CHAPTER-1

PART – A

Introduction to Liquid crystals
1.1 Introduction to Liquid crystals

From year’s research in science had been conditioned into recognizing three states of matter - solid, liquid and gas. It was anticipated that if we take a crystalline solid and heat it then it will step through the phases solid-liquid-gas, unless it sublimes and evaporates before the gas phase is reached. The interconversion of phases, particularly, in case of organic compounds, usually takes place at well defined temperatures. In the year 1888 an unusual sequence of phase transition was observed by an Austrian Botanist Reinitzer (Figure1a) [1] while investigating some esters of cholesterol compounds (cholesterly benzoate). After Reinitzer study on these samples of cholesterol a German Physicist Lehmann (Figure1b) [2] who was studying the crystallization properties of various substances observed the same samples with his polarizing microscope and noted its similarity to some of his own samples. He observed that they flow like liquids and exhibit optical properties like that of a crystal. The most important properties which differentiate between solids and liquids are flow, optical, electrical, magnetic properties and molecular ordering. Lehmann first referred to them as flowing crystals and later used the term "liquid crystals". Hence, “liquid crystals” must possess some typical properties of a liquid (e. g. fluidity, inability to support shear, formation and coalescence of droplets) as well as some crystalline properties (anisotropy in optical, electrical, and magnetic properties, periodic arrangement of molecules in one spatial direction, etc). Liquid crystal materials are unique in their properties and uses.
Some features that are important in this field of research are summarized as follows:

- The two most common states of condensed matter phases are the isotropic liquid phase and the crystalline solid phase.
- In a crystal, the molecules or atoms have both orientational and three dimensional positional order over a long range.
- In a liquid, the molecules have neither positional nor orientational order, they are distributed randomly. There is no degree of order and no preferred direction in liquid, hence they are named as “isotropic”.
- The transition from one state to another normally occurs at a very precise temperature commonly known as “Phase transition temperature”. These transitions are definite and precisely reversible.
- Many organic compounds do not immediately transform to liquid phase during heating from solid to its melting temperature, but exhibit one or
more intermediate phases having the properties of both solid and liquid. These types of materials exhibiting intermediate phases are known as “Liquid crystals” and the phase is called “Liquid Crystal phase” or “Mesophase”.

- In a liquid crystal phase, the molecules possess both orientational and one or two dimensional positional order i.e. it has order like solid and flow like liquid.
- In this phase the unique axis of the molecules remain on an average parallel to each other, leading to a preferred direction in space. This direction of alignment is described by a unit vector ‘\( \mathbf{n} \)’ (figure 2), the director, which gives at each point in a sample, the direction of a preferred axis.
- The structural features in molecules that exhibit liquid crystal nature are more likely have anisotropic shape (elongated), flat segments like benzene rings, rigid double bonds which define the long axis of the molecules.

Till 1890, all the liquid crystalline substances that had been investigated were naturally occurring and after that the first synthetic and most readily prepared liquid crystal is \( p \)-azoxyanisole came into existence [3]. Subsequently more liquid crystals were synthesized and it is now possible to synthesize liquid crystals with specific predetermined material properties.
1.2 Types of Liquid crystals:

Liquid crystals are of two types based on the process that drives them to liquid crystal phase to a conventional liquid phase. The two categories are

1. Thermotropic liquid Crystals
2. Lyotropic Liquid Crystals

1.2.1 Thermotropic liquid crystals

Liquid crystal materials in which the transitions to the mesophases are obtained purely by thermal process are called thermostropic or non-amphiphillic liquid crystals [4,5]. If the temperature rise is too high, thermal motion will destroy the delicate cooperative ordering of the liquid crystal phase, pushing the
material into a conventional isotropic liquid phase. In contrast to the high temperature, at too low temperature, most liquid crystal materials will form a typical crystal. As the temperature is raised, their state changes from crystal to liquid crystal at temperature $T_1$. Raising the temperature further changes the state from liquid crystal to isotropic fluid at temperature $T_2$. For a thermotropic liquid crystal, the essential requirement is, in it the molecules must have a structure consisting of central rigid aromatic core and flexible peripheral aliphatic groups. Thermotropic liquid crystals are divided into two types:

1.2.1 a) Monotropic Liquid Crystals:

This type of thermotropic liquid crystals exhibit liquid crystal state either in heating or cooling process as shown in figure3. Mostly many compounds exhibit the mesophase in the cooling process. In monotropic materials, the liquid-crystal phase is not thermodynamically stable and is only observed on cooling due to kinetic reasons [6].

1.2.1 b) Enantiotropic Liquid Crystals:

This type of thermotropic liquid crystals exhibit liquid crystal phase both on heating and cooling process as shown in figure4 i.e. mesomorphic transitions occur on increasing the temperature of compounds and also in the reverse process of decreasing the temperature. Enantiotropic liquid crystalline phases are thermodynamically stable in a temperature region between the crystal melting temperature and the isotropic temperature
Figure 3 LC’s phase in cooling process, structure and schematic representation of transitions sequence for cholesteryl nonanoate.
Figure 4 Liquid Crystal phase in both heating and cooling process, structure and schematic representation of transitions sequence for para-Azoxylanisole.
1.2.2 Lyotropic liquid crystals

Liquid crystalline behavior is also found in certain colloidal solutions such as aqueous solutions of tobacco mosaic virus and certain polymers. This class of liquid crystals is called lyotropic or amphiphillic Liquid Crystals. The lyotropic liquid crystals are formed by the dissolution of amphiphilic molecules of a material in a suitable solvent and consists a hydrophilic polar “head” and a hydrophobic “tail”. In blends of different components phase transitions depend on concentration. Thus, lyotropic mesophases are concentration and solvent dependent. Examples of Lyotropic liquid crystals are soap (figure 5a) and various phospholipids (figure 5b) like those present in cell membranes [7, 8]. These materials have been widely used in various applications [9] and are also important for biological systems [10, 11]. The lyotropic liquid crystals are composed of hexagonal (figure 6a), cubic (figure 6b), lamellar, reverse hexagonal phase, etc…

![Chemical structure of sodium dodecylsulfate (soap)](image)

**Figure 5(a)** Chemical structure of sodium dodecylsulfate (soap)
Figure 5(b) phospholipids (lecitine) present in cell membranes

6(a) Schematic diagram of hexagonal phase
1.3 Structural Classification of Liquid Crystals

In thermotropic liquid crystals regarding the shape of molecular structure they are two types of LC molecules a) rod type liquid crystals b) Disc type liquid crystals (Figure 7).

Figure 7 Types of shape of thermotropic liquid crystal; rod and disc shapes.
Calamatic or rods like LC’s are the compounds that possess an elongated shape responsible for anisotropic nature of molecular structure. This type of molecular structure consists of a ring systems attached by linking units with flexible terminal groups at the end. The linking groups together with ring structure are called “Rigid Core” forming calamatic molecules as shown in figure8.

![Figure8 Block diagram of molecular structure for Calamatic or rod LC’s](image)

a) Calamatic LC’s: Depending on the nomenclature proposed by G. Friedel [12] the mesophases that Calamatic thermotropic liquid crystals exhibit are shown as follows:

1.3.1 Nematic phase (In Greek word nematos means “thread”)

The nematic phase of calamatic LC’s is the simplest liquid crystal phase which is characterized by long-range orientational order, i.e. the long axes of the molecules tend to align along a preferred direction (Figure9c). Therefore, the molecules flow just like in a liquid, but they all point in the same direction. Molecules can rotate about both the axes and the molecules have several possibilities of intermolecular mobility. Because of the high mobility, the nematic phases have low viscosities. Most nematics are uniaxial. Some liquid crystals are
biaxial nematics, meaning that in addition to the orientation along the long axis, they also orient along a secondary axis.

