Liquid Crystals: a Dielectric and Electro-optical Study

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Thanks For your Love and support

Dedicated to my beloved parents for their eternal support
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Acknowledgement

"Take up one idea. Make that one idea your life - think of it, dream of it, live on that idea. Let the brain, muscles, nerves, every part of your body, be full of that idea, and just leave every other idea alone. This is the Way to Success.

- Swami Vivekananda

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“To be able under all circumstances to practice five things constitutes perfect virtue; these five things are gravity, generosity of soul, sincerity, earnestness and kindness.”

(Sudhaker Dixit)
This is to certify that Mr. Sudhaker Dixit has carried out this work under my supervision. The contents of this thesis are original and have not been presented elsewhere for award of Ph.D. degree.

(Dr. Rajiv Manohar)
Associate Professor
Supervisor
CERTIFICATE

This is to certify that all regulations necessary for the submission of Ph.D. thesis of Mr. Sudhaker Dixit have been fully observed.

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List of Publication

Published and Accepted Papers


**Communicated Papers**

1. **Sudhaker Dixit**, Rajiv Manohar and A.K. Arora, “Gamma induced modifications on two newly synthesized liquid crystals”, *communicated in Radiation Measurements*.


4. Kamal Kumar Pandey, Abhishek Kumar Misra, **Sudhaker Dixit**, Satya Prakash Yadav and Rajiv Manohar, “Nano doped weakly polar versus highly polar liquid crystal”, *Communicated in Applied Nano Science*
Conference Papers

More than thirty conference papers have been selected and presented in several national and international conferences:

Few Selected Presentations:


Abstract

Liquid crystals were accidentally discovered by Austrian botanist Friedrich Reinitzer in 19th century. Study of this phase spread to all the continents, although very slowly in the beginning and then there was an explosive growth during 1970’s and 1980’s. Theories for the liquid crystal phases added a new dimension of study and the invention of liquid crystal displays gave the field, a practical dimension. Scientific studies of liquid crystals involve both the chemistry and physics of this state, being concerned with liquid crystal synthesis and investigation of structure-property relationships.

Liquid-crystal physics, although a field in itself, is often included in the larger area called ‘soft condensed matter’, which includes polymers, colloids and surfactant solutions, all of which are highly deformable materials. This property leads to many unique and exciting phenomena not seen in the ordinary condensed phases, having possibilities of novel technological applications.

The subject of liquid crystal is multidisciplinary and has for years impinged upon chemistry, physics, biology and mathematics and more recently, as consequence of the applications of liquid crystals upon applied chemistry, applied physics, electrical and electronic engineering and
engineering itself. Success in these areas has however arisen only through the collaborations among different disciplines of science. The reason liquid crystal research is an important and active field of science has changed over the last twelve years. New substances showed new properties, and the new theoretical ideas necessary to understand these properties has implications beyond the area of liquid crystals. In addition, the market for lightweight and low power computer displays was growing exponentially, fueling a boom in the application of liquid crystals to displays. In the 1990s, the rate at which discoveries concerning liquid crystals Nematic liquid crystals are the most simplest and the fascinating phase of liquid crystals. Their properties make them applicable for displays. Even though Ferroelectric liquid crystals have fast response and memory effect yet they are not being used in displays because of low contrast and small vision angle.

Liquid crystals have many wide and varied applications apart from high profile uses in displays. In such a short amount of time between its discovery and application in industrial field they become very popular because liquid crystals have technological importance. This is due to the fact that liquid crystal offers a unique and delicate collection of phase of matter that are precariously balanced between the organized solid state
and the amorphous liquid, and which can be accessed by the all type of material and not just organic compounds.

In 1907 Vorlander proposed his rule that “the liquid crystalline state is obtained for the most linear of the molecules”, but in the last few years, details of their molecular structure and micro -segregation have attracted much attention for producing novel, self- organizing systems. These types of molecular topology and their ability to form mesophases are fundamental topics in the investigation of molecular assembly, as these new molecular architectures can be important in critical applications as they widen the temperature range of functionality.

In the present thesis, along with gamma ray modification technique on nematic liquid crystals, newly synthesized H- Shaped dimeric liquid crystal has been analyzed. For H- Shaped dimeric liquid crystal, influences on the molecular orientation have been studied with the help of dielectric spectroscopy. The dielectric parameter have been analyzed thoroughly and there practical applications have also been mentioned. The gamma irradiation induced transformational changes in nematic liquid crystals have also studied in the present thesis. The variation in the dielectric and electro-optical properties in different nematic liquid crystals have been analyzed and well explained in this thesis. To examine the effect of applied
electric field on the dielectric properties the bias voltage study has also
done for nematic liquid crystals.

**Chapter 1** basically deals with the introduction to the family of
liquid crystals. History of the liquid crystals and recent development has
been introduced in the chapter. The basic classification scheme has also
been discussed. The chapter ends with the application of liquid crystals
and their importance in various fields.

**Chapter 2** is an introduction to the theoretical background of liquid
crystalline phase. The brief discussion about basic terms related with
liquid crystals such as director, order parameter, anisotropy etc, have
been given in this chapter. The elastic properties including viscosity,
elasticity, response time etc. have also been discussed in the mid of the
chapter. The chapter also includes the broad discussion about the
dielectric spectroscopy. The phase transition theories of liquid crystals
such as Landau-de Gennes theory, Maier-Saupe theory etc have also been
discussed. In the last the description about the gamma ray modification
technique has also given.

**Chapter 3** is an introduction to the experimental techniques used in
the present thesis. Sample holder preparation is the most important part
of the investigation. The complete fabrication technique and precautions
related with each step has been discussed extensively. Two basic
alignment techniques have been given in this chapter. Different dielectric methods are also given in this chapter.

In the chapter 4, we analyze the dielectric behaviour of unusual H-Shaped liquid crystal dimer named Bis[5-(4'-n-dodecyloxybenzoyloxy)-2-(4''-chlorophenyldazo)phenyl]butylethers (12-Cl-H4). The observations suggest that relaxation mode observed in MHz region for the sample. The relaxation mode follows Cole-Cole theory. Various dielectric parameters such as relaxation frequency, effective dielectric permittivity, distribution parameter, activation energy for the sample (12-Cl-H4) using Cole-Cole plot. The dielectric study for the given sample has been done with variation in both temperature and frequency. Also a strong theoretical background has been given, to minimize one of the liquid crystal defects - splay defect with this new molecular topology. Thus, this new molecular topology could trigger a revolution in liquid crystalline devices and could be used in future from application point of view.

The chapter 5 reports comparative dielectric study of gamma irradiated and unirradiated nematic liquid crystal. This study is an attempt to see the irradiation effect in the alignment and dielectric parameters of nematic liquid crystal. The dielectric measurements have been done with the temperature variation in the frequency range 100 Hz to 10 MHz. The dielectric data show relaxation modes which follow Cole-
Cole theory. The Cole-Cole plots have been used to determine the dielectric parameters such as relaxation frequency and relaxation strength. The dielectric permittivity is found to increase for gamma irradiated sample as compared to the unirradiated sample with variation in temperature and frequency and well explained in this chapter.

In the chapter 6 dielectric as well as electro optical parameters have been investigated for unirradiated 4-Cyano-4’-pentylbiphenyl (5CB) along with gamma radiated 5CB, as a function of temperature and voltage. The sample exhibits a strong positive dielectric anisotropy due to the presence of a large dipole moment along with the major molecular axis. The dielectric anisotropy $\Delta \varepsilon$ decreases for the irradiated 5CB sample as a result of gamma radiation. Some electro-optical parameters such as rotational viscosity, response time have also been determined and compared with the unirradiated 5CB samples.

Chapter 7 reports the comparative study of dielectric and electrot-optical properties of unirradiated EBHA nematic liquid crystal (NLC) with gamma irradiated EBHA NLC. The dielectric measurement has been performed with the variation in voltage and temperature within the frequency range 100 Hz to 10 MHz. Variation in response time for both gamma irradiated and unirradiated samples have also been measured and well explained in the present chapter.
In the end I conclude that our experimental findings backed by theoretical model and explanations presented in the thesis provides a broad information about the modification techniques as well as the gamma ray modification technique, their consequences on the dielectric and electro-optical properties of liquid crystalline materials. **Chapter 8** reports the final conclusions drawn from the experimental findings and some crucial suggestions.
Basic terms related to liquid Crystals
Basic Terms Related To Liquid Crystals

Alignment layer
A layer and/or surface treatment applied to the boundary of a liquid crystal cell to induce a particular director orientation. For example, a layer of polyimide buffed in one direction induces alignment parallel to the buffing direction, or a surfactant may be polymerized on a boundary surface to induce perpendicular alignment.

Amorphous
Irregular; having no discernible order or shape. In the context of solids, the molecules are randomly arranged, as in glass, rather than periodically arranged, as in a crystalline material.

Amphiphilic
A molecule with a hydrophilic head and a hydrophobic tail. That is, a molecule that has one end which attracts water and one end which repels water.

Anisotropic
Having properties which vary depending on the direction of measurement. In liquid crystals, this is due to the alignment and the shape of the molecules.

Aromatic
A compound containing a series of benzene (6 Carbon) rings; so named because many have a distinctive odour.

Axial ratio
The ratio of the length of the molecule to the diameter of the liquid crystal molecule.

Biaxial
Possess two directions along which monochromatic light vibrating in any plane will travel with the same velocity. The optic axis lies just between these directions.

Bilayer
A double layer of amphiphilic molecules, arranged such that either the nonpolar ends are on the inside screened by the polar ends or the polar ends are on the inside screened by the nonpolar ends, depending on whether the solvent is polar or nonpolar.
**Birefringence**

Also called double refraction. The property of uniaxial anisotropic materials in which light propagates at different velocities, depending on its direction of polarization relative to the optic axis. A wave with polarization perpendicular to the optic axis will exhibit an "ordinary" index of refraction, \( n_o \) (this is often referred to as the ordinary ray). In contrast, a wave with polarization parallel to the optic axis exhibits an "extraordinary" index, \( n_e \) (the extraordinary ray). The ordinary index, \( n_o \), is isotropic with respect to direction of propagation while the extraordinary, \( n_e \), varies depending on the direction of propagation with a maximum value for light travelling perpendicular to the optic axis and, of course, polarized parallel to it. The difference \( \Delta n = n_e - n_o \) is also referred to as the birefringence or the optical anisotropy.

**Blue phases**

Blue phases are special types of liquid crystal phases that appear in the temperature range between a chiral nematic phase and an isotropic liquid phase. Blue phases have a regular three-dimensional cubic structure of defects with lattice periods of several hundred nanometers, and thus they exhibit selective Bragg reflections in the wavelength range of light (visible part of electromagnetic radiation) corresponding to the cubic lattice.

**Bond orientational order**

Describes a line joining the centers of nearest-neighbor molecules without requiring a regular spacing along that line. Thus, a relatively long-range order with respect to the line of centres but only short range positional order along that line.

**Chiral molecule**

A molecule that is not identical to its mirror image. This gives a chiral substance its characteristic twisted shape, due to the fact that its molecules do not line up when combined.

**Cholesteric liquid crystals**

Also known as Chiral Nematic. Similar to the nematic phase, however, in the cholesteric phase, molecules in the different layers orient at a slight angle relative to each other (rather than parallel as in the nematic). Each consecutive molecule is rotated slightly relative to the one before it. Therefore, instead of the constant director of the nematic, the cholesteric director rotates helically throughout the sample. Many cholesterol esters exhibit this phase, hence the name cholesteric. See also chiral.

**Cholesteric mesophase**

Nematic liquid crystals with chiral centers form in two dimensional nematic-like layers with directors in each layer twisted with respect to those above and
below so that the directors form a continuous helix about the layer normal. Many cholesteric esters exhibit this phase, hence the name cholesteric. This mesophase exhibits circular dichroism and is optically active.

Circular polarization
A condition caused by two waves whose electric field components are 90 degrees out of phase, causing an effective rotation of the electric field about an axis in direction of propagation.

Cis (configuration)
A polymer configuration in which adjacent bonds are coplanar and on the same side of the carbon-carbon double bond.

Columnar phase
A liquid crystal phase characterized by disc-shaped molecules that tend to align themselves in vertical columns.

Contrast ratio
The contrast ratio is a property of a display system, defined as the ratio of the luminance of the brightest color (white) to that of the darkest color (black) that the system is capable of producing. A high contrast ratio is a desired aspect of any display.

Crystallinity
The presence of three-dimensional order on the level of atomic dimensions. In polymers, the range of order may be as small as about 2 nm in one (or more) crystallographic direction(s) and is usually below 50 nm in at least one direction. Polymer crystals frequently do not display the perfection that is usual for low-molecular mass substances. Polymer crystals that can be manipulated individually are often called polymer single crystals.

Defects
A local break in the translational or orientational symmetry of the material.

Deformation
The condition where the director in a liquid crystalline material changes its orientation from one molecule to the next.

Dendrimers
Highly branched molecules that have several layers of branching. These molecules exhibit a characteristic spherical shape.

Dichroism
Refers to the selective difference in absorption between the two orthogonal components of the polarization state of light propagating in a given direction in an anisotropic medium. Generally applied to linearly polarized light. This is how a sheet polarizer works with one direction of polarization transmitted and the perpendicular directions absorbed. Circular dichroism describes the corresponding effect for circularly polarized light where one “handedness” of circularly polarized light is absorbed more strongly than the opposite “handedness.” Solutions of chiral molecules will produce this effect as will cholesteric liquid crystals for wavelengths well removed from the pitch value.

Dielectric anisotropy
A condition arising when the dielectric constant parallel to the length of a mesogen, is different from that perpendicular to it. This occurs when the charge distribution along the molecule responds differently to the parallel component of the local electric field than the distribution perpendicular to the length does to the perpendicular component, yielding a difference in dielectric constants. See the LC properties section.

Dielectric breakdown
Dielectric breakdown is a sudden increase in current when the voltage exceeds a critical value $V_b$.

Dielectric loss
The liquid crystal sample cell (parallel plate capacitor) treated as a RC network in which current is made up of two parts; capacitive current (out of phase part) and resistive current (in phase part). The resistive current is the property of dielectric and entirely due to the dielectric medium arises between the plates of sample cell. Therefore we characterize it by a component of the permittivity by defining relative permittivity as $\varepsilon_r=\varepsilon'-j\varepsilon''$. The magnitude of the $\varepsilon''$ component is called dielectric loss.

Dielectric strength
For a given material, the insulating properties can be described in terms of the dielectric strength, expressed as the field which, when applied to the material, causes an uncontrollable current to flow through or across it.

Dielectric susceptibility
The dielectric susceptibility of the medium is given as the ratio of bound charge density to the free charge density. It is dimensionless constant.

Dimer
The liquid crystal compound is dimer which means that it is composed of molecules containing the two conventional mesogenic groups linked via a
flexible spacer. This liquid crystal dimer shows quite different behaviour to the conventional liquid crystals.

**Dipole**
Two equal electric or magnetic charges of opposite sign, separated by a small distance. In the electric case, the dipole moment is given by the product of one charge and the distance of separation. Applies to charge and current distributions as well. In the electric case, a displacement of charge distribution produces a dipole moment, as in a molecule.

**Director**
The molecular direction of preferred orientation in liquid crystalline mesophases.

**Disclination**
Line defects arising from singularities in orientational order in a director field.

**Discotic liquid crystal**
The component disc-shaped molecules self-assemble in a way that resembles stacks of coins. The discs are stacked on top of each other to form columns, which in turn are packed on a two-dimensional, usually hexagonal, lattice.

**Dislocations**
Line defects arising from singularities in translational order in a crystalline lattice.

**Domain**
A domain is a region where the spontaneous polarization is uniform. Adjacent domains can have different polarization, much like in ferromagnetism.

**Elastomers**
A class of polymers that have some degree of cross linking and are rubbery. Elastomers possess memory, that is, they return to their original shape after a stress is applied.

**Electro-optical materials**
Materials whose optical properties are changed under the application of an electric field.

**Emulsion**
A mixture of two mutually insoluble liquids such that one is dispersed in the other in droplets which often cause the solution to be cloudy or translucent.

**Enantiomers**

XX
Molecules which exist in two nonsuperimposable mirror images, analogous to human hands. Chiral molecules are perfect physical and chemical models of each other with the exception of their rotation of polarized light and those interactions that involve other chiral systems, such as chiral molecular recognition. A racemic mixture contains equal amounts of two enantiomers and thus produces no rotation of the plane of polarization of light.

**Enantiotropic liquid crystal**
Exhibit the liquid crystal state both when the temperature rises from the solid state side or when it falls from the liquid state. Monotropic liquid crystals exhibit the liquid crystalline state only when the temperature changes in one direction.

**Extraordinary ray**
The optical ray which not follow the law of refraction in the double refraction phenomenon. See birefringence section.

**Ferroelectric material**
One that produces domains of spontaneous polarization whose polar axis can be reversed in an electric field directed opposite to the total dipole moment of the lattice.

**Freedericksz transition**
The point at which a liquid crystal changes from an aligned to a deformed state under the influence of an external electric or magnetic field.

**Free radical**
A molecule with an unpaired electron, making it highly reactive.

**Grandjean texture**
A specific pattern of defects found in chiral nematic liquid crystals that is caused by the chiral nature of the crystal. Named for the French scientist F. Grandjean who worked with chiral nematic liquid crystals.

**Helix**
The molecular conformation of a spiral nature, generated by regularly repeating rotations around the backbone bonds of a macromolecule.

**Homeotropic texture**
A mesogen configuration in which the molecules are aligned normal to the boundary surfaces, as at the faces of a liquid crystal cell, as illustrated. Consequently the director will be normal to the surface. This orientation is generally obtained by the application of an electric field normal to the surface but can be achieved through surface treatment.
**Homogeneous**
An uniform structure or composition throughout. Having or possessing the same properties.

**Homogeneous (planar) texture**
A mesogen configuration in which the molecules are aligned parallel to the boundary surfaces, as at the faces of a liquid crystal cell.

**Hydrophilic**
"Water loving"; describes a molecule which is attracted to water.

**Hydrophobic**
"Water fearing"; describes a molecule which is repelled by water.

**Index of refraction**
Ratio of the phase velocity of electromagnetic radiation in free space divided by the phase velocity in a given medium. It is greater than one except for rather special cases.

**Isomer**
A molecule which has an identical molecular formula to another molecule, but has a different structure.

**Isotropic**
Having properties that are the same regardless of the direction of measurement. In the isotropic state, all directions are indistinguishable from each other. See also anisotropic.

**ITO**
Indium Tin Oxide (indium oxide doped with tin). A transparent conductive material very commonly used for electrodes in displays or other applications which require conductivity along with light transmission.

**Lipophilic**
Describes a molecule which is attracted to hydrocarbons.

**Liquid crystal**
A thermodynamic stable phase characterized by anisotropy of properties without the existence of a three-dimensional crystal lattice, generally lying in
the temperature range between the solid and isotropic liquid phase, hence the
term mesophase.

