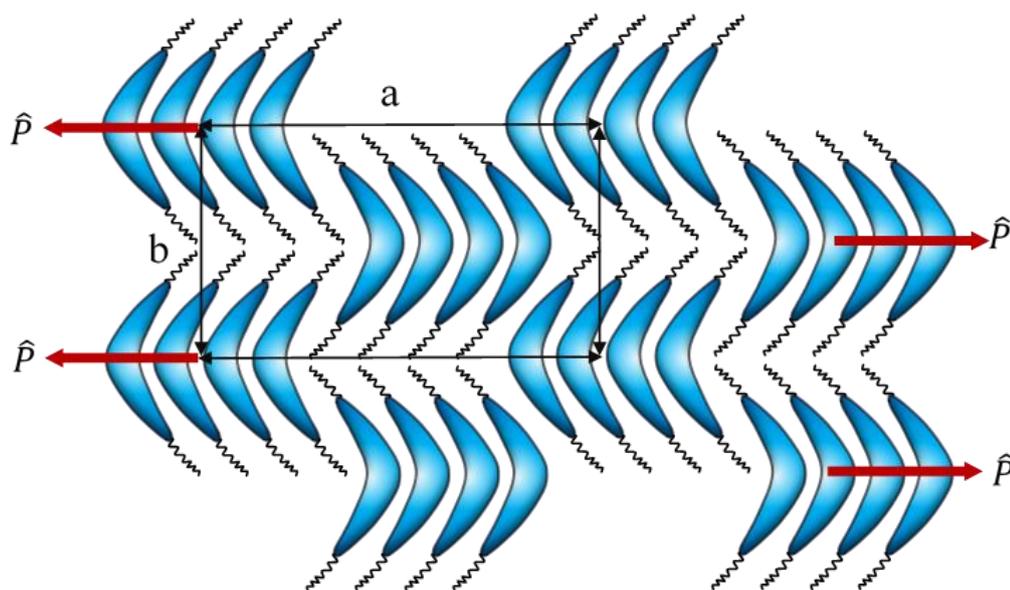


Figure 1.13. Schematic illustration of molecular geometry in B_1 mesophase. a and b give the measure of periodicities in the two perpendicular directions.

polarization. The wide-angle scattering of X-ray diffraction pattern demonstrates this B_1 phase as liquid-like in plane ordered phase, while the small angle pattern indicates an intercalation in the structure, *i.e.*, it reveals a two-dimensional frustrated layer structure [90,99]. In contrast to response of external field, the B_1 phase can be further classified into two distinct classes – $B_{1\text{rev}}$ and $B_{1\text{revtilt}}$. In $B_{1\text{rev}}$ phase, the polarization direction is parallel to columnar axis whereas $B_{1\text{revtilt}}$ phase is the tilted analogous of the $B_{1\text{rev}}$ phase and both are switchable in response to applied field [123-125].

b. B_2 phase

The B_2 phase is the most common and widely popular mesophase among all the banana phases which are generally observed in some bent-core compounds with long terminal alkyl chain. In 1997, Link *et al.* represented that the molecular long axis in this mesophase is tilted with respect to layer normal in each layer which leads to a C_{2v} structural symmetry and the effective direction of polarization is orthogonal to the tilt direction [98]. The closed packed structure of parallel aligned molecules in each layer produces the layer polarization and it alternates the direction from one layer to adjacent another.

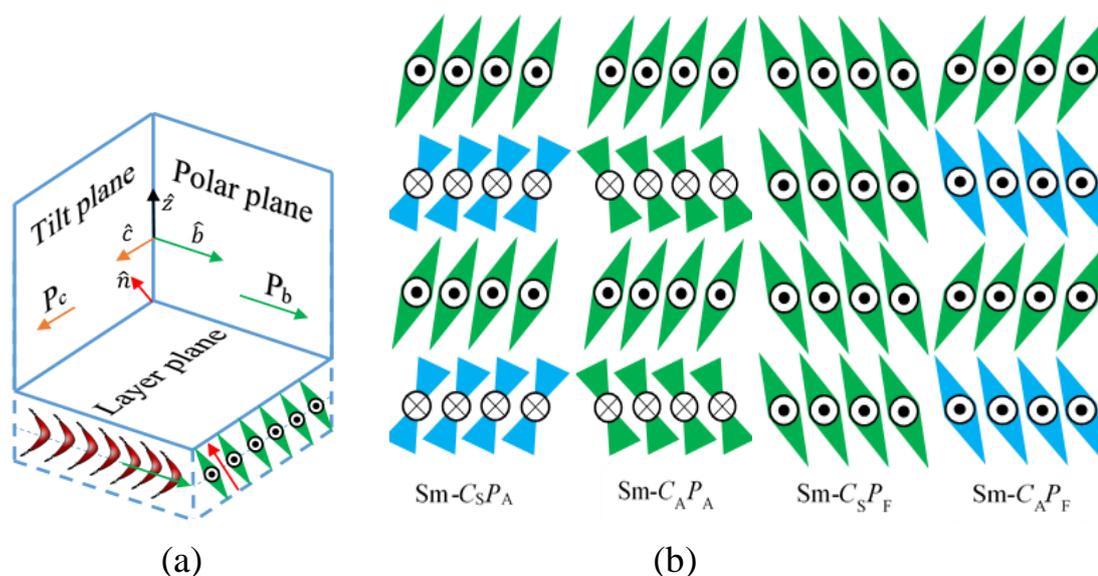


Figure 1.14. Representations of molecular geometry in (a) three mutually orthogonal planes and (b) four fundamental variants of Sm-CP phase in the B_2 phase.

Therefore, the complete mesophase structure can be considered to be consisting of three distinct mutually orthogonal planes, a tilt plane, a polar plane and a layer plane in each layer, as shown in Fig. 1.14(a). The mirror image of such mutual orthogonal planes does not superimpose with the original one. Thus the layer chirality produces in this mesophase, although the individual banana molecules are achiral in nature. However, the associated mesophase can be designated as Sm-CP phase (P symbolizes as polar order). Furthermore depending upon the molecular tilt direction and the effective polarization direction in adjacent layers, this phase is also further classified into– $Sm-C_S P_A$, $Sm-C_A P_A$, $Sm-C_S P_F$, and $Sm-C_A P_F$ phases [34-36,98] as illustrated in Fig. 1.14(b), where $Sm-C_S$ and $Sm-C_A$ represent the layer structure as in Sm-C type with synclinal and anticlinal arrangement of tilt direction in adjacent layers respectively. Conversely, P_F and P_A correspond to ferroelectric and anti-ferroelectric type of polarization in the adjacent layers respectively. Furthermore, on application of external electric field, a switching process by a collective rotation of the molecules around a cone from antiferroelectric to ferroelectric state is usually observed in such Sm-CP phases. At the time of

switching, the polar direction as well as the tilt direction gets reverses, but they preserve the layer chirality. Thus the anti-ferroelectric ground state of Sm- CP or B_2 phases of banana-shaped molecules switches to ferroelectric state by applying external electric field.