1.3.2 Smectic phase

When the crystalline order is lost in two dimensions, one obtains stacks of two dimensional liquid. Such systems are called smectics (In Greek word smectos means “soap”). The important feature of the smectic phase, which distinguishes it from the nematic, is its stratification. The smectic phases, which are found at lower temperature, form well-defined layers that can slide over one another in a manner similar to that of soap. The molecules exhibit some correlations in their positions in addition to the orientational ordering [13]. Different classes of smectics have been recognized by differing the smectic phases from each other in the way of layer formation and the existing order inside the layers like Smectic – A, B,C,D,E,F,G,H,I. The increased order means that the smectic state is more "solid-like" than the nematic. Two commonly occurring smectic phases are

i) **Smectic A:** It has a layer structure. Inside the layers, the molecules are parallel to their long axes and perpendicular to the plane (Figure9a). These are optically uniaxial. The flexibility of layers leads to distortions which give rise to beautiful optical patterns known as focal-conic textures.

ii) **Smectic C:** Smectic C is a tilted form of Smectic A as shown in figure9b. The major difference between the two is the tilt of the molecular long axes inclined with respect to the layers. This phase is optically biaxial.
1.3.3 Cholesteric phase (or defined as “chiral Nematic”)

The cholesteric phases show chirality nature (twist or helical) and are often called the “chiral Nematic”. This phase exhibits a twisting of the molecules perpendicular to the director, with the molecular axis parallel to the director. In this structure, the directors actually form in a continuous helical pattern about the layer normal (Figure 9d). That helical path is known as a pitch, p, refers to the distance over which the liquid crystal molecules undergo a full 360° twist but, the structure of the chiral phase repeats itself every half-pitch, since in this phase directors at 0° and 180° are equivalent. The angle at which the director changes can be made larger and thus tighten the pitch, by increasing the temperature of the molecules, hence giving them more thermal energy. Liquid crystals of this type are mostly optically active. The cholesteric liquid crystals are optically uniaxial with negative character; it can scatter the light to give bright colour.

Thermotropic liquid crystal molecules also exist in disc shapes. This disc-shape molecules exhibit two distinct classes of phases, the columnar (or canonic) and the discotic nematic phases. When the crystalline order is lost in one direction one obtains a periodic stack of discs in columns (Figure 10); such systems are called columnar phases. In 1977, a second type of mesogenic structure, based on discotic (disc) shaped) molecular structures was discovered. The discotic nematic phase includes nematic liquid crystals composed of flat-shaped discotic molecules without long-range order. In this phase, molecules do
not form specific columnar assemblies but only float with their short axes in parallel to the director.

Figure 9 Phases existing in liquid crystal materials according to molecular arrangement.

Figure 10 Typical discotic: a) Columnar hexagonal phase b) example molecular structure of 2,3,6,7,10,11-hexakis(hexyloxy)triphenylene
Similarly to the calamitic LCs, discotic LCs possess a general structure comprising a planar (usually aromatic) central rigid core surrounded by a flexible periphery, represented mostly by pendant chains. When temperature decreases, the translational symmetry is broken too. The usual structure of disc-like molecules consists of a rigid central part and flexible hydrocarbon chains, which lie in the plane terminal by the rigid core. Such structure of molecules gives rise to a possibility of partial leaking of the translational symmetry, namely, the interaction of the molecular tails in the plane disc-like molecules is stronger than that between different planes. So, in principle such interaction may give rise the creation of a two-dimensional lattice.

1.4 Physical Properties of Liquid Crystals

Many applications of thermotropic liquid crystals rely on their physical properties and how they respond to the external perturbations. The physical properties can be distinguished into scalar and nonscalar properties. Typical scalar properties are the thermodynamic transition parameters (transition temperature, transition enthalpy and entropy changes, transition density and fractional density changes). The dielectric, diamagnetic, optical, elastic and viscous coefficients are the important nonscalar properties.

1.4.1 Anisotropy

The order existing in the liquid crystalline phases destroys the isotropy, and introduces anisotropy; it means that all directions are not equivalent in the system. This anisotropy manifests itself in the elastic, electric, magnetic and
optical properties of a mesogenic material. The macroscopic anisotropy is observed because the molecular anisotropy responsible for any property does not average out to zero as in the case of an isotropic phase. The liquid crystalline states can be characterized through their orientational, positional and conformational orders. The orientational order is present in all the liquid crystal phases and is usually the most important ones. The positional order is important to characterize the various mesophases (nematic, smectic A, smectic C, etc.) and can be investigated by their textures.

1.4.2 The Phase transitions and transition temperatures

The transition temperatures are the important quantities which represent a scalar property characterizing the materials. The difference in the transition temperatures between the melting and clearing points gives the range of stability of the liquid crystalline phases. For polymorphous substances the higher ordered phase exhibits the lower transition temperatures. The compounds with odd chain length have lower values of clearing points and an "even-odd effect" is observed in a homologous series. A rough estimate on the purity of a substance can be made from the temperature range over which the clearing takes place. High purity compounds have narrow clearing ranges of typically 0.3 to 0.5K. With increasing amounts of impurities this range will steadily increase to over 1K.

Several analytical techniques are in use at present for the characterization and identification of phase structures. In some liquid crystal phases the classification is relatively simple and these phases can be identified by employing just one technique. Whenever minimal differences exist in the phase structures the
precise classification often requires the use of several different techniques. The phase classification can be done on the basis of different criteria such as structures, microscopic textures, miscibility rules. The structure is characterized by the arrangement and the conformation of the molecules and intermolecular interactions. The textures are pictures which are observed microscopically usually in polarized light and commonly in thin layers between glass plates. They are characterized by defects of the phase structure which are generated by the combined action of the phase structure and the surrounding glass plates.

When a material melts, a change of state occurs from a solid to a liquid and this melting process requires energy (endothermic) from the surroundings. Similarly the crystallization of a liquid is an exothermic process and the energy is released to the surroundings. The enthalpy changes of transition between various liquid crystal phases are also small.

(a) **Crystal to smectic** - Molecules which are held together in a parallel regular arrangement by both lateral and terminal attractive forces in a crystal lattice undergo a loosening of terminal forces due to increased thermal motions. This allows a sliding of layer planes containing regular parallel arrangements of molecules.

(b) **Smectic to nematic** - A loosening of primary lateral attractions between molecules occurs so that molecules may slide longitudinally over one another. Still there is sufficient attraction to prevent complete disordering.
Smectic polymorphism may occur if there are more than one stable parallel packing arrangement for molecules.

(c) Nematic to isotropic - Thermal motion increases to a point where random orientation occurs within the material.

1.4.3 Polymorphism

These mesogenic materials exhibit the richest variety of polymorphism in their phases. They pass through more than one mesophases between solid and isotropic liquid. The transition between different phases corresponds to the breaking of some symmetry. When a mesophase can be formed by both the cooling and heating processes, it is known as "enantiotropic". Those liquid crystal phases which are obtained during cooling process are called "monotropic". One can predict the order of stability of the different phases on a scale of increasing temperature simply by utilizing the fact that a rise in temperature leads to a progressive destruction of molecular order. Thus, the less symmetric the mesophase, the closer in temperature it lies to the crystalline phase. Exceptions to the below sequence have been observed [14-16] in which higher symmetric mesophase re-appears in-between two lower symmetric mesophases. This kind of phenomenon is known as "reentrant polymorphism".

\[
\text{L-blue-N-S}_A-S_C-S_B-S_I-S_{Bcry}-S_F-S_I-S_G-S_E-S_K-S_H=\text{Solid/Crystal}
\]

(From Liquid to crystal)

Figure 11 Polymorphism in liquid crystals
1.4.4 The Refractive Index

Normally, liquid crystals are formed by rod or disc-like molecules with different molecular orientations in different directions arising to anisotropy. Liquid crystals are found to be birefringent, due to their anisotropic nature. When light wave is incident on anisotropic LCs difference in their refractive indices is observed in different directions [17, 18]. That is, they demonstrate double refraction (having two indices of refraction). Light polarized parallel to the director has a different index of refraction (that is to say it travels at a different velocity) than light polarized perpendicular to the director. It is the ability of aligned liquid crystals to control the polarization of light as it depends upon the direction and polarization of the light waves through the material. Accordingly, uniaxial liquid crystals are found to exhibit two principal refractive indices, the ordinary refractive index \( n_0 \), and the extraordinary refractive index \( n_e \).