**Lyotropic**
Materials in which liquid crystalline properties appear induced by the presence
of a solvent, with mesophases depending on solvent concentration, as well as
temperature.

**Macromolecule**
A very large molecule. Many polymers are composed of hundreds of thousands
of atoms, and are thus characterized as macromolecules.

**Melting transition temperature**
The temperature at which the substance loses its translational and
orientational order, changing from a solid phase to a liquid phase.

**Mesogen**
Rigid rodlike or disclike molecules which are components of liquid crystalline
materials.

**Mesomorphic substance**
Another term for a liquid crystal material.

**Mesophase**
Equilibrium liquid crystalline phases formed with order less than three
dimensional (like crystals) and mobility less than that of an isotropic liquid.
Parallel orientation of the longitudinal molecular axes is common to all
mesophases (long-range orientational order). See the Liquid Crystal
introduction section

**Micelle**
A spherical formation caused by an amphiphilic substance in a solution. The
lyophilic end of the molecule tends to orient itself toward the outside of the
sphere while the lyophobic end tends to orient itself toward the inside of the
sphere.

**Monolayer**
A layer of amphiphilic molecules on the surface of a solvent, arranged such
that the ends attracted to the solvent are in contact with it and the other ends
point into the air.
Monomer

The simple chemical unit which, when many are joined together, form a polymer.

Monotropic

A type of material which exhibits the liquid crystalline state only when the temperature changes in one direction. This is generally a result of the liquid crystal phase being below the melting temperature of the solid, where the liquid crystal phase is only observed if the liquid is supercooled below the melting point.

Nano particle

In nanotechnology, a particle is defined as a small object that behaves as a whole unit in terms of its transport and properties. It is further classified according to size: In terms of diameter, fine particles cover a range between 100 and 2500 nanometers, while ultrafine particles, on the other hand, are sized between 1 and 100 nanometers.

Nematic mesophase

Liquid crystals are characterized by long-range orientational order and the random disposition of the centers of gravity in individual molecules. Nematics may be characterized as the simplest spontaneously anisotropic liquids. Nematic phases are composed of rod-shaped molecular aggregates that are arranged with parallel but not lateral order.

See Liquid Crystal classification section.

Optical activity

The plane of vibration of linearly polarized light rotates as it propagates through a medium. This rotation can occur in either a right or left handed direction. Since linearly polarized light can be regarded as the sum of right and left hand circularly polarized components, this optical activity corresponds to different indices of refraction for the two circular components (circular birefringence).

Optic axis

In a uniaxial material, a single direction of propagation along which double refraction does not occur. The index of refraction for both polarization directions is n_o along this axis. This axis lies along the director for nematic liquid crystal.

Order parameter

S describes the orientational order of liquid crystalline material, allowing for the individual orientational deviation of the molecules from the director, which represents the average over the collection. Typically, S ranges from 0.3 to 0.9,
depending on the temperature, with a value of unity for perfect order. See Introduction to Liquid Crystal phases section.

**Orientational order**
Measure of the tendency of the molecules to align along the director on a long-range basis. See order parameter.

**Permittivity**
When a dielectric material is placed in an electric field already existing in a homogeneous medium, it has the effect of changing the distribution of the field to a degree depending upon its relative permittivity; i.e. the electric field intensity is a function of the medium in which it exists. In general the dielectric permittivity is defined as the ratio of the flux density to field.

**Piezoelectricity**
A mechanical strain produces dielectric polarization and vice versa, an applied electric field causes mechanical strain. Materials which lack a center of symmetry are piezoelectric.

**Pitch**
An important characteristic of the cholesteric mesophase is the pitch. The pitch, \( p \), is defined as the distance it takes for the director to rotate one full turn in the helix.

**Polarizability**
Relates the induced electric dipole moment, \( p \), of an atom or molecule to the local electric field it experiences as \( \alpha = p / E_{\text{local}} \), hence depending on the displacement by the field of the electronic charge from its equilibrium position in the atom or molecule.

**Polarization**
The dipole moment per unit volume of the sample is called the polarization.

**Polymer liquid crystals**
Polymers that contain mesogen units and thus have liquid crystal properties.

**Positional order**
The extent to which the position of an average molecule or group of molecules shows translational symmetry.

**Prolate**
Elongated at the poles.

**Relaxation**
A term used to mean all irreversible processes which bring a system back to equilibrium after it has been perturbed by some external force. For instance, if an electric field is applied to a fluid of polar materials a polarization will be induced, but this will disappear after the field is removed, because of the randomization of the molecular orientations produced by Brownian motions.

**Resonance**
A method of stabilizing a bond by delocalizing the electrons around the molecule.

**Rotational symmetry**
Consider the example of an unmarked billiard ball. Rotation of any amount about any axis through its center will take the ball into itself so it has complete rotational symmetry. However, the stitching on a baseball places several restrictions on the axes about which it can be rotated into itself.

**Schlieren texture**
The texture that appears in the optical microscopy of nematic and related smectic C phases under crossed polarizers when the planarity of the phase is interrupted by defects. The schlieren, dark streaks or brushes, form in the liquid crystal, connecting the defect points. The dark streaks or brushes that are characteristic of this texture may also appear along disclinations in a liquid crystal.

**Self-assembly**
The aggregation of molecular moieties into more ordered structures that are thermodynamically stable and involve noncovalent bonds. Crystallization is an example of such self-assembly. Self-assembly is used to build nanostructures such as inorganic clusters and lattices, nanotubes and channels, host-guest complexes, monolayers, hydrogen-bonded networks and systems of intertwined molecules.

**Smectic mesophase**
The molecules organize themselves into layers. The smectic phases form a one dimensional periodic lattice in which the individual layers are two dimensional liquids. Now 12 different smectic phases have been identified.

**Spacer**
Flexible section of polymer chain between two mesogens or the mesogen and the backbone of a polymer.

**Steric hindrance**
A condition when the rotation of a given group is restricted due to the size of neighbouring groups.
**Super critical fluids**
A substance above its critical point on the temperature/pressure phase diagram. Above the critical point, the fluid is neither a gas nor a liquid but possesses properties of both. The viscosity of a supercritical fluid is at least one order of magnitude higher than the viscosity in the gaseous state, but is one or two orders of magnitude less than in the liquid state.

**Surfactants**
Surface active agents. Organic compounds consisting of two parts: a water-attracting (hydrophilic) portion and a water-resistant (hydrophobic) portion. Detergents may contain more than one kind of surfactant. The hydrophobic ends attach themselves to the soil particles or to the fabrics being washed while the hydrophilic ends are attracted to the water. The surfactant molecules surround the soil particles, break them up, force them away from the surface of the fabric, then suspend the soil particles in the wash water. Surfactants are classified by their ionic (electrical charge) properties in water.

**Symmetry**
The invariance of some properties of the object being investigated with respect to all the transformations considered.

**Thermoplastics**
Linear plastics of finite molecular weight that can be fabricated into complex shapes by melting and injection molding.

**Thermotropic**
Liquid crystal molecules which exhibit temperature dependent liquid crystalline behavior. See also: lyotropic

**Topology**
A branch of mathematics concerned with those properties of geometric configurations which remain unaltered under very general kinds of elastic deformations (transformations such as stretching or twisting) where length, angles, and shapes are changed.

**Translational order**
A condition when molecules have some arrangement in space. Crystals have three degrees of translational order (each molecule is fixed in space with an x, y, and z coordinate) and liquids have no translational order.

**Uniaxial materials**
Possess only one direction along which monochromatic light vibrating in any plane will travel with the same velocity. This direction is known as the optic axis.
**Unit cell**
The smallest, regularly repeating material portion contained in a parallelepiped from which a crystal is formed by parallel displacements in three dimensions. Unlike the case of low-molar mass substances, the unit cell of polymer crystals usually comprises only parts of the polymer molecules, and the regularity of the periodic repetition may be imperfect.

**Vander Waal's forces**
Forces which act between molecules that are caused by small random fluctuations in the polarity of the liquid crystal molecules.

**Viscosity**
The internal resistance to flow existing between two liquid crystal layers when they are moved relative to each other. This internal resistance is a result of interaction between liquid crystal molecules in motion.

**Vulcanization**
A process by which a network of crosslinks is introduced into an elastomer to strengthen it.
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References
1.1 Introduction

Since school we distinguish mainly three states of matter: solids, liquids, and gases. But it was already at the late nineteenth century, some scientists were in doubt of this classification. Solids, namely crystals, are highly ordered, the constituting atoms or molecules possessing positional as well as orientational order. On contrary, simple liquids like water or gases exhibit no order at all.

Ordinary fluids are isotropic in nature: they appear optically, magnetically, electrically, etc. to be the same from any perspective. Although the molecules which comprise the fluid are generally an isometric in shape, this anisometry generally plays little role in anisotropic macroscopic behaviour (aside from viscosity). Nevertheless, there exists a large class of highly an isometric molecule which gives rise to unusual, fascinating, and potentially technologically relevant behaviour. There are many interesting fields of this type for study, including polymers, micelles, micro emulsions, and materials of biological significance, such as DNA and membranes. Although at times the investigations on all of these materials are continuing, my primary effort is centred on liquid crystals [1-2].

This chapter is an introduction to “Liquid Crystals”. Chapter starts with basic definitions of liquid crystals followed by classification scheme and history of liquid crystals. At the end of the chapter, the applications of liquid crystals have also been discussed.

1.2 Beginning With Liquid Crystal

There is always a reason behind everything and this principle does not exclude naming conventions in physics. Hence, to understand what is a “liquid crystal” we need to clarify why would one give such a name to a substance. Hence to get into the root of liquid crystals, we must clarify the name first. At first sight, it looks absurd. But it gives an idea that this phase of the matter must have properties associated with both solids and liquids. From our basic perception, the order in a crystal is usually both positional and orientational, i.e. the molecules are constrained both to occupy specific sites in lattice and to point their molecular axes in specific direction. On the other hand, diffuse
randomly through the sample container with the molecular axes tumbling wildly. The forces holding the liquid molecules are much weaker than the forces in the solids. When these phases are grouped together, the new phase liquid crystal shares properties associated with both liquids and crystals [3, 4]. The molecules in all liquid crystal phases diffuse about much like the molecules of liquid, but they do so maintaining some degree of orientational order and sometimes some positional order also [4, 5]. The amount of order in the liquid crystal is quite small relative to crystal. In general, the solid crystal phase of a material exhibits more order than the liquid phase (see figure 1.1).

**Figure 1.1** Arrangement of molecules with an increase in temperature in a (A) Crystalline Solid (B) Liquid Crystal (C) Isotropic Liquid.

### 1.3 History of Liquid Crystals

Between 1850 and 1888, researchers in different fields such as chemistry, biology, medicine and physics found that several materials behaved strangely at temperatures near their melting points. It was observed that the optical properties of
these materials changed discontinuously with increasing temperatures. For example W. Heintz reported in 1850 that stearin melted from a solid to a cloudy liquid at 52°C, changed at 58°C to an opaque and at 62.5°C to a clear liquid. Others reported observing blue colours when compounds synthesized from cholesterol were cooled. Biologists observed anisotropic optical behaviour in "liquid" biological materials, behaviour usually expected only in the crystal phase.

An important invention of the time was the heating state microscope by Otto Lehmann [5], a physicist from Karlsruhe, Germany. This microscope allowed control of the temperature of the sample. In a later version, with polarizers added, it became the standard equipment in every liquid crystal research laboratory.

In 1888, an Austrian botanist named Friedrich Reinitzer [6], interested in the biological function of cholesterol in plants, was looking at the melting behaviour of an organic substance related to cholesterol. (The chemical structure of cholesterol was still unknown. Today we know that the observed substance was cholesteryl benzoate). He observed, as W. Heintz did with stearin 38 years before, that the substance melted to a cloudy liquid at 145.5°C and became a clear liquid at 178.5°C. He repeated an earlier observation which showed that upon cooling the clear liquid, a brief appearance of blue color could be seen at the transition temperature, and that a blue violet color appeared just before crystallization. Reinitzer sent his early work to Otto Lehmann, a professor of natural philosophy (physics) in Germany. Lehmann had constructed a polarizing microscope [5] with a stage to control precisely the temperature of his samples. He examined Reinitzer’s substance with his microscope and noticed its similarity to other samples he was studying then. The term ‘liquid crystal’ was coined by him in 1900 (although at first he called them ‘flowing crystals’ (1889) and ‘crystalline solids’ (1890)). Research in the area of liquid crystals burgeoned in the years after 1888. Some of the more important results are listed below.
The claim that a new phase of matter was found was challenged by important scientists like Walter Nernst and Gustav Tamman. They argued that the phenomena could be explained as an effect of an emulsion of two distinct phases or compounds. Further experiments by Lehmann and others supported his theory. Later theoretical work by Emil Bose also gave rise to arguments against the hypothesis of an emulsion.

Max Born suggested a theoretical description of liquid crystals as molecules with permanent electric dipoles. This theory unfortunately leads to faulty results.

A German chemist David Vorlander [7] was the first to observe a single substance that possessed more than one liquid crystal phase. Out of this work Vorlander [6] was able to identify what kinds of substances were likely to be liquid crystal.

In 1922 in Paris, France, Georges Freidel [8] suggested the classification scheme which is used today with different phases of liquid crystals called nematic, smectic and cholesteric.

Carl Oseen in Sweden worked on elastic properties of liquid crystals and his results were used on the continuum theory by England's F.C. Frank [9]. This theory is one of the basic theories to describe liquid crystals today.

Alfred Saupe [10, 11], a German physicist, later working at Kent State University, worked together with his advisor Wilhelm Maier in Karlsruhe 1958 on his thesis ("Diplomarbeit"), a molecular theory of liquid crystals not involving permanent dipoles as Max Born's theory did. This work gave rise to the Maier-Saupe Theory, another well-known basic theory of liquid crystals.

From 1945 to 1958 all was quiet on the liquid crystal front. People thought they knew everything about liquid crystals and that nothing new could be expected in this area. Even worse, they were not even included in textbooks. An entire decade of growing scientists did not have contact with liquid crystals. No one could yet imagine how large a role liquid crystals would play in technical applications today.
In 1958 Glenn Brown, an American chemist, published an article in Chemical Reviews on the liquid crystal phase and subsequently sparked an international resurgence in liquid crystal research.

Slowly the study of this phase spread to all the continents and there was an explosive growth during the 1970s and 1980s. It was always interesting and famous topic for even early physicists and crystallographers who worked on various aspects of liquid crystals, for example, Born, Ewald, Ornstein, Mauguin, Zsigmondy, Hückel, Bernal, and Landau, as well as the more familiar and more recent contributions of Onsager, Flory, Frank, Leslie, Ericksen and De Gennes have contributed a lot in the field of liquid crystals [7-11]. A surprising omission is the paper reporting the discovery of discotic liquid crystals by Chandrasekhar in 1977. Furthermore, the emphasis is rather firmly on thermotropic systems, with relatively little on lyotropic or polymeric liquid crystals, although these latter fields are at least as extensive as thermotropics [9, 10]. Vittorio Luzzati’s Group pleased the world, who first deduced the structures of most of the lyotropic phases known today. Theories for the liquid crystal phases added a new dimension of study and the invention of liquid crystals displays gave the field a practical dimension.

The future of liquid crystals has just begun. There are still unsolved physical problems in this area, despite the fact that researchers in the fifties had already withdrawn form this area, thus giving an interesting field for the pure scientist. The need for liquid crystal applications grew; requiring engineers specialized in this field. Statistics show that cathode ray tube displays in TVs and computer monitors will be overtaken by liquid crystal displays in the near future. More recent applications involve switchable windows that can be changed from clear and opaque with the flip of a switch, liquid crystal displays with wider viewing angles, and displays that can remain in use for years without the need of power.

Knowledge in the field of liquid crystals is crucial for an understanding of biological membranes, thus biologists, medical researchers and pharmacists are also interested in liquid crystal research.
It is very proud for all the researchers that in the 1960s, a French theoretical physicist, Pierre-Gilles de Gennes, who had been working with magnetism and superconductivity, turned his interest to liquid crystals and soon found fascinating analogies between liquid crystals and superconductors as well as magnetic materials. His work was rewarded with the Nobel Prize in Physics 1991. The modern development of liquid crystal science has since been deeply influenced by the work of Pierre-Gilles de Gennes [12].

Therefore, today, thanks to Reinitzer, Lehmann and their followers [13], we know that literally thousands of substances have a diversity of other states. Some of them have been found very usable in several technical innovations [14], among which liquid crystal screens and liquid crystal thermometers may be the best known.

1.4 Criteria to achieve the Liquid Crystalline phase

After a number of experiments in past years it has now become clear, what type of molecules are likely to be liquid crystalline at some temperature [15]. Liquid crystalline materials are normally constituted by aromatic ring attached with aliphatic tail (Figure 1.2). The aromatic ring provides the rigidity like solids whereas the aliphatic tail provides the fluidity to the liquid crystal molecules. Due to the presence of aromatic ring and aliphatic tail the liquid crystals are capable to show the characteristics of both solids and liquids.
Chapter 1: Introduction to Liquid Crystal

Figure 1.2 (A) Basic requirements for molecules a molecule to show the liquid crystalline behaviour (B) Basic molecular structure of a liquid crystal molecule 5CB.

1.5 Classification of Liquid Crystals

Condensed matter which exhibits intermediate thermodynamic phases between the crystalline solid and simple liquid state are now called liquid crystals or mesophases (Figure 1.1). This fourth state of matter generally possesses orientational or weak positional order and thus reveals several physical properties of crystals but flow like
liquids. There are several bases that have been used till date to classify the liquid crystals as shown in figure 1.3.

![Classification scheme of liquid crystal.](image)

**Figure 1.3 Classification scheme of liquid crystal.**

### 1.5.1 Chemical Concept

Liquid crystals fall in two basic classes Lyotropic and Thermotropic [16, 17]. This classification of liquid crystal If transitions between the phases are due to temperature change, they are called thermotropic. In blends of different components phase transitions may also depend on concentration, and these liquid crystals are called lyotropic. Thermotropic liquid crystals are mostly used for technical applications at present, while lyotropic liquid crystals are important for biological systems, e.g. membranes.
1.5.1.1 Lyotropic Liquid Crystals

Lyotropic liquid crystals were the first liquid crystals to be discovered in 1850. In contrast to thermotropic mesophases, lyotropic liquid crystal transitions occur with the influence of solvents, not by a change in temperature. Lyotropic mesophases occur as a result of solvent-induced aggregation of the constituent mesogens into micellar structures. Lyotropic mesogens are typically amphiphilic, meaning that they are composed of both lyophilic (solvent attracting) and lyophobic (solvent-repelling) parts. This causes them to form into micellar structures in the presence of a solvent, since the lyophobic ends will stay together as the lyophilic ends extend outward toward the solution. As the concentration of the solution is increased and the solution is cooled, the micelles increase in size and eventually coalesce. This separates the newly formed liquid crystalline state from the solvent. For example, the “goo” that sometimes collects in the bottom of your soap dish is a lyotropic liquid crystal phase of the soap/water mixture.

