INTRODUCTION
TO
LIQUID CRYSTALS
1.1 INTRODUCTION

The study of liquid crystals began in 1888 when an Austrian botanist, Friedrich Reinitzer observed two distinct melting points in the compound cholesteryl benzoate. A German physicist, Otto Lehmann later confirmed this discovery and coined the name 'liquid crystal'. Liquid crystals are known as the fourth state of matter and exhibit phases, which flow like a liquid but also have properties of crystalline solids i.e. the term liquid crystal describes a state of matter that is intermediate between an isotropic liquid and a crystalline solid. Materials that exhibit such unusual phases are often called mesogens (i.e., they are mesogenic) and the various phases in which they could exist are termed mesophases. Since their discovery in the late 19th century by Reinitzer (1888) and Lehmann¹ (1889) there have been thousands of compounds identified to exhibit this unusual phase of matter the liquid crystalline or mesogenic phase. Most molecules with liquid crystalline properties are geometrically anisotropic with a rod or a disc-like shape. The molecules in crystals are ordered (positional and orientational) whereas in the liquid they are not.² In crystals the molecules are held in fixed positions by intermolecular forces that need not be the same in all directions. On heating, the molecules vibrate and overcome the weaker organizing forces first but they
remain bound by the stronger forces and lose some or all of their positional order, while maintaining the orientational order. The molecular axes of the individual molecules remain relatively aligned and parallel to each other leading to a preferred direction in space. In some cases the molecules tend to further associate in layers (a modulation in density in planes that intersect the molecular directors). Liquid crystals are usually anisotropic materials and the physical properties of the bulk system vary with the average alignment of the director in which large alignment tends towards anisotropic materials while small alignment tends towards isotropic materials. In the case of liquid crystals, the transition from the isotropic liquid phase to a crystal phase is not a single step but occurs by one or more intermediary steps. The shapes of the individual molecules and incompatibility of molecular segments are two key factors that drive organization in liquid crystal phases. Research in this area was originally motivated by the desire to understand the behavior of this interesting state of matter. More recently research is motivated by applications of these materials which have led to significant invention and technological development. From the earliest days and even now over a century after their discovery, liquid crystals continue to provide surprises.

To understand the physical and optical properties of these materials, it is necessary to know their constituent molecules. Figure 1.1a shows the basic structures of the most commonly occurring liquid crystal molecules. They are aromatic, and if they contain benzene rings, they are often referred to as benzene derivatives. In general, aromatic liquid crystal molecules such as those shown in Fig: 1.1a comprise a side chain \( R \), two or more aromatic rings \( A \) and \( A^1 \), connected by linkage groups \( X \) and \( Y \), and at the other end connected to a terminal group \( R^1 \).

Examples of side-chain and terminal groups are alkyl \( (C_nH_{2n+1}) \), alkoxy \( (C_nH_{2n+1}O) \) and others such as acyloxy, alkylcarbonate, alkoxy carbonyl, and the nitro and cyano groups.

The linkage groups are simple bonds or groups such as ester, stilbene \(-CH=CH-\), tolane \(-C=C-\), azoxy \(-N=N-\) , Schiff base \(-CH=N-\), acetylene and diacetylene \(-C\equiv C\equiv C-\). The names of liquid crystals are often fashioned after the linkage group (e.g., Schiff base liquid crystal).

There are quite a number of aromatic rings. These include saturated cyclohexane or unsaturated phenyl, biphenyl, and terphenyl in various combinations.
The majority of liquid crystals are benzene derivatives mentioned previously. The rest include heterocyclic's, organometallics, sterols, and some organic salts or fatty acids. Their typical structures are shown in figure 1.1b-d.

Heterocyclic liquid crystals are similar in structure to benzene derivatives, with one or more of the benzene rings replaced by a pyridine, pyrimidine, or other similar groups. Cholesterol derivatives are the most common chemical compounds.
that exhibit the cholesterol (or chiral nematic) phases of liquid crystals. Organometallic compounds are special in that they contain metallic atoms and possess interesting dynamical and magneto-optical properties. All the physical and optical properties of liquid crystals are governed by the properties of these constituent group and how they are chemically synthesized together.

1.2 TYPES OF LIQUID CRYSTALS

There are two very general types of liquid crystals, which can be distinguished by their composition and method of formation. Depending on their molecular ordering, each of these two types of liquid crystals may form a number of specific structures.4

1.2.1 Thermotropic liquid crystals

Thermotropic liquid crystals exhibit a variety of phases as the temperature is changed. At high temperature, the thermal motion destroys the ordering of the liquid crystal phase and transforms the material into a conventional isotropic liquid phase. At low temperature, most liquid crystal materials form a conventional crystal. A liquid crystal phase may be formed either by cooling an isotropic liquid below the clearing point or by heating a solid crystal above the melting point. There are two types of thermotropic liquid crystals which are called enantiotropic where the liquid crystal phase can be achieved either by heating or cooling (reversible cycles) and monotropic which is an irreversible process where the liquid crystal phase can only be reached from one direction (upon cooling) in the thermal cycle.5 Of course, a liquid crystal phase may also be obtained by heating or cooling from a different adjacent liquid crystal phase.