The ordinary refractive index \( n_0 \) is observed with a light wave where the electric vector oscillates perpendicular to the optic axis. The extraordinary refractive index \( n_e \) is observed for a linearly polarized light wave where the electric vector is vibrating parallel to the optic axis. In case of chiral nematics the optic axis coincides with the helix axis which is perpendicular to the local director; \( n_e = n_x \), and \( n_0 \) is a function of both \( n_e \) and \( n_x \) and depends on the relative magnitude of the wavelength with respect to the pitch. The refractive index is an essential physical property for the optimization of liquid crystal mixtures for application in liquid crystal display devices. However, it is the optical properties of liquid crystals that most resemble those of crystalline solids.
There are various methods for measuring refractive indices described in literature like Abbe refractometer [19], Wedge shaped technique, Newton’s ring technique [20,21], Rayleigh interferometer [22]. The standard graphical variation of refractive indices $n_c$ and $n_o$ with temperature is shown in figure 12 [23].

The optical dispersion of a material is the dependence of the refractive index upon the wavelength. The determination of the refractive indices at different wavelengths in the visible spectrum enables a subsequent fit to the Cauchy equation [24].

$$n(\lambda) = n_\infty + \frac{\alpha}{\lambda^2}$$

where $n_\infty$ (infinity) is the refractive index extrapolated to infinite wavelength and $\alpha$ is a material specific coefficient. Using the fit, it is possible to calculate the respective refractive indices $n_c$ and $n_o$ and consequently the optical anisotropy or so called birefringence.

![Figure 12](image.png)

**Figure 12** Temperature dependence of the refractive indices $n_c$ and $n_o$ for 4-(trans-4'-pentylcyclohexyl)-benzonitrile (PCH-5) determined at 589.3 nm.
1.4.5 Effective Geometry Parameter

“Effective geometry parameter”, one of the important parameter is helpful in understanding the influence of measurable physical parameters like temperature, birefringence and order parameter on the behavior of light propagation in liquid crystals. Satiro and Moraes [25,26] described the propagation of light near disclinations lines in liquid crystals from a geometric point of view, the effective geometry parameter ($\alpha_g$) which is the ratio of $n_o$ and $n_e$ is used. Topological defects in liquid crystals cause light passing by to deflect and the deflection is due to the particular orientation of director associated to the defect as shown in figure13 [27,28].

The intensity of the deflection depends on the effective geometry parameter ($\alpha_g$) which is the ratio between the ordinary and extraordinary refractive indices. Barriola [29] described the effective geometry perceived by light in the presence of a hedgehog point defect. This hedgehog point defect is described by its metric, Riemann tensor and curvature scalar which coincides with the space part of the geometry associated to a global monopole, a topological defect of spacetime. A geometrical model was developed by Joets and Ribotta [30] for anisotropic media to study the propagation of light in the nematic phase with topological defects.
Figure 13 (a) Director field (b) light paths for the $\theta = \pi/2$ section of the hedgehog for $k = 1, c = 0$ disclination and $k = 1, c = \pi/2$ disclination (line defects), respectively.

1.4.6 The Birefringence

It is a very important property of LC materials. Anisotropic nature of LC’s results in this phenomenon. When an electromagnetic wave propagates through a medium its wavelength and velocity decrease by a factor called index of refraction. In case of anisotropic materials the permittivity is different in different directions and hence the two components of polarizations have different indices of refraction and different velocities. The anisotropy of nematic LCs causes polarization of light. The component of light polarized along the director propagates with different velocity from the velocity of light polarized perpendicular to the director. These birefringent materials have two indices of refraction $n_{\parallel}$ and $n_{\perp}$ in the parallel and perpendicular direction respectively. The
difference between these indices \( \Delta n = n_e - n_o = n || - n_\perp \) gives optical anisotropy.

For rod-like molecules \( n|| > n_\perp \); \( \Delta n \) is, therefore, positive and can be between 0.02-0.4. If \( \Delta n \) is +ve (Figure14) then the material is said to be positive uniaxial and if \( \Delta n \) is –ve the material is said to be negative uniaxial. The biaxial materials have three indices of refraction [31].

Hence, because of its double refraction or birefringence property, a liquid crystal exhibits the following optical characteristics [32].

1) It redirects the direction of incoming light along the long axis (director) of the liquid crystal.

2) It changes the direction of polarization.

![Figure14](image.png)  
**Figure14** Birefringence with positive optical anisotropy
1.4.7 The Order Parameter

One mesophase differs from another with respect to its symmetry. The transition between different phases corresponds to the breaking up of some symmetry and can be described in terms of the so-called order parameter. It represents the extent to which the configuration of the molecules in the less symmetric (more ordered phase) differs from that in the more symmetric (less ordered phase). In general, an order parameter $S$ may be defined and represented (figure 15) as shown below

(i) $S = 0$, in the more symmetric (less ordered) phase, and
(ii) $S \neq 0$, in the less symmetric (more ordered) phase.

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

**Figure 15** Schematic diagram of ordering of molecules with respect to director ‘n’

where ‘$\theta$’ is the angle between the director and long axis of each molecule. The brackets denote an average over all of the molecules in the sample.
The order parameter, \( S \), varies between 1 and 0, depending upon whether there is perfect order or no order at all. Typical values of \( S \) in nematic phase range from 0.7 to 0.3 for liquid crystal molecules as the temperature of the sample is varied from the freezing point to the isotropic liquid where the value of \( S \) abruptly goes to zero. This is illustrated below for a nematic liquid crystal material shown in figure 16. Values of \( S \) have been determined, however, in a number of compounds with sufficient accuracy to compare with existing theories on mechanisms responsible for molecular order in liquid crystals. It has been found that Mayer-Saupe's theory based on dispersion interactions is generally in good agreement at the low temperature end of the nematic phase. Near the isotropic transition deviations from this theory become pronounced. In order to test the influence of other mechanisms on molecular order such as the electric dipole moment of a molecule or molecular shape, experiments have been performed using solute molecules. The order existing in liquid crystalline phases can also be measured by using the relationship between microscopic and macroscopic properties. However, no simple formalism is appropriate for all the mesophases and the difficulties are further compounded because of complex chemical structure and non-rigidity of the molecules.
Figure 16 Example of order parameter variation as a function of temperature in LCs

The order parameter can be directly related to certain experimentally measurable quantities, for example, diamagnetic anisotropy (susceptibility), dielectric anisotropy, optical anisotropy (birefringence or refractive indices and linear dichroism), etc. A number of techniques have been developed for the determination of order parameter; the most commonly used are optical methods [33-35]. These include local field models of Vuks [36] and Neugebauer [37]; normalisation procedures of Haller [38], Averyanov [39]. Wu [40,41] further developed other models. Kuczynski’s extrapolation technique [42] does not consider a local field and thereby eliminates the determination of density and molecular polarisability. The measurements of these anisotropies can give the value of orientational order parameter. Other important techniques sensitive to local fluctuations are magnetic resonance spectroscopy, neutron scattering, X-ray
scattering, electron paramagnetic resonance, infra-red and Raman spectroscopies, etc.

A number of techniques (e.g. optical microscopy, mettler oven, microscope hot stage, differential thermal analysis, calorimetry, Raman spectroscopy, etc.) are available for the measurement of transition quantities. Most of these quantities may be determined for both pure mesogens and mixtures. The main instruments which may be used for the measurement of phase transition temperatures and the characterization of liquid crystal phases can be done concurrently using a hot-stage under a polarizing microscope. Some researchers [43-45] proposed an image processing and analysis methodology in conjunction with POM to investigate the phase transitions of liquid crystals.

1.4.8 Theory for liquid crystals

a) **Onsager hard-rod model:** Onsager hard-rod model [46,47] predicts lyotropic phase transitions. This theory considers the volume excluded from the center of mass of one idealized cylinder as it approaches another.

b) **Maier-Saupe mean field theory:** Maier-Saupe mean field theory [48-50] proposed by Dr. Alfred Saupe and Dr. Wilhelm Maier, includes contributions from an attractive intermolecular potential from an induced dipole moment between adjacent liquid crystal molecules. This theory considers a mean-field average of the interaction. This theory predicts thermotropic nematic-isotropic phase transitions, consistent with experiment.
c) **Mcmillan’s model:** Third, Mcmillan’s model [51] is an extension of the Maier-Saupe mean field theory used to describe the phase transition of a liquid crystal from a nematic to a smectic A phase. This predicts that the phase transition can be either continuous or discontinuous depending on the strength of the short-range interaction between the molecules. As a result, it allows for triple critical point where the nematic, isotropic, and smectic A phase meet.