In general different types of optical textures are observed in this phase, among them the schlieren and the focal-conic textures and quite often fingerprint texture are also observed. Sometimes chiral domains of opposite handedness are also recognized during slow cooling from the isotropic phase.

c. B_3 phase

During cooling from isotropic phase, another type of banana phase named as B_3 phase generally appears in between B_2 and B_4 phases, where B_2 phase is the higher temperature mesophase [99]. However, in a fast cooling process from B_2 to B_3 phase, the appearance of the optical textures is found to identical as that of B_2 phase, while a broken fan-shaped texture appears on slow cooling. An inspection of X-ray diffraction pattern for this phase in non-oriented sample representing several diffraction peaks at wide angle as well as in small angle region which indicates a crystal-like ordered structure [101,126,127], whereas the 2-D X-ray diffraction pattern in planar oriented sample reveals that the layer thickness is smaller than the molecular length of all *trans*-conformation. Therefore, it has been predicted that the molecules are tilted within the layer [98,101,126] to accomplish such condition. Further study from the dielectric [128] and terahertz spectroscopy [129] in B_3 phase also suggest the same molecular dynamics as in B_2 phase, which indicates a higher-ordered smectic-like nature of this mesophase.

d. B_4 phase

During cooling from the higher temperature B_3 or B_2 phase, a dark bluish type optical texture of another banana phase named as B_4 phase appears in crossed polarizing microscope and hence this mesophase is designated as

smectic blue phase [101,126,130]. However, by rotating one of the polarizer in any direction, optical texture exhibits some tiny domains with different brightness and again they interchanges their brightness by rotating the polarizer further in clockwise or anticlockwise directions [131]. Such an appearance is identical to chiral phases which clearly suggesting the B_4 phase as a chiral mesophase. Moreover, the XRD patterns in wide angle and small angle region in B_4 phase implying the layer spacing comparable to length of the molecule, which is an indication of non-tilted smectic ordering of the molecules and packed as a crystalline phase. However, the low-frequency dielectric study reveals this mesophase as non-crystalline in nature. Although the FFTEM study demonstrates that this phase is fabricated by chiral nano-bundles associated with twisted layers of molecules [117], it does not possess any switchable property. Furthermore, in the absence of any external electric field, the simple harmonic generation (SHG) signal was observed in this mesophase, which indicates a spontaneous non-centrosymmetric ordering [132,133].

e. B_5 phase

The B_5 phase is rare among all the banana phases and it appears in few compounds just below the B_2 phase with a small change in transition enthalpy [98,99,134]. Both the B_2 and B_5 phases appeared to be identical in textural appearance and also in the electro-optical response. However, the XRD pattern

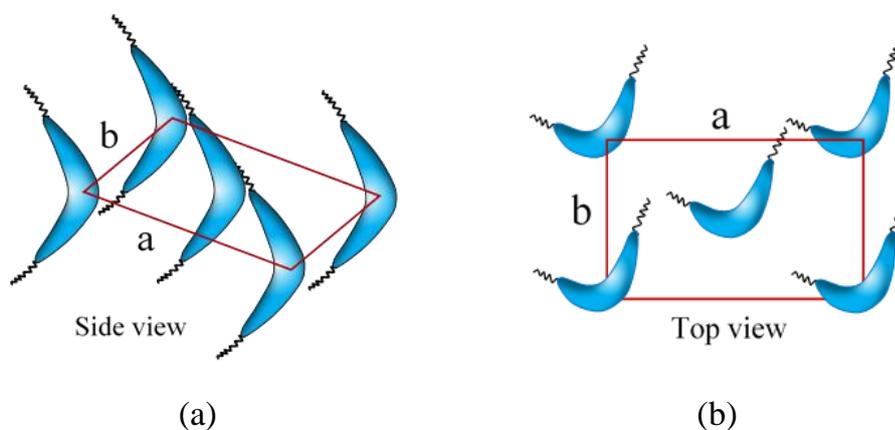


Figure 1.15. Schematic representation of the in-plane molecular packing in the B_5 phase. Vectors **a** and **b** suggests the presence of in-plane order.

is quite different than B_2 phases because additional reflection has been observed in wide angle region and perpendicular to the small-angle layer-reflection. This is due to the presence of in-plane positional ordering of the molecules within the smectic layers (Fig. 1.15), which again has been described by considering the existence of a 2D rectangular lattice within the layers [99,105,134].

f. B_6 phase

The B_6 phase is generally observed in some bent-core compounds having short alkyl chain. Although a typical fan-shaped optical texture similar to that of Sm-A phase formed by calamitic molecules is visible in the B_6 phase for a homogenous aligned sample [111], it is difficult to obtain a homeotropically aligned texture. From the lamellar reflection of XRD pattern in small angle region reveals that a periodicity of the molecules is present in this phase which is less than half of the molecular length, *i.e.*, an intercalated smectic structure of the molecules [99,135] observed in this phase. However, the wide-angle reflection represents four broad diffuse peaks, specifying a liquid-like in-plane ordering of the molecules. The inclination between the neighboring diffuse peaks corresponds to a molecular tilt organization in this

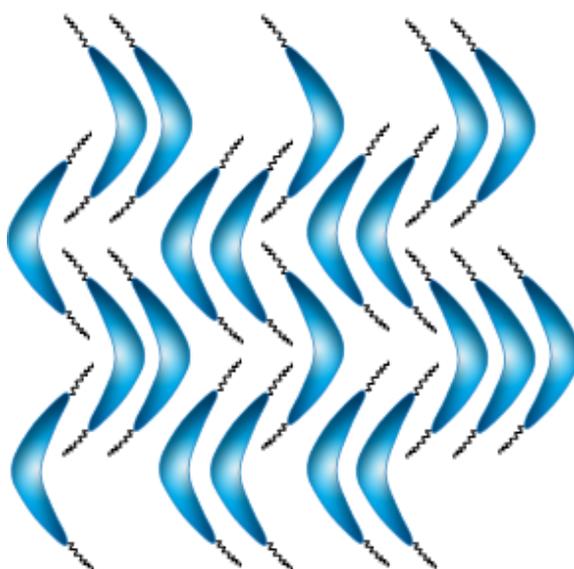


Figure 1.16. Schematic illustration of molecular ordering in the B_6 phase.

phase [99,135] and the tilt angle varies from 20° to 30° in each layer [99]. Furthermore, by increasing the chain length, the B_6 phase transform to B_1 and B_2 phases as observed in some homologous compounds [111,135,136]. The intercalated structure of B_6 phase is shown in Fig. 1.16.

g. B_7 phase

B_7 phase is the most unique mesophase among all the banana phases due to revelation of a number of distinct textural appearances much disparity than other phases. On cooling from isotropic phase the optical textures appear a number of unique pattern like – helical smectic filament, twisted helical filaments with single, double or triple coils, myelin-like, accordion-like, checkerboard-like, lancet-like or thread-like germs, banana-leaf-like, and circular domain textures etc. [99,106,137-141]. However, the spirals of smectic filaments are the most interesting texture among them and it has been assumed that such helical textures are the indication of chirality [137] for B_7 phase. However, as a result of applying electric field on B_7 phase, a ferroelectric-like switching is observed, which again transform to tristable switching state on lowering the temperature [142]. Investigation of X-ray diffraction pattern for B_7 phase illustrates several sharp reflections in the small angle region as well as liquid-like diffuse broad scattering at wide-angle region [139,142,143]. Therefore, this phase supposed to be considered as two dimensional ordered modulated layer structures caused by the polarization splay modulation in the ferroelectric state [144] and this 2D structure is quite different from those found in B_1 phases.

h. B_8 phase

In 2001, Bedel *et al.* observed another banana phase named as B_8 phase. He reported that a few bent-core compounds having n -alkyl carboxylate groups as a terminal chain exhibit a fan-shaped texture, in which the extinction direction is parallel to the layer normal. However, the X-ray diffraction study

proclaimed a bi-layer structure of the molecules in B_8 phase [106]. Additionally, by applying external electric field in this phase, it possesses an anti-ferroelectric switching. Since limited information has been reported on B_8 phase so far, further investigations are required to understand the actual molecular structure and associated mesophase behavior.