Just as there are different types of structural modifications for thermotropic liquid crystals, there are several different type lyotropic liquid crystal phases. The concentration of material in solvent dictates the types of Lyotropic liquid crystals [18, 19].
Figure 1.4 Schematic showing the aggregation of amphiphiles into micelles and then into lyotropic liquid crystalline phases as a function of amphiphile concentration and of temperature.

Lyotropic phases are classified into three different types viz. lamellar, cubic and hexagonal as shown in figure 1.4 [1]. Lyotropic liquid crystals are also extremely important because of their role in biological membranes. Membranes are composed of amphiphilic liquids - mostly phospholipids and cholesterol, with a small percentage of glycolipids.

1.5.1.2 Thermotropic Liquid Crystals

Thermotropic transitions occur in most liquid crystals, and they are defined by the fact that the transitions to the liquid crystalline state are induced thermally. That is, one can arrive at the liquid crystalline state by raising the temperature of a solid and/or lowering the temperature of a liquid. The temperature at which phase transition occurs is called phase transition temperature.

Liquid crystal mesophases are indefinitely stable at a defined temperature and pressure. The vast majority of thermotropic liquid crystals are composed of rod-like molecules (one molecular axis is much longer than the other two) and they are known as calamitic liquid crystals (As shown in figure 1.1).

Thermotropic liquid crystals can be classified into two types: enantiotropic liquid crystals, which can be changed into the liquid crystal state by either lowering the temperature of a liquid or by raising the temperature of a solid, and monotropic liquid crystals, which can only be changed into the liquid crystal state by either an increase in the temperature of a solid or a decrease in the temperature of a liquid, but not both [20-22]. In general, thermotropic mesophases occur because of anisotropic dispersion forces between the molecules and because of packing interactions. The liquid crystals in which mesophase is defined by melting temperature of crystalline phase $T_m$ and below the clearing point of $T_{IN}$ (as shown in figure 1.5) i.e. phase transitions occur due to change in temperature are called thermotropic liquid crystals.
1.5.2 Molecular Shape Concept

On the basis of molecular shape the liquid crystals are classified into three classes i.e. they are rod shape, disk like and banana shape liquid crystals. A broad classification is shown in the figure 1.6. Instead of this broad classification the range of this concept is still growing. The most recent additions are lambda, hockey, U, Y and H shaped liquid crystal molecules.

1.5.2.1 Rod Shape Molecules

The classical liquid crystals are constituted from rod shape molecules and usually known as Calamatic. The word Calamatic is derived from Greek word calamos which means rod as shown in figure 1.6.
1.5.2.2 Disc Shape Molecules

It was originally thought that the mesophase could only be generated by molecules of rod-like structure. The existence of mesophase generated by disk shaped molecules was theoretically predicted in 1970 and mesomorphism in discotic materials was first reported by Chanderashekar in 1977 [22].

There are several different types of columnar mesophases exhibited by discotic materials; these arise because of the different symmetry classes of the two dimensional lattice of columns and the order or disorder of the molecular stacking within the columns. Different structures formed by disc shape molecules are shown in figure 1.7.
Transformation between phases with respect to the temperature is like the rod-like molecules. At high temperature molecules are in isotropic liquid phase (see in figure 1.8). By decreasing the temperature the material transform into nematic phase which has orientational order but no positional order. The average direction of the short axis perpendicular to the disk is oriented along a preferred direction which is also called the liquid crystal director. When the temperature is decreased further, liquid crystal transforms into columnar phase where they have partial positional order. The molecules stack up in columns in which they have two-dimensional liquid behaviour.
1.5.2.3 Banana Shaped Liquid Crystals

Liquid crystal molecules with a bent molecular shape, so called banana-shaped liquid crystals, have attracted special attention. It has been known since 1923 that bent core molecules can show liquid crystalline phases [7]. However, at that time they were just called “bad rods” and no body anticipated the noise these substances would make later on due to the discovery of polar switching. Liquid crystals composed by banana shape molecules as shown in figure 1.9 provide now a new and hot area of liquid crystal research, as such materials organize into fluid phases with polar order and supermolecular chirality [21, 23] properties which are of current interest in different areas of science.
Figure 1.9 Banana shaped liquid crystal

### 1.5.2.4 Unusual Shaped Liquid Crystals

In addition to the conventional molecular shape of liquid crystals described above, many more molecular shapes have been added to the liquid crystals. As early as 1907 Vorlaender [24, 25] proposed his rule that the liquid crystalline state is obtained for the most linear of ring and indeed a wide variety of rod-like mesogenic molecules have been synthesized. Disubstitution of the benzene ring in the 1, 2- or 1, 3-positions results in U-shaped or bent molecules that deviate significantly from the `ideal’ elongated lath-like structure. Consequently very few such systems have been reported to form liquid crystal phases. The first such report was by Vorlaender himself in conjunction with Apel. Yoshizawa and Yamaguchi [24- 27] have reported layered structure in the nematic phase consisting of U shaped molecule. Yamaguchi et. al. [27, 28] has reported synthesis of homologous series of novel \( \lambda \)-shaped mesogenic compounds which showed unusual smectic phases. Yoshizawa et. al. [27] have designed novel Y-shaped shown in figure 1.10 (a) Liquid crystal oligomers in which three mesogenic units are connected via 3, 5-dihydroxybenzoic acid. The Y-shaped liquid crystal oligomers [27] were found to show a direct phase transition from isotropic liquid to anticlinic SmC phase. They observed that the Y-shaped compounds are quite different from that of the corresponding \( \lambda \)-shaped figure 1.10 (b) mesogenic compounds. Since different possible orientations of the net molecular moment dipole are allowed at the air-water interface, one may speculate on the existence of monolayers and thin films of new structures. These compounds are also a good candidate for a better understanding of the correspondence between the phases of amphiphilic compounds in monolayers at the air-water interface and bulk mesophases. Figure 1.10 shows some of different shape showing liquid crystalline behavior like lambda, bowlic compound, hockey shape, star shape, U shape, S shape and H shape [24-33].
Figure 1.10 Different unusual shaped liquid crystals.
1.5.3 Molecular arrangement Concept

1.5.3.1 Nematic Liquid crystal

Nematic liquid crystal is a translucent liquid that changes the polarity of light waves passing through it. The word “nematic” comes from the Greek word for thread, and describes the thread-like formations that can be formed in the liquid crystal [8]. The nematic liquid crystal phase is characterized by long range orientational order and the random disposition of the centres of gravity in individual molecules. It has a high degree of long-range orientational ordering of the molecules i.e., the long axes of the molecules tend to be parallel to a particular direction, called the director [34, 35] (designated by a unit vector \(\mathbf{n}\), as shown in the figure 1.11). There is no long range order in the position of the centres of mass of the molecules of a nematic liquid crystal but a certain amount of short range order may exist as in ordinary fluids. The constituent molecules rotate (freely or hindered) around both their short and long axes.

![Figure 1.11 Schematic illustration of (a) Ordinary Nematic Phase (b) Chiral Nematic Phase (c) Smectic A Phase and (d) Smectic C Phase.](image)

*Figure 1.11 Schematic illustration of (a) Ordinary Nematic Phase (b) Chiral Nematic Phase (c) Smectic A Phase and (d) Smectic C Phase.*
Many compounds are known to form nematic mesophase. A few of them are shown in figure 1.12. Optically, a nematic phase can be uniaxial or biaxial [19]. The latter is formed by elongated lath like molecules. Conventional nematic liquid crystals formed by rod like molecules constitute a uniaxial medium with non polar symmetry.

![Chemical structures of PAA, MBBA, and 5CB](image)

*Figure 1.12 Typical compounds forming nematic mesophase.*

The alignment of the molecules of nematic liquid crystals can be deformed by even small external influences. They are able to translate weak external signals viz. electrical, magnetic, and mechanical into visible optical effects for which they are extremely useful in various display devices. Nematic liquid crystals usually show dark threads on a bright background when observed under polarizing microscope. These lines are defects in the orientational order and are called disclinations. The preferred direction is undefined at these disclinations.

### 1.5.3.2 Chiral Nematic Or Cholesteric Liquid Crystal

The cholesteric (or chiral nematic) liquid crystal phase is typically composed of nematic mesogenic molecules containing a chiral center which produces intermolecular forces that favor alignment between molecules with a slight angle to one another. This leads to the formation of a structure which 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. In this structure, the directors actually form in a continuous helical pattern about the layer normal as illustrated by the black arrow in the following figure. The black arrow in the figure represents director orientation in the succession of layers along the stack [36].

![Figure 1.13 Schematic representations of the periodic helical structures of the chiral nematic (cholesteric) phase. The pitch of the helix corresponds to the rotation of the director through 360°.](image)

The molecules shown are merely representations of many chiral nematic mesogens lying in the slabs of infinitesimal thickness with a distribution of orientation around the director. This is not to be confused with the planar arrangement found in smectic mesophases. An important characteristic of the cholesteric mesophase is the pitch. The pitch, $p$, is defined as the distance it takes for the director to rotate one full turn in the helix as illustrated in the figure 1.13. A byproduct of the helical structure of the chiral nematic phase, is its ability to selectively reflect light of wavelengths equal to the pitch length, so that a color will be reflected when the pitch is equal to the
corresponding wavelength of light in the visible spectrum. The effect is based on the temperature dependence of the gradual change in director orientation between successive layers, which modifies the pitch length resulting in an alteration of the wavelength of reflected light according to the temperature. 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. Similarly, decreasing the temperature of the molecules increases the pitch length of the chiral nematic liquid crystal [36]. The pitch length is temperature dependent and hence so is the colour of the reflected light. This is the basis behind the commercially successful use of chiral nematic materials in thermo chromic thermometer devices and other devices that change colour with temperature e.g. articles of clothing, inks and paints. The wavelength of the reflected light can also be controlled by adjusting the chemical composition, since cholesterics can either consist of exclusively chiral molecules or nematic molecules with a chiral dopant dispersed throughout. In this case, the dopant concentration is used to adjust the chirality and thus the pitch [37-40].

1.5.3.3 Smectic Liquid Crystal

The word smectic has been derived from the Greek word ‘Smectos’ which means soap like [34, 41]. The smectic phase of a liquid crystal represents a higher state of ordering than nematics. In addition to the orientational ordering the molecules are arranged in layers [41]. A great variety of smectic phases can be observed depending on the molecular arrangements in the layers. The molecules may be upright or inclined to the layers and may or may not have long range positional ordering in each layer, but long range orientational ordering is always present in all layers of the smectic liquid crystal [38, 39-42]. Some of the smectic liquid crystals have three dimensional long range positional order as in a crystal while some others have three dimensional long range ‘bond orientational order’ without any long range positional order. The interlayer attractions are weaker than the lateral forces between molecules and hence the layers can easily slide over one another. Hence smectics have fluidity though these are much more viscous than nematics. The lamellar smectic state can be divided into four
subgroups by considering the extent of the in-plane positional ordering of the constituent molecules, and the tilt orientational ordering of the long axes of the molecules relative to the layer planes. Two groups can be defined where the molecules have their long axes essentially normal to the layers. These two groups are distinguished from each other by the extent of the positional ordering of the constituent molecules. For example, smectic A and hexatic B are smectic liquid crystals in which the molecules have only short-range positional order, whereas crystal B and crystal E are smectic crystal modifications where the molecules have long-range orientational order in three dimensions. Two other classes can be distinguished where the molecules are tilted with respect to the layer planes. In smectic C, smectic I, and smectic F, the molecules have short-range orientational ordering, whereas in crystal G, crystal H, crystal J, and crystal K the molecules have long-range three-dimensional ordering [38, 43]. Thus, as already noted, smectics C, I, and F are essentially smectic liquid crystals, whereas G, H, J, and K are crystal phases. These latter phases, however, have somewhat different properties than normal crystals, for example, their constituent molecules are reorienting rapidly about their long axes ($10^{11}$ times s$^{-1}$). Smectic phase is also divided into many subclasses; some of them are as follows:

### 15.3.3.1 Smectic A Liquid Crystal

In the smectic A phase the molecules are arranged in diffuse layers so that their long axis are on the average in perpendicular to the layer planes. The molecules are undergoing rapid reorientational motion about their long axis on a timescale of $10^{11}$ times per second, and also undergoing relaxations about their short axis but on a much longer timescale of $10^6$ times per second. The molecules are arranged in such a way that there is no translational periodicity in the planes of the layers or between the layers. Therefore, the molecules have only short range hexagonal ordering extending over a few molecular centres at most. Although the phase has been described as having a layered structure, in the direction perpendicular to the layer planes the molecules are arranged in a one dimensional density wave, indicating that the layers are relatively diffuse [44, 45]. As a consequence, the concept of a layered mesophase is somewhat
misleading because the layers are so diffuse that in the macroscopic phase they are almost non-existent. Within these loosely constructed layers the molecules are arranged in such a way that they are often at slight angles to the layered planes. The long axes of the molecules can be tilted anywhere up to about 14 to 15° from the layer normal, and this makes the layer spacing, on average, slightly shorter than the molecular length. However, as this tilting occurs randomly across the bulk phase, the average direction of the long axes of the molecules is perpendicular to the layer planes. Consequently the director, \( \mathbf{n} \), is perpendicular to the layers, and the phase is therefore uniaxial. As the phase is uniaxial, it is also optically uniaxial, with the optic axis perpendicular to the layer planes [44,45].

The sub-phases of smectic A are described as monolayer smectic A (SmA\(_1\)), bilayer smectic A (SmA\(_2\)), partially bilayer smectic A (SmA\(_d\)). Partial bilayer ordering is typically caused either by interdigitation or pairing of the molecules with partial overlap and found to happen in materials where the molecules have terminal polar groups. Another smectic modification called ‘ribbon’ or antiphase has also been reported where an undulating bilayer is observed. Sub-structures of SmA phases are shown in figure 1.14. Details regarding this polymorphism of smectic A have been reported by many authors [44, 45].
1.5.3.2 Smectic C Liquid Crystal

In the smectic C phase the constituent molecules are arranged in diffuse layers where the long axes of the molecules are tilted at a temperature-dependent angle, $q$, with respect to the layer planes. The smectic C phase can be formed, via a first order phase transition, by cooling the isotropic liquid, the nematic, smectic A or the D phases, or via a second order phase transition from the smectic A phase. Typically, for first order phase transitions there is a jump in the value of the tilt angle at the transition, i.e., from a value of zero to a large finite value of usually more than 20°. After the initial jump in the value of the tilt angle, which occurs over only a few degrees, the angle remains fairly temperature independent. For a second order transition to the smectic C phase, the tilt angle usually continues to rise with falling temperature over the entire temperature range of the mesophase. However at lower temperatures there is a tendency for the tilt angle to saturate. Mathematically the temperature dependence of the tilt angle takes the form

$$\theta_T = (\theta)_0 (T_c - T)^a$$

where $\theta_T$ is the tilt angle at temperature $T$ °C, $(\theta)_0$ is a constant, $T_c$ is the smectic A to smectic C transition temperature, $T$ is the temperature and $a$ is an exponent theoretically predicted to be equal to 0.5. This power law dependence of the tilt angle ensures that the value of the tilt angle will essentially saturate with falling temperature. The molecules within the layers are locally hexagonally close-packed with respect to the director of the phase; however, this ordering is only short range, extending over distances of approximately 15 Å. Locally the molecules may also have bond orientational ordering, but the extent of this structural feature has not yet been fully examined. Over large distances, therefore, the molecules are randomly packed, and in any one domain the molecules are tilted roughly in the same direction. Thus the tilt orientational ordering between successive layers is preserved over long distances [46-51].

Figure 1.14 Bilayer and monolayer structures of the smectic A phase.
In SmC phase, when the constituent molecules are strongly axially polar, four sub phases are observed identical to those of the SmA phase, except that the molecules are tilted with respect to the layer planes. In this case an additional subgroup has been found where the tilt direction appears to flip as one moves from one layer to the other and is called alternating smectic C (SmC) [46-51].

1.5.3.3 Smectic B Liquid Crystal

Two distinct types of smectic B phase have been identified; one is called hexatic B (SmB\textsubscript{hex}) [48-50] and the other one is crystal B (B) [38]. In SmB\textsubscript{hex} phase the molecular arrangement is close to that of the SmA phase, however, within a layer the molecules are arranged in close packed hexagonal symmetry. Although the positional ordering within the layer is short range, there is long range bond orientational order in this phase. If the line joining the centers of mass of a molecule and its nearest neighbor is called a ‘bond’ then by ‘long range bond orientational order’ it is meant that the orientation of the hexagonal packing array is of long range [34, 50]. In crystal B phase, additionally the molecules have long range positional order within the layers as well as along the layer normal. However, in crystal B [34] phase the inter-layer stacking sequence may be of mono- (AAAA type), bi- (ABAB type) and tri- (ABCABC type) layers. Even random ABCABC type packing is also reported. Structures of SmB\textsubscript{hex} and B phases have been shown in Figure 1.15.
1.5.3.4 Smectic E Liquid Crystal

The smectic E phase is now designated as crystal E (E) phase since it can also be considered as a ‘soft’ crystal like the B phase [34, 51-52]. The lath-like molecules rotate cooperatively about their long axes on a time scale of $10^{11}$ times per second but unlike in B phase the motion is not full free rotation rather of an oscillatory nature. SmE phase is also found to have bilayer structure as in B phase [51-52].

1.5.3.5 Smectic I and Smectic F Liquid Crystals

The structures of smectic I phase are similar to SmB_{hex} but the molecules in this case are tilted within the layers [34, 53-56], direction of tilt being towards an apex of the hexagonal packing net. Thus it has short range in-plane and quasi-long range out-of-plane positional order as well as long-range bond orientational order in three dimension. The only difference in the molecular arrangement of smectic F phase is that the tilt of the molecules is towards an edge of the hexagonal packing net. In addition slightly longer correlation has been observed in the in-plane positional ordering than that found in smectic I phase [34, 35].