### 1.5 History of Liquid Crystals

Friedrich Reinitzer is credited with the discovery of liquid crystals. He prepared cholesteryl benzoate and briefly sketched its properties. However, the properties of liquid crystalline were correctly described by Lehmann, who explained that the liquid crystalline state shows turbidity. On studying cholesteryl benzoate he found that in the liquid crystalline state the material flowed like "oil" and that it changed color with change in temperature. Lehmann was the first to suggest the name liquid crystals for those substances which are liquid in their mobility and crystalline in their optical properties. Research in the 1920's and 1930's resulted in some outstanding observations of properties and structure of liquid crystals. Friedel assigned names to the classes of liquid crystals based on their optical properties. He identified the nematic and smectic classes and first proposed that the cholesteric class was a special kind of nematic structure. Liquid-crystal phases formed by mineral moieties have been known for almost as long as organic liquid crystals. Renewed interest in them has arisen because of the ability to combine the properties of liquid crystals, in particular anisotropy and fluidity, with the electronic and
structural properties of minerals. They may also be cheaper to produce than conventional liquid crystals, which require organic synthesis. Rodlike mineral systems that form nematic phases have been well studied. Sheet-forming mineral compounds that form smectic (layered) structures in solution are also known.

In earlier periods of 1957 to 1965 research is carried out by number of scientists like Maier and Saupe [48] developed a statistical theory of the nematic phase considered outstanding contribution of the field. Maier and Saupe gave convincing evidence that the forces predominantly responsible for parallel orientation in the nematic phase are the dipole-dipole dispersion forces which are highly angularly dependent because of the anisotropy of the optical transition moments of the elongated aromatic molecules. Optical properties, field effects, scattering and other physical properties were being studied. Any realistic theory of liquid crystal structure has to account for the remarkably diverse and subtle changes in physical and optical properties brought about by surfaces and weak external forces. Bose proposed the swarm theory to explain the structure of liquid crystals. This theory was the predominant one for approximately fifty years. Kast and Ornstein [52] expanded the swarm theory which explained many of the optical, electric and magnetic properties of nematic liquid crystals and their structures.

Most mathematical work has been on the Oseen-Frank theory [53], in which the mean orientation of the rod-like molecules is described by a vector field. However, more popular among physicists is the Landau - de Gennes theory
[54], in which the order parameter describing the orientation of molecules is a matrix, the so-called Q-tensor. The first continuum theory for smectic A was proposed by de Gennes [55]. Later Martinet al. [56] established a general framework for developing hydrodynamic theories which in principle is applicable to liquids, liquid crystals, and in particular to smectic A. This theory had a profound influence on the study of hydrodynamics of condensed matter. Zocher [57] introduced the concept of the continuum theory explaining the molecular arrangement in liquid crystals. Leslie continuum theory [58] explains the nematic and the cholesteric (twisted nematic) structures and the role of enantiomorphy. An effect of primary importance in nematic liquid crystals is the alignment produced by a static electric or magnetic field. Dielectric properties were studied extensively. Fields which are far too weak to produce a torque sufficient to align single molecules at the temperature of the liquid crystal phase however are strong enough to affect the weak elastic constants described in the continuum theory. In the case of a magnetic field, the coupling to the director occurs through the anisotropy of the molecular susceptibility associated primarily with the pi electrons of the characteristically aromatic molecules. There have been a large number of investigations related to the effects of electric and magnetic fields on the structure and morphology of liquid crystals. The dielectric dispersion over a range of frequencies has been studied by Maier and Saupe [59] and by Axmann et al. [60-62]. Compounds with negative dielectric anisotropy, such as $p$-azoxyanisole, are aligned parallel to a d.c. or low frequency electric
field but they are aligned perpendicular to a high frequency (300 kHz) electric field.

The early literature contained primarily the optical properties of liquid crystals, their flow properties, theory of their structure, and the discovery of new compounds. Bragg made a valuable contribution to the structures of the various phases. He carefully explained the stratification in their structure. The first data was taken by him on viscosity, surface tension, refractive index, optical rotation and magnetic susceptibility. Aside from the anisotropy and surface orienting effects, the flow of nematic liquids appears not to be much different from that of isotropic liquids. In the similar way, the disc shape molecules discovered by Chandrasekhar et al. [63] and predicted by Peierls and Landau [64, 65] called as discotics, are the field of interest of many groups. The reasons for the interest are on the one hand the potential applications of such systems and on the other hand the very interesting physical properties of these mesophases. Discotic liquid crystals (DLCs) are a more recent and less familiar form than the ubiquitous calamitics. DLCs are formed from triphenylenes or phthalocyanines, which have an aromatic core and a series of alkyl side chains. DLCs can exhibit a nematic phase, with one-dimensional ordering, but also exhibit a columnar hexagonal phase, in which molecules stack, core on core, to form a hexagonal array of molecular columns. In this phase, the electrical conductivity is highly anisotropic, with the axial conductivity being up to 100 times greater than the in-plane conductivity. The absence or presence of
correlations in some directions is very important for a structural classification and for investigation of phase transitions in such crystals.

As the field matured, it became apparent that these materials present supramolecular properties, which lend themselves towards device application, and this in turn has led to an enhanced effort on the synthesis and the investigation of new discotic materials with a view to understand the molecular features that govern mesophase behaviour in disc-like systems. Researchers have paid particular attention to the triphenylene core [66,67].

Recently, triphenylene based discotics have emerged as a new class of fast photoconductive materials. In that work, two novel triphenylene – ammonium – ammonium – triphenylene diads were synthesised. The effect of the peripheral chain length around triphenylene and the length of the linker connecting triphenylene with an ammonium moiety on the liquid crystalline behaviour was studied. The molecular structures were verified using proton and carbon nuclear magnetic resonance, mass spectrometry and elemental analysis. The liquid crystalline properties of these compounds were determined by polarising optical microscopy, differential scanning calorimetry and X-ray diffraction studies. These triphenylene–ammonium-based gemini dimers with tetrafluoroborate as the counter ion were found to exhibit liquid crystalline behaviour with a hexagonal columnar phase morphology [68-72].
1.6 Applications of Liquid Crystals

Liquid crystals have the optical properties of certain liquid crystalline substances in the presence or absence of an electric field. In a typical, a liquid crystal layer sits between two polarizers that are crossed. The liquid crystal alignment is chosen so that its relaxed phase is a twisted one. So, if we would apply to electric field, the device would not appear transparency. If not, the device would appear transparency. In these days, liquid crystals are being used at flat screen television, laptop screens, digital clocks and thermometers etc which are briefly explained.

1.6.1 Display application of liquid crystals

The most common application of liquid crystal technology is liquid crystal displays (LCDs.) [73-76]. This field has grown into a multi-billion dollar industry, and many significant scientific and engineering discoveries have been made. Liquid crystal display devices consisting of digital readouts are used in watches, calculators, and several other instruments like mobile and many household electric appliances [77]. Some liquid crystal substances could be useful in computer industry, for making new computer elements with high memory capacity. LCDs had a humble beginning with wrist watches in the seventies. Continued research and development in this multidisciplinary field have resulted in display with increased size and complexity. After three decades of growth in performance, LCDs now offer a formidable challenge to cathode ray tubes (CRT). There are many types of liquid crystal displays, each with unique properties. The
most common LCD that is used for everyday items like watches and calculators is called the twisted nematic (TN) display. This device consists of a nematic liquid crystal sandwiched between two plates of glass. A special surface treatment is given to the glass so that the director at the top of the sample is perpendicular to the director at the bottom. This configuration sets up a 90 degree twist into the bulk of the liquid crystal, hence the name of the display. The underlying principle in a TN display (figure17) is the manipulation of polarized light.