1.2.4.2. Nematic phases of bent-core liquid crystals

Due to the presence of bend angle in the molecular structure of bent-core molecules (absence of rotational symmetry around long axis), they try to form a layer structure to fill the available space in order to minimize the excluded volume in liquid crystal material. Therefore, it is easy for the molecules to form tilted or non-tilted layered structure of smectic mesophases, while such molecular structure is quite incompatible to form the nematic phase. Therefore, the nematic mesophase is quite rare than smectics for such bent-core molecules as they distorted the translational symmetry which resists to form N phase. Hence, to overcome this problem for the appearance of nematic phase, certain specific structural modification has been introduced to bent-core molecules. Subsequently, a number of distinct bent-core molecules have been synthesized to manifest the nematic phase by some particular techniques, such as by the extending aromatic core with shorter terminal chains as in different bent oligophenyleneethynylenes [145,146], *m*-terphenyls [111], and naphthalene derivatives [112-115]. Another technique is to reduce the molecular bend-angle as obtained in 5-membered heterocycles, like oxadiazoles [32-34,38,107] or some di-mesogens composed of rod-like and bent-units [147-149]. Due to the presence of such kink in the molecular structure and hence an inter-molecular lateral correlation, the bent-core molecules has an affinity to form certain small clusters within nematic phase even also in the isotropic phase [43]. Such domains are called “cybotactic cluster” and the molecules are arranged in smectic like layer within such short-range domains [37-44] as indicated in Fig. 1.17. Moreover, the cybotactic

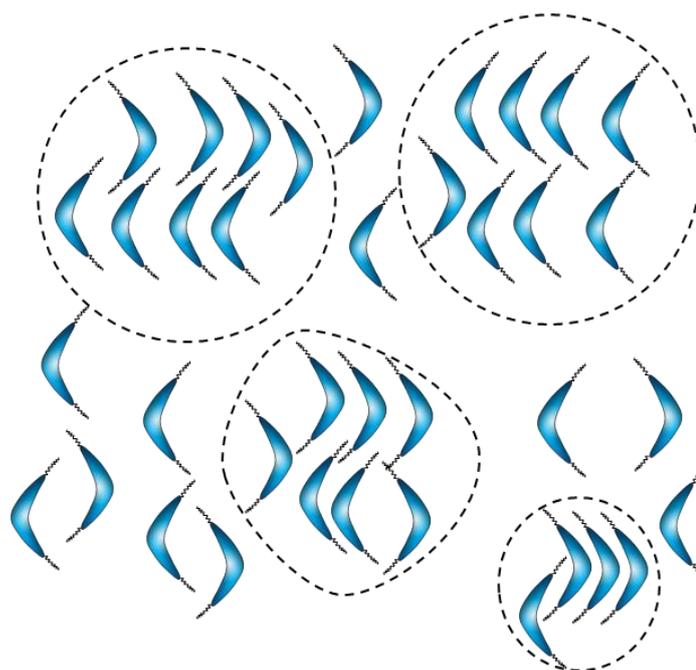


Figure 1.17. Sketch of the molecular arrangement in bent-core nematic liquid crystals comprising smectic-like cybotactic clusters.

clusters shows a microscopic polar order, effect of which makes the bent-core nematic phase an exclusive phase quite different from usual calamitic nematics. As the bent-core molecules in general are biaxial in nature, cybotactic clusters also exhibit biaxiality, although on the average the entire nematic phase is uniaxial in nature. Therefore, the existence of such unique features of cybotactic clusters in nematic phase, the bent-core nematic reveals a number of intriguing mesomorphic properties such as great flexo-electricity [150,151], extraordinary electro-convection patterns [152-154], a considerable Kerr effect [155], unique rheological properties [156,157] etc., which are absent in usual nematic phases formed by rod-like molecules. Moreover, in recent times, attention has grown up to understand some unusual characteristics like field induced biaxiality in nematic phase [158], twist-bend nematic phase [159,160], and ferroelectric switching in nematic phase [161] for bent-core liquid crystals to employ them in technological applications.

1.2.5. Hockey stick-shaped liquid crystals

The hockey stick-shaped LC compound is the unique variant of bent-core liquid crystal, in which the molecules are asymmetric in contrast to the position of structural bend-angle in aromatic core. Fig. 1.18, represents a hockey stick-shaped compound in which the bend-angle has been introduced by attaching an alkyl or alkyloxy chain at the *meta*-position of a terminal phenyl ring [162-169]. These types of mesogens are intermediate in shape between usual calamitic and the bent-core liquid crystals, and also exhibit some

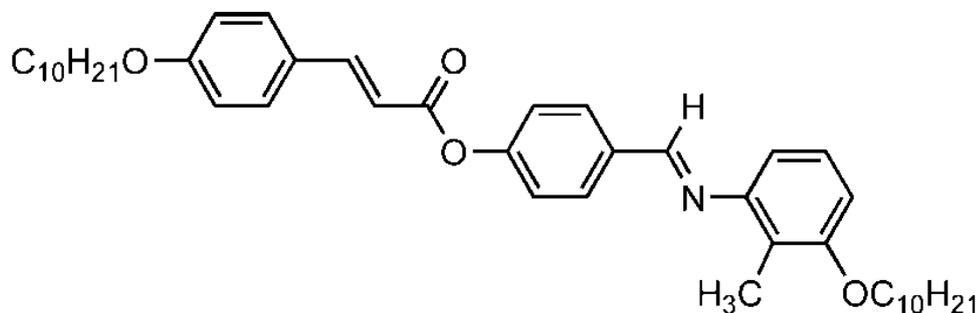


Figure 1.18. Structural representation of a hockey stick-shaped compound H-22.5 [details in Chapter 5].

unusual mesophases with greater temperature stability. Moreover, based on the terminal chain length, orientation of the linking groups and number of aromatic rings present in such asymmetrical bent-shaped molecules, they exhibit a number of exotic mesophases displaying both calamitic and bent-core like properties [170]. Recent discovery on some hockey stick-shaped liquid crystal reveals two polymorphic tilted smectic phases – the synclincic smectic *C* ($Sm-C_s$) as well as the anticlinic smectic *C* ($Sm-C_a$) phases [163,171]. Furthermore, some other characteristics such as the dark conglomerate phases [172], the co-occurrence of two different molecular tilts at the *N*–*Sm-C* transition [173], a transition having layer thinning [174] etc. also been discovered in hockey stick-shaped compound which bring them as a potential candidate for designing the future noble materials.

1.3. Liquid crystal mixtures

Although different liquid crystal compounds have its inherent unique mesophase characteristics, all the desired properties for practical applications cannot be fulfilled by a single mesogenic compound. Hence, by choosing the appropriate pure compounds, mixtures are prepared in certain specific concentrations to acquire the desired material for application purpose. As a result of mixing the individual LC components in particular proportion, the effective clearing temperature can be lowered as well as the thermal mesophase stability can be achieved higher than the pure compounds. At the same time different physical properties like dielectric permittivity and anisotropy, optical birefringence, elastic constant, rotational viscosity, threshold voltage etc. can be tuned so far [175-179]. Moreover, a proper understanding can be acquired about the mutual interactions of the constituent molecules having similar or dissimilar conformers such as calamitic-calamitic, calamitic-discotic, calamitic and bent-core along with some nano-doped systems with LC compounds [180-183]. The transitional phenomena at several mesophase transitions and associated critical behavior can be investigated more rigorously by the mixtures of LC compounds [184-188]. However, always it is not possible to interpolate the physical properties of the mesophases in mixtures by an assumption for that of the pure compounds. In certain cases several new mesophases developed in mixtures called “induced mesophase”, even they are not present in pure compounds [189,190]. Furthermore, some less ordered mesophases also re-appears in the mesomorphic range at lower temperature region, called the “re-entrant mesophase” [191-194]. In order to improve the mesophase behavior and to study associated physical properties, in some cases the multi-component mixtures also been developed rather than binary mixtures [195-196]. Such mixtures are of great interest not only for application purpose but they also extract some important characteristics regarding phase transition behavior and molecular interaction in such soft condensed matter systems.

1.4. Phase transitions

Transition between different LC mesophases occurs due to the external influence of temperature, pressure, concentration, electric or magnetic field etc. Actually the phase transition is a transformation of a thermodynamic function from one mesophase to another. Typically this thermodynamic function is the free energy and this free energy does not change smoothly at the phase transition point, *i.e.*, a non-analytic property (critical phenomena) of the system which is present at that point (critical point). In order to understand the actual phenomena at this phase transition point, it is necessary to consider a physical quantity that distinguishes both the phases before and after the transition. Such an observable physical quantity is the order parameter which represents how the microscopic constituents organize the macroscopic mesophases that are ordered. Choosing of such order parameter varies from system to system like as the magnetization (M) for ferromagnet to para-magnetic transition, density difference (ρ) for liquid to gas transition, shear modulus (G) for liquid to solid transition, pair wave function (ψ_S) for superconductor to metal transition, the electrical polarization (P) for a ferroelectric system etc. However, in liquid crystal system this order parameter is the degree of molecular ordering [1] which is associated with spontaneous symmetry breaking. The value of it is found to be identically zero in case of completely disordered state or more symmetric mesophases and found to be some non-zero value for relatively more ordered or less symmetric phases [197,198]. The order parameter is a physical observable parameter which is correlated to first derivative of the Gibbs free energy (G). Hence, the behavior of order parameter may changes gradually or abruptly at the phase transition point. Thus it is quite significant to classify the possible types of phase transitions which are somewhat more complicated.