1.5.3.6 Smectic G, G', H And H' Liquid Crystal

All these smectic phases are now termed respectively as crystal G, crystal J, crystal H and crystal K phase since they have long range three dimensional order and they are like ‘soft’ crystals. In these cases the molecules are tilted with respect to the layer planes [35, 57-60]. The crystal J and G modifications are like the tilted crystal B phase, direction of the tilt being that in SmI and SmF phases respectively. The best way to keep tracks of all these phases is to use a chart as shown in figure 1.16. No single liquid crystal material is found to exhibit all the phases but many
compounds are found to exhibit complex polymorphism, for example, the compound N-(4-n-pentyloxybenzylidene)-4’-n-hexylaniline possess the phases N, SmA, SmC, SmB, SmF and SmG phases. Current knowledge of phase sequencing with respect to temperature is found to be as follows:

Iso, N\textsubscript{O}, N\textsubscript{SC} (or Ch), SmA, SmC, SmB\textsubscript{hex}, SmI, SmF, B, J, G, E, K, H, Crystal

Decreasing temperature

Increasing order

<table>
<thead>
<tr>
<th>Phase type</th>
<th>Molecular orientation</th>
<th>Molecular packing</th>
<th>Molecular orientational ordering</th>
<th>Bond orientational ordering</th>
<th>Positional ordering</th>
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</thead>
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<tr>
<td>Isotropic</td>
<td>Random</td>
<td>Random</td>
<td>SRO</td>
<td>SRO</td>
<td>SRO</td>
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<tr>
<td>N</td>
<td>Parallellism of long molecular axis</td>
<td>Random</td>
<td>LRO</td>
<td>SRO</td>
<td>SRO</td>
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<tr>
<td>SmA</td>
<td>Orthogonal</td>
<td>Random</td>
<td>LRO</td>
<td>SRO</td>
<td>QLRO</td>
</tr>
<tr>
<td>SmC</td>
<td>Tilted</td>
<td>Random</td>
<td>LRO</td>
<td>SRO</td>
<td>QLRO</td>
</tr>
<tr>
<td>SmB\textsubscript{hex}</td>
<td>Orthogonal</td>
<td>Hexagonal</td>
<td>LRO</td>
<td>LRO</td>
<td>QLRO</td>
</tr>
<tr>
<td>SmI</td>
<td>Tilt to apex of hexagon</td>
<td>Pseudo hexagonal</td>
<td>LRO</td>
<td>LRO</td>
<td>QLRO</td>
</tr>
<tr>
<td>SmF</td>
<td>Tilt to side of hexagon</td>
<td>Pseudo hexagonal</td>
<td>LRO</td>
<td>LRO</td>
<td>QLRO</td>
</tr>
<tr>
<td>B</td>
<td>Orthogonal</td>
<td>Hexagonal</td>
<td>LRO</td>
<td>LRO</td>
<td>LRO</td>
</tr>
<tr>
<td>J</td>
<td>Tilt to apex of hexagon</td>
<td>Pseudo hexagonal</td>
<td>LRO</td>
<td>LRO</td>
<td>LRO</td>
</tr>
<tr>
<td>G</td>
<td>Tilt to side of hexagon</td>
<td>Pseudo hexagonal</td>
<td>LRO</td>
<td>LRO</td>
<td>LRO</td>
</tr>
<tr>
<td>E</td>
<td>Orthogonal</td>
<td>Orthorhombic</td>
<td>LRO</td>
<td>LRO</td>
<td>LRO</td>
</tr>
<tr>
<td>K</td>
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<td>Monoclinic</td>
<td>LRO</td>
<td>LRO</td>
<td>LRO</td>
</tr>
<tr>
<td>H</td>
<td>Tilted to shorter side of cell</td>
<td>Monoclinic</td>
<td>LRO</td>
<td>LRO</td>
<td>LRO</td>
</tr>
</tbody>
</table>
Twisted grain boundary phases (TGB) have been known since 1988 [61-63] and have attracted great attention during the last 10 years. Chiral liquid crystals have tendency to form a cholesteric-like helical director field. On the other hand, the molecular interaction may favour a smectic layer structure. However it is impossible to realize a continuous structure which exhibits both a cholesteric director field and a smectic layer structure at the same time. The competition between these two structural features can result in frustrated structures containing a regular lattice of grain boundaries which in turn consist of a lattice of screw dislocations. This defected structure exhibits an interesting theoretical analogy to the flux line lattice which occurs in the type 2 superconductors. However the range of parameters determining the structure is larger in liquid crystals than in superconductors. Thus a large variety of new phases, such as the TGB$_A$, TGB$_C$, TGB$_{2q}$, melted grain boundary (MGB) phases [61-
63], antiferroelectric crystals of twist grain boundaries, and smectic blue phases have been predicted and/or experimentally observed.

Figure 1.16 (a) Structure of a phase which shows a local smectic order and a helical director field at the same time (b) Structure of the TGBA phase proposed by Renn and Lubensky. In addition to the structural features displayed in (a), the grain boundaries and the screw dislocations are shown. Characteristic lengths: $d =$ smectic layer spacing, $lb =$ thickness of the smectic slabs, $ld =$ distance between neighbouring screw dislocations, and $p =$ pitch of the director field [55-56].
Twist grain boundary (TGB) phases usually appear in the temperature range between the cholesterics N* phases with short pitch and a smectic phase, typically a SmA or SmC*. One of their remarkable properties is the selective reflection of circularly polarized light. This feature shows that the director field has a helical structure similar to the cholesteric phase. On the other hand X-ray investigations of TGB phases indicate a layer structure as occurring in smectic phases. Chirality of the system is an essential precondition for the occurrence of TGB phases. The table 1.1 shows some chemical compounds showing twist grain boundary (TGB) phases [61-63]:

<table>
<thead>
<tr>
<th>No.</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a)</td>
<td><img src="image" alt="Chemical Structure" /> e. g. m=6, n=14 (14P1M7): SmC* 89.7°C TGBA 93.8°C I</td>
</tr>
<tr>
<td>1b)</td>
<td><img src="image" alt="Chemical Structure" /> a = H, b = F, m = 6, n = 14: Cr 48.9°C SmC* 72.6°C SmA 80.8°C TGBA 85.8°C I</td>
</tr>
</tbody>
</table>

Table 1.1 shows chemical compounds showing twist grain boundary (TGB) phases.

The other common examples of frustrated phase are the so called BLUE PHASES [1-2]. There are generally three types of blue phases BPI, BPII and BPIII. These are exhibited by materials that are highly chiral and occur at a temperature above a chiral nematic phase and exist for only a few °C before the material clears to the isotropic liquid. As shown before, the chiral nematic phase has a helical, twisted structure and the structure of the blue phase is similar except that a double twist exists. The axes of the
two twists or helices shown are perpendicular, but in reality twist axes exist in all directions in the plane containing the two twist axes [15].

Blue phases are so called because when first discovered they appeared blue when viewed by eye as thin films. However the blue phases of many compounds exhibit other colors such as red and green when viewed by optical polarizing microscope.

### 1.5.3.3.8 The Chiral Line Liquid

The chiral line liquid NL* predicted by Kamien and Lubensky [64] is the analog of the flux line liquid occurring in type 2 superconductors with strong fluctuations. Instead of forming a regular array, the defects are rather disordered. However the precise structure of the NL* are still unknown [64].

### 1.5.3.3.9 Bend Grain Boundary (BGB) Phases

Eleven years were necessary to recognize that the mixed state predicted by de Gennes [65] cannot only be induced by mechanical deformation of the director field, but can even occur spontaneously due to the presence of the chiral Molecules. The experimental evidence for the occurrence of the mixed state in the form of TGB phases has initiated a revival of the search for regular defect structures in nonchiral materials due to mechanical forces [65-67].

![Diagram of molecules with bent molecular core](image)

*Figure 1.17 Molecules with a bent molecular core are expected to show a high flexoelectric coefficient. Thus, an electric field-induced bend deformation may be suitable to generate a lattice of edge dislocation, thereby leading to a bend grain boundary phase.*
1.5.3.3.10 Reentrant Phases Of Polar Liquid Crystals

In condensed matter physics phenomenon of <<reentrance>> of more ordered phases from less ordered phases by cooling or compressing can generally be argued to occur from competition of tendencies towards different orderings. Recently a molecular theory has been developed which exemplifies the potentialities of a microscopic approach in accounting for the observations of multiply re-entrant nematic and smectic phases in polar liquid crystals. The thermodynamic phases and phase transitions in these systems are very sensitive to details of the molecular structure. In some liquid crystals of molecules with strongly dipolar heads (-CN or –NO₂) nematic phases (orientational order) and smectic phases (smectic phase and partial positional order) reenter. Experimentally observed reentrances typically involve nematic (N), monolayer smectic A(A₁), and interdigitated partial bilayer smectic A(A₂) phases. The reentrance sequence include <<single reentrances>> (N-A₂-N), <<double reentrances>> (N-A₂-N-A₂-N-A₁), and <<reentrance below A₁>>(N-A₁-N-A₂(-A₁)). On the theoretical side all of these reentrances have been obtained with the spin gas model of liquid crystals [66-67].

1.6 Applications Of Liquid Crystal

Liquid crystals have found wide commercial application over the last 25–30 years in the electro-optical flat panel display (FPD) devices for consumer audiovisual and office equipment, such as watches, clocks, stereos, calculators, portable telephones, personal organizers, notebooks, and laptop computers. There are many other applications for liquid crystal displays (LCDs), such as information displays in technical instruments and in vehicle clocks, speedometers, navigation and positional aids [4]. They are also used in low-volume, niche products, such as spatial light modulators and generally as very fast light shutters. More importantly, they have come to dominate the displays market in portable instruments due to their slim shape, low weight, low-voltage operation, and low power consumption. LCDs are now starting to
win market shares from cathode ray tubes (CRTs) in the computer monitor market. The market share of LCDs in the total market for displays is expected to significantly increase over the next decade. There are a number of existing competing FPD technologies, such as plasma displays (PDs), vacuum fluorescence displays (VFDs), inorganic light-emitting diodes (LEDs), and micro mirrors (MM). However, these have relatively small shares of the overall displays market.

1.6.1 Applications Of Thermotropic Liquid Crystal

A strange form of matter which piqued the curiosity of scientists at the end of the last century has grown into an enormous industry with a great variety of application and is still growing. The need for liquid crystal application grew, requiring engineers specialized in this field [1, 2]. Statistics shows that cathode ray tube displays in TVs and computer monitors will be over taken by liquid crystal displays in the near future. Since liquid crystals are very sensitive to even weak external perturbations they are used in measurement of temperature, pressure and chemical contamination. Thermotropic chiral liquid crystals whose pitch varies strongly with temperature can be used as crude thermometers, since the colour of the material will change as the pitch is changed. Liquid crystal colour transitions are used on many aquarium and pool thermometers. Other liquid crystal materials change colour when stretched or stressed. Thus, liquid crystal sheets are often used in industry to look for hot spots, map heat flow, measure stress distribution patterns, and so on [1-2]. Liquid crystal in fluid form is used to detect electrically generated hot spots for failure analysis in the semiconductor industry. The helical pitch of cholesteric liquid crystals is highly sensitive to temperature and hence a slight change in temperature changes colour of the sample. Thus cholesteric liquid crystals have got interesting sensing applications. One of these is the so called thermal mapping of components of electronic devices. The use of cholesteric liquid crystals as an investigative and diagnostic tool in medicine has become widespread. For example skin infections and skin tumors may be detected and located by the use of the devices made by cholesteric liquid crystals. It is possible due
to the fact that the portion of the infected skin or tumor has higher temperature than the surrounding uninfected area.

1.6.1 Displays

Liquid crystal display devices have been typically used because they consume low power and provide a high picture quality. Liquid crystal technology has a major effect in many areas of science and engineering, as well as device technology. A liquid crystal display device is formed by attaching a thin film transistor array substrate and a colour filter substrate face to face with a uniform interval between them and placing a liquid crystal layer between the thin film transistor array substrate and the colour filter substrate. Of course display applications are not only the possible applications of liquid crystals. Researchers investigated more exotic and new applications of liquid crystals [6-18]. Uses of the non-linear properties of liquid crystal mediums (the material parameters are not only direction depended, but also depend on the intensity of the entering light and the wavelength) have generated a lot of novel applications.

1.6.2 Solitary Wave Propagation in Liquid Crystal

A high intensity laser beam injected in a liquid crystal can produce a local reorientation of the director molecules. In this way the light produces it's own waveguide and the laser light will not diffract but stays confined in a narrow beam [15, 18, 61-67]. The soliton application can lead to an addressable liquid crystal waveguide to switch light between several optical fibers shown in figure 1.19.
1.6.1.3 Hollow Liquid Crystal Fibres

Hollow optical fibers have already proved their use. If we fill them with liquid crystals they can give interesting controllable behaviour to the optical fibers. An application of polymer liquid crystals (figure 1.20) that has been successfully developed for industry is the area of high strength fibers. Kevlar, which is used to make such things as helmets and bullet-proof vests, is just one example of the use of polymer liquid crystals in applications calling for strong, light weight materials.

Ordinary polymers have never been able to demonstrate the stiffness necessary to compete against traditional materials like steel. It has been observed that polymers with long straight chains are significantly stronger than their tangled counterparts. Main chain liquid crystal polymers are well-suited to ordering processes. For example, the polymer can be oriented in the desired liquid crystal phase and then quenched to create
a highly ordered, strong solid. As these technologies continue to develop, an increasing variety of new materials with strong and light-weight properties will become available.

1.6.14 Liquid Crystal Solar Cell

A new and promising application using liquid crystals is the liquid crystal semiconductor. Liquid crystals are organic molecules similar to polymers. In polymers containing conjugated systems (alternating single and double bond) the creation of a higher and lower pi-bond leads to the creation of a band gap similar to semiconductors.

![Liquid Crystal Solar Cell](image1.png)  ![Liquid Crystal Shutters](image2.png)

*Figure 1.21 (a) Liquid Crystal Solar Cell (b) Liquid Crystal Shutters.*

The use of such a liquid crystal in a device similar to the Grätzel cell can lead to new types of solar cells (figure 1.21).

1.6.15 Optical Imaging

In this technology, a liquid crystal cell is placed between two layers of photoconductor. Light is applied to the photoconductor, which increases the material’s conductivity. This causes an electric field to develop in the liquid crystal corresponding to the intensity of light. The electric pattern can be transmitted by an electrode, which enables the image to be recorded. This technology is still being developed. The other potential optical applications of liquid crystals are as follows

(A) Light Shutters
16.2 Applications And Importance Of Lyotropic Liquid Crystal

One material that demonstrates lyotropic liquid crystalline behavior is simple household soap. Soaps work better than pure water in removing dirt and grease because the nonpolar insides of the micelles are capable of dissolving nonpolar substances that will not dissolve in water (This also works in reverse if the solvent is nonpolar and some of the substance to be removed is polar). Soaps also help water dissolve more because the molecules tend to remain at the surface, hydrocarbon tail away from the water, thus lowering the surface tension of the water and allowing more material to enter it and be dissolved. Other diverse applications exist for amphiphilic molecules. Because of their ability to dissolve both polar and nonpolar substances, a mixture of water and an amphiphilic compound can be pumped into a depleted oil well in order to remove much of the residual oil. In the medical professions, a lyotropic liquid crystal can coat a drug to keep it from being destroyed in the digestive tract [1]. The drug can then be taken orally, and after it reaches the proper location in the body, the liquid crystal breaks down and the drug is released.

Lyotropic liquid crystals have been used to make stable hydrocarbon foam [2]. Hydrocarbon foams have been difficult to produce in the past because the surface tension of the hydrocarbon is low enough that adsorption to an oil-soluble surfactant would have no significant effect. Without the adsorption, the hydrocarbon simply behaves as a liquid. When lyotropic liquid crystal molecules change from inverse micelles to lamellar sheets, they lower the surface tension enough for foam to form. The hydrocarbon and the surfactant can dissolve in each other, and the surfactant cannot dissolve in water, although water can dissolve in the surfactant and mix into the liquid crystal. Many other substances are also more soluble in lyotropic liquid crystals. One example is the drug hydrocortizone. It is often taken in topical applications, but its uses have been limited because the highest concentration possible has been only 1%. When the drug was blended into a liquid crystal of lecithin and water, the concentration went
up to 4%. In time, liquid crystals may become a primary solvent for topical medications. The outermost layer of skin is primarily a lyotropic liquid crystal made of fatty acids. At least some of the fatty acids must be unsaturated because saturated chains will simply crystallize rather than forming a liquid crystal structure. Experiments with crystals made only from saturated fatty acids produced layers that did not prevent water transport across them. This is a symptom that sometimes occurs in people whose diets are deficient in essential fatty acids of the sort found in unsaturated fats [1-3].
References

[38] Srivastava, A.K. A Ph. D thesis, Department of Physics, University of Allahabad, India, 2005.
[65] de Gennes, P.G. Solid state communication 1972, 10, 753.
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2.1 Basic Properties of Liquid Crystal

Investigations on the structure and physical properties of liquid crystals have greatly increased in the last decades and are now an integral part of solid state physics. Certain organic materials do not show a single transition from solid to liquid, but rather a cascade of transitions involving new phases. The mechanical properties and the symmetry properties of these phases are intermediate between those of a liquid and those of a crystal [1-5]. Depending upon the nature of the building blocks and upon external parameters (temperature, solvents, etc.) a wide variety of phenomena and transitions amongst liquid crystals are observed some of them are discussed below.

2.1.1 Order Parameter

Liquid crystalline mesophases have different sort of orientational and positional order. To describe the different degree of molecular order in different liquid crystals mesophases, in 1942 Tsvetkov had introduced a concept of order parameter [1]. The average direction of liquid crystal molecules is called the director axis [2]. The amount of orientational order in liquid crystals can be obtained by averaging macroscopic molecular orientation with respect to this direction.

![Diagram of Nematic Director](image)

**Figure 2.1 The Nematic Director making an angle with the long molecular axis of the molecule.**

In contrast, we cannot observe any intrinsic order in the liquid phase. The degree of the order in a liquid crystal is denoted by the orientational order parameter (S), as given by the equation below. Typical values for the order parameter of a liquid...
crystal range between 0.3 and 0.9, with the exact value a function of temperature, as a result of kinetic molecular motion.

![Diagram](image)

**Figure 2.2** The distribution function $f(\theta)$ for a system of rod-like molecules in the nematic phase, $f(\theta)$ is large around $\theta = 0, \pi$ and is small for $\theta = \pi/2$.

\[
S = \frac{\int f(\theta) \left( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) d\Omega}{\int f(\theta) d\Omega} = \frac{3}{2} \langle \cos^2 \theta \rangle - \frac{1}{2} \tag{2.1}
\]

Here $\theta$ is the angle between the long axis of each molecule and director. For an isotropic liquid, the order parameter is zero, as we expected, in contrast to isotropic liquids, order parameter is one in a perfect crystal. The orientational order parameter is typically a function of temperature. Figure 1.1 (from previous chapter) represents the relationship between temperature and order parameter. In this figure $T_{NI}$ is the temperature of transition between the crystals - liquid states. The order parameter can be measured experimentally by using several types of experimental technique, for
example, nuclear magnetic resonance (NMR), optical birefringence and Raman scattering experiments. With the help of order parameter different phases can be characterized easily (figure 2.1).