**Figure17** Principle of twisted nematic LCDs

### 1.6.2 Thermal mapping and non-destructive testing

Chiral nematic (cholesteric) liquid crystals reflect light with a wavelength equal to the pitch. Because the pitch is dependent upon temperature, the color reflected also is dependent upon temperature. Liquid crystals make it possible to accurately gauge temperature just by looking at the color of the thermometer. By mixing different compounds, a device for practically any
temperature range can be built. More important and practical applications have been developed in such diverse areas as medicine and electronics. Special liquid crystal devices can be attached to the skin to show a "map" of temperatures. This is useful in physical problems, such as tumors which have a different temperature from the surrounding tissues. Liquid crystal temperature sensors can also be used to find bad connections on a circuit board by detecting the characteristic higher temperature. The sensitivity of cholesteric liquid crystals to react to pressure as well as temperature by colour change is used to make some very interesting publicity materials and toys. Cholesteric liquid crystals can be used as an analytical tool to detect the presence of very small amounts of gases or vapours by colour changes to the extent of about 1ppm [78].

1.6.3 Medical Uses

Cholesteric liquid crystal mixtures have also been suggested for measuring body skin temperature, to outline tumors etc. Any inflammation or constriction of the vessels will naturally affect the temperature of the skin. This will help in the location of inflammation, since the warmer areas will outline by the color pattern. In gynecology, where there is a necessity of cesarian section, liquid crystals can be used to locate the plecenta, thus avoiding the need for X-ray. They are also useful in controlled drug delivery [79]. Recently their biomedical applications such as protein binding, phospholipids labeling and inmicrobe detection [80] have been demonstrated. In psychology, cholesteric liquid crystals could be used in lie detectors [81].
1.6.4 Optical Imaging and Liquid Crystal Interactions with Nanostructure

An application of liquid crystals that is only now being explored is optical imaging and recording. This technology is still on growth and is one of the most promising areas of liquid crystal research. The use of the mesomorphic state for the organization of nanoparticles opens up the utilization of techniques employed for fabrication of large panel displays. Alternatively, higher ordered LC phases are used for the controlled bottom-up self organisation in two or three-dimensional lattices, depending on the type of mesophase. This might be particularly valuable in applications associated with the optical, magnetic or conducting properties of nanoparticles [82-84].

1.6.5 Other Liquid Crystal Applications

Liquid crystals have a multitude of other uses. They are used for nondestructive mechanical testing of materials under stress. This technique is also used for the visualization of RF (radio frequency) waves in waveguides. They are used in medical applications, for example, transient pressure transmitted by a walking foot on the ground is measured. Low molar mass (LMM) liquid crystals have applications including erasable optical disks, full color" electronic slides" for computer- aided drawing, and light modulators for color electronic imaging. They are also used in Chromatography, as Solvents in Spectroscopy [85] and Guest-Host type Display etc.
CHAPTER-1

PART – B

Introduction to Image Analysis
1.7 Introduction to Image Analysis

Image analysis or image processing is another field of research that is used in this work in combination with liquid crystals in order to extract properties of LC’s from their textures. To study any property regarding a texture or image, pixel values with different intensities are to be extracted from the image. From 1950 till now image analysis has it importance in many research fields and applications mainly like interpretation of medical images which is usually the preserve of radiology and medical science (neuroscience, cardiology, psychiatry, psychology, etc). Image processing could be used for astronomy, music, agriculture, travel etc and has become a vital part of the modern movie production process. Digital image processing has become a vast domain of modern signal technologies. Digital image processing requires the most careful optimizations and especially for real time applications. It involves changing the nature of an image in order to either improve its pictorial information for human interpretation or for recognizing the object and renders it more suitable for autonomous machine perception. Most image processing techniques involve treating the image as a two dimensional (Figure18) signal and applying standard signal processing technique to it.

Some important features that are important in image analysis are summarized as follows:

- Image is matrix of intensity pixels. A digital image can be considered as a large array of sampled points from the continuous image, each of which has a particular quantized brightness.
Figure 18 2-dimensional distribution of image Points (Pixels)

- These points are called picture elements, or simply pixels. The pixels surrounding a given pixel constitute its neighborhood. A neighborhood can be characterized by its shape in the same way as a matrix.
- Each of the pixels in a region is similar with respect to some characteristic or computed property, such as color, intensity, or texture. Adjacent regions are significantly different with respect to the same characteristics [86].
- The intensity of each pixel is variable. In color image systems, a color is typically represented by three component intensities such as red, green, and blue i.e. having 3 values per pixel. A monochrome image (Figure 19) system has 1 value per pixel, represented by gray in color.
Figure 19 Examples of color and monochrome image systems

- The more pixels used to represent an image, the closer the result can resemble the original. Spatial resolution is the density of pixels over the image. The greater the spatial resolution, the more pixels are used to display the image.

- Each image pixel has its own gray level (dynamic range). The number of distinct colors that can be represented by a pixel depends on the number of bits per pixel (bpp) as shown below.
  
  a) 1 bpp, $2^1 = 2$ colors (monochrome)
  
  b) 2 bpp, $2^2 = 4$ colors
  
  c) 3 bpp, $2^3 = 8$ colors
The image signal is coded in a two dimensional spatial domain. In image processing, feature extraction is a special form of dimensionality reduction. Transforming the input data into the set of features is called feature extraction. Features often contain information relative to gray shade, texture, shape, or context.

1.8 Types of Digital Images:

The various types of digital images are as follows

1. Binary-scale image

2. Gray-scale image or Intensity Image

3. Color image or RGB Image

4. Indexed Color image

1.8.1 Binary-scale image

In this type of image each pixel is just black or white. Since there are only two possible values for each pixel (0,1), one bit per pixel is needed. Most monochrome image processing operations are carried out using binary or gray-scale images. Such images can therefore be very efficient in terms of storage. Images for which a binary representation may be suitable include (printed or handwriting) text. Binary images often arise in digital image processing as masks or as a result of certain operations such as segmentation, thresholding, and dithering.
1.8.2 Gray-scale image or Intensity Images

These images contain the brightness information. A gray-scale image is a data matrix whose values represent shades of gray. When the elements of a gray-scale image are of class uint8 or uint16, they have integer values in the range (0, 255) or (0, 65535), respectively. Values of double and single gray-scale images normally are scaled in the range (0, 1), although other ranges can be used. Grayscale images can be transformed into a sequence of binary images by breaking them up into their bit-planes. Mostly the gray value of each pixel of an 8-bit image is considered. The range of 0-255 was agreed for two good reasons: The first is that the human eye is not sensible enough to make the difference between more than 256 levels of intensity (1/256 = 0.39%) for a color. The
second reason for the value of 255 is obviously that it is convenient for computer storage.

![Figure 21 Example of gray scale image](image)

Figure 21 Example of gray scale image

To obtain the image of a color by a grayscale transform, it must be applied to the red, green and blue components separately and then reconstitute the final color. The graph of grayscale transform is called an output look-up table, or gamma-curve (figure 22). The shades of grays have equal components in red, green and blue, thus their decomposition must be between 0 and 255 (example (0,0,0) black, (32,32,32) dark gray, (128,128,128) intermediate gray, (192,192,192) bright gray, (255,255,255) white etc…). The effects of increasing contrast and lightness to the gamma-curve of the corresponding grayscale transform are shown in figure 22.
1.8.3 Color image or RGB Image

Normally, images are represented as RGB (Red, Green, Blue) modes, and each pixel has 24 bits. The brightness information and color information are coupled and represented in many applications. The color image can be converted
into binary or gray color image in order to reduce the time consumption and difficulty in image analysis. The decomposition of a color in the three primary colors is quantified by a number between 0 and 255. For example, white will be coded as \((R,G,B) = (255, 255,255)\); black will be known as \((R,G,B) = (0,0,0)\); and bright pink will be \((R,G,B) = (255,0,255)\). In other words, an image is an enormous two-dimensional array of color values, pixels, each of them coded on 3 bytes, representing the three primary colors. This allows the image to contain a total of 256x256x256 = 16.8 million different colors. This technique is also known as RGB encoding, and is specifically adapted to human vision.

![Figure 23 Example of color scale image](image-url)
1.8.4 Indexed Color image

Most color images have only a small subset of the more than sixteen million possible colors. For convenience of storage and file handling, the image has an associated color map which is simply a list of all the colors used in that image. Each pixel has a value which does not give its color (as for an RGB image), but an index to the color in the map. It is convenient if an image has 256 colors or less, for then the index values will only require one byte each to store.