Thermotropic calamitic liquid crystals usually consist of rigid units (usually one or more rings) which comprise the molecular long axis to which is attached some flexible alkyl chains. These molecules are able to orient themselves so their long axes (along the director, \( n \)) are on average parallel to each other. The simplest thermotropic bulk liquid crystal order is the nematic (N) where the molecules have no positional order but possess a spontaneous long range orientational order6. As the chains are elongated, further segregation of the rigid units and the alkyl chains may occur. In such a case, the calamitic molecules tend to also become arranged in layers to form smectic phases.

On the other hand, discotic molecules form the discotic nematic phase or columns to exhibit either the columnar nematic (Nc) or other columnar phases (Colh, Colr)7. The discotic nematic phase is composed of flat-shaped disc molecules without long-range
order. The discotic nematic molecules do not form specific columnar assemblies but are organized with their short axes parallel to the director. The columnar nematic (Nc) has no long-range order and are less organized than other columnar liquid crystals which have long-range order with two-dimensional lattices, such as the hexagonal (Colh), rectangular (Colr), oblique, plastic and helical. Our discussion will only focus on the columnar hexagonal phase. Relatively few thermotropic compounds with cubic phases are known.

The mesophase morphologies for thermotropic LCs are summarized, as shown in Figure 1.2

![Figure 1.2: Mesophase morphologies for thermotropic mesogens.](image)

1.2.2 Lyotropic liquid crystals

Lyotropic liquid crystals were discovered well before their thermotropic counterparts were known. In 1850, their texture was noticed in a mixture of the phospholipid myelin and water. For both the thermotropic and lyotropic liquid crystals, temperature is an important condition for the appearance of liquid crystal phases. Because lyotropics are comprised of at least two chemical constituents, concentration is a much more important parameter compared to temperature. Lyotropic liquid crystal transitions occur with the primary influence of solvents, not by a change in temperature. Different phases can be observed as the concentrations of the solutions change. In these phases, solvent molecules fill the space around (and/or in) the structures to provide fluidity to the system. The mesophase morphologies for lyotropic LCs are summarized, as shown in Figure 1.3.

At very low concentrations, the molecules are distributed randomly without order throughout the water but as the concentration increases, the molecules agglomerate as amphiphiles called micelles, with the hydrophobic tail inside the micelle core, exposing a hydrophilic head to the aqueous component. These micelles separate into two shapes that are either spherical or rod-like. These shapes are influenced by the relative volume of the
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alkyl chains and the headgroups\textsuperscript{18}. As the concentration increases, the micelles increase in size and eventually coalesce to separate the newly formed liquid crystalline state from the solvent\textsuperscript{16}. Since lyotropic liquid crystals rely on a subtle balance of intermolecular interactions amongst more diverse components, it is sometimes more difficult to analyze their structures and properties than those of thermotropic liquid crystals.

When the concentration is increased, cubic phases are formed where spherical molecules form the I-type cubic phases and the rod-like molecules form the V-type cubic phases. Further increase in the concentration forms the hexagonal phase. At even higher concentration, a lamellar phase may be formed where the polar head is now at the outer layer and the non-polar tails are sandwiched in the middle. The normal phase (type 1) is common where the hydrophobic tails are located inside the aggregates surrounded by the polar head groups. For some systems, inverse phase (type 2) liquid crystals can also be observed at high concentration\textsuperscript{19} where the polar head groups are inside the core.

![Figure 1.3: Mesophase morphologies for lyotropic mesogens\textsuperscript{17}](image)

The driving forces for the formation of liquid crystalline phases of these amphiphilic molecules are the micro-segregation of hydrophilic and hydrophobic molecular parts into different regions (interface curvature), as well as the strong attractive forces between the hydrophilic head groups, such as intermolecular hydrogen bonding. The interface curvature between hydrophilic and hydrophobic regions is directed away from the water with stronger cohesive interaction (hydrogen bonding). The normal phase (type 1) shows positive interface curvature where the interface is curved away from the water while on the other hand, the inverse phases (type 2) show negative interface curvature in which the interface is curved towards the water with stronger cohesive interaction.\textsuperscript{20} At zero interface curvature, the lamellar (Smectic A) phase occurs. The
interface curvature (ratio between the hydrophilic and hydrophobic regions) determines the structure, its mesophase and also whether it is the normal (type 1) or inverse (type 2) phases.

1.2.3 Amphotropic or Amphitropic Liquid Crystals

Another type of liquid crystal which has received special attention is termed amphotropic\textsuperscript{21} or amphitropic\textsuperscript{22-24}. These materials can form liquid crystalline phases not only in the lyotropic systems but also as pure compounds in the thermotropic systems\textsuperscript{25,26,20}. However, the mesophases observed in these two regimes are often quite different owing to the temperature, shapes and chemical structures\textsuperscript{20}. Examples of such amphotropic molecules are amphiphilic polyhydroxy compounds and carbohydrate derivatives.

1.3 STRUCTURAL CLASSIFICATION OF THERMOTROPIC LIQUID CRYSTALS

There are different types of liquid crystal phases which can be distinguished based on their distinct optical texture and the amount of order in the material, depending on the temperature\textsuperscript{4}. These liquid crystalline phases are characterized by molecular orientational order when cooling from the isotropic phase to the crystalline phase\textsuperscript{27}. The observation of the optical textures of these phases by polarized optical microscopy is one of the most important methods for the identification and classification of different liquid crystalline phases.