According to P. Ehrenfest, the first-order phase transition of the system possesses a discontinuity in the first order derivative of Gibb's free energy (G)

($G(T, p) = U - TS + PV$, U is energy, T is temperature, S is entropy, P is pressure and V is volume) with respect to some thermodynamic variable, while in case of the second order transition the first order derivative of Gibb's free energy is continuous but second order derivative is discontinuous [199,200]. Mathematically, $\left(\frac{\partial G}{\partial T}\right)_P = -S$, and $\left(\frac{\partial G}{\partial P}\right)_T = V$ are discontinuous at first order transition, but $\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\frac{C_p}{T}$ and $\left(\frac{\partial^2 G}{\partial P^2}\right)_T = -V\Delta K$, $\left(\frac{\partial^2 G}{\partial T \partial P}\right) = V\Delta\alpha$ are discontinuous at second order transition. Hence, it is possible to obtain phase transitions above the second order in accordance with Ehrenfest classification. Moreover, the modern classification suggesting only two types of transition, the first order and the second order, associated with latent heat of the system [201]. The discontinuous transition or first-order phase transition involves a latent heat of the system, while continuous or second order transition does not involve any latent heat. The thermodynamic function G is correlated with order parameter in different systems. In this context, degree of molecular ordering, which is the order parameter of liquid crystal system changes continuously or abruptly at the transition points. However, most of the phase transitions in liquid crystal belong to either weakly first order or second order depending on the small enthalpy change (ΔH) and $\Delta V/V$. Hence, in accordance with the change in order parameter value, it is more interesting to take an insight into the critical anomaly at the transition point for different phase transitions in liquid crystal system.

1.5. Critical exponents

The asymptotic critical behavior (degree of singularity or diverging behavior) of any physical quantity for thermodynamical systems in the vicinity of the transition point can be classified into universality classes characterized by some critical indices or critical exponents like α , β , γ , ν etc. [202-204]. They exhibit either branch point singularity or diverging singularity. The order parameter of any thermodynamical system approaches to zero at the critical

point and represents a branch point singularity. However, the physical quantities generally have power-law divergence as a function of the difference between the control parameter (say temperature, T) and their critical values (T_c). For example, the magnetization density (m) as referred to as the order parameter of a magnetic system and can be expressed by, $m = M/V$ (M = total magnetization, V = volume). The value of m is zero for paramagnet while it assumes a non-zero value for ferromagnetic sample without any external field, *i.e.*, $m \propto 0$ at $T > T_c$ and $m \propto |\tau|^\beta$ at $T < T_c$, where $\tau = (T - T_c)/T_c$, is called the reduced temperature. Hence the singular behavior or non-analyticity of magnetization order parameter is characterized by the critical exponent β . Similarly, for liquid-gas phase transition, the isothermal susceptibility (divergence of compressibility) is governed by similar critical exponent γ and expressed as, $\chi^\pm \propto |\tau|^{-\gamma^\pm}$ where \pm denotes both sides of phase transition point and in most of the cases γ^+ and γ^- are equal. Moreover, the singularity for the thermal response function as heat capacity is governed by critical exponent α and can be expressed as, $C^\pm \propto |\tau|^{\alpha^\pm}$ where $\alpha^+ = \alpha^-$. Furthermore, the correlation length (characteristic distance over a local fluctuation in one part of the system affected by other) expressed as ξ , diverges as $\xi^\pm \propto |\tau|^{-\nu^\pm}$ at the critical temperature and also again in this case $\nu^+ = \nu^-$. The experimental evidences reveal that these sets of critical exponents are independent of materials whether it is dependent on the range of interaction (it may be long-range or short-range), spatial dimensionality, spin dimensionality, symmetry of the ordered state, and the number of components of the order parameter [205]. Thus in general they are found to belong in the same universal class in nature because several system exhibits the same critical behavior [201,202]. Moreover, such exponents are also correlated to each other by some inequalities such as Rushbrooke inequality $\alpha + 2\beta + \gamma \geq 2$, the Griffiths inequality $\gamma \geq \beta(\delta - 1)$, the Fisher inequality $(2 - \eta)\nu \geq \gamma$, the Josephson inequality $d\nu \geq 2 - \alpha$, etc. [206-209], where δ and η relates the order parameter to the source field and the size

of correlations respectively at the critical temperature. Study of the critical phenomena in liquid crystal systems has become a fundamental importance in soft condensed matter physics. In order to deal with the critical fluctuations of physical parameters at critical region, the theory of renormalization group has been introduced, which also becomes a plausible calculation tool to deal with the critical phenomena of the universal quantities. Therefore, by using renormalization group theory it is possible to investigate critical phenomena in detail for different mesophase transitions of liquid crystal systems.

References:

- [1] E.B. Priestley, P.J. Wojtowicz, and P. Sheng, (Eds.) in *Introduction to liquid crystals*, Plenum, New York (1974).
- [2] B. Bahadur (Ed.), in *Liquid crystals: Applications and uses*, World Scientific, Singapore (1992).
- [3] P.G. de Gennes, and J. Prost, in *The Physics of Liquid Crystal*, Clarendon Press, Oxford (1993).
- [4] S. Kumar, in *Experimental Study of Physical Properties and Phase Transitions*, Cambridge University Press, New York (2011).
- [5] P. Oswald, and P. Pieranski, in *Nematic and Cholesteric Liquid Crystals*, CRC Press, Taylor & Francis, Boca Raton (2005).
- [6] (a) F. Reinitzer, *Monatshefte fur Chemie*, **9**, 421 (1988); and (b) F. Reinitzer, *Liq. Cryst.*, **5**, 7 (1989).
- [7] O. Lehmann, Über fließende Krystalle. *Zeitschrift für Physik. Chemie.*, **4**, 462 (1889).
- [8] G. Friedel, *Ann. Physique.*, **18**, 273 (1922).
- [9] G. Friedel, in *Colloid chemistry*, The chemical catalogue company inc., New York (1926).
- [10] P. Kirsch, and M. Bremer, *Angew. Chem. Int. Ed.*, **39**, 4216 (2000).
- [11] J.P.F. Lagerwall, and G. Scalia, *Curr. Appl. Phys.*, **12**, 1387 (2012).
- [12] R. Stannarius, *Nat. Mater.*, **8**, 617 (2009).
- [13] Q. Li, in *Liquid crystals beyond displays: chemistry, physics, and applications*, John Wiley & Sons, USA (2012).
- [14] W.A. Crossland, T.D. Wilkinson, T.M. Coker, T.C.B. Yu, and M. Stanley, *OSA TOPS.*, **14**, 102 (1997).
- [15] C.J. Henderson, B. Robertson, D.G. Leyva, T. Wilkinson, D. O'Brien, and G. Faulkner, *Opt. Eng.*, **44**, 75401 (2005).
- [16] R.K. Komanduri, W.M. Jones, C. Oh, and M.J. Escuti, *J. Soc. Inform. Disp.*, **15**, 589 (2007).