![Example of indexed color image](image)

**Figure24** Example of indexed color image
Extraction of features from the different kinds of images is useful to interpret the images. Various techniques have been developed to extract features from images.

1.9 FEATURE EXTRACTION TYPES

Various techniques have been used to extract features from images. Some of the commonly used methods are discussed below.

1. Spatial features
2. Transform features
3. Edges & boundaries
4. Shape features
5. Moments
6. Texture

1.9.1 Spatial Features

Spatial features of an object may be characterized by its gray levels, their amplitude features, histogram features, spatial distribution etc. For example, in x-ray images, the gray level amplitude represents the absorption characteristics of the body masses and enables discrimination of bones from tissue or healthy tissue from diseased tissue. Some of the common histogram features are dispersion, mean, variance, mean square value or average energy, skewness, kurtosis. Other useful features are median and mode. A narrow histogram indicates a low contrast region.
1.9.2 Transform Features

Image transforms provide the frequency domain information in the data. Transform features are extracted by zonal filtering of the image in the selected transform space. The zonal filter, also called the feature mask, is simply a slit or an aperture. Generally the high frequency components can be used for boundary and edge detection, and angular slits can be used for detection of orientation.

1.9.3 Edge Detection

Edges characterize the object boundaries and are useful for segmentation, registration and identification of objects in scenes. The goal of edge detection is to mark the points in a digital image at which the luminous intensity changes sharply. Sharp changes in image properties usually reflect important events and changes in properties of the world. These include (i) discontinuities in depth, (ii) discontinuities in surface orientation, (iii) changes in material properties and (iv) variations in scene illumination.

1.9.4 Boundary Extraction

Boundaries are linked edges that characterize the shape of an object. They are useful in computation of geometrical features such as size or orientation. Different methods used are:
a) Connectivity

Boundaries can be found by tracing the connected edges. On a rectangular grid, a pixel is said to be four or eight-connected when it has the same properties as one of its nearest four or eight neighbors.

b) Contour Following

Contour following algorithms trace boundaries by ordering successive edge points. This algorithm can trace an open or closed boundary as a closed contour.

c) Edge Linking

A boundary can also be viewed as a path through a graph formed by linking the edge elements together. Linkage rules give the procedure for connecting the edge elements. Such features are useful because they frequently correspond to an object or material boundaries, which are of interest. e.g., object recognition systems.

1.9.5 Shape Extraction

The shape of an object refers to its physical structure and profile. Example: Moments, perimeter, area, orientation etc. These characteristics can be represented by the previously discussed boundary, region, moment, and structural representations. These representations can be used for matching shapes, recognizing objects or for making measurement of shapes.
1.9.6 Texture Extraction

Texture analysis is defined as the classification or segmentation of textural features with respect to the shape of a small element, density, and direction of regularity. Texture is a property that represents the surface and structure of an Image. Generally speaking, texture can be defined as a regular repetition of an element or pattern on a surface. Image textures are complex visual patterns composed of entities or regions with sub-patterns with the characteristics of brightness, color, shape, size, etc. An image region has a constant texture if a set of its characteristics are constant, slowly changing or approximately periodic. Texture can be regarded as a similarity grouping in an image [87,88]. Several definitions of textures have been formulated by various researchers [89,90].

1.10 Approaches to Texture Analysis

As texture has so many different dimensions, there is no single method of texture representation that is adequate for a variety of textures. Texture analysis refers to a class of mathematical procedures and models that characterize the spatial variations within imagery as a means of extracting information. Therefore texture analysis is usually defined as the classification or segmentation of textural features with respect to the shape of a small element, density, and direction of regularity. Most texture analysis operators provide a measure of the image texture for each pixel, or for small areas in an image. Texture analysis by mathematical procedures falls into some major categories.
1.10.1 Structural approach

The structural approach, introduces the concept of texture primitives, often called texels or textons. To describe a texture, a vocabulary of texels and a description of their relationships are needed. The goal is to describe complex structures with simpler primitives, for example via graphs. Structural texture models work well with macrotextures with clear constructions. Through the pioneering work of [91,92], primitive-based models have been widely used in explaining human perception of textures. Application of structural techniques to textural analysis is a difficult undertaking unless the textures under analysis are also uniform and structured. For this reason, structural techniques have limited applications for analysis of textures.

1.10.2 Statistical or Stochastic approach

Statistical approaches compute different properties and are suitable if texture primitive sizes are comparable with the pixel sizes. These include Fourier transforms, convolution filters, co-occurrence matrix, spatial autocorrelation, fractals, etc. Statistical methods represent the texture indirectly according to the non-deterministic properties that manage the distributions and relationships between the gray levels of an image. This technique is one of the first methods in machine vision [89]. By computing local features at each point in the image, and deriving a set of statistics from the distributions of the local features, statistical methods can be used to analyze the spatial distribution of gray values. Based on
the number of pixels defining the local feature, statistical methods using various algorithms can be classified into first-order (one pixel), second-order (two pixels) and higher-order (three or more pixels) statistics. The difference between these classes is that the first-order statistics (Histogram of intensities) estimate properties (e.g. Mean, variance, Skewness, Kurtosis, Energy and Entropy ) of individual pixel values by waiving the spatial interaction between image pixels, but in the second-order and higher-order statistics estimate properties of two or more pixel values occurring at specific locations relative to each other. The most popular second-order statistical features for texture analysis are derived from the co-occurrence matrix [93].

1.10.3 Moments

Research on the utilization of moments for object characterization in both invariant and noninvariant tasks has received considerable attention in recent years. Image moments and their functions have been utilized as features in many image processing applications, viz., pattern recognition, image classification, target identification, and shape analysis. Moments of an image are treated as region-based shape descriptors. The principal techniques explored include moments invariant, Geometry moments, rotational moments, orthogonal moments and complex moments. The mathematical concept of moments has been used for many years in many diverse fields ranging from mechanics and statistics to pattern recognition and image understanding. Describing image with moments instead of other more commonly used image features means that global properties of the image are used rather than local properties. Hu [94,95] published the first
significant paper on the utilization of moment invariants for image analysis and object representation. Various moments have their uses and disadvantages like using geometric moments a set of invariable moments which has the desirable properties of being invariant under image translation, scaling and rotations are derived. But the reconstruction of image from these geometric moments is deemed to be quite difficult. In general orthogonal moments are better than other types of moments in terms of information redundancy and image representation.

1.10.4 Orthogonal moments

Teague [96] suggested the notion of orthogonal moments to recover the image from moments based on the theory of orthogonal polynomials. He introduced the rotationally invariant Zernike moment, which employs the complex Zernike polynomials as moment basic set and also by using Legendre polynomials as basic sets. Many variations have been done by various researchers [97,98] both on Zernike and Legendre moments.

The $n^{th}$ order Legendre polynomial is defined by

$$P_n(x) = \sum_{j=0}^{n} a_{n,j} x^j = \frac{1}{2^n n!} \frac{d^n}{dx^n} (x^2 - 1)^n.$$

The Legendre polynomial has the generating function

$$\frac{1}{\sqrt{1 - 2rx + r^2}} = \sum_{s=0}^{\infty} r^s P_s(x), \quad r < 1.$$ 

From the generating function the recurrent formula of the Legendre polynomials can be acquired as
Then we have the recurrent formula of the Legendre polynomials as

\[
\frac{d}{dr} \left( \frac{1}{\sqrt{1-2rx+r^2}} \right) = \frac{d}{dr} \left( \sum_{s=0}^{\infty} r^s P_s(x) \right)
\]

\[
\frac{x-r}{(1-2rx+r^2)^{3/2}} = \sum_{s=0}^{\infty} s r^{s-1} P_s(x)
\]

\[
(x-r) \sum_{s=0}^{\infty} r^s P_s(x) = (1-2rx+r^2) \sum_{s=0}^{\infty} s r^{s-1} P_s(x).
\]

Then we have the recurrent formula of the Legendre polynomials as

\[
P_{n+1}(x) = \frac{2n+1}{n+1} x P_n(x) - \frac{n}{n+1} P_{n-1}(x).
\]

The legendre polynomials \( P_m(x) \) [99] are a complete orthogonal basis set on the interval \([-1,1]\).

\[
\int_{-1}^{+1} P_m(x) P_n(x) dx = \frac{2}{2m+1} \delta_{mn},
\]