1.3.1 Nematic phase

The nematic (N) phase is the most common liquid crystal phase. The molecules have long-range orientational order but no positional order. As such, it is the least ordered thermotropic phase and thus the closest to the isotropic liquid. They have the ease of fluidity in which molecules slide past one another while retaining their average parallel positions (Figure 1.4).
A nematic phase may be comprised of individual molecules with substantially anisotropic electrical and optical properties. In such a case, and because of their tendency to organize themselves in a parallel fashion, they may also demonstrate corresponding interesting and useful bulk electrical and optical properties. The nematic to isotropic liquid transition phase is a first order transition with relatively small transition energy. In general, the transition energies increase with increasing molecular length within a homologous series.

Viewed by polarizing optical microscope (POM), on cooling from the isotropic liquid, nematic layers between glass plates show the defect regions linking these domains as a threaded schlieren texture which appears between crossed polarizers in POM (Figure 1.5). The simple nematic with a single axis (uniaxial) perpendicular to the director (actually the two minor axes are identical in the case of the simple nematic) is different from the biaxial nematic which is a spatially homogeneous liquid crystal with three distinct optical axes. Some nematic liquid crystals are biaxial, meaning that in addition to orienting along their long axis, they also can orient preferentially along one of the pair of secondary orthogonal axes. For example, a biaxial nematic with a boomerang-shaped oxadiazole bent-core mesogen was first reported in 2004.
1.3.2 Smectic phases

There are a number of different categories of smectic phases amongst which the best known are the smectic A (SmA) and smectic C (SmC) phases.

1.3.2.1 Smectic A phase

The smectic phases are found at temperatures below the nematic and they have at least one more increased degree of order, which means that the smectic state is more 'solid-like' than the nematic. They maintain the general orientational order of nematics but also show a degree of translational order not present in the nematic. As such, they form well-defined layers that can slide by one another. Molecules in SmA possess the least order amongst all smectic phases and they align with their directors on the average perpendicular to the layer planes. These molecules are able to rotate freely about their long axes and the individual molecules are able to move from one layer to another but spend most of their time associated with a layer. Most mesogens that exhibit the SmA phase have molecular structures that consist of a rigid core and one or two alkyl chain(s). The molecular order of the SmA phase is as illustrated in Figure 1.6.

The SmA phase can be obtained by cooling either a nematic or the isotropic phase. Two important microscopic textures of SmA are the homeotropic texture and the focal-conic fan texture. Observation using POM shows a black area of homeotropic
The common texture for SmA is the focal-conic fan, which is formed upon cooling the isotropic phase. The phase separates out initially in the form of bâtonnets which then coalesce to form the focal-conic fan texture (Figure 1.7).

![Figure 1.7: POM photographs of (a) homeotropic texture of SmA; (b) bâtonnets growing from the isotropic; (c) formation of the focal-conic fan texture of SmA from coalescence of bâtonnets](image)

1.3.2.2 Smectic C phase

Closely related to the SmA phase is the smectic C (SmC) phase. Here the molecules are not on average orthogonal to the layer plane, and hence the molecular directors, lie at an average angle, 0 to the layer plane (Figure 1.8).

![Figure 1.8: Schematic representation of molecular order in the SmC phase](image)

This angle is temperature dependent and the SmC phase is the tilted analogue of a SmA phase. The tilt is caused by dipole-induced intermolecular interactions. The formation of SmC is influenced by the molecular structure; particularly symmetrical molecules with two terminal alkyl or alkoxy chains. In some cases, branching in the terminal chain can increase the chances for a material to exhibit the SmC phase. The zig-zag molecular shapes produce the necessary tilting within the layers to form the SmC phase. The usual microscopic textures exhibited by the SmC phase are the schlieren and the broken focal-conic fan textures. The SmC can be obtained either by cooling the
isotropic, the nematic or the SmA phases. Cooling the focal-conic fan texture of SmA shows the broken focal-conic fan texture of the SmC phase (Figure 1.9).

![Figure 1.9: POM photographs of (a) broken focal-conic fan texture of SmC (b) schlieren texture of SmC](image)

**1.3.3 Cholesteric phase**

Intrinsically chiral molecules can also form a special nematic phase called the chiral nematic but usually called the cholesteric phase ($N^*$) because it was first observed for cholesterol derivatives. The cholesteric phase can also be produced by mixing a nematic material with a chiral dopant. These molecules often have a chiral center and the molecular order remains the same as the nematic except the director makes a twist about a single axis with a constant angle in the preferred direction throughout the sample. The twist produces the molecules perpendicular to the director with the molecular axis parallel to the director and this creates the intermolecular forces between alignments of the molecules at a slight angle to one another. This can be visualized as a stack of very thin 2-D nematic-like layers with the director in each layer twisted with respect to those above and below, as illustrated in Figure 1.10. The distance over which the director rotates by 360 degrees is called the chiral pitch, $p$. When the temperature is altered (and/or the amount of chiral dopant is altered), the pitch often changes and can be tuned accordingly. The structure of the cholesteric phase repeats itself every half-pitch, since in this phase directors at 0 degrees and +/-180 degrees are equivalent. In this structure, the directors actually form a continuous helical pattern about the layer normal.
Figure 1.10: Schematic representation of cholesteric phase for (a) half pitch, \( p/2 \)
(b) one complete chiral pitch, \( p \). Note the pitch axes in (a) and (b) have
different orientations.