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- [17] W.A. Crossland, I.G. Manolis, M.M. Redmond, K.L. Tan, T.D. Wilkinson, M.J. Holmes, T.R. Parker, H.H. Chu, J. Croucher, V.A. Handerek, S.T. Warr, B. Robertson, I.G. Bonas, R. Franklin, C. Stace, H.J. White, R.A. Woolley, and G. Henshall, *J. Lightwave Technol.*, **18**, 1845 (2000).
- [18] S. Muto, T. Nagata, K. Asai, H. Ashizawa, and K. Ariei, *Jpn. J. Appl. Phys.*, **29**, 1724 (1990).
- [19] L.L. Lai, E. Wang, Y.H. Liu, and Y. Wang, *Liq. Cryst.*, **29**, 871 (2002).
- [20] F. Nilsson, O. Siderman, and I. Johansson, *Langmuir*, **12**, 902 (1996).
- [21] D.W. Bruce, D.A. Dunmur, E. Lalinde, P.M. Maitlis, and P. Styring, *Nature*, **323**, 791 (1986).
- [22] B.-G. Kim, E.J. Jeong, J.W. Chung, S. Seo, B. Koo, and J. Kim, *Nat. Mater.*, **12**, 659 (2013).
- [23] A.M.F. Neto, and S.R.A. Salinas, in *The physics of lyotropic liquid crystals*, Oxford University Press, Oxford (2005).
- [24] A.G. Petrov, in *The lyotropic state of matter: molecular physics and living matter physics*, Gordon and Breach Science, Amsterdam (1999).
- [25] G.W. Gray, in *Liquid crystals and plastic crystals*, Ellis Harwood, Chichester, England (1974).
- [26] W.H. de Jeu, in *Physical properties of liquid crystalline materials*, Gordon and Breach, New York (1980).
- [27] L.M. Blinov, and V.G. Chigrinov, in *Electro-optic effects in liquid crystal materials*, Springer-Verlag, New York (1994).
- [28] K. Merkel, A. Kocot, J.K. Vij, R. Korlacki, G.H. Mehl, and T. Meyer, *Phys. Rev. Lett.*, **93**, 237801 (2004).
- [29] K. Neupane, S.W. Kang, S. Sharma, D. Carney, T. Meyer, G.H. Mehl, D.W. Allender, S. Kumar, and S. Sprunt, *Phys. Rev. Lett.*, **97**, 207802 (2006).
- [30] F. Hessel, and H. Finkelmann, *Polym. Bull.*, **15**, 349 (1986).
- [31] K. Severing, and K. Saalwächter, *Phys. Rev. Lett.*, **92**, 125501 (2004).
-
-

-
-
- [32] B.R. Acharya, A. Primak, T.J. Dingemans, E.T. Samulski, and S. Kumar, *Pramana*, **61**, 231 (2003).
- [33] L.A. Madsen, T.J. Dingemans, M. Nakata, and E.T. Samulski, *Phys. Rev. Lett.*, **92**, 145505 (2004).
- [34] B.R. Acharya, A. Primak, and S. Kumar, *Phys. Rev. Lett.*, **92**, 145506 (2004).
- [35] A. de Vries, *Mol. Cryst. Liq. Cryst.*, **10**, 31 (1970); *ibid*, **10**, 219 (1970); *ibid*, **11**, 36 (1970).
- [36] O. Francescangeli, M. Laus, and G. Galli, *Phys. Rev. E*, **55**, 481 (1997).
- [37] S. Stojadinovic, A. Adorjan, S. Sprunt, H. Sawade, and A. Jákli, *Phys. Rev. E*, **66**, 060701 (2002).
- [38] O. Francescangeli, V. Stanic, S.I. Torgova, A. Strigazzi, N. Scaramuzza, C. Ferrero, I.P. Dolbnya, T.M. Weiss, R. Berardi, L. Muccioli, S. Orlandi, and C. Zannoni, *Adv. Funct. Mater.*, **19**, 2592 (2009).
- [39] N. Vaupotic, J. Szydłowska, M. Salamonczyk, A. Kovarova, J. Svoboda, M. Osipov, D. Pocięcha, and E. Gorecka, *Phys. Rev. E*, **80**, 030701 (2009).
- [40] C. Bailey, K. Fodor-Csorba, J.T. Gleeson, S.N. Sprunt, and A. Jákli, *Soft Matter*, **5**, 3618 (2009).
- [41] C. Keith, A. Lehmann, U. Baumeister, M. Prehm, and C. Tschierske, *Soft Matter*, **6**, 1704 (2010).
- [42] O. Francescangeli, and E.T. Samulski, *Soft Matter*, **6**, 2413 (2010).
- [43] S.H. Hong, R. Verduzco, J. Williams, R.J. Twieg, E. DiMasi, R. Pindak, A. Jákli, J.T. Gleeson, and S.N. Sprunt, *Soft Matter*, **6**, 4819 (2010).
- [44] V. Domenici, *Soft Matter*, **7**, 1589 (2011).
- [45] I. Dierking, in *Textures of liquid crystals*, WILEY-VCH Verlag GmbH & Co.KGaA, Weinheim (2003).
- [46] C. Druon and J.M. Wacrenier, *Mol. Cryst. Liq. Cryst.*, **98**, 201 (1983).
- [47] I. Hatta, Y. Nagai, T. Nakayama, and S. Imaizumi, *J. Phys. Soc. Jpn.*, **52**, 47 (1983).
-
-

-
-
- [48] C. Chiang, and C.W. Garland, *Proc. of 10th ILCC*, York, July, abstract E20 (1994).
- [49] F. Hardouin, A.M. Levelut, M.F. Achard, and G. Sigaud, *J. de Chemie Physique.*, **80**, 53 (1983).
- [50] R. Berardi, S. Orlandi, D.J. Photinos, A.G. Vanakaras, and C. Zannoni, *Phys. Chem. Chem. Phys.*, **4**, 770 (2002).
- [51] D. Apreutesei, and G.H. Mehl, *Chem. Commun.*, 0, 609 (2006).
- [52] A. Chakraborty, B. Das, M.K. Das, S. Findeisen-Tandel, M.-G. Tamba, U. Baumeister, H. Kresse, and W. Weissflog, *Liq. Cryst.*, **38**, 1085 (2011).
- [53] D. Demus, J.W. Goodby, G.W. Gray, H.W. Spiess, and V. Vill, (Eds.), in *Handbook of liquid crystals*, Wiley-VCH, Weinheim (1998).
- [54] D.R. Nelson, and B.I. Halperin, *Phys. Rev. B*, **19**, 2457 (1979).
- [55] B.I. Halperin, and D.R. Nelson, *Phys. Rev. Lett.*, **41**, 121 (1978).
- [56] P.J. Collings, and J.S. Patel (Eds.), in *Handbook of liquid crystal research*, Oxford University Press, Oxford (1997).
- [57] R.J. Birgeneau, and J.D. Lister, *J. Phys. Lett.*, **39**, 399 (1978).
- [58] J.J. Benattar, F. Moussa, M. Lambert, and C. Germain, *J de Phys. Lett.*, **42**, 67 (1981).
- [59] T. Miyazawa, Y. Yamamura, M. Hishida, S. Nagatomo, M. Massalska-Arodz, and K. Saito, *J. Phys. Chem. B*, **117**, 8293 (2013).
- [60] P.S. Pershan, in *Structure of liquid crystal phases*, World Scientific Lecture Note in Physics, Singapore (1988).
- [61] G.W. Gray, and J.W. Goodby, in *Smectic liquid crystals: textures and structures*, Leonard Hill, London (1984).
- [62] S. Singh, in *Liquid crystals: Fundamentals*, World Scientific, Singapore (2002).
- [63] I. Dierking, *Symmetry*, **6**, 444 (2014).
- [64] A.Y. Bobrovsky, N.I. Boiko, and V.P. Shibaev, *Liq. Cryst.*, **27**, 219 (2000).
-
-