\( \delta_{mn} \) is the Kronecker symbol

Legendre orthogonal moments have been widely used in the field of image analysis. An efficient method for computing 3D Legendre moments is developed. Various algorithms are proposed which improve the computational efficiency significantly and can be implemented easily for higher order of moments [100]. Content Based Image Retrieval (CBIR) system using Exact Legendre Moments (ELM) for gray scale images is proposed. CBIR is orthogonal, computationally faster, and can represent image shape features compactly. Superiority of the proposed CBIR system is observed over other moment based methods, viz., moments invariant and Zernike moment in terms of retrieval efficiency and retrieval time. Further, the classification efficiency is improved by employing Support Vector Machine (SVM) classifier [101].
The speed of computing image moments is extraordinarily important when higher order moments are involved. The Legendre moments depend only on the geometric moments of the same order and lower. However, computation of moments specifically at higher order moments is involved is a time-consuming procedure. Because their computation by a direct method is very time expensive, recent efforts have been devoted to the reduction of computational complexity [102]. To speed up the computation the most important method is to avoid using the recurrent formula of the Legendre polynomials. A recurrence formula is used to compute the Legendre moments of the liquid crystal textures based on the Legendre polynomial. The abrupt change in the values of Legendre moments as a function of temperature gives the phase transitions of liquid crystals [103]. Some of the standard techniques for texture description are [104], for instance, based on the analysis of light intensity difference [105] reported as a function of the distance from an arbitrary point of the image frame. Other methods are based on so-called ‘run length statistics’ [106,107] characterized by moving in chosen direction from an image arbitrary point, looking for the number of pixels with the same intensity as the starting point.

Various approaches for describing texture have to use statistical moments of the intensity histogram of an image or region. Using only histograms in calculation will result in measures of texture that carry only information about distribution of intensities, but not about the relative position of pixels with respect to each other in that texture. Using a statistical approach such as co-occurrence
matrix will help to provide valuable information about the relative position of the
neighbouring pixels in an image.

1.10.5 Gray-level Co-occurrences Matrix

The Gray Level Co-occurrence Matrix (GLCM) is a widely used
texture analysis method which estimates image properties related to second-order
statistics. It enhances the details of the image and gives the interpretation. The
GLCM is a tabulation which represents how often the different combinations of
pixel brightness values (gray levels) occur in an image. The GLCM indicates the
frequency occurrence of pixel pairs. From this principle, it used to compute the
relationships of pixel intensity to the intensity of its neighbouring pixels. They are
used on the hypothesis that the same gray level configuration is repeated in a
texture [108-110]. Since the co-occurrence matrix collects information about pixel
pairs instead of single pixels, it is called a second-order statistical method. The
actual features are derived from an averaged co-occurrence matrix, or by
averaging the features calculated from different matrices.

The GLCM, is defined with respect to the given row and column. A
GLCM element \( GLCM_{(i, j)} \) represents the number of times a point having gray
level \( j \) occurs relative to a point having gray level \( i \) as shown in figure 25. This is
explained with an example is shown as.
In above example, each element of Gray level co occurrence matrix represents the probability of occurrence of pixel pair. In the above example, the pixel pair (1,1) occurs one time and hence the element of the GLCM (1,1) is 1. Next, the pixel pair (1, 2) occurs two times, giving the element of the GLCM (1, 2) is 2. Similar procedure is repeated for all pixel pairs to construct the GLCM of the image. Each element of GLCM represents the probability of occurrence of pixel pairs. In order to estimate the similarity between different gray level co-occurrence matrices, some statistical features are extracted from them. The statistical features are energy, entropy, correlation and homogeneity which are defined and described in chapter 2 part B.
Gray level co-occurrence matrix (GLCM) has been proven to be a very powerful tool for texture image segmentation. The only shortcoming of the GLCM is its computational cost. Such restriction causes impractical implementation for pixel-by-pixel image processing. Various methods were proposed to reduce the GLCM computational burden at the computation architecture level and hardware level [111-113]. Valkealahti and Oja (1998) [114] have presented a method in which multi-dimensional co-occurrence distributions are utilized. In their approach, the gray levels of a local neighborhood are collected into a high-dimensional distribution, whose dimensionality is reduced with vector quantization. For example, if the eight-neighbors are used, a nine-dimensional (eight neighbors and the pixel itself) distribution of gray values is created instead of eight two-dimensional co-occurrence matrices. An enhanced version of this method was later utilized by Ojala et. al. [115] with signed gray-level differences.

It is apparent that LBP can be regarded as a specialization of the multi-dimensional signed gray-level difference method. The reduction of dimensionality is directly achieved by considering only the signs of the differences, which makes the use of vector quantization unnecessary. A comprehensive comparison of the original LBP, GLCM and many other methods has been carried out by Ojala et. al. [116].
1.10.6 Local Binary Operator (LBP)

The Local Binary Pattern (LBP) operator is defined as a gray-scale invariant texture measure, derived from a general definition of texture in a local neighbourhood. The LBP operator can be seen as a unifying approach to the traditionally divergent statistical and structural models of textural analysis. Perhaps the most important property of the LBP operator in real-world applications is its invariance against monotonic gray level change. Another equally important thing is its computational simplicity, which makes it possible to analyze the images in challenging real-time settings [117-119]. The LBP operator was originally designed for texture description. This concept was developed by Ojala et al attempting to decompose the texture into small units where the texture features are defined by the distribution of the calculated LBP values for each pixel in the image. The LBP texture unit is calculated in a 3 X 3 square neighborhood by applying a simple threshold operation with respect to the central pixels.

\[ T = \{t(g_0 - g_c), \ldots, t(g_{P-1} - g_c)\}, \quad t(x) = \begin{cases} 1 & x \geq 0 \\ 0 & x < 0 \end{cases} \]

Where \( T \) is the texture unit, \( g_c \) is the grey level value of the central pixel, \( g_o \) are the grey values of the pixels adjacent to the central pixel in the 3 X 3 neighbourhood, \( P \) defines the number of pixels in the 3 X 3 neighbourhood and function \( t(x) \) defines the threshold operation. For a 3 X 3 neighbourhood the value of \( P \) is 8. To encompass the spatial arrangement of the pixels in the 3 X 3 neighbourhood, the LBP value for the tested (central) pixel is calculated using the following relationship.
The LBP values calculated are in the range (0, 255). It concerns the spatial relationship between patterns while ignoring the magnitude of grey level differences and also invariant against grey scale shifts. Hence, the texture features are invariant when all of the pixels in the neighborhood show plus or minus values at the same time so that sign of differences can be ignored [120].

The first incarnation of the operator worked with the eight-neighbors of a pixel, using the value of the center pixel as a threshold. An LBP code for a neighborhood was produced by multiplying the thresholded values with weights given to the corresponding pixels and summing up the result (Figure26).

\[
LBP = \sum_{i=0}^{P-1} t(g_i - g_c) * 2^i
\]

where \( t(g_i - g_c) \) is the value of the thresholding operation illustrated using \( T \) value.

Figure26 Calculating the LBP code and contrast measure
1.11 History of Image Analysis

In 1973, Haralick et al proposed a general procedure for extracting textural properties of blocks of image data. These features were calculated in the spatial domain, and the statistical nature of texture was taken into account in the procedure, which was based on the assumption that the texture information in an image “I” was contained in the overall or "average" spatial relationship which the gray tones in the image had to one another. They computed a set of gray tone spatial-dependence probability-distribution matrices for a given image block and suggested a set of 14 textural features, which could be extracted from each of these matrices. These features contain information about such image textural characteristics as homogeneity, gray-tone linear dependencies (linear structure), contrast, number and nature of boundaries present, and the complexity of the image. The number of operations required for computing any one of these features was proportional to the number of resolution cells in the image block. It was for this reason that these features were called quickly computable [121]. In 1988, John S. DaPonte et al proposed a method for choosing the direction of the displacement vector that was based on the most dominant edge obtained from gradient analysis [122]. In 1992, Chung-Ming W. et al studied the classification of ultrasonic liver images by making use of some powerful texture features, including the spatial gray-level dependence matrices, the Fourier power spectrum, the gray-level difference statistics, and the Laws’ texture energy measures [123]. In 1995, Mir A.H. et al in did some work in the use of texture for the extraction of diagnostic information from CT scan images. They obtained a number of features
from abdominal ct scans of liver using the spatial domain texture analysis methods. The result was that the texture features were helpful in diagnosing the onset of disease in liver tissue, which cannot be done by visible eye. Three texture features namely - entropy, homogeneity, and gray level distribution were found to be effective [124]. In 2001, Sharma M. et al used five different texture feature extraction methods that were most popularly used in image understanding studies. Their results show that there was considerable performance variability between the various texture methods. Their finding, that co-occurrence matrices and Law’s method perform better than other techniques, was supported by previous comparative studies in this area. The best overall result was obtained by using nearest neighbor methods with co-occurrence matrices, whereas the best result was obtained in linear analysis using combined set of features [125]. Moment functions of image intensity values have been successfully used in object recognition [126,127], image analysis [128,129], object representation [130], edge detection [131], and texture analysis [132]. Legendre moment for image reconstruction and feature representation, accuracy and efficiency in 2D and 3D Legendre moment are studied [102].