1.3.4 Blue phase

Blue phases are among the most interesting self-organized structure in the field of
liquid crystals. These are liquid crystal phases that may appear between a cholesteric
phase and an isotropic liquid and usually with a very narrow temperature range of
only a few degrees Kelvin\(^4\). In this phase, the molecular directors rotate in a helical
fashion perpendicular to lines that form a number of helical axes in different
directions. It is sometimes called a double twist structure even though an unlimited
number of axes are present and is more stable than the single twist structure found in
cholesteric molecules. The double twist structures are limited in all directions to the
distance from the center line where the twist amounts to \( 45^\circ \) and a double twist
cylinder results. Such a cylinder is more stable because of its small radius compared
to the same volume filled with only one single twist of cholesteric liquid crystal\(^4\)
(Figure 1.11).

Figure 1.11: (a) Perspective view of a double twist structure with two helical axes,
h\(_1\) and h\(_2\).
(b) Top view of a double twist cylinder with three helical axes;
(c) Perspective view of a double twist cylinder (outside lines indicate a
\( 45^\circ \) rotation of the director).\(^4\)
Blue phases have a regular three-dimensional cubic structure of defects. If the spacing between the defects is in the range of the wavelength of light, interference occurs in a certain wavelength range for light reflected from the lattice (especially blue colored light). These double twist cylinders form a cubic lattice wherein the defects occur at the contact point of the cylinders\(^4\) (Figure 1.12).

Figure 1.12: (a) A cylindrical region of double twist structure; (b) Intersection of three double twist cylinders which form a defect; Arrangement of double twist cylinders which may exist in (c) BPI and (d) BPII\(^4\).

Liquid crystals are typically rod like anisotropic materials with parallel orientation and limited positional order, forming one or several mesophases between the solid crystal and isotropic liquid phase. The refractive index and the static dielectric constant depend on the orientation of the director and the electric field which cause the birefringence and dielectric anisotropy, respectively. This phenomenon is exceptional for blue phases materials which appear in chiral systems in the temperature range just below the isotropic liquid phase\(^5\). These phases are optically isotropic and they are not birefringent\(^6\). However, they may show colors due to the selective reflection of circularly polarized light. Three different thermodynamically stable blue phases, BPI, BPII and BPIII have been observed on cooling from the isotropic phase to the chiral nematic phase\(^7\). They are the colorful BPI and BPII and the misty blue BPIII which are separated by first order transitions. Both BPI and BPII have long-range orientational order with 3-D cubic symmetry that is the body-centered cubic (BPI) and simple cubic (BPII) while BPIII is only isotropic\(^8\) (Figure 1.13).
It was reported that some new materials possess blue phases with enhanced thermal stability from 1°C range to 30°C range and the flexoelectricity effects observed in them are profound. This report is of interest as most any practical application of some electro-optical phenomenon in a blue phase will require an operating temperature regime well in excess of the few degree range characteristic of conventional materials. Coles reported that the stabilization of these blue phases over a wide temperature range of 60°C in a mixture of three homologous dimers mixed in equal proportion with a small amount of chiral dopant.

1.3.5 Cubic phase

Thermotropic cubic phases show a variety of morphologies as the temperature is changed.

1.3.5.1 Thermotropic cubic mesophase

Thermotropic cubic mesophases have received considerable attention due to their complex three dimensional (3-D) structures in different self-organizing systems. Their molecules are often highly anisotropic, and the bulk phase is optically isotropic and highly viscous in their cubic phase even when it appears between adjacent SmA and SmC phases. Examples of molecular structures producing these thermotropic Cub phases include the bisbenzoyl hydrazines, disk-shaped molecules, block copolymers, polyhydroxy amphiphiles and carbohydrates. They have been widely used as a building block of supramolecular materials and have a wide variety of different mesophases driven by the intermolecular hydrogen bonding between the hydroxy groups in the molecules.
and the segregation of the non-polar hydrophobic chains. Therefore, the number, length, location and composition of the alkyl chains attached to the rigid moiety and the number and type of hydrogen bonding sites determines the identity of the resulting mesophase(s).

These types of cubic phases show a variety of morphologies. The most common is the bicontinuous $la3d$, followed by the space group $lm3m$ and the $Pm3n$\textsuperscript{86}. In order to determine the exact symmetry of these cubic phases, X-ray diffraction studies are required. The Bragg peaks in the X-ray detects the cubic polar and a polar interfaces due to the electron density contrast but it is not sensitive to the position of the alkyl chain regions with respect to the polar/a polar interfaces thus is not sufficient to identify whether it is a normal or inverted type\textsuperscript{86}. Examples of the cubic phases (I- and V-phases) structures in thermotropic mesogens include the bicontinuous structures with a body centered lattice ($la3d$, $lm3m$)\textsuperscript{87,88} and the primitive cubic lattice ($Pm3n$)\textsuperscript{83}, as shown in Figure 1.14.