2.1.2 Uniaxial Versus Biaxial Media

The uniaxial media is the media with a single director and a single order parameter have been considered. However, liquid crystals may be biaxial - described by two mutually orthogonal directors, \( \mathbf{n} \) and \( \mathbf{m} \), and two order parameters, \( S_1 \) and \( S_2 \). The molecules themselves might be biaxial - book-shaped, rather than rod-shaped, or a mixture of rod- and disc- shaped particles. Even if the molecules are uniaxial, they can form biaxial arrangements [3].

2.1.3 Curvature Elasticity

The basic difference between deformations in a liquid crystal and in a solid is that in liquid crystals, there is no translational displacement of molecules on distortion of a sample. This is due to slippage between liquid layers. A purely shear deformation of a liquid crystal conserves elastic energy [4, 5]. The elasticity of an isotropic liquid is related to changes in density. In liquid crystals, variations in density can also be characterized by a suitable modulus, but the elasticity that is related to the local variation in the orientation of the director is their principal characteristic. In the description of elasticity of a (nematic) liquid crystal, the following assumptions are made:

a) Director \( \mathbf{n} \) reorients smoothly compared to the molecular dimension of a liquid crystal. Thus, we may conclude that the order parameter \( S \) remains constant throughout the whole volume of a liquid crystal at a fixed temperature \( T \), while only director field varies in accordance with external electric (or some other) fields.

b) The only curvature strains of the director field, which must be considered, correspond to the splay, bend, and twist distortions figure 2.3. Other types of deformation either do not change the elastic energy (e.g., above-mentioned pure shears) or are forbidden due to the symmetry [6]. In nematic liquid crystals, the
cylindrical symmetry of the structure as well as the absence of polarity (head to tail symmetry) must be taken into account.

c) Following the Hooke’s law, only squares of the director deformations are included into the expression for the free energy [7].

Figure 2.3 Basic types of liquid crystal deformations: (a) S deformation (splay), (b) B deformation (bend), and (c) T deformation (twist).

In the case of nematic liquid crystal possesses curvature elasticity. In a uniformly orientated, mono-domain sample of nematic liquid crystal, the director \( \mathbf{n} \) is in the same direction throughout the medium. When a distortion is induced in \( \mathbf{n} = \mathbf{n}(r) \) and the derivatives of \( \mathbf{n} \) exist, an elastic restoring torque comes into play tending to restore \( \mathbf{n} \) to the undistorted state. Any deformation is a combination of three basic curvature deformations, as described before. The deformation free energy density is defined as,

\[
F_d = \frac{1}{2} K_{11} [\nabla \cdot \mathbf{n}]^2 + \frac{1}{2} K_{22} [\mathbf{n} \cdot \nabla \times \mathbf{n}]^2 + \frac{1}{2} K_{33} [\mathbf{n} \times \nabla \times \mathbf{n}]^2 \quad (2.2)
\]
Where $K_{11}, K_{22}$ and $K_{33}$ are the splay, twist and bend elastic constants respectively. The constants are positive and usually $K_{33} > K_{11} > K_{22}$. The typical magnitudes of these constants are $\sim 10^{-12}$ Newton.

The theory of elasticity in smectic liquid crystals has its own features. Deformations related to a change in the spacing between the layers are common to all smectic phases. The deformations are, in general, not related to a change in director orientation, and here an additional modulus of elasticity $B$ occurs. In smectic A liquid crystals, the only allowed deformation is specific undulation of the smectic layers, such that interlayer distance is kept constant and director remains normal to the layer. There are a number of experimental data on elastic moduli of liquid crystals, which are only qualitatively explained. The existing molecular approaches do not directly correspond to the real situation because molecules are considered to be spherocylinders or hard rods, far from the reality [6-10]. The methods of the measurements of the liquid crystal elastic moduli are various and so we constraint ourselves hereby and not going into much detail.

### 2.1.4 Flexoelectricity

The nematic medium does not exhibit spontaneous polarization due to the apolar nature of the director. A macroscopic polarization can be induced in a nematic liquid crystal by splay and bend distortions of the director field. This was first shown by Meyer in 1969 [11]. The flexoelectric polarization is given by,

$$
P = e_{11} (\nabla \cdot n) n + e_{33} (\nabla \times n) \times n$$

(2.3)

Where $e_{11}$ and $e_{33}$ are the two flexoelectric coefficients corresponding to splay and bend distortions respectively. According to Meyer’s model [11-14] only nematics made of polar molecules with shape anisotropy can be expected to exhibit flexoelectricity.
For example, a nematic consisting of pear shaped molecules with longitudinal dipole moments become polarized under splay distortion (see figure 2.4) and a nematic made of banana shaped molecules with transverse dipole moments becomes polarized under bend distortion (see figure 2.5). In the undistorted state, the dipole moments of the molecules are oriented with equal probability in opposite directions. They cancel each other and the net dipole density is zero.

**Figure 2.4** A nematic consisting of pear-shaped molecules with longitudinal dipole moments becomes polarized under splay deformation

**Figure 2.5** A nematic consisting of banana-shaped molecules with transverse dipole moments becomes polarized under bend deformation.
Another microscopic model was developed by Prost and Marcerou [11-17] in which the flexoelectric effect arises due to quadrupolar moments of the molecules. The splay deformation develops a net dipole moment and the medium gets polarized. The quadrupolar contribution to flexoelectric effect is of the same magnitude as due to dipolar contribution. The quadrupolar contribution is independent of the shape of the molecules. Since all nematic molecules have finite quadrupole moments, flexoelectric effect is an universal property of nematics.

### 2.1.5 Dielectric Constants

Dielectric constant is a measure of the response of the given material to an external electric field. It depends on the intrinsic properties of the material like distribution of the charges in the molecules and also intermolecular interactions. The dielectric constant changes with the temperature and the frequency of the applied electric field. In a medium with polar molecules in addition to the induced polarization an orientational polarization occurs due to the tendency of the permanent dipole moments to orient parallel to the electric field [18-22]. The orientational polarization in liquid crystals has a major contribution to the dielectric constants. But in a solid crystal the orientational polarization does not contribute significantly to the permittivity due to the fixed orientations of the molecules. In liquid crystals, \( \varepsilon_H \) and \( \varepsilon_\perp \) represent the dielectric constants measured with an electric field parallel and perpendicular to the director \( \mathbf{n} \) respectively. The dielectric anisotropy is the difference of parallel and perpendicular dielectric constants i.e. \( \Delta \varepsilon = \varepsilon_H - \varepsilon_\perp \). The sign of \( \Delta \varepsilon \) depends upon the permanent dipole moments of the molecules. It is positive, if the component of the net dipole moment of the molecule along the long axis is larger than that along the transverse axis and vice versa.
Figure 2.6 Schematic illustration of positive and negative dielectric anisotropy

Using Maier and Meier’s theory the expressions of two dielectric constants [11] can be written:

\[
\varepsilon_\parallel = 1 + 4\pi \frac{N_A \rho h F}{M} \left[ \tilde{\alpha} + \frac{2}{3} \Delta \alpha_0 S + \frac{F \mu^2}{3k_BT} \left\{ 1 - (1 - 3\cos^2 \beta)S \right\} \right] \quad (2.4)
\]

\[
\varepsilon_\perp = 1 + 4\pi \frac{N_A \rho h F}{M} \left[ \tilde{\alpha} - \frac{1}{3} \Delta \alpha_0 S + \frac{F \mu^2}{3k_BT} \left\{ 1 + \frac{1}{2}(1 - 3\cos^2 \beta)S \right\} \right] \quad (2.5)
\]

where \(\Delta \alpha_0\) is the polarizability anisotropy of a perfectly oriented medium, \(N_A\) is the Avogadro number, \(\rho\) the density, \(M\) the molecular weight, \(h = \frac{3\pi}{2(2\pi + 1)}\), is the cavity field factor and \(F = 1/(1 - f \tilde{\alpha})\) where, \(f = (\tilde{\varepsilon} - 1)/[2\pi a^3 (2\tilde{\varepsilon} + 1)]\) is the reaction field factor for a spherical cavity and \(\alpha\) is the average polarizability and \(\beta\) is the angle between permanent dipole moment \(\mu\) and the long axis of the molecule. The average dielectric constant and dielectric anisotropy can be obtained from Equation (2.4) and Equation (2.5) as,

\[
\bar{\varepsilon} = \frac{\varepsilon_\parallel + 2\varepsilon_\perp}{3} = 1 + 4\pi \frac{N_A \rho h F}{M} \left[ \tilde{\alpha} + \frac{F \mu^2}{3k_BT} \right] \quad \text{and} \quad (2.6)
\]
\[ \Delta \varepsilon = (\varepsilon_{||} - \varepsilon_{\perp}) = 4\pi \frac{N_A \rho F}{M} \left[ \Delta \alpha_0 - \frac{F \mu^2}{2k_B T} (1 - 3 \cos^2 \beta) \right] S \quad (2.7) \]

The relative magnitudes of the two terms within the square brackets of Equation (2.7) determine the sign of \( \Delta \varepsilon \). When \( \beta < 54.7^0 \), the two terms add up and the compound exhibits positive dielectric anisotropy. For \( \beta \approx 54.7^0 \), the second term vanishes and only \( \Delta \alpha_0 \) contributes to \( \Delta \varepsilon \). For \( \beta > 54.7^0 \), \( \Delta \varepsilon > 0 \) or <0 depending on whether the dipolar contribution is less or more than the contribution due to polarizability anisotropy. The dielectric displacement \( \mathbf{D} \) induced in a nematic liquid crystal by an electric field \( \mathbf{E} \) is given by,

\[ \mathbf{D} = \epsilon_0 \epsilon_{\perp} \mathbf{E} + \epsilon_0 \Delta \varepsilon (\mathbf{n} \cdot \mathbf{E}) \mathbf{n} \quad (2.8) \]

and the dielectric energy density of a nematic is given by,

\[ W_{\text{die}} = -\int_0^E \mathbf{D} \cdot d\mathbf{E} = -\frac{1}{2} \epsilon_0 \epsilon_{\perp} \mathbf{E}^2 - \frac{1}{2} \epsilon_0 \Delta \varepsilon (\mathbf{n} \cdot \mathbf{E})^2 \quad (2.9) \]

It is clear that the dielectric energy is lowered by an alignment of \( \mathbf{n} \) with respect to \( \mathbf{E} \), which depends on the sign of \( \Delta \varepsilon \).

### 2.1.6 Electrical Conductivity

The origin of electrical conductivity in liquid crystals is the mobility of the residual ionic impurities under the application of an electric field. The conductivity is usually of the order of \( 10^{-11} \) /m. The conductivity anisotropy is given by,

\[ \Delta \sigma = \sigma_{||} - \sigma_{\perp} \quad (2.10) \]

where \( \sigma_{||} \) and \( \sigma_{\perp} \) are the principal components of conductivity parallel and perpendicular to \( \mathbf{n} \) respectively. The sign of \( \Delta \sigma \) depends on the direction along which the ions can flow easily. Usually for nematics \( \Delta \sigma \) is positive as the ions can move more freely along \( \mathbf{n} \) than perpendicular to it. In smectics usually \( \Delta \sigma \) is negative as it is easier for the ions to flow in the layers than perpendicular to the layers. In usual liquid
crystals, the ionic effects can be usually ignored for frequencies $\geq 1$ kHz of the applied electric field.

### 2.1.7 Polarizability Anisotropy and Birefringence

The order parameter can be directly related to a few experimentally determined quantities viz diamagnetic anisotropy, dielectric anisotropy, birefringence etc. Let us choose a space-fixed coordinate system $xyz$ with $z$ parallel to $\mathbf{n}$.

![Diagram of principal components of polarizabilities of the molecule.](image)

**Figure 2.7 Schematic representation of the principal components of the polarizabilities of the molecule.**

If $\alpha_l$ and $\alpha_s$ are the principal polarizabilities of the molecule along its long and short axes, the average $z$ component of the polarizability in the nematic phase can be written as,

$$\alpha_z = \alpha_l \langle \cos^2 \theta \rangle + \alpha_s \langle \sin^2 \theta \rangle$$  \hspace{1cm} (2.11)

Using equations (2.1) and (2.11) we get,

$$\alpha_z = \left( \frac{\alpha}{3} + \frac{2}{3} \Delta \alpha_0 S \right)$$  \hspace{1cm} (2.12)
It can be shown that,

\[
\alpha_x = \alpha_y = \left(\frac{\alpha}{3} - \frac{1}{3} \Delta \alpha_0 S\right)
\]  

(2.13)

where \( \alpha = (\alpha_l + 2\alpha_t)/3 \), and \( \Delta \alpha_0 = (\alpha_l - \alpha_t) \), is the polarizability anisotropy of a perfectly aligned medium. The absolute value of the order parameter is expressed as,

\[
S = \frac{(\alpha_z - \alpha_x)}{(\alpha_l - \alpha_t)} = \frac{\Delta \alpha}{\Delta \alpha_0}
\]  

(2.14)

Refractive index is the property of a material that determines the relative speed of light in the material.

![Figure 2.8 Sketch of the anisotropy in the refractive indices for a uniaxial liquid crystal.](image)

In the case of uniaxial nematic liquid crystals the direction of optic axis is along the director \( \mathbf{n} \). The uniaxial nematic phase has two principal refractive indices called \( n_e \) and \( n_o \). \( n_e \) is the extraordinary refractive index for a light wave propagating with electric vector parallel to \( \mathbf{n} \). \( n_o \) is the ordinary refractive index for a light wave propagating with electric vector perpendicular to \( \mathbf{n} \). The birefringence is given by,

\[
\Delta n = n_e - n_o
\]  

(2.15)
\( \Delta n \) can be used to calculate the approximate orientational order parameter \( S \) of nematic liquid crystals using the relation,

\[
S \approx \frac{\Delta n}{\Delta n_o}
\]  

(2.16)

where \( \Delta n_o \) is the birefringence of the medium in the fully aligned state. The exact relationship between the principal polarizabilities \( \alpha_e \) and \( \alpha_o \) and the refractive indices \( n_e \) and \( n_o \) is not known in strongly anisotropic media like liquid crystals. In the Vuks approach, the local field is considered to be isotropic and the Lorentz-Lorentz formula works fairly well for the average polarizability of strongly anisotropic organic molecules. The relation is given by,

\[
\frac{\bar{n}^2 - 1}{\bar{n}^2 - 2} = \frac{4\pi}{3} \nu \bar{\alpha}
\]  

(2.17)

where \( \nu \) is the number of molecules/cc and,

\[
\bar{n}^2 = \frac{n_x^2 + n_y^2 + n_z^2}{3}
\]  

\[
\bar{\alpha} = \frac{\alpha_x + \alpha_y + \alpha_z}{3}
\]

Here, \( n_x \), \( n_y \) and \( n_z \) are the principal refractive indices of the crystal and \( \alpha_x \), \( \alpha_y \) and \( \alpha_z \) are the corresponding principal polarizabilities. In the isotropic medium, the polarization \( \vec{P} \) is given by,

\[
\vec{P} = \frac{n^2 - 1}{4\pi} \vec{E}
\]  

(2.18)

where \( \vec{E} \) is the applied electric field.

Also,

\[
\vec{P} = \alpha \nu \vec{F} = \alpha \nu \frac{n^2 + 2}{3} \vec{E}
\]  

(2.19)
\[ \bar{F} = \frac{n^2 + 2}{3} \bar{E}^3 \]

Where, \( \bar{F} \) is an internal field.

For an anisotropic medium,

\[ P_i = \frac{(n^2_{ik} - \delta_{ik})}{4\pi} E_k \quad i, k = x, y, z \] (2.20)

Assuming that the internal field is isotropic, we can write,

\[ P_i = \frac{\nu}{3} (n^2 + 2) \alpha_{ik} E_k \] (2.21)

From these equations we get,

\[ \frac{n^2_{i} - 1}{n^2 + 2} = \frac{4\pi}{3} \nu \alpha_i \] (2.22)

which is the Vuks formula. Equation (2.17) follows from Equation (2.22). From Equations (2.14), (2.17) and (2.22) we get,

\[ S = \frac{\Delta \alpha}{\Delta \alpha_0} = \frac{\bar{\alpha}}{\Delta \alpha_0} \frac{n^2_e - n^2_o}{n^2 - 1} \] (2.23)

### 2.18 Anchoring Energy

Surface effects (e.g., anchoring) for a long time was considered as a side topic of liquid crystals, but with the increasing importance of weak anchoring it entered in the spotlights in the past few years. Now days, many of the mechanisms are being studied and it is a main challenge for chemists to develop new materials with specific anchoring properties. In classic liquid crystal devices such as displays strong anchoring is used, which implies that the surface director is fixed. The anchoring of the liquid crystal molecules at the surface is intended to control the alignment of the surface director.
Therefore it is an important aspect while designing liquid crystal devices. Different alignment materials have been compared on their anchoring properties with as ultimate goal finding a surface material in which the azimuthal anchoring, the anchoring strength related to changes of the director twist angle at the surface, is reduced to a minimum. Numerous potential applications of liquid crystals allow researchers to study different aspects of their basic properties particularly surface anchoring effect, which forces near surface molecules to align molecules in bulk in different modes. Thus interfacial interaction between the liquid crystal molecules and substrate surface is an important phenomenon. The liquid crystal with lesser anchoring energy (i.e. the energy of the molecules and surface interaction) will be better for display due to the need of laser electric field for anchoring the molecules. Classic alignment layers hold the liquid crystal director at their surface tightly in a fixed orientation. This is referred to as strong anchoring and is widely used in lots of liquid crystal applications. The nature of the anchoring process is the anisotropy of the surface in contact with the liquid crystal. The origin of this anisotropy can be very different. Some surfaces like crystalline solids or polymers have an inherent anisotropy, which results in molecular interaction between the liquid crystal and the surface. Alignment layers are manufactured by a large variety of processes rubbing, photoalignment structured surfaces surfactants. For a rubbed surface, the azimuth and pretilt of the surface director are determined by the rubbing parameters. For other
processes like photo-alignment, the orientation of the surface director is not so strict. With a strong electric field or a torque on the liquid crystal director, the surface director can turn away from the preferential direction; therefore, the principle of weak anchoring is introduced.

Weak anchoring is a generic term for all situations where the surface director can be altered. Such surfaces exhibit one or more stable orientations of the surface director, but electric or mechanical torques can change the orientation of the surface director. In practice different surface conditions are possible:

A. Monostable surfaces: a single stable orientation of the surface director.
B. Bistable or multistable surfaces: two or more stable orientations of the surface director.
C. Degenerated anchoring surfaces: the director prefers to be oriented in a certain plane or on a cone.
D. Surface gliding: By application of a strong temporary electric field and/or heating of the liquid crystal cell, the stable direction of the surface director can be modified permanently.