In 2002, Clausi David A. et al studied the effect of grey level quantization on the ability of co-occurrence probability statistics to classify natural textures. None of the individual statistics showed increasing classification accuracy throughout all grey levels. Correlation analysis was used to rationalize a preferred subset of statistics. The preferred statistics set (contrast, correlation, and entropy) was demonstrated to be an improvement over using single statistics or
using the entire set of statistics [133]. In 2007, Mark Sheppard and Liwen Shih studied to double the accuracy of ultrasound diagnosis and biopsy guidance, which was an efficient, integrated platform for image textural analysis and also for clustering of transrectal prostate ultrasound images that potentially represents cancerous or normal tissue areas. An efficient Image Texture Analysis tool platform on Window PC was constructed via innovative sparse co-occurrence matrix techniques with linked lists to speedup the processing from 8 days to about 5 seconds per image on a PC [134]. In 2006, A. Sparavigna et al and J. Eccher et al used the statistical parameters of the first, second kind to identify the phase transitions temperatures of liquid crystals [135,136]. Sparavigna et al considered in their study the position and dispersion indices, i.e. the mean intensity of the transmitted light (averaged over the whole window, which can be the entire beam cross section, or a certain part of it) and the $k^{th}$ order moments of the light intensity distribution (with $k=1$, $n$ with $n$ defined a priori). These parameters are extremely sensitive to changes in the textures of liquid crystals and thus can be very useful for the investigation of structural changes due to both order and phase transitions in the materials. In fact, the application of the moments method to the optical investigations of (i) phase transitions (in the case of similar textures in both phases) and (ii) order transitions (within the same phase) represents a significant improvement in the detection sensitivity. The major limitation of any moments description is that it cannot follow the local spatial character of the image frame, since this particular information is drowned in the average sea. In 2012, S. Sreehari Sastry et al studied the phase transition temperatures of liquid
crystals using image moments (Legendre moments) and through statistical image analysis using MATLAB software, the statistical parameters, such as mean, standard deviation, root mean square, contrast and entropy of the textures are computed as a function of temperature [105,137].

1.12 Applications of image analysis

Image processing has an enormous range of applications; almost every area of science and technology can make use of image processing methods. Here is a short list just to give some indication of the range of image processing applications.

A. Medicine
- Inspection and interpretation of images obtained from X-rays, MRI or CAT scans
- Analysis of cell images, of chromosome karyotypes.

B. Agriculture
- Satellite/aerial views of land, for example to determine how much land is being used for different purposes, or to investigate the suitability of different regions for different crops
- Inspection of fruit and vegetables—distinguishing good and fresh produce from old.

C. Industry
- Automatic inspection of items on a production line,
- Inspection of paper samples.
D. Law enforcement

- Fingerprint analysis
- Sharpening or de-blurring of speed-camera images.

E. LCD’s

- The vast majority of color digital cameras use a Bayer filter, resulting in a regular grid of pixels where the color of each pixel depends on its position on the grid. In October 2011, Toshiba announced $2560 \times 1600$ pixels on a 6.1-inch LCD panel, suitable for use in a tablet computer, "Toshiba announces 6.1 inch LCD panel with an insane resolution of 2560 x 1600 pixels". October 24, 2011, especially for Chinese character display.

- Vertical alignment displays are a form of LCDs in which the liquid crystals naturally align vertically to the glass substrates. When no voltage is applied, the liquid crystals remain perpendicular to the substrate creating a black display between crossed polarizers. When voltage is applied, the liquid crystals shift to a tilted position allowing light to pass through and create a gray-scale display depending on the amount of tilt generated by the electric field.

- In 1992, engineers at Hitachi work out various practical details of the IPS technology to interconnect the thin-film transistor array as a matrix and to avoid undesirable stray fields in between pixels [138].
1.13 A Computational Tool: MATLAB

Computation is fast becoming the third pillar of modern science and engineering. Selecting a particular computational environment sets up a number of logistical challenges. Some environments are specialized for particular task (e.g., numerical integration and algebraic manipulation), requiring a secondary environment to perform other tasks (e.g., data acquisition, analysis and modeling). The tools which are used for computation must be easy to use, well-documented, flexible, and powerful for professional environment. Various computational tools appeared due to presence of different environmental purposes like numerical computation for science and engineering, graphical plotting, computer algebra, specialized curve fitting, 2D/3D visualization etc. Some of the computational tools are DSP development, Euler math toolbox, free math, Guass, j software, labview, maple software, math cad, mathematica, matlab, origin, simplex numerica etc. In this purpose of study the “Matlab” tool is chosen for the statistical programming as it is a versatile piece of software. It can perform symbolic manipulation, numerical integration, solve PDEs, acquire and process images and interface with data acquisition tools.

The power of MATLAB brings to digital image processing an extensive set of functions for processing multidimensional arrays of which images (two-dimensional numerical arrays) are a special case. The Image Processing Toolbox is a collection of functions that extend the capability of the MATLAB numeric computing environment. These functions, and the expressiveness of the MATLAB language, make image-processing operations
easy to write in a compact, clear manner, thus providing an ideal software prototyping environment for the solution of image processing problems.

Some important points on MATLAB are as follows:

- Matlab means, MAT – **matrix** LAB – **laboratory**.
- Images are just matrices (arrays) where the elements mean something (visually).
- Each pixel in an image has an intensity value. Arrays are of size MxN.
- A digital image can be represented as a MATLAB matrix:

$$f = \begin{bmatrix}
  f(1,1) & f(1,2) & \cdots & f(1,N) \\
  f(2,1) & f(2,2) & \cdots & f(2,N) \\
  \vdots & \vdots & \ddots & \vdots \\
  f(M,1) & f(M,2) & \cdots & f(M,N)
\end{bmatrix}$$

- All the operators in MATLAB defined on matrices can be used on images: +, -, *, /, ^, sqrt, sin, cos etc. Images in MATLAB are given for Binary images: \{0,1\}, Intensity images : \{0,1\} or uint8, double etc, RGB images : m-by-n-by-3, Indexed images : m-by-3 color map and multidimensional images m-by-n-by-p (p is the number of layers).
- MATLAB functions are useful for extending the MATLAB language for the applications. They can accept input arguments and return output arguments and also store variables in a workspace internal to the function.
Using MATLAB software, the statistical parameters, such as mean, standard deviation, root mean square, contrast and entropy of the textures as a function of temperature, are computed. These results show abrupt changes as a function of temperature, indicating the phase transition of the sample [137]. The processing of an image by using MATLAB tool is easy and important in extracting image features through matrix coding.

The potential scientific importance in fundamental research and the growing number of applications of liquid crystals, this motivated the author to carryout studies on liquid crystals. The parameters like refractive index, effective geometry parameter, birefringence, order parameter and other physical parameters are different in different liquid crystal phases. The orientational order is always significant factor which cannot be neglected as it is important to many industrial and medical applications for which they are used as LCD’s. Important categories in statistical methods for image characterization are Gray Level Co-occurrence matrix and Local Binary operator. Liquid crystals having one and two phases are selected and their nature of physical properties is studied by important techniques. The process of choosing good techniques and better liquid crystal compounds are discussed in chapter 2.