![Figure 1.14: Schematic representation of cubic phases (I- and V-phases) in the thermotropic system.\textsuperscript{89}](image)

Cubic phases are characterized by a long range positional order but without orientational order\textsuperscript{90}. The cubic phase was initially called the SmD phase\textsuperscript{91}. Under POM, the cubic phases do not show any texture in both lyotropic and thermotropic systems. They look isotropic but have a highly viscous character. In the lyotropic system, the cubic phases were often called a ringing phase\textsuperscript{92}. Earlier work on the refractive index\textsuperscript{93} and X-ray diffraction of this phase showed no layered structure in the molecules\textsuperscript{94}. Instead, the structure was discovered to have positional order similar to that of the isotropic liquid but it coexists with a crystalline cubic lattice. Etherington et al\textsuperscript{95} argued that SmD phase should not be called a smectic phase, but simply the D phase since it is clearly established to have three dimensional order and is definitely cubic. Later, it was known as D phase and now is known as the cubic phase. It presents an optically black area and its transformation from the isotropic
liquid or from a homeotropic smectic phase is hard to observe (black to black area) and it could be mistaken for an isotropic liquid.  

1.3.6 Columnar phase

Columnar liquid crystals are different from the previous types because the molecules that form them are usually shaped like disks instead of long rods. The discotic molecules tend to arrange themselves and become the discotic nematic, the nematic columnar and other more stable columnar phases with two dimensional lattices. The discotic nematics are composed of flat-shaped discotic molecules stacked in one dimension. The nematic columnar phase do not form two-dimensional lattice but display a positional short-range order and an orientational long-range order. They are less organized than other columnar liquid crystals which have long-range order with two-dimensional lattices (Figure 1.15).

![Figure 1.15: Schematic representation of the nematic columnar phase.](image)

These latter phases consist of five types of columnar arrangements based on the geometry of molecular stacking (Figure 1.16).

![Figure 1.16: Schematic representation of columnar: (a) hexagonal (Colh) (b) rectangular (Colr) (c) oblique (d) plastic (Colp) (e) H phase columnar helical columns which interdigitate in groups of three stacks.](image)

The typical columnar liquid-crystalline molecules have a π-electron-rich aromatic core surrounded by multiple flexible alkyl chains. The π-π interaction is a noncovalent interaction caused by intermolecular overlapping of p-orbitals in π-conjugated systems.
As flexible long aliphatic chains surround the core, the intercolumnar distance is usually 20-40 Å, depending on the lateral chain length. Therefore, the interactions between neighbor molecules stacked in the same column are stronger than the interactions between molecules in the neighboring columns.

1.4 STRUCTURAL CLASSIFICATION OF LYOTROPIC LIQUID CRYSTALS

There are different types of lyotropic liquid crystal phases which can be distinguished by their bulk organization depending on the temperature and concentration. At certain conditions of concentration and temperature, the amphiphilic molecules form aggregates with different shapes. Ordering of the structural units forms specific structures such as cubic, hexagonal and lamellar.

1.4.1 Cubic phase

Cubic phases in the lyotropic system are more commonly observed than in thermotropic systems. By changing the concentration of the solvent, several different cubic phases may be observed in lyotropic systems.

1.4.2 Lyotropic cubic mesophase

Cubic phases are more commonly observed in the lyotropic systems. The individual micelles arrange themselves and form the cubic phase, which may exist in three different packing arrangements including the cubic, cubic face-centered and cubic body-centered lattices. By changing the concentration of the solvent, several different cubic phases may be observed in lyotropic systems. Micellar aggregates separate into two distinct shapes; the spherical shape which forms the I-phase (discontinuous cubic phase) while the other shape is rod-like which is interconnected in three dimensional patterns to form the V-phase (bicontinuous cubic phase). In a lyotropic system, there are four different cubic structures of the I- and V-phases in the normal and inverted types (Figure 1.17).
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Figure 1.17: Schematic representation of cubic phases from spherical molecules, I-phase (top) and from rod-like molecules, V-phase (below), in the lyotropic system.

The microphase separation between hydrophilic and hydrophobic parts of the aggregates formed by the amphiphilic molecules is known as interfacial curvature. This is an important factor that determines the structure and the phase sequence of the molecules based on the concentration of the solvent. If both regions are equal with respect to the required space, a lamellar structure ($L_a$) with zero curvature is observed. Smaller deviations show the bicontinuous cubic phase (V-phase) while greater deviations show the micellar structure (I-phase). Detailed information from the crystallographic point of view helps to distinguish different types of cubic lattices. In the I-phase, the spherical normal structure of the primitive ($Pm3n$), cubic face centered ($Fm3m$) and cubic body centered ($Ia3d$). This I-phase also shows one inverse structure ($Fd3m$). In the V-phase, the rod-like shows three different structures of 3-D interwoven networks consist of short rod-like micelles with the face curvature facing water ($V_1$) or nonpolar solvent ($V_2$). These arrangements organize into different bicontinuous cubic lattices of $Pn3m$, $Ia3d$ and $Ia3d$ (Figure 1.17). These cubic phases (I- and V-phases) can be differentiated from one another by their position in sequence between other phases. In the increasing surfactant concentration, the I-phase is located in between the isotropic micellar and the hexagonal phase while the V-phase is between the hexagonal and the lamellar phase.