-
-
- [65] D.K. Yang, J.L. West, L.C. Chien, and J.W. Doane, *J. Appl. Phys.*, **76**, 1331 (1994).
- [66] Y. Takanishi, Y. Ouchi, H. Takezoe, A. Fukuda, A. Mochizuki, and M. Nakatsuka, *Jpn. J. Appl. Phys. Lett.*, **29**, L984 (1990).
- [67] J.P.F. Lagerwall, in *Phase characterization of polar liquid crystals using dielectric spectroscopy*, Licentiate thesis, Chalmers, Göteborg (2000).
- [68] J.V. Selinger, P.J. Collings, and R. Shashidhar, *Phys. Rev. E*, **64**, 61705 (2001).
- [69] J.P.F. Lagerwall, and F. Giesselmann, *Chem. Phys. Chem.*, **7**, 20 (2006).
- [70] P. Mach, R. Pindak, A.-M. Levelut, P. Barois, H.T. Nguyen, H. Baltes, M. Hird, K. Toyne, A. Seed, J.W. Goodby, C.C. Huang, and L. Furenlid, *Phys. Rev. E*, **60**, 6793 (1999).
- [71] R.B. Meyer, L. Liebert, L. Strzelecki, and P.J. Keller, *Phys. Lett. (Orsay, Fr.)*, **36**, L-69 (1975).
- [72] P. Collings, and M. Hird, in *Introduction to Liquid Crystals: Chemistry and Physics*, Taylor & Francis, London, (1997).
- [73] N.A. Clark, and S.T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).
- [74] J.W. Goodby, R. Blinc, N.A. Clark, S.T. Lagerwall, M.A. Osipov, S.A. Pikin, T. Sakurai, K. Yoshino, and B. Žekš, in *Ferroelectric liquid crystals: principles, properties and applications*, Gordon & Breach, Philadelphia (1991).
- [75] S.T. Lagerwall, in *Ferroelectric and antiferroelectric liquid crystals*, Wiley-VCH, Weinheim (1999).
- [76] I. Musevič, R. Blinc, and B. Žekš, in *The physics of ferroelectric and antiferroelectric liquid crystals*, World Scientific, Singapore (2000).
- [77] A.M. Levelut, C. Germain, P. Keller, and L. Liebert, *J. Phys. (Paris)*, **44**, 623 (1983).
- [78] Y. Galerne, and L. Liebert, in *Abstract Book of 2nd International Conf. Ferroelectric Liq. Cryst.*, **O27** (1989).
-
-

-
-
- [79] A.D.L. Chandani, Y. Ouchi, H. Takezoe, A. Fukuda, K. Terashima, K. Furukawa, and A. Kishi, *Jpn. J. Appl. Phys.*, **28**, L 69 (1989).
- [80] H.S. Kitzerow, and C. Bahr, in *Chirality in Liquid crystals*, Springer-Verlag, New York, Inc., (2001).
- [81] P.P. Crooker, in *Chirality in Liquid Crystals*, Ed. H.S. Kitzerow, C. Bahr Springer-Verlag, New York (2001).
- [82] (a) P.P. Crooker, *Liq. cryst.*, **5**, 751 (1989); (b) D.C. Wright, and N.D. Mermin, *Review of Modern Physics.*, **61**, 385 (1989).
- [83] F. Castles, S.M. Morris, E.M. Terentjev, and H.J. Coles, *Phys. Rev. Lett.*, **104**, 157801 (2010).
- [84] T.C. Lubensky, *Physica A*, **220**, 99 (1995).
- [85] R. Dhar, *Phase Transit.*, **79**, 175 (2006).
- [86] S.R. Renn, and T.C. Lubensky, *Phys. Rev. A*, **38**, 2132 (1988).
- [87] S.R. Renn, and T.C. Lubensky, *Mol. Cryst. Liq. Cryst.*, **209**, 349 (1991).
- [88] J.W. Goodby, M.A. Waugh, S.M. Stein, E. Chin, R. Pindak, and J.S. Patel, *J. Am. Chem. Soc.*, **111**, 8119 (1989).
- [89] I. Dierking, *Symmetry*, **6**, 444 (2014).
- [90] H. Takezoe, and Y. Takanishi, *Jpn. J. Appl. Phys.*, **45(2A)**, 597 (2006).
- [91] D. Vorlander, *Ber. Dtsch. Chem. Ges.*, **62**, 2831 (1929).
- [92] D. Vorlander, and A. Apel, *Ber. Dtsch. Chem. Ges.*, **65**, 1101 (1932).
- [93] M. Kuboshita, Y. Matsunaga, and H. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, **199**, 319 (1991).
- [94] T. Matsuda, and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **64**, 2192 (1991).
- [95] H. Matsuzaki, and Y. Matsunaga, *Liq. Cryst.*, **14**, 105 (1993).
- [96] T. Akutagawa, Y. Matsunaga, and K. Yasuhara, *Liq. Cryst.*, **17**, 659 (1994).
- [97] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, and H. Takezoe, *J. Mater. Chem.*, **6**, 1231 (1996).
- [98] D.R. Link, G. Natale, R. Shao, J.E. Maclennan, N.A. Clark, E. Körblova, and D.M. Walba, *Science*, **278**, 1924 (1997).
-
-

-
-
- [99] G. Pelzl, S. Diele, and W. Weissflog, *Adv. Mater.*, **11**, 707 (1999).
- [100] T. Sekine, T. Niori, J. Watanabe, T. Furukawa, S.W. Choi, and H. Takezoe, *J. Mater. Chem.*, **7**, 1307 (1997).
- [101] T. Sekine, T. Niori, M. Sone, J. Watanabe, S.W. Choi, Y. Takanishi, and H. Takezoe, *Jpn. J. Appl. Phys.*, **36**, 6455 (1997).
- [102] R. Macdonald, F. Kentischer, P. Warnick, and G. Heppke, *Phys. Rev. Lett.*, **81**, 4408 (1998).
- [103] R.A. Reddy, and C. Tschierske, *J. Mater. Chem.*, **16**, 907 (2006).
- [104] D.M. Walba, D.J. Dyer, T. Sierra, P.L. Cobben, R. Shao, and N.A. Clark, *J. Am. Chem. Soc.*, **118**, 1211 (1996).
- [105] S. Diele, S. Grande, H. Kruth, Ch. Lischka, G. Pelzl, W. Weissflog, and I. Wirth, *Ferroelectrics*, **212**, 169 (1998).
- [106] J.P. Bedel, J.C. Rouillon, J.P. Marcerou, M. Laguerre, H.T. Nguyen, and M.F. Achard, *Liq. Cryst.*, **28**, 1285 (2001).
- [107] J.A. Olivares, S. Stojadinovic, T. Dingemans, S. Sprunt, and A. Jákli, *Phys. Rev. E*, **68**, 041704 (2003).
- [108] M.G. Tamba, B. Kosata, K. Pelz, S. Diele, G. Pelzl, Z. Vakhovskaya, H. Kresse, and W. Weissflog, *Soft Matter*, **2**, 60 (2006).
- [109] G. Shanker, M. Prehm, and C. Tschierske, *J. Mater. Chem.*, **22**, 168 (2012).
- [110] Y. Wang, H.G. Yoon, H.K. Bisoyi, S. Kumar, and Q. Li, *J. Mater. Chem.*, **22**, 20363 (2012).
- [111] D. Shen, S. Diele, G. Pelzl, I. Wirth, and C. Tschierske, *J. Mater. Chem.*, **9**, 661 (1999).
- [112] R.A. Reddy, and B.K. Sadashiva, *J. Mater. Chem.*, **14**, 1936 (2004).
- [113] R.A. Reddy, B.K. Sadashiva, and V.A. Raghunathan, *Chem. Mater.*, **16**, 4050 (2004).
- [114] N.S. Novikova, E. Gorecka, R.V. Kondratyeva, and E.D. Kilimenchuk, *Liq. Cryst.*, **35**, 743 (2008).
-
-