At such a surface, also referred to as a slippery surface, the director has a preference to lie in the plane parallel to the substrate, but can rotate freely in the azimuthal direction. The applications of weak anchoring are situated in the field of multistable nematic liquid crystal devices, electrically controllable anchoring and reduction of the threshold voltage and power consumption of liquid crystal devices. The behavior of the surface anchoring is determined by the surface material, treatment or structure. The applications of weak anchoring are situated in the field of multistable nematic liquid crystal devices, electrically controllable anchoring and reduction of the threshold voltage and power consumption of liquid crystal devices [23-28]. The behavior of the surface anchoring is determined by the surface material, treatment or structure. The anchoring strength is presumed strong, medium or weak, as shown in figure 2.10.
Therefore we can say that, The description of how strongly the director is aligned on the boundary surface is called anchoring. The anchoring energy measures the strength of anchoring of the director along a well defined direction, called as easy axis at the surface. The simplest surface energy density is of a form first proposed by Rapini and Papoular [29], and can be written as,

$$W_s(\theta) = \frac{1}{2} W_\theta \sin^2(\theta - \theta_0)$$  \hspace{1cm} \text{(2.24)}$$

where $\theta$ and $\theta_0$ are polar angles made by the director $\mathbf{n}$ and the easy axis with the surface normal respectively. $W_\theta$ is the anchoring energy for tilt orientation of the director.

2.19 Freedericksz Transition

The competition between orientation produced by surface anchoring and by electric field effects is often exploited in liquid crystal devices. Consider the case in which liquid crystal molecules are aligned parallel to the surface and an electric
field is applied perpendicular to the cell. At first, as the electric field increases in magnitude, no change in alignment occurs. However at a threshold magnitude of electric field, deformation occurs. Deformation occurs where the director changes its orientation from one molecule to the next. The occurrence of such a change from an aligned to a deformed state is called a Freedericksz transition and can also be produced by the application of a magnetic field of sufficient strength. The Freedericksz transition is fundamental to the operation of many liquid crystal displays because the director orientation (and thus the properties) can be controlled easily by the application of a field.

Another important example of the electro-optic effect, fundamental to the operation of many liquid crystal displays, is the Freedericksz transition. It is an electric-field induced transition in nematic liquid crystals oriented homogeneously between two glass plates, from an unperturbed to a non-uniformly deformed state. In the unperturbed state, which is maintained as long as the electric field $\vec{E}$ is below a threshold value $E_{th}$, the director (and the optic axis) is uniformly oriented parallel to the glass plate figure 2.11. If the sample is kept between two crossed polarizers and the optic axis is rotated by $45^\circ$ with respect to one of the polarizers, below the threshold voltage the light will pass through the sample. When the dielectric anisotropy of the molecules is positive, if an electric field is applied perpendicular to the glass plate, the molecules try to align along the field direction. In the deformed state which results, many molecules become perpendicular to the glass plate and the intensity falls down. Thus, depending on the off and on state of the applied field we can get on and off states in the transmitted intensity [30, 31]. The threshold field arises due to the competition between the elastic energy cost for the deformation of the director, and the dielectric energy gained by the alignment of the liquid crystal molecules.
Figure 2.11 Influence of external electric field. At some critical Electric Field ($E_c$), the director rotates while before $E_c$ nothing happens. Here $d$ is the cell thickness and electric field $E$ is along $z$-axis.

Therefore, in case of nematic liquid crystals, competition between the effect of a wall and the effect of an external torque results in a director distribution that minimizes the free energy. The re-orienting torque arises due to a coupling between an external field and the corresponding susceptibility anisotropy. In a homogeneously (planar) aligned sample with positive $\Delta \varepsilon$, when an electric field is applied perpendicular to the director, a distortion takes place only when the strength of the applied field exceeds a certain well defined threshold value. This transition is called Freedericksz transition. The threshold voltage (independent of cell thickness) is given by,

$$V_{Th} = \pi \sqrt{\frac{K_{11}}{\varepsilon_0 \Delta \varepsilon}}$$ (2.25)

where $K_{11}$ is the splay elastic constant and $\Delta \varepsilon$ is the dielectric anisotropy of the medium. $K_{11}$ can only be measured if the sample has a positive dielectric anisotropy.

The director orientation above the threshold depends on both $K_{33}$ and $K_{11}$ and can be used to measure $K_{33}$ also.

### 2.1.10 Response Time

The response time of liquid crystal molecules depends on elastic constants of liquid crystalline system. Another liquid crystal property that is closely related to the response time is the viscosity $\nu$ and $\eta$ given by:
\[ \eta = \rho \nu \]  

(2.26)

Where \( \eta \) is the dynamic viscosity, \( \rho \) is the density and \( \nu \) is the kinematic viscosity. Liquid crystal density is typically 0.98 – 1.02 gm/cm\(^3\), same as water.

The transition time when liquid crystal materials are rotating on each of the required white/black or gray levels is called "rise time" and "fall time,.

High speed operation needs small viscosity. Few general rules are

- High polar molecules => larger \( \nu \)
- Longer Y, Z groups => larger \( \nu \)
- More benzene rings => larger \( \nu \)
- More side chains => larger \( \nu \)
- Low temperature => large \( \nu \)

Also notice that large \( \Delta n \) requires high polar molecules. So large birefringence and higher viscosity goes hand in hand. Typical \( \nu = 5-100 \text{ mm}^2/\text{s} \) at room temp. It can be larger than 5000 at low temp. The dynamics of liquid crystal molecule realignment due to external fields involves solving the Erickson-Leslie equations. The results for the H-cell and low twist TN cells are,
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\[ \tau_{on} = \frac{\eta d^2}{|\Delta e| V^2 - K_{ij} \pi^2} \]  
(2.27)

And

\[ \tau_{off} = \frac{\eta d^2}{K_{ii} \pi^2} \]  
(2.28)

The total response time is defined as  \[ \tau = \tau_{on} + \tau_{off} \]  
(2.29)

i.e. the response time depends upon the viscosity, applied electric field, dielectric anisotropy and the elastic constant. Notice that the response time is proportional to \(d^2\). Therefore very thin cells are needed for fast response time, e.g. for video applications.

Example: \(V = 100 \text{ mm}^2/\text{s}, \ \rho = 1 \text{ gm/cm}^3, \ K_{11} = 12.6 \times 10^{-12} \text{ N}, \ d = 6 \ \mu\text{m}. \)

Substitute into formula, get \(\tau_d = 30 \text{ ms}\). this is a typical number for TN. Typical response times for LCD:

- STN (super twisted nematic) 100-200 ms
- TN (twisted nematic) 10-50 ms
- H-cell (homogeneous) 2-5 ms
- B-cell (bend) 0.5 ms
- Ferroelectric 20 \(\mu\)s

The response time of ferroelectrics (FLC) is very fast than to nematics because FLC is based on a dipole force rather than a dielectric energy force, i.e. the force is first order in \(E\) rather than \(E^2\) [22-34].

### 2.1.11 Alignment of Liquid Crystals

In an unaligned liquid crystalline medium the director \(n\) varies gradually from point to point. In order to measure physical properties, the director should be aligned in a specific direction in the cell. In general the director is aligned either parallel or perpendicular to the plane of the glass substrate, called homogeneous and homeotropic alignment respectively. **Homogeneous Alignment**: A glass plate coated with a thin
layer of polyimide and rubbed in a specific direction gives rise to planar or homogeneous alignment. The rubbing on polyimide generates micro-grooves along which the long axes of the molecules get aligned.

![Schematic diagrams of the two types of alignment of the molecules.](image)

**Figure 2.13 Schematic diagrams of the two types of alignment of the molecules.**

**Homeotropic Alignment**: A glass plate coated with a surfactant which has long chain molecules like ODSE (octadecyl triethoxy silane) gives rise to a homeotropic alignment.

Detail description is given in Chapter 3.

### 2.1.12 Phase Transition

Phase transitions are ubiquitous in nature. Examples include magnets, liquid crystals, superconductors, crystals, amorphous equilibrium solids, and liquid condensation. These transitions occur between equilibrium states as functions of temperature, pressure, electric field etc.; and define the nature of the matter.

### 2.2 Theoretical Treatment of Liquid Crystalline Material

Microscopic theoretical treatment of fluid phases can become quite complicated, owing to the high material density, meaning that strong interactions, hard-core repulsions, and many-body correlations cannot be ignored. In the case of liquid crystals, anisotropy in all of these interactions further complicates analysis [2, 30-39]. There are a number of fairly simple theories, however, that can at least predict the general behavior of the phase transitions in liquid crystal systems.
2.2.1 Nematic-Isotropic Phase Transition Theories

2.2.1.1 Landau-de Gennes Theory

The Landau-de Gennes theory is a phenomenological model for the nematic-isotropic phase transition. It is based on the Landau’s general description of phase transitions and was first developed by De Gennes [30-39]. It is the theory that describes the nematic-isotropic phase transition. The strengths of this theory are its simplicity and its ability to capture the most important elements of the nematic-isotropic transition.

This theory starts with the assumption that the order parameter S is small in the nematic phase in the vicinity of the transition and thus the difference between the free energy per unit volume of the two phase’s can be expanded in power of S [30-39]. Of course a term linear in the order parameter is not allowed since this would mean that the free energy per unit volume of the nematic phase would be less than the free energy per unit volume of the isotropic phase at all temperatures.

\[ G(S,T) = \frac{3}{4} A(T)S^2 + \frac{1}{4} BS^3 + \frac{9}{16} CS^4 \]  (2.30)

The first term in the above equation drives the transition; the second term ensures asymmetry of S by breaking the S to –S invariance and the third term bounds the values of S. The parameter A (T) is most important in determining when G(S, T) is greater or less than zero, so it is given by:

\[ A(T) = A_0 (T-T^*_{NI}) \]  (2.31)

Where AO and T^*_{NI} are constant. Since the phase transition take place in the vicinity of where A (T) changes sign, T^*_{NI} locates this temperature region [30-39]. The parameter B and C are also constant. The equilibrium nematic degree of order S_{eq} is found by minimizing the free energy. The minimization gives the value as:

\[ S_{eq} = 0 \quad T > T_{NI} \]  (2.32)
\[ S_{eq} = \frac{1}{2} \left[ -\frac{B}{3C} + \left\{ \frac{B}{3C} \right\}^2 - \frac{8A_0(T - T_{NI}^*)}{3C} \right]^{1/2} \quad \text{T}<T_{NI} \quad (2.33) \]

Where \( T_{NI} \) is the Nematic-Isotropic transition temperature. The super cooling temperature \( T_{NI}' \) and superheating temperature \( T_{NI}^{**} \) are related via materials parameters as :

\[ T_{NI}' = T_{NI} + \frac{B^2}{27A_0C} \quad (2.34) \]

\[ T_{NI}^{**} = T_{NI}' + \frac{B^2}{24A_0C} \quad (2.35) \]

### 2.2.12 Maier-Saupe Theory

Maier and Saupe in a series of paper have given a microscopic model for the phase transition in a nematic liquid crystal. This statistical theory, proposed by Alfred Saupe and Wilhelm Maier, includes contributions from an attractive intermolecular potential from an induced dipole moment between adjacent liquid crystal molecules. The anisotropic attraction stabilizes parallel alignment of neighboring molecules, and the theory then considers a mean-field average of the interaction. Solved self-consistently, this theory predicts thermotropic nematic-isotropic phase transitions. [30-39]

The fundamental assumption of their theory is as follows:

The molecules are assumed not to posse’s permanent dipole moment. This means that the dominant force between the molecules is an interaction between induced dipoles. A momentary dipole moment on one molecule induces a momentary dipole moment on the neighboring molecules, resulting in an attractive dispersion force. Such force varies with distance to the minus sixth power. That’s why mean field potential \( U_i(\theta_i) \) varies as the inverse square of the volume.

It is assumed that molecules are cylindrically symmetric about their long axes. Thus the potential energy between two molecules can only depends on the
angle between their long axes with an angular dependence proportional to the second Legendre polynomial of this angle. It is assumed that the degree of orientational order of the molecules enters into the mean field potential in a linear way figure 2.14.

The mean field potential is given by-

$$U_i(\theta_i) = -\frac{A}{V^2} S \left(\frac{3}{2} \cos^2 \theta_i - \frac{1}{2}\right)$$

(2.36)

The Maier-Saupe theory predicts-

1. A first order phase transition
2. The qualitatively correct temperature dependence of $S$.

The stable mesophase is given by the solutions which minimizes the free energy, which may be calculated as -

$$F(T,S) = -\frac{1}{2} A_o S^2 + K T \ln \left(\frac{C}{4\pi}\right)$$

(2.37)

The Maier-Saupe theory predicts a first-order phase transition at a temperature $T_c$ defined by-

$$K_B T_c = 0.22 A_0$$

(2.38)

And the value of the order parameter at the transition is -

$$S_c = 0.43$$

(2.39)
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One of the theory’s shortcomings is that it predicts a universal function $S(T)$ for all materials. This does not confirm to the materials such as MBBA (methoxy benzylidene butyl aniline) and BEHA (4-butoxyphenyl ester of 4’-hexyloxybenzoic acid). Repeated corrections have been made to Maier-Saupe theory in order to improve the agreement with experiments.

2.2.1.3 Onsager Hard-Rod Model

A simple model which predicts lyotropic phase transitions (discussed later) is the hard-rod model proposed by Lars Onsager. This theory considers the volume excluded from the center-of-mass of one idealized cylinder as it approaches another. Specifically, if the cylinders are oriented parallel to one another, there is very little volume that is excluded from the center-of-mass of the approaching cylinder (it can come quite close to the other cylinder). If, however, the cylinders are at some angle to one another, then there is a large volume surrounding the cylinder which the approaching cylinder's center-of-mass cannot enter (due to the hard-rod repulsion between the two idealized objects). Thus, this angular arrangement sees a decrease in the net positional entropy of the approaching cylinder (there are fewer states available to it). The fundamental insight here is that, while parallel arrangements of anisotropic objects lead to a decrease in orientational entropy, there is an increase in...
positional entropy. Thus in some case greater positional order will be entropically favorable. This theory thus predicts that a solution of rod-shaped objects will undergo a phase transition, at sufficient concentration, into a nematic phase. Although this model is conceptually helpful, its mathematical formulation makes several assumptions that limit its applicability to real systems [30-39].

### 2.2.14 McMillan’s Model

McMillan’s model, proposed by William McMillan 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. It 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 a triple critical point where the nematic, isotropic, and smectic A phase meet. Although it predicts the existence of a triple critical point, it does not successfully predict its value. The model utilizes two order parameters that describe the orientational and positional order of the liquid crystal. The first is simply the average of the second Legendre polynomial and the second order parameter is given by:

\[ \sigma = \left\langle \cos \left( \frac{2\pi z_i}{d} \right) \left( \frac{3}{2} \cos^2 \theta_i - \frac{1}{2} \right) \right\rangle \]  \hspace{1cm} (2.40)

The values \( z_i, \theta_i, \) and \( d \) are the position of the molecule, the angle between the molecular axis and director, and the layer spacing. The postulated potential energy of a single molecule is given by:

\[ U_i(\theta_i, z_i) = -U_0 \left( S + \alpha \sigma \cos \left( \frac{2\pi z_i}{d} \right) \left( \frac{3}{2} \cos^2 \theta_i - \frac{1}{2} \right) \right) \]  \hspace{1cm} (2.41)

Here constant \( \alpha \) quantifies the strength of the interaction between adjacent molecules. The potential is then used to derive the thermodynamic properties of the system assuming thermal equilibrium. It results in two self-consistency equations.
that must be solved numerically, the solutions of which are the three stable phases of the liquid crystal.

2.3 Dielectric Spectroscopy

2.3.1 Electric polarization

Consider a capacitor made of conducting parallel plates as depicted in figure 2.15, each carrying an equal charge of opposite sign, +Q and –Q respectively. Then

\[ C_0 = \varepsilon_0 A / d \]  \hspace{1cm} (2.42)

\( A = \) plate area

\( d = \) plate separation

Fig. 2.15 A charged parallel plate capacitor (a) with vacuum (b) filled with dielectric material.

Now fill the capacitor with non-conducting material, the positive charge will be attracted towards the negatively charged plate and negative charges will be attracted towards positively charged plate. The system will be stabilizing in this state as shown in figure 2.15(b). This means that electric field induces an internal charge reorganization or distortion, in the material, such that a net electric dipole moment per unit volume \( P \) (Cm\(^{-2}\)) appears.

The magnitude and direction of the polarization induced by a unit electric field is a characteristic of the material and it is given by the tensorial material parameter \( \chi \), which is called dielectric susceptibility.
\[ P = \chi \varepsilon_0 E \]  

(2.43)

In dielectric spectroscopy we usually deals with another material parameter that is known as relative dielectric permittivity

\[ \varepsilon_r = 1 + \chi \]  

(2.44)

So we obtain the field induced polarization by following relation

\[ P = \varepsilon_0 E (\varepsilon_r - 1) \]  

(2.45)

2.3.2 Polarization Mechanism

In any material, there are various types of charges and charge association, which contributes to the polarization. They are as follows [40-42]:

a) The “inner electrons” bound to the nuclei. Although little affected by the applied field, they “resonate” with high energy (≈10^4 eV), short wavelength (≈10^{10} mm) electromagnetic fields corresponding to the X-ray range.

b) The “outer electrons”, these are valence electrons which contribute to the atomic and molecular polarizabilities and also, in the case of elongated molecular structures, to their orientation with respect to the applied field.

c) The “free electrons’ which contributes to the “in phase” conduction.

d) The “bound ions” or ions bound to oppositely charged ions, forming molecular dipoles. These permanent dipoles experience an orientation torque in a uniform field.

e) The “free ions” as in electrolytes, which moves in the applied field, usually with a low mobility ionic dipole.

f) Finally “the multipoles” and mainly “quadrupoles” or an “antiparallel association” of two dipoles, which undergoes only a configurational strain in a uniform field. Each configuration has its own critical frequency, above which the interact in with the field becomes
vanishingly small, the lower the frequency, the more configurations is excited.

The electronic polarizability contributes at optical frequencies and is usually considered in terms of the refractive index. It takes place at frequency of around $10^{14}$ Hz. The frequency range for orientational polarization is broad. Typically the value ranges from $10^9$ Hz for the reorientation of small molecules to $10^2$ for certain cooperative reorientation in liquid crystals or motion in polymers. The redistribution of free charges is generally the slowest process, since it involves the movement of the charge carrier through the material.

Fig. 2.16 Electric field interactions with an atom under the classical dielectric model.
Fig. 2.17 Typical behavior of the real (upper) and imaginary (lower) parts of the dielectric permittivity as a function of frequency.