1.4.3 Hexagonal phase

If the solvent concentration in the cubic phase is increased, the hexagonal phase may occur and depending on the solvent polarity, the normal ($H_n$) or inverse structures ($H_o$) will be formed. Micelles aggregate themselves and become cylindrical shaped
micelles of indefinite length, forming hexagonal arrays with six rods grouped around a central one where the micelle surface is composed of hydrophilic heads while the hydrophobic tails are isolated inside the micelle. This phase has long-range orientational order\textsuperscript{106}. In the normal hexagonal phases (type 1), hydrocarbon chains are contained within the cylindrical aggregates and shows positive mean curvature for polar-apolar interface ($H_i$). The inverse hexagonal phases ($H_i^\text{a}$) have water within the cylindrical aggregates and the hydrocarbon chains fill the voids between the hexagonally packed cylinders\textsuperscript{106}. Both normal and inverse phases are highly viscous and show textures as smoke-like, fan-like or mosaic (Figure 1.18).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure18.png}
\caption{Schematic representation of hexagonal phase of (a) rod micelle close up (b)normal and (c) inverse types\textsuperscript{106}.}
\end{figure}

1.4.4 Lamellar phase

At even higher concentrations (Figure 1.18) the molecules move into another liquid crystalline phase – the lamellar phase. This structure has a double layer of molecules with one dimensional stacking and zero interfacial curvature. This lamellar structure is formed with the polar heads on the outer layer and the nonpolar tails sandwiched in the middle.\textsuperscript{15} This pattern is similar to that of smectic liquid crystals in the thermotropic category, which form a focal conic texture. This lamellar phase is less viscous than the hexagonal phase because the sheet-like layers can slide easily past each other despite its lower water content. If the molecules are placed on the surface of water without actually being dissolved in it, they can form a monolayer in which the polar heads are in contact with the water and the hydrophobic tails point into the air. These monolayers are often referred to as Langmuir films\textsuperscript{16} (Figure 1.19).
A precursor to the bilayer is the ribbon phase which involves finite bilayers that end in cylindrical half-micelles. These ribbons will fuse together to form the bilayers. If the amphiphile concentration is lower, the mixture reverts to a hexagonal phase or a solution of micelles.  

1.5. MATERIAL PROPERTIES OF LIQUID CRYSTALS - NEMATIC LIQUID CRYSTALS

1.5.1 Birefringence (Δn)

A monodomain specimen of nematic medium is optically uniaxial, positive and strongly birefringent. The value of Δn depends on the structure of the compound, but for a given compound it decreases appreciably with rise of temperature. If the molecules are highly conjugated and made up of groups having strong anisotropy of polarizability, Δn is larger.

1.5.2 Dielectric Anisotropy (Δε)

If the molecule is nonpolar (as in the case of quino-phenyl) or if the net dipolar moment μ = 0, Δε arises entirely from the anisotropy of the low frequency molecular polarizability and has a positive value normally between 0.5 and 1.0. The presence of a strong polar group with μ pointing long the long molecular axis enhances Δε. For example, the C = N group at one end (as in 5 CB) increase Δε by a factor of about 10^{107,108}. However, if the polar group makes a large angle with the long axis, Δε may become negative as in PAA, for example^{109}. In the case of the -C ≡ N group attached to the axis, Δε will be nearly equal to ~5^{110}.

The component of μ perpendicular to the length of the molecules has a dielectric relaxation frequency in the microwave region, arising from the rapid
rotation of the molecule about its long axis. On the other hand, the parallel component of $\mu$ has to work against the nematic orienting potential as well as the viscous torque, and the relaxation frequency comes down considerably, usually to the mega hertz region and in special cases to the kilo hertz region. Hence $\Delta \varepsilon$ drops to a low value beyond this frequency, $\nu_0$ and in some cases even changes sign from a positive to a negative value beyond $\nu_0$. This is a useful property in multiplexed display devices.

1.5.3 Viscous properties

The viscosity is an important parameter in determining the on and off times of display devices. A complete distribution of the viscous behaviour of a nematic requires five viscosity coefficients, but for most practical purposes an appropriate average value $\eta$ is adequate. As a rule, the longer and stiffer the molecule the greater the value of $\eta$. It has a high value for esters and a relatively low value for the biphenyl’s and an even lower value for the phenyl cyclohexanes and cyclohexyl cyclohexanes. For a room temperature nematic like pentyl cyanophenyl cyclohexanes, $\eta \approx 20$ cP about 20 times that of water. The value decreases rapidly with rise of temperature.

1.5.4 Conductivity Anisotropy

Nematogenic molecules are electrically neutral. However, the presence of ionic impurities, accidentally or deliberately introduced in the liquid crystal, makes the medium electrically conducting. Because of the anisotropic viscosity of the liquid crystal, the ions can flow more easily along with director than in direction perpendicular to it. The conductivity anisotropy ($\Delta \sigma$) is positive, $\sigma$ usually being about 1.4. The actual value of $\sigma$ depends on the nature of the liquid crystal, the nature and concentration of the dopant, and the temperature. If the liquid crystal shows smectic and nematic phases, smectic-like short range order (sometimes called cybotactic groups) builds up in the nematic phase close to the transition, in this regime $\Delta \sigma$ changes sign and becomes negative.