-
-
- [115] S.K. Lee, X. Li, S. Kang, M. Tokita, and J. Watanabe, *J. Mater. Chem.*, **19**, 4517 (2009).
- [116] E.-J. Choi, X. Cui, C.-W. Ohk, W.-C. Zin, J.-H. Lee, T.-K. Lim, and W.-G. Jang, *J. Mater. Chem.*, **20**, 3743 (2010).
- [117] L.E. Hough, M. Spannuth, M. Nakata, D.A. Coleman, C.D. Jones, G. Dantlgraber, C. Tschierske, J. Watanabe, E. Körblova, D.M. Walba, J.E. MacLennan, M.A. Glaser, and N.A. Clark, *Science*, **325**, 452 (2009).
- [118] S.T. Wang, X.F. Han, A. Cady, Z.Q. Liu, A. Kamenev, L. Glazman, B.K. Sadashiva, R.A. Reddy, and C.C. Huang, *Phy. Rev. E*, **70**, 061705 (2004).
- [119] R.A. Reddy, C. Zhu, R. Shao, E. Körblova, T. Gong, Y. Shen, E. Garcia, M.A. Glaser, J.E. MacLennan, D.M. Walba, and N.A. Clark, *Science*, **332**, 72 (2011).
- [120] N. Chattham, M.-G. Tamba, R. Stannarius, E. Westphal, H. Gallardo, M. Prehm, C. Tschierske, H. Takezoe, and A. Eremin, *Phys. Rev. E*, **91**, 030502 (2015).
- [121] P. Grzybowski, and L. Longa, *Phys. Rev. Lett.*, **107**, 027802 (2011).
- [122] J. Watanabe, T. Niori, T. Sekine, and H. Takezoe, *Jpn. J. Appl. Phys.*, **37**, L139 (1998).
- [123] J. Szydłowska, J. Mieczkowski, J. Matraszek, D.W. Bruce, E. Gorecka, D. Pocięcha, and D. Guillon, *Phys. Rev. E*, **67**, 031702 (2003).
- [124] K. Pelzl, W. Weissflog, U. Baumeister, and S. Diele, *Liq. Cryst.*, **30**, 1151 (2003).
- [125] R.A. Reddy, V.A. Raghunathan, and B.K. Sadashiva, *Chem. Mater.*, **17**, 274 (2005).
- [126] J. Thisayukta, H. Takezoe and J. Watanabe, *Jpn. J. Appl. Phys.*, **40**, 3277 (2001).
- [127] H. Chan, and I. Dierking, *Phys. Rev. E*, **70**, 021703 (2004).
- [128] J. Salfetnikova, H. Schmalfuss, H. Nadasi, W. Weissflog, and H. Kresse, *Liq. Cryst.*, **27**, 1663 (2000).
-
-

-
-
- [129] Y. Takanishi, K. Ishikawa, J. Watanabe, H. Takezoe, M. Yamashita, and K. Kawase, *Phys. Rev. E*, **71**, 061701 (2005).
- [130] G. Heppke, D. Krueker, C. Lohning, D. Lotzsch, S. Rauch, and N.K. Sharma, in *Frieburger Arbeitstagung Flussige Kristalle*, Freiburg, Germany, P 70 (1997).
- [131] P. Collings *et al.*, Abtr. Workshop on *Banana-Shaped Liquid Crystals: Chirality by Achiral Molecules*, P-15, Berlin, Germany (1997).
- [132] F. Kentischer, R. Macdonald, P. Warnick, and G. Heppke, *Proc. SPIE*, **3143**, 128 (1997).
- [133] S.-W. Choi, Y. Kinoshita, B. Park, H. Takezoe, T. Niori, and J. Watanabe, *Jpn. J. Appl. Phys.*, **37**, 3408 (1998).
- [134] H. Nádasi, W. Weissflog, A. Eremin, G. Pelzl, S. Diele, B. Das, and S. Grande, *J. Mater. Chem.*, **12**, 1316 (2002).
- [135] W. Weissflog, I. Wirth, S. Diele, G. Pelzl, H. Schmalfuss, T. Schoss, and A. Würflinger, *Liq. Cryst.*, **28**, 1603 (2001).
- [136] H.N.S. Murthy, and B.K. Sadashiva, *Liq. Cryst.*, **29**, 1223 (2002).
- [137] A. Jákli, Ch. Lischka, W. Weissflog, G. Pelzl, and A. Saupe, *Liq. Cryst.*, **27**, 1405 (2000).
- [138] R.A. Reddy, and B.K. Sadashiva, *Liq. Cryst.*, **30**, 273 (2003).
- [139] H.N. Shreenivasa Murthy, and B.K. Sadashiva, *Liq. Cryst.*, **30**, 1051 (2003).
- [140] Y.A. Nastishin, M.F. Achard, H.T. Nguyen, and M. Kleman, *Eur. Phys. J. E*, **12**, 581 (2003).
- [141] A. Jákli, D. Krüerke, and G.G. Nair, *Phys. Rev. E*, **67**, 051702 (2003).
- [142] G. Pelzl, S. Diele, A. Jakli, Ch. Lischka, I. Wirth, and W. Weissflog, *Liq. Cryst.*, **26**, 135 (1999).
- [143] G. Pelzl, M.W. Schröder, U. Dunemann, S. Diele, W. Weissflog, C. Jones, D. Coleman, N.A. Clark, R. Stannarius, J. Li, B. Das, and S. Grande, *J. Mater. Chem.*, **14**, 2492 (2004).
-
-

-
-
- [144] D.A. Coleman, J. Fernsler, N. Chattham, M. Nakata, Y. Takanishi, E. Körblova, D.R. Link, R.-F. Shao, W.G. Jang, J.E. Maclellan, O. Mondainn-Monval, C. Boyer, W. Weissflog, G. Pelzl, L.-C. Chien, J. Zasadzinski, J. Watanabe, D. M. Walba, H. Takezoe, and N. A. Clark, *Science*, **301**, 1204 (2003).
- [145] M. Lehmann, and J. Levin, *Mol. Cryst. Liq. Cryst.*, **411**, 273 (2004).
- [146] M. Lehmann, S.-W. Kang, C. Köhn, S. Haseloh, U. Kolb, D. Schollmeyer, Q. Wang, and S. Kumar, *J. Mater. Chem.*, **16**, 4326 (2006).
- [147] C.V. Yelamaggad, S. Shashikala, D.S. Shankar Rao, C.V. Lobo, and S. Chandrasekhar, *Angew. Chem., Int. Ed.*, **43**, 3429 (2004).
- [148] R. Stannarius, A. Eremin, M.-G. Tamba, G. Pelzl, and W. Weissflog, *Phys. Rev. E*, **76**, 061704 (2007).
- [149] P. Kumar, Y.G. Marinov, H.P. Hinov, U.S. Hiremath, C.V. Yelamaggad, K.S. Krishnamurthy, and A.G. Petrov, *J. Phys. Chem. B*, **113**, 9168 (2009).
- [150] J. Harden, B. Mbanga, N. Éber, K. Fodor-Csorba, S. Sprunt, J.T. Gleeson, and A. Jákli, *Phys. Rev. Lett.*, **97**, 157802 (2006).
- [151] J. Harden, R. Teeling, J.T. Gleeson, S. Sprunt, and A. Jákli, *Phys. Rev. E*, **78**, 031702 (2008).
- [152] D. Wiant, J.T. Gleeson, N. Éber, K. Fodor-Csorba, A. Jákli, and T. Tóth-Katona, *Phys. Rev. E*, **72**, 041712 (2005).
- [153] S. Tanaka, S. Dhara, B.K. Sadashiva, Y. Shimbo, Y. Takanishi, F. Araoka, K. Ishikawa, and H. Takezoe, *Phys. Rev. E*, **77**, 041708 (2008).
- [154] S. Tanaka, H. Takezoe, N. Éber, K. Fodor-Csorba, A. Vajda, and A. Buka, *Phys. Rev. E*, **80**, 021702 (2009).
- [155] S. Dhara, F. Araoka, M. Lee, K.V. Le, L. Guo, B.K. Sadashiva, K. Song, K. Ishikawa, and H. Takezoe, *Phys. Rev. E*, **78**, 050701 (2008).
- [156] E. Dorjgotov, K. Fodor-Csorba, J.T. Gleeson, S. Sprunt, and A. Jákli, *Liq. Cryst.*, **35**, 149 (2008).
-
-