2.3.3 The Complex Dielectric Permittivity

The macroscopic quantity of interest in dielectric spectroscopy is the polarization of the sample. Suppose that E(t) is a time dependent electric field that changes such that the polarization P(t) is always in equilibrium with the field. If we turn on the field at t=0, after a long period of time the saturation value $P_s$ is given by

$$P_s = \chi(0) \varepsilon_0 E$$  \hspace{1cm} (2.46)

$\chi(0) =$ static (at zero frequency) susceptibility

It is reasonable to assume that, before reaching the equilibrium value, P will change at a rate which is proportional to its deviation from that value.

$$-\frac{\partial}{\partial t} (P_s - P) = \frac{1}{\tau} (P_s - P)$$  \hspace{1cm} (2.47)

Integrating the above

$$-\ln (P_s - P) = \frac{t}{\tau} + K$$  \hspace{1cm} (2.48)

K=constant

Applying boundary condition at t=0, P=0

$$K = -\ln P_s$$  \hspace{1cm} (2.49)

Hence

$$\ln (P_s - P) - \ln P_s = -\frac{t}{\tau}$$  \hspace{1cm} (2.50)

$$\frac{P_s - P}{P_s} = e^{-\frac{t}{\tau}}$$  \hspace{1cm} (2.51)
This can also be written as

\[ P = P_s (1 - e^{-\frac{t}{\tau}}) \]  

(2.52)

As this equation shows, the polarization is approaching its saturation value in an exponential way, with a characteristic time constant \( \tau \), known as Relaxation Time. If after a long time, we turn off the field \( (E=0) \), the polarization decays to zero according to

\[ P = P_s e^{-\frac{t}{\tau}} \]  

(2.53)

If we now instead apply an AC field, \( E = E_0 e^{i\omega t} \), to a dielectric with a given relaxation time \( \tau \), we want to investigate the response of the medium as we vary the frequency \( \omega \).

\[ P = \chi \varepsilon_0 E = P = \chi(0) \varepsilon_0 E_0 e^{i\omega t} \]  

(2.54)

A phase long between \( E \) and \( P \) is hidden in \( \chi(0) \) which in general will be complex, from Eq. We have,

\[ i\omega P = i\omega \chi(0) \varepsilon_0 E = (\chi(0) \varepsilon_0 E - \chi(\omega) \varepsilon_0 E) / \tau \]  

(2.55)

Hence

\[ i\omega \tau \chi(\omega) = \chi(0) - \chi(\omega) \]  

(2.56)

\[ \chi(\omega) = \frac{\chi(0)}{1 + i\omega \tau} \]  

(2.57)

Separating real and imaginary part

\[ \chi'(\omega) = \frac{\chi(0)}{1 + \omega^2 \tau^2} \]  

(2.58)

\[ \chi''(\omega) = \frac{\omega \tau \chi(0)}{1 + \omega^2 \tau^2} \]  

(2.59)
The above results are first reported by Peter Debye in 1927. The above equation involves only one excited dielectric mode in the system. The electronic excitation always contributes to $\chi'$ in dielectric spectroscopy as their relaxation times are vanishingly small. Thus their high frequency contribution $\chi'$ and $\varepsilon''$, have to be added at any applied frequency. Therefore the complete equation is given by

$$\chi'(\omega) = \chi_\infty + \frac{\chi(0)}{1 + i\omega\tau}$$  \hspace{1cm} (2.60)

$$\chi''(\omega) = \chi_\infty + \frac{\chi(0)}{1 + \omega^2\tau^2}$$  \hspace{1cm} (2.61)

$$\varepsilon''(\omega) = \varepsilon_\infty + \frac{\omega\tau\chi(0)}{1 + \omega^2\tau^2}$$  \hspace{1cm} (2.62)

Same equation in terms of dielectric permittivity can be written as

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_f - \varepsilon_\infty}{1 + i\omega\tau}$$  \hspace{1cm} (2.63)

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_f - \varepsilon_\infty}{1 + \omega^2\tau^2}$$  \hspace{1cm} (2.64)

$$\varepsilon''(\omega) = \frac{\omega\tau(\varepsilon_f - \varepsilon_\infty)}{1 + \omega^2\tau^2}$$  \hspace{1cm} (2.65)

This is the more general form of Debye equation, commonly used. The above equation in terms of relaxation frequency can be written as

$$\varepsilon'(f) = \varepsilon_\infty + \frac{\chi}{1 + (\frac{f}{f_R})^2}$$  \hspace{1cm} (2.66)

$$\varepsilon''(f) = \frac{f}{f_R} \frac{\chi}{1 + (\frac{f}{f_R})^2}$$  \hspace{1cm} (2.67)
Fig. 2.18 The real (continuous curve) and imaginary (dashed curve) parts of the Debye equation as a function of angular frequency.

All the above equations shown here represent only single relaxation mode as shown in figure 2.18. If there are several modes present in our systems, then every mode will have its own values from $\chi$ and $f_R$. Each mode will then also get its specific set of $\varepsilon_f$ and $\varepsilon_\infty$. The susceptibility is equal to the maximum contribution to the real part of the dielectric permittivity of one specific mode, the effective $\varepsilon_\infty$ value is the permittivity at the minimum frequency of no contribution from the mode and the effective $\varepsilon_f$ is the sum $\varepsilon_\infty + \chi$ shown in figure 2.19.

There are many ways to represent Debye equation or Debye relaxation function. The above methods use the time dependent of the polarization of the sample, which is on macroscopic level. From microscopic point of view, Debye supposed that rotation of the molecule in an electric field is interrupted collision with the neighbor. This obstruction can be described by a resistive couple proportional to the angular velocity of the molecule.
Fig. 2.19 Behavior of real $\varepsilon'$ and imaginary $\varepsilon''$ part of dielectric permittivity as function of frequency in the case of two modes within measured frequency.

### 2.3.4 Non Debye Type Relaxation Functions

On experimental ground, Debye equation does not fit well for all the systems. For polymeric system and low molar mass liquid crystals, the relaxation modes turns out to be characterized by a distribution of relaxation times and therefore it is impossible to obtain a good fit of Debye equation. Although a number of approaches are possible, here we will discuss some of them. The collection given here is based on the Debye function that has been extended empirically to account for the broadening of spectra.

#### 2.3.5 The Cole-Cole Relaxation Function

Since in reality a perfect Debye relaxation is rare, some empirical modification have been made, as a result of broadened peak in the imaginary parts and measures out steps in real part. The Cole-Cole function is aimed at the description of a symmetric broadening of the peak [40-49]. This is done by modifying equation (2.58) and (2.59) (frequency domain form)
\[ \varepsilon^*(f) = \varepsilon_\infty + \frac{\chi}{1 + (i \frac{f}{f_R})^{1-\alpha}} \quad (2.68) \]

Separating real and imaginary part gives us the following equations

\[ \varepsilon'(f) = \varepsilon_\infty + \frac{\chi(1 + (\frac{f}{f_R})^{1-\alpha} \sin(\alpha \pi / 2))}{1 + 2\left(\frac{f}{f_R}\right)^{1-\alpha} \sin^2(\frac{\alpha \pi}{2}) + \left(\frac{f}{f_R}\right)^{2(1-\alpha)}} \quad (2.69) \]

\[ \varepsilon''(f) = \frac{\chi(\frac{f}{f_R})^{1-\alpha} \cos(\alpha \pi / 2)}{1 + 2\left(\frac{f}{f_R}\right)^{1-\alpha} \sin^2(\frac{\alpha \pi}{2}) + \left(\frac{f}{f_R}\right)^{2(1-\alpha)}} \quad (2.70) \]

When \( \alpha = 0 \), the Cole-Cole equation reduces to the Debye equation. But for non zero values of \( \alpha \), we get a distribution of Relaxation times. The distribution or shape parameter \( \alpha \), which lies between 0 and 1, describes the broadening of the curve; \( \alpha = 0 \) corresponds to the situation of no broadening, with increasing \( \alpha \) the peaks becomes lower and broader. The parameter \( \alpha \) is purely empirical and there is no microscopic theory for it. If we imagine a certain dipole being in liquid crystal containing only one simple molecular specifies. We would find a pure Debye behavior. However for multi component mixtures, in which each particular dipole would not have a unique environment, this would lead to a smear out the relaxation process and to \( \alpha \neq 0 \).
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Figure 2.20 The Cole–Cole relaxation function. The full lines are the real parts $\varepsilon'$ and the dashed lines are the imaginary parts $\varepsilon''$. Curves are plotted for $\alpha = 0$, $\alpha = 0.2$, $\alpha = 0.4$, $\alpha = 0.6$ and $\alpha = 0.8$.

2.3.6 The Cole-Davidson Relaxation Function

For unsymmetrical distribution of Relaxation time, Cole-Davidson Relaxation function is used [46-49]. Generally the broadening occurs at high frequency side. The expression is given as

$$
\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_f - \varepsilon_\infty}{1 + (i\omega \tau)^\beta}
$$

(2.71)

For $\beta=1$, this expression reduces to the Debye function. $\beta$ takes values between 0 and 1. Plot is shown in figure 2.21.

From the figure it is clear that the maximum of the peak does not correspond any more to $\omega = \tau^{-1}$ but is shifted to higher frequencies. Another observation that can be made from the figure is that apart from the shift to higher frequencies; there is no change to the low frequency wing of the relaxation peak. This means that a Cole-Davidson function cannot be distinguished from a Cole-Cole function on the basis of the low frequency information alone, a fact that must be taken into account to interpret certain analyses correctly.
Figure 2.21 The Cole-Davidson relaxation functions. The full lines are the real parts \( \varepsilon' \) and the dashed lines are the imaginary parts \( \varepsilon'' \). Curves are plotted for \( \beta = 1, \beta = 0.8, \beta = 0.6, \beta = 0.4 \) and \( \beta = 0.2 \).

### 2.3.7 The Cole-Cole Plot

The equation is given by:

\[
(\varepsilon' - (\varepsilon_\infty + \frac{\chi}{2}))^2 + (\varepsilon'')^2 = \left(\frac{\chi}{2}\right)^2
\]  

(2.72)

The above equation represents a circle, centered on \( \varepsilon' = \varepsilon_\infty + \chi/2 \) and \( \varepsilon'' = 0 \). Such plot is known as Cole-Cole plot. The Cole-Cole plot does not have frequency axis, instead \( \varepsilon' \) works as frequency axis. As we already know \( \varepsilon' \) is monotonously decreasing function of the frequency, higher \( \varepsilon' \), lower the frequency. Since the maximum absorption occurs at the relaxation frequency \( f_R \), means top of the semicircle represents this frequency. The radius of the circle is \( \chi/2 \) and the point where the graph cuts the \( \varepsilon' \) axis are \( \varepsilon_\infty \) and \( \varepsilon_t \). Thus Cole-Cole plot is the quick way of obtaining both the absorption frequency and the susceptibility of a mode [44-50].

It can be easily shown that Cole-Cole equation is made up of an infinite number of Debye relaxation process. In a gas where the molecules are relatively simple and independent, a single time constant dominates. In liquid crystals and solids, the molecules can be very large or to be bound with the lattice. This makes
reorientation of polar molecules subjected to an electric field a slow and complicated process.

![Figure 2.22 The Cole-Cole plot for (a) Debye type process (b) Cole-Cole process.]

### 2.3.8 Physical Interpretation of Relaxation

Whenever electric field is applied to a system, the dipole present in the system tries to align themselves in the direction of the applied field. This reorientation will surely minimize the energy of the system, thus stabilizing the whole system. However during this whole reorientation process, the dipole must have to overcome certain forces present in the system such as Vander Waals forces, Hydrogen bonds, surface anchoring etc. these forces resists the reorientation of the dipole. Thus every dipole takes some time to reorient. This time is known as relaxation time $\tau$.

If an oscillating field is applied with a frequency that is much larger than $1/\tau$ then all dipoles can reorient themselves and contribute to the polarization. However if the applied frequency is within the range of $1/\tau$ then not all polarization contributes to $\varepsilon'$, as a result dielectric permittivity decreases. This is the step in $\varepsilon'$ and the peak in $\varepsilon''$. Finally when the applied frequency rises above $1/\tau$, no molecules can catch up with the electric field anymore and the contribution to this dipole motion to the polarization ceases to exist. $\varepsilon'$ is flat again and $\varepsilon''$ has returned to zero.
Relaxation time has been determined by the fitting of the dispersion/absorption curves. The temperature dependency of the relaxation time is generally analyzed using Arrhenius equation and Vogel-Fulcher-Tamman (VFT) equation. VFT equation was introduced to describe the non-Arrhenius dependence in glass forming systems.

### 2.3.9.1 Arrhenius Equation

The Arrhenius equation describes the temperature dependence of the relaxation times of a process where a temperature-independent potential barrier has to be crossed. The Arrhenius equation is usually given in the form

$$\tau = A \exp\left(\frac{-\Delta E}{K_b T}\right) \quad (2.73)$$

Where $A$ is temperature independent factor and $\Delta E$, the activation energy, does not depend on temperature either.

Linearization of this equation shows that an Arrhenius process shows up as a straight line when the relaxation times are plotted with respect to the inverse of temperature and the slope of this line gives the activation energy [48-52]. Therefore the relaxation time data will mainly be presented in terms of Arrhenius plot.

![Arrhenius Plot for determining Activation Energy.](image)
References


[34] Jiang, Y.W.; Yu, X.H.; Chen, Y. G.; Yao, Y.M. Chinese Physics B 2009, 18, 0238.


Chapter 3

Experimental Details
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3.1 Introduction

Liquid crystals have application in various fields. The appropriate application of any particular liquid crystal depends upon its characteristics [1]. This chapter is about the experimental techniques that have been followed in the present work to characterize different liquid crystalline materials. In the present work, different dielectric and electro-optical techniques has been used to study various properties of liquid crystals.

In order to explore and understand the properties of liquid crystals, sample holders (cells) preparation is the most important part. Therefore before coming to actual experimental techniques, the sample holder fabrication technique is discussed.

3.2 Sample Holder Fabrication Techniques

This section deals with the detail and essential points of fabrication procedure of the liquid crystals sample cell. To construct the sample cell ITO coated optical flat glass plates have been imported from the Diamond coatings U. K. From displays point of view the sheet resistance and the visible light transmission must be of the order of $10\,\Omega/\square$ and 90% respectively, which in our case is $10\,\Omega/\square$ and more than 90%.

These ITO coated glass plates have been used as electrodes to construct the sandwich type of sample holder. There are few treatments which must be employed before using them as electrode, they are discussed as follows-

![Figure 3.1 ITO Coated Liquid Crystal Plates](image_url)
3.2.1 Photolithography

Photolithography is a technique to transfer any particular pattern on the ITO coated glass plates. For device application the photolithography is the fundamental requirement to produce a preferred pattern on the ITO substrate. But for the characterization procedure, it is required to remove the different inadequacies in the various experiments and make them easy.

The photolithography comprises of many steps as follows and must be carried out in the dark room [1, 2].

3.2.1.1 Photoresist Application

The first step after unpacking the imported ITO glass plate is cleaning them with soap water and acetone to avoid any traces of organic impurities employed during the packing (like wax) and dust particles. Just after the cleaning process, photoresist is applied to the conducting surface of the ITO coated glass plate through spin coating technique. There are two types of photoresist positive and negative.

When positive photoresist coated substrate is exposed through the UV light, the UV light exposure results in change in the chemical structure of the photoresist and make it soluble in the respective developer. The developer washes out the exposed portion and leaves a window on the substrate.

Whereas negative photoresist works in just opposite manner. The exposure makes them harder by polymerization. Therefore the developer solution does not
affect the exposed portion on the surface while the rest of the unexposed portion washes out. Therefore after the washing through developer only the exposed portion stays [2]. Therefore one may use positive or negative photoresist depending upon the need. In our case it is negative photoresist, which can be prepared by chlorobenzene, 2-ethoxyethanol cyclohexanane and polyvinyl cinnamate.

3.2.1.2 Soft Baking

Once the homogeneous layer of photoresist appears on the glass plates the substrates are used to keep at temperature of 90 °C for ten minutes. This process is called as soft baking. During soft baking the layer of negative photoresist on the ITO substrate becomes harder.

3.2.1.3 Mask Alignment

After soft baking, the substrate is set against the photomask and exposed through the pattern on the mask with a high intensity ultra violet light. The ITO electrode pattern style and way of exposing the UV light is shown in the figure 3.3 and figure 3.4 respectively. The distance of the ultra violet light from the substrate and its duration of exposure have to be optimized. In our case it was 15” (approx.) and the exposure time was 45 seconds.

Figure 3.3 ITO electrode pattern
3.2.1.4 Development And Hard Baking

For developing the exposed photoresist the substrates are washed by developer. As similar to the photoresist, developers also are of two types positive and negative. Both the photoresist and developer must be of the same type, in our case both of them are negative. After washing through developer the Benzene is employed on the glass substrate.

Benzene is used as a fixer to stop the reaction of the developer with the photoresist. The pattern obtained is now baked at 220°C for three hours. This process of heating the developed pattern is called hard baking. This step is necessary in order to harden the photoresist and improve adhesion of the photoresist to the surface.

3.2.2 Etching

This process is used to remove the extra ITO other than ITO below the pattern of photoresist from the substrate. Two type of etching process are well known i.e. dry etching and wet etching. Dry etching dissolves the ITO using Liquid Crystal Research Lab, Physics Department, University of Lucknow, Lucknow-226007.
reactive ions or vapour phase etchant, whereas wet etching involves the chemical
treatments to remove extra ITO from substrate. Wet etching process has been used
in our case.

The Indium Tin Oxide (ITO) is composed of indium oxide (In$_2$O$_3$) and tin
Oxide (SnO$_2$) in the ratio of 9:1 wt/wt., therefore the etchant material can be HCl
+ Zn dust or HCl +HNO$_3$ [3]. In our case earlier one has been used, Zinc dust is
spread uniformly into the diluted HCL (15 %). The substrates found after the hard
baking, are immersed in the mentioned solution just after this, chemical reactions
start. The reaction between the Zinc dust and HCl produces nascent hydrogen that
reacts with the ITO and removes extra ITO on the substrate in following steps:

\[
\text{Zn} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + 2\text{H}^+ \\
\text{SnO}_2 + 4\text{H}^+ \rightarrow \text{Sn} +2\text{H}_2\text{O} \\
\text{In}_2\text{O}_3 + 6\text{H}^+ \rightarrow 2\text{In} +3\text{H}_2\text{O}
\]

Dipping the substrates into water can stop these reactions. To insure that
the extra ITO has been removed or not, the conductivity of substrate has been
checked by a multimeter. After the full assurance that no extra ITO is present on
the substrate, the substrates are cleaned with soap solution and acetone. Finally the
desired pattern is on the glass plates. Now the substrates are ready for the
alignment and further procedures needed for the fabrication of sample cell.

### 3.2.3 Alignment

Alignment of the liquid crystal is most important step in the fabrication of a
liquid crystal cell. Various methods for obtaining uniform alignment have been
proposed by many workers [4-7]. The molecular alignment of liquid crystal is
influenced by the forces acting between the liquid crystal molecules as well as
between the liquid crystal molecules and the surface of substrate. Basically two
types of alignment are found in liquid crystals, i.e. homogenous and homeotropic alignment. In homogenous alignment (also known as planar alignment), the long molecular axis are constrained to align perpendicular to the surface normal as shown in lower part of figure 3.5, whereas in homeotropic alignment the liquid crystal molecules are subjected to the surface interaction such that the molecules align parallel to the surface normal as shown in upper part of figure 3.6. The different alignments are used according to their requirement in display devices.