1.5.5 Elasticity

Nematic liquid crystals exhibit curvature elasticity, i.e., a restoring torque comes into play if the local director changes its orientation at a given point. There are
three fundamental types of distortion: Splay, twist and bend (Fig. 1.19). The corresponding curvature elastic constants are denoted by $k_{11}$, $k_{22}$ and $k_{33}$ respectively. The units of $k_{11}$ are dynes. For normal nematics, the value is around $10^{-6}$ dyne and $k_{33} > k_{11} > k_{22}$. Like all order-dependent properties ($K_{11} \propto s^2$ approximately) all three constants decrease with rise of temperature. In the case of cybotactic nematics, anomalous behavior is observed for $k_{22}$ and $k_{33}$ usually close to the smectic-nematic transition. These two constants increase very rapidly as the transition temperature is approached.

1.5.6 Flexoelectricity

Meyer\textsuperscript{117} argued that if the molecules are pear shaped with a permanent dipole moment along the long axis, for geometrical reasons a splay deformation should produce an electric polarization in the liquid crystal. Similarly, if the molecules are banana shaped with a dipole moment along the short axis, a bend should produce the same effect. This is the analogue of piezoelectricity in solids. Later, Prost and Marcerou\textsuperscript{118} showed that even quadrupoles are sufficient to give flexo- (or curvature) electricity under deformation. Experiments have confirmed the existence of both types of effects\textsuperscript{119}.

When a homogeneously aligned sample is subjected to a dc or to an ultra low frequency ac electric field, certain periodic instabilities can be observed owing to the flexoelectric torque produced in the sample\textsuperscript{120,121}. However, even for relatively low frequency of the applied ac voltage, the flexoelectric effects are marked by electrohydrodynamic instabilities and hence have not so far found any application.

1.5.7 Surface Alignment

Unidirectional rubbing of a glass substrate produces a homogeneously aligned nematic with its director oriented along the direction of the rubbing\textsuperscript{122,123}. Alignment can be reproducibly achieved by vacuum-coating the substrate at an oblique angle\textsuperscript{124}. In this case the angle made by the director with substrate depends on the angle of coating\textsuperscript{125}.

To produce homotropic alignment (the director perpendicular to the substrate), a monolayer of a long chain compound with a polar head, e.g., acetyl trimethyl ammonium bromide (CTAB)\textsuperscript{126}, is coated on the surface. The polar groups attach themselves to the glass plate and, if the density of CTAB is sufficiently high, the alkyl
chains stand out of the glass plate and align the nematic normal to the substrate. The anchoring energy of courses depends on the mode of preparation of the substance.

1.6 APPLICATIONS OF LIQUID CRYSTALS

1.6.1. Applications of Liquid Crystals in Optical Computing

Liquid crystals by virtue of their orientational order can be made highly birefringent or dichroic with refractive index anisotropies as large as $\Delta n = 0.2^{128}$. Under the condition of partial translational ordering, liquid crystals generally exhibit, 'soft' degree of freedom for which the mean molecular orientation and therefore the optic axes are easily manipulated by weak external forces, such as those produced by surfaces or applied fields. Thus, a few volts applied to a 10 $\mu$m thick LC layer can reorient its optic axis through 90° in a time $\tau$ in the range $1\mu$ sec $< \tau < 100$ m sec. This electric field induced reorientation of the mean molecular axis of rod shaped molecules has become the basis for LC electro-optic technology.

The principal electro-optic application of LC's has been to information display. LC watches, calculators, and instrument displays are by now household items, and handled flat panel colour video displays and laptop computer displays are currently making major market entries. In point of fact, the LC display revolution has only just began. By the turn of the century LC displays will be the mode of choice for most major display applications, and will fuel a revolution based on powerful portable information processing with Active Matrix Twisted Nematic (AMTN) $^{129}$ and Ferroelectric Liquid Crystal (FLC) $^{130}$ technologies leading the way.

In exploring the applications of LC's to optical computing (OC), it is instructive to consider the reasons for the success of LC's in displays. As employed in displays the optical rise time of LC's in response to an applied voltage step is in the 10 m sec to 10$\mu$ sec regime. Despite this rather slow response speed LC displays are the technology of choice for the following reasons.

1. **Flexibility:** LC's lend themselves to hundreds of different molecular and optical geometrics with properties optimized for particular applications. This is an important consequence of their fluidity and high birefringence which yields dramatic optical effects in cells of a few optical wave lengths thick.