-
-
- [157] P. Tadapatri, U.S. Hiremath, C.V. Yelamaggad, and K.S. Krishnamurthy, *J. Phys. Chem. B*, **114**, 1745 (2010).
- [158] M. Nagaraj, Y.P. Panarin, U. Manna, J.K. Vij, C. Keith, and C. Tschierske, *Appl. Phys. Lett.*, **96**, 011106 (2010).
- [159] V.P. Panov, M. Nagaraj, J.K. Vij, Yu. P. Panarin, A. Kohlmeier, M.G. Tamba, R.A. Lewis, and G.H. Mehl, *Phys. Rev. Lett.*, **105**, 167801 (2010).
- [160] V.P. Panov, R. Balachandran, M. Nagaraj, J.K. Vij, M.G. Tamba, A. Kohlmeier, and G.H. Mehl, *Appl. Phys. Lett.*, **99**, 261903 (2011).
- [161] S. Ghosh, N. Begum, S. Turlapati, S.K. Roy, A.K. Das, and N.V.S. Rao, *J. Mater. Chem. C*, **2**, 425 (2014).
- [162] M. Hird, J.W. Goodby, N. Gough, and K.J. Toyne, *J. Mater Chem.*, **11**, 2732 (2001).
- [163] B. Das, S. Grande, W. Weissflog, A. Eremin, M.W. Schröder, G. Pelzl, S. Diele, and H. Kresse, *Liq. Cryst.*, **30**, 529 (2003).
- [164] H. Okamoto, Y. Morita, Y. Segawa, and S. Takenaka, *Mol. Cryst. Liq. Cryst.*, **439**, 221 (2005).
- [165] T. Kajitani, S. Kohmoto, M. Yamamoto, and K. Kishikawa, *Chem. Mater.*, **17**, 3812 (2005).
- [166] F.C. Yu, and L.J. Yu, *Chem. Mater.*, **18**, 5410 (2006).
- [167] C.D. Jones, R.-F. Shao, A.G. Rappaport, J.E. MacLennan, N.A. Clark, E. Körblova, and D.M. Walba, *Liq. Cryst.*, **33**, 25 (2006).
- [168] F.C. Yu and L.J. Yu, *Liq. Cryst.*, **35**, 799 (2008).
- [169] E. Enz, S. Findeisen-Tandel, R. Dabrowski, F. Giesselmann, W. Weissflog, U. Baumeister, and J. Lagerwall, *J. Mater. Chem.*, **19**, 2950 (2009).
- [170] A. Chakraborty, M.K. Das, B. Das, U. Baumeister, and W. Weissflog, *J. Mater. Chem. C*, **1**, 7418 (2013).
- [171] V. Novotná, J. Žurek, V. Kozmík, J. Svoboda, M. Glogarová, J. Kroupa, and D. Pocięcha, *Liq. Cryst.*, **35**, 1023 (2008).
-
-

-
-
- [172] A. Belaisaoui, S.J. Cowling, and J.W. Goodby, *Liq. Cryst.*, **40**, 822 (2013).
- [173] L. Chakraborty, N. Chakraborty, D.D. Sarkar, N.V.S. Rao, S. Aya, K.V. Le, F. Araoka, K. Ishikawa, D. Pocięcha, E. Gorecka, and H. Takezoe, *J. Mater. Chem. C*, **1**, 1562 (2013).
- [174] M.K. Paul, R.K. Nath, B. Moths, L. Pan, S. Wang, R. Deb, Y. Shen, N.V.S. Rao, and C.C. Huang, *Phase Transitions*, **85**, 1070 (2012).
- [175] S. DasGupta, S.K. Roy, *Phys. Lett. A*, **306**, 235 (2003).
- [176] A. Kubono, K. Yoshino, T. Ninomiya, R. Akiyama, K. Tanaka, *Liq. Cryst.*, **29**, 1089 (2002).
- [177] R. Dabrowski, *Mol. Cryst. Liq. Cryst.*, **191**, 17 (1990).
- [178] M.F. Grebyonkin, G.A. Beresnev, V.V. Belyaev, *Mol. Cryst. Liq. Cryst.*, **103**, 1 (1983).
- [179] H. Schad, *J. Appl. Phys.*, **54**, 4994 (1983).
- [180] S.K. Sarkar, and M.K. Das, *RSC Adv.*, **4**, 19861 (2014).
- [181] D. Venkata Sai, G. Mirri, I. Musevic, and S. Dhara, *Liq. Cryst.*, **43**, 1884 (2016).
- [182] P. Salamon, N. Éber, A. Buka, J.T. Gleeson, S. Sprunt, and A. Jákli, *Phys. Rev. E*, **81**, 031711 (2010).
- [183] M.K. Das, P.C. Barman, and S.K. Sarkar, *Eur. Phys. J. B*, **88**, 175 (2015).
- [184] M.B. Sied, S. Diez, J. Salud, D.O. Lopez, P. Cusmin, J.L. Tamarit, and M. Barrio, *J. Phys. Chem. B*, **109**, 16284 (2005).
- [185] Y. Sasaki, K. Ema, K.V. Le, H. Takezoe, S. Dhara, and B.K. Sadashiva, *Phys. Rev. E*, **82**, 011709 (2010).
- [186] M.B. Sied, J. Salud, D.O. Lopez, M. Barrio, and J.L. Tamarit, *Phys. Chem. Chem. Phys.*, **4**, 2587 (2002).
- [187] M.G. Lafouresse, M.B. Sied, H. Allouchi, D.O. Lopez, J. Salud, and J.L. Tamarit, *Chem. Phys. Lett.*, **376**, 188 (2003).
-
-

- [188] M.A. Anisimov, in *Critical phenomena in liquids and liquid crystals*, Gordon and Breach, New York (1991).
- [189] A. Buka, (Ed.), in *Modern topics in liquid crystals*, World Scientific (1993).
- [190] C.S. Oh, *Mol. Cryst. Liq. Cryst.*, **42**, 1 (1977).
- [191] T. Narayanan, and A. Kumar, *Phys. Rep.*, **249**, 135 (1994).
- [192] G. Pelzl, C. Scholz, S. Diele, H.-J. Deutscher, D. Demus, H. Sackmann, *Mol. Cryst. Liq. Cryst.*, **168(1)**, 197 (1989).
- [193] F. Hardouin, G. Sigaud, M.F. Achard, and H. Gasparoux, *Phys. Lett. A*, **71**, 347 (1979).
- [194] K.W. Evans-Lutterodt, J.W. Chung, B.M. Ocko, R.J. Birgeneau, C. Chiang, C.W. Garland, E. Chin, J. Goodby, and N.H. Tinh, *Phys. Rev. A*, **36**, 1387 (1987).
- [195] A. Pramanik, B. Das, M.K. Das, K. Garbat, S. Urban, and R. Dabrowski, *Liq. Cryst.*, **40**, 149 (2013).
- [196] A. Chakraborty, S. Chakraborty, M.K. Das, and W. Weissflog, *J. Mol. Liq.*, **265**, 536 (2018).
- [197] J.M. Yeomans, in *Statistical mechanics of phase transitions*, Clarendon, Oxford (1992).
- [198] H.B. Callen, in *Thermodynamics*, J. Wiley and Sons, New York, 376 (1960).
- [199] G. Jaeger, *Arch. Hist. Exact Sci.*, **53**, 51 (1998).
- [200] P. Ehrenfest, *Proc. R. Acad. Sci. Amsterdam*, **36**, 153 (1933).
- [201] R.K. Pathria, in *Statistical mechanics*, Butterworth-Heinemann, Jordan Hill, Oxford (1996).
- [202] I. Herbut, in *A modern approach to critical phenomena*, Cambridge University Press, New York (2007).
- [203] H.E. Stanley, in *Introduction to phase transitions and critical phenomena*, Oxford University Press (1971).

- [204] J.J. Binney, N.J. Dowrick, A.J. Fisher, and M.E.J. Newman, in *The theory of critical phenomena*, Clarendon Press, Oxford (1992).
- [205] J. Przystawa, *Physica A*, **114(1–3)**, 557 (1982).
- [206] H. Eugene Stanley, in *Introduction to Phase Transitions and Critical Phenomena*, Clarendon Press. Oxford (1971).
- [207] Robert B. Griffith, *Phys. Rev. Lett.*, **14**, 623-624 (1965).
- [208] M.E. Fisher, *Phys. Rev.*, **180**, 594 - 600 (1969).
- [209] B.D. Josephson, *Proc. Phys. Soc. (London)*, **92**, 276 (1967).