2. **Low voltage, Low power Operation:** Obviously a key property for portable display applications but also an important consideration when comparing the
speed of LC devices with other electro-optic technologies for optical computing applications. The operating speed practically attainable for intrinsically faster technologies is in fact limited by power dissipation in many interesting applications to times comparable to those obtainable in LC devices configured for optical computing applications.\(^{31}\)

3. **Ease of Fabrication**: Liquid crystal cells of high optical quality and controllable characteristics can be mass produced so that sophisticated devices, for example, mega pixel light valve arrays, can be made at moderate rate. It is evident that these characteristics will also be important in the use of LC’s for optical computing. An important theme in optical computing is the exploitation of the intrinsic parallelism of optics to do processing and it is in this area that liquid crystals are especially useful. A particularly elegant and ancient realization of this idea is optical Fourier transformation wherein the optical electric field distribution in the Fraunhofer diffraction plane is the Fourier transforms of an image field.\(^{32}\) The ready availability of coherent light sources has made Fourier optics a powerful image filtering and processing technique.\(^{33}\) The basic advantage of optics in this application derives from its intrinsic parallelism, the ability of light rays of different wave vector to occupy the same space and to pass through each other, and from the analog nature of light. To take advantage of this parallelism in processing application, the positional dependence in one or two dimensions of the electric field of an optical wave front must be manipulated in a way that can be easily and quickly changed, leading to the requirement for Spatial Light Modulators (SLMs), dynamically changeable devices which modify the amplitude, phase, and/or polarization of an optical wave front as a function of time and position across it.

### 1.6.2 Liquid Crystal Light Valves for Schlieren Optical Projection

Large-Screen projectors for video applications and computer monitors are convenient instruments for promotional or conference presentations as well as for TV use at home. Light valve displays using the schlieren optical principle show improved brightness and resolution of the image compared to those of cathode ray tube (CRT) projectors.
A schlieren optical projector consists of a light source, a separator to split the light into RGB colours, three colour tuned imaging elements, the schlieren lens and bar and a projection lens.

The projection system for one colour is shown in Fig. 1.20. The imaging element is a controllable phase grating with a reflective backplane. The light coming from the illumination system is reflected and diffracted towards the screen. The diffraction maxima are focused in the focal plane of the schlieren lens. If the system is used in dark field projection mode the central maximum is mirrored back into the light source. The phase information of the imaging element is transformed into amplitude information on the screen. The imaging element shifts light waves which pass its active zones compared to light in non-active zones. In Fig. 1.21a, a wave is shown which propagates through reflective phase modulators of different technologies. In the case of a modulator with reflective oil film (Fig. 1.21b) the film thickness is controlled in order to shift the light waves by $\Delta \phi^{134}$. The same phase shift can be obtained using a liquid crystal material with a constant thickness but a controllable refractive index $^{135}$ (Fig. 1.21c). A third technique is to displace a metallic mirror which is coated on a visco-elastic layer $^{136}$ (Fig. 1.21d).
Liquid crystal phase modulation is based on the optical anisotropy of the LC material. The optical properties of LC devices depend on the orientation of the LC molecules. In order to calculate the molecular orientation and the optical properties, the LC material is usually divided into thin layers with homogeneous molecular
orientation. The refractive index for the birefringent LC layers can be determined using the refractive index ellipsoid, whose longitudinal axis is parallel to the director. The liquid crystal material Merck ZLI 5049 - 000 with a cell gap of 4 μm is generally used for phase modulator applications. The technical details of this application is well discussed in the references\textsuperscript{137,138}.

1.6.3 Liquid crystals in medicine

The medical applications of cholesteric - nematic liquid crystals include oral thermometry, cutaneous thermography, gynecology, neurology, oncology, pediatrics, surgery, podiatry and dentistry. To be more specific, these medical applications include detection of breast cancer, location of the placenta, blood flow patterns in extremities of the human anatomy, and observation of skin temperature changes following blockage of the sympathetic nervous system. The observation of skin temperature changes following blockage of the nervous system enables the physician to determine if neurological and vascular pathways are open. Continuous monitoring of the skin temperature over an extended area provides the physician with a detailed and more easily interpreted indication of circulatory pattern than point measurements with thermocouples and thermistors.

A tumor is generally warmer than the surrounding tissue, which makes it easy to identify its contours and thus guide a surgeon where to cut to extract the tumor and leave as much healthy tissues as possible to enhance healing. The placenta is warmer than the surrounding tissue, and knowing its location aids the obstetrician in determining if the baby can be expected to have normal delivery or whether a caesarian is in order. Third degree burns are cooler than second degree burns because the blood circulation in the third degree area is less than in a second degree burn. Use of liquid crystals to identify the extent of a burn can speed up treatment and avoid the delay of several days for development of scab.

The liquid crystals also find application in the diagnosis of several diseases. In addition to hardening of the arteries, gallstone formation, and sickle cell anemia, we can name a few rather rare diseases that involve liquid crystal applications. It is well known that phospholipids such as lecithin and sphingomyelin swell in water to give a lamellar, liquid crystalline structure. These water-lipid compositions are
sensitive to temperature changes and will undergo order-disorder transitions as the temperature is lowered. Phospholipids from living systems, such as brain tissues and red cell membranes interact with water to give liquid crystalline structures. Cholesterol is insoluble in water and in living systems it can precipitate as cholesterol mono hydrate to form, for example, gallstones and arteriosclerosis lesions. Cholesterol esters behave in a comparable way. However, if one takes a three-component system of lecithin, cholesterol, and water, the cholesterol will be solubilized by the water and lecithin to form a liquid crystalline system. The compositions can be as high as a mole of lecithin to a mole of cholesterol. With higher concentrations of cholesterol, it precipitates as cholesterol mono hydrate. Chemical analysis of the deposits on artery walls can give some guidelines on the chemicals that are involved in hardening of the arteries. Analysis of the deposits indicates that cholesterol esters make up most of the deposit.
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