3.2.3.1 Homogenous (Planar) Alignment

Parallel alignment is usually obtained as long as the surface is microscopically flat and liquid crystal does not contain amphiphilic impurity as well as surface polarity is too low to absorb the impurity. Normally, surface coated with fluorinated material gives low surface energy. Therefore, stable parallel alignment is obtained by decreasing the surface polarity by coating polymer or surface coupling agent, of which molecules tend to adsorb parallel to the surface. However, these alignments are random parallel alignment. In order to obtain homogenous alignment, unidirectional rubbing is necessary. The mechanism of parallel alignment to the rubbing direction is analyzed by Berreman [8]. There are a number of methods employed for homogenous alignment.

1. Rubbed Polyimide
2. Silicon Monoxide And Other Similar Dielectrics

There are several polyamides like Nolimid 32, Hitachi PIQ and Merck ZLI 2650 available in the market. In our case, the alignment was achieved by using polymer NYLON 6/6 coated and rubbed on substrates. The etched plates obtained were dipped in adhesion promoter e.g. Silane solution (0.2% solution of Phenyl-Trichlorosilane in Toluene) for 10 minutes and then washed with propanol. This procedure is immediately followed by deposition of the polyamide coating on the substrate. For this 0.5% solution of NYLON 6/6 is prepared in a solvent mixture of 60% m-Cresol and 40% methanol. This solution is spin coated on the glass substrate at a rotational speed of 50 rpm. The excess solvent is then evaporated by keeping the coated glass plates at 120°C for 1 hour. Now, the polymer treated substrates are rubbed unidirectional with a good quality velvet cloth or cotton [2, 9].

3.2.3.2 Homeotropic Alignment

There are three proposed alignment mechanisms to obtain perpendicular alignment. Amphiphilic materials (surfactants) assisted alignment, i.e., amphiphilic material absorbs perpendicular to the polar surface and liquid crystal aligns according to the amphiphilic material, as shown in figure 3.6. The second mechanism is the use of surface coupling agents such as silanes (silicon-hydrogen compound: a compound of silicon and hydrogen belonging to a group analogous to the paraffin hydrocarbons. Formula: \( \text{Si}_n\text{H}_{2n+2} \) with long alkyl chains. The third mechanism is microscopic
columnar structure-assisted alignment which is obtained by SiO\textsubscript{x} relatively oblique evaporation as reported by Hiroshima et al [10].

In our case for homeotropic alignment, the substrates are cleaned with the acetone and then simply coated with the dilute solution of Lecithin. Solution of Lecithin has been prepared by dissolving Lechithin (Cetyl Trimethylammonium Bromide) in ethyl alcohol. The substrates have been dried at 200 °C for ten hours before assembling of the cell.

### 3.2.4 Assembling

After treating the substrate for any particular alignment they are ready for assembling. Before assembling, two small pieces of Mylar spacers have been placed in between the two substrates outside the active area. The Mylar spacers of thickness from 5 to 15 µm have been used. Now the sandwiched substrates have been sealed at the corners by U.V sealant and dried well at room temperature before making the connections. Figure 3.8 shows the detailed structure of the constructed cell.
Figure 3.8 The Detailed structure of the finally constructed liquid crystals sample cell.

There may be some fabrication tolerance in the thickness of the cell, therefore before filling the sample in cell it is very necessary to measure the thickness. The thickness of the cell can be measured either by capacitor measurement method or by optical interference method and both of them are very well known to scientific regime.

3.2.5 Filling

Last but not least step in the fabrication procedure is sample filling. For filling, the material has been introduced to the opening of the cell and heated up to temperature 10°C higher than its isotropic temperature. At this temperature the material is sucked inside the cell due to capillary action. Now in order to obtain perfect alignment, filled cell is cooled very slowly up to room temperature in the presence of low frequency electric field. Now, the liquid crystal sample cells are ready to characterize different properties.

3.3 Dielectric Spectroscopic Study

Dielectric spectroscopic study is one of the important tools to study the molecular dynamical properties over a wide range of characteristic time for $10^{-12}$ s to $10^5$ s. Dielectric spectroscopy also provides information about the intermolecular interaction. It also gives link between the investigation of the properties of the individual constituents of a complex material and the characterization of its bulk properties. This section deals with dielectric measurement technique used in the present work and other important points regarding dielectric spectroscopy.

Before starting discussion about measurement techniques, we would like to discuss about stray capacitance problem.
3.3.1 Calibration Of Cell

The cell constructed is simply a parallel plate capacitor. So a stray capacitance arises when it is subjected to an electric field due to the lead attached and the non-homogeneities of the field lines at the edges of the active area. In this condition the air capacitance ($C_o$) of the cell can be written as-

$$C_o = C_L + C_S$$

(3.1)

Here $C_L$ is the capacitance of the empty cell without the stray capacitance ($C_S$) [2, 11-12]. For the measurement of stray capacitance of the constructed cell two standard liquids of known relative permittivity i.e. Benzene and CCl$_4$ [13] are used. The cell capacitance filled with any of these liquids can be written as-

$$C_{SL} = \varepsilon'_SL C_L + C_S$$

(3.2)

By using the equation 3.1 and 3.2 we can calculate the live capacitance of the cell as-

$$C_L = \frac{C_{SL} - C_o}{\varepsilon'_SL - 1}$$

(3.3)

Here $C_{SL}$ represents the capacitance of the cell field with the standard liquid of known relative permittivity ($\varepsilon'_SL$). Now, any one can calculate the value of stray capacitance.

3.3.2 Measurement

3.3.2.1 Measurement Techniques

The complex dielectric permittivity function $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ can be measured in the extraordinary broad frequency region from $10^{-6}$ Hz to $10^{12}$ Hz. To span this dynamic range different measurement systems based on different
measurement principal have to be combined. From $10^{-6}$ to $10^7$ Hz, lumped circuit methods are used in which the sample is treated as a parallel or serial circuit of an ideal capacitor and an ohmic resistor. With increasing frequency the geometrical dimensions of the sample capacitor become more and more important limiting this approach to about 10MHz. In addition parasitic impedances caused by cables, connectors etc. becomes important at frequencies $>$10MHz [14-17].

There are a number of possibilities to determine $\varepsilon^*(\omega)$. The basis of any measurement of $\varepsilon^*$ is essentially a determination of the Impedance $Z$ of the sample.

$$Z_c = \frac{1}{\omega C}$$

(3.4)

For the case of a dielectric sample cell, one can use either a measured value of the vacuum capacitance $C_0$ or the equation for geometrical capacitance

$$\varepsilon = \frac{C}{C_0}$$

(3.5)

In reality the Impedance is a complex value $Z^*$

$$Z_c^* = \frac{1}{i\omega C}$$

(3.6)

If sinusoidal voltage is applied to the sample and the voltage over and current through the sample are determined, including the phase information

$$V(t) = V_0 \exp(i\omega t)$$

(3.7)

$$I(t) = I_0 \exp(i\omega t + i\phi)$$

(3.8)
\[ Z^* = \frac{V_o}{I_o} \exp(i\phi) \]

Then

\[ \varepsilon^* = \frac{-i}{\omega Z^* C_o} \]

Then for \( \varepsilon^* \), we have

The value obtained for \( \varepsilon^* \) is that corresponding to the frequency of the applied field. The value of \( C_o \) can be measured from the empty cell or directly from the geometry of the cell. A number of techniques can be used for the measurement of dielectric permittivity. Some of them are discussed here. All of them belong to the frequency domain techniques.

![Diagram](image-url)
Figure 3.9 Survey of different measurement techniques used in the frequency range $10^6$ Hz to $10^{15}$ Hz [18].

### 3.3.2.1.1 The Bridge Method

This is one of the simples and oldest methods in use, essentially the principle of the Wheatstone bridge applied to AC circuits, shown in figure 3.10. If there is no current or voltage at the detector, simple calculation shows that

$$Z_x = \frac{Z_1 Z_3}{Z_2}$$

(4.1)

This method is suitable for frequencies below 100 kHz. The impedance was formed by a combination of capacitors and resistors.

![Bridge Method Diagram](image)

Figure 3.10 The circuit for a Bridge measurement.

### 3.3.2.1.2 The I-V Method

Another simple method, now based on the fact that

$$Z_x = \frac{V}{I}$$

(4.2)
Thus one has to apply an electric field to the sample and measure the voltage over and current through the sample. This works for frequencies below 1 MHz. The over simplified diagram is shown in figure 3.11.

![Simplified circuit for I-V measurement.](image)

**Figure 3.11 The simplified circuit for I-V measurement.**

### 3.3.2.1.3 The RF I-V Method

Measurement at high frequency becomes difficult and at frequencies above 1 MHz most methods fail. One of the solutions is this RF I-V method, which allows measurements up to 1 GHz. The basic idea of this type of measurement is that current and voltage over the sample (DUT) is measured to obtain the impedance. Because of the high frequencies, precautions have to be made, like matching the impedance of different parts of the circuit. The basic trick appears to be the reduction of the frequency before the actual measurement is performed by digitizing (ADC) the amplified signal (IF Amp). The circuit for RF I-V measurement is shown in figure 3.12.
3.3.2.1.4 The Auto Balancing Bridge

An oscillator (OSC) generates a sinusoidal field of the wanted frequency and delivers that to the sample at H. The feedback loop (Auto Balancing Bridge) tries to maintain a zero voltage at L. The impedance is then calculated from the voltage measurement by the voltmeter V and the current is obtained with the help of the current meter A. This type of circuit, in different versions depending on the frequency range, has been implemented for frequencies from 20 Hz to 110 MHz.
3.3.2.2 Measurement of Dielectric Properties

Here we have performed the dielectric measurements by Impedance/gain phase analyzer Hewlett-Packard (4194A), which is a highly accurate instrument that has the measurable frequency range from 100 Hz to 40 MHz. The complete dielectric measurement setup is shown in figure 3.14. The instrument employs microprocessor controlled built-in bridges and resonant circuits to cover a wide range of frequencies. The instrument can measure eleven different parameters, which are impedance (Z), admittance (Y), phase angle (θ), resistance (R), reactance (X), conductance (G), susceptance (B), inductance (L), capacitance (C), dissipation factor (D) and Q (= I/D) with 20 parameter combinations [14]. HP-4194A has an impedance measurement range from 0.1 mΩ to 1.6 MΩ with accuracy of 0.17%. The AC signal of the HP-4194A may vary between 10mV\text{rms} to 1V\text{rms} and DC signal may vary from 0 to ± 40V. The default values of AC and DC signals are kept at 0.5V\text{rms} and 0V respectively. The Impedance/gain phase analyzer Hewlett-Packard (4194A) works on the principle of auto balancing and consist of three sections (1) signal source section, (2) auto balancing bridge section and (3) vector ratio detector section.

The signal source section consist a microprocessor based frequency synthesizer that generates the test signal of variable frequency with a high resolution of 1 mHz. These test signals are directly fed to the device under test (DUT). Internal reference signals are also generated in this section.
Figure 3.14 Experimental setup for dielectric measurement

Figure 3.15 shows the block diagram of the auto balancing section. The auto balancing section balances the range resistor current with the DUT current to keep the lower terminal at same zero potential. The detector observes the potential at the lower terminal and manages the magnitude of the phase generated by oscillator OSC2 to bring potential back to zero. The vector ratio section measures two vector voltages, one across DUT ($V_{DUT}$) and other across the range resistor $R_r$ ($V_{rr}$) series circuit. Since the range resistor value is known, measuring two voltages will give the impedance vector $Z_x = R_r (V_{DUT}/V_{rr})$. Each vector voltage is separated into its $0^\circ$ and $90^\circ$ components by a phase detector, and each component is measured using dual-slope A to D converter. Either $V_{DUT}$ or $V_{rr}$ signal is selected by a selector to that the $V_{DUT}$ and $V_{rr}$ signals follows identical path to eliminate tracking error between the two signals. To measure the dielectric properties of the
liquid crystals filled cell terminals have been connected to Impedance / Gain Phase Analyzer by a text fixture (16047 D) [14].

![Block diagram for the auto balancing section of the HP-4194A.](image)

Figure 3.15 Block diagram for the auto balancing section of the HP-4194A.

To record the values of capacitance and conductance of the sample holder the Impedance / Gain Phase Analyzer has been interfaced with a P (IV) computer using a GPIB card. The values of the capacitance and conductance can be recorded by software. The beauty of this software is that we can program it to acquire the data according to our need and data can be processed directly by any scientific software like Origin or Mat Lab. The value of relative permittivity ($\varepsilon'$) and dielectric dispersion ($\varepsilon''$) can be directly calculated from recorded values of capacitance and conductance for with and without sample and by using following equations -

$$\varepsilon' = \frac{C_m - C_0}{C_L} + 1$$

(4.3)
\[ \varepsilon'' = \frac{G_m - G_0}{2\pi f C_L} \]  

(4.4)

Here \( C_m \) and \( G_m \) are the capacitance and conductance respectively for the cell filled with the liquid crystal material while \( C_o \) and \( G_o \) are capacitance and conductance for empty cell.

### 3.3.3 Dealing With Unwanted Absorption

Instead of great accuracy of the measurement, the experimental data suffers from the two basic problems. Liquid crystal compounds are unfortunately never free from ionic impurities, and this has severe effects on dielectric spectroscopy measurement. There are two main types of ionic contributions i.e. ionic space charge polarization and charge build up at the cell electrodes [15-17]. The first problem is in low frequency range which is due to the presence of free charge particles. The second is due to the sheet resistance of ITO coated sheet and lead inductance of the wires attached as terminals. These problems can be sorted out by the best theoretical fitting of some functions discussed below [15-17].

#### 3.3.3.1 Low Frequency Ionic Contribution

Since the liquid crystals are improper dielectrics, they have some concentration of the charge carriers that can move freely in the presence of electric field. This conduction of charge carriers offers conductivity effect in the low frequency range and affects the dielectric results considerably. This conductivity effect can be resolved by assuming a resistance attached parallel to the cell as shown in figure 3.16 (a). Here \( R_i \) represents the additional resistance and works in the inverse manner, subscript \( i \) refers to the ions. The measured data in low frequency range also shows an effect of ionic conductance, therefore for our fitting
purpose it is therefore sufficient to model that the ionic contribution with simple inverse temperature dependence instead of separate Cole -Cole process [19]

\[ \varepsilon' = \varepsilon'(dc)f^{-n} \quad \text{and} \quad \varepsilon''_{\text{ions}} = \frac{\sigma(\Delta f)}{\varepsilon_0} \frac{1}{2\pi f^k} \]

Here \( f \) is measurement frequency, \( \varepsilon_0 \) is vacuum permittivity, \( \sigma, n \) and \( k \) are fitting parameters. The parameter \( \sigma \) denotes the conductivity of the sample and \( m \) is needed because often absorption does not have a perfectly inverse linear dependence of frequency. The value should however normally be close 1. The conductivity is related to the conductance \( G = \frac{A}{l} \) where \( A \) is area and \( l \) is length.

According to Iwamoto [20], ionic contribution of space charge polarization decrease if applied voltage is increased. This is often seen when performing dielectric spectroscopy measurement with varying applied voltage, thus indicating that this kind of ionic contribution rather usual in liquid crystals. When performing measurements in these phases, one therefore has to find an optimum measuring voltage, where ionic contributions are suppressed as much as possible. The second type of ionic contribution due to surface charges at the electrodes is not affected by measurement voltage [21, 22]. If such contribution is present, it will thus always give a constant contribution in low frequency end of the dielectric spectrum. After adding low frequency terms effect due to the electrode polarization in Cole Cole equation, the real and imaginary part of the dielectric permittivity can be written as

\[ \varepsilon' = \varepsilon'(dc)f^{-n} + \left( \varepsilon'(\infty) + \frac{\Delta \varepsilon}{1 + \left(2\pi f\tau\right)^{l-a}} \right) \]

(4.6)
The first terms of both the equations are for the contribution due to the ionic conductivity, while bracket terms of the above equations represent real and imaginary part of the Cole-Cole equation.

### 3.3.3.2 High Frequency Cell Relaxation Problem

The measurement cells used for dielectric spectroscopy, as well as for many standard liquid crystal characterization techniques, are normally coated with ITO electrodes which are transparent to visible light [20]. Due to the low resistivity of ITO unfortunately leads to a spurious absorption centred on a frequency \( f_{\text{ITO}} \) in the dielectric spectrum.

![Equivalent circuit of the sample cell in (a) low frequency range (b) in high frequency region.](image)

**Figure 3.16 Equivalent circuit of the sample cell in (a) low frequency range (b) in high frequency region.**

The effect is seen as a local increase in dielectric loss centred on a frequency \( f_{\text{ITO}} \) and a corresponding decrease in dielectric loss above \( f_{\text{ITO}} \) and it thus
minimize a polarization processes in the dielectric spectrum. The frequency \( f_{\text{ITO}} \) of this spurious mode is called cell relaxation decreased with decreasing cell thickness and with increasing electrode resistance. For this reason one must take care in using cells coated with low resistive ITO and for thin cell measurement it is actually worthwhile considering using really low resistive but unfortunately non transparent electrodes like gold or copper, in order not have the interesting part of the dielectric spectrum completely obscured. At the frequencies beyond 10 MHz, the ionic conduction contribution becomes small whereas the ITO sheet resistance becomes active and results in pronounced increase in the dielectric absorption at higher frequencies. The equivalent circuit of the measurement in high frequency region is as shown in figure 3.16 (b). In addition to the time constant of the dipolar reorientation, the cell also offers a cut off frequency given by the inverse of the \( R_{\text{ITO}}C_{\infty} \). Therefore the measured dielectric data shows problem only in absorption and after including the contribution of ITO the measured absorption can be written as

\[
\varepsilon'' = A f^m + \text{Im} \left( \varepsilon'(\infty) + \frac{\Delta \varepsilon}{1 + (2\pi f \tau)^{1-\alpha}} \right)
\]

(4.8)

Here \( A \) and \( m \) are the fitting parameters and depend upon the \( RC \) constant of the cell. Overall contribution due to the ionic conductivity and ITO resistance can be written as

\[
\varepsilon' = \varepsilon'(\text{dc}) f^{-n} + \left( \varepsilon'(\infty) + \frac{\Delta \varepsilon}{1 + (2\pi f \tau)^{1-\alpha}} \right)
\]

and
\[ \varepsilon'' = \frac{\sigma_{dc}}{\varepsilon_0 2\pi f^k} + \text{Im} \left( \varepsilon'(\infty) + \frac{\Delta\varepsilon}{1 + (2\pi f\tau)^{1-\alpha}} \right) + A f^n \] (4.9)

Figure 3.17 Equivalent circuit for sample cell suitable for complete frequency range.

Figure 3.17 shows the equivalent circuit valid for both high and low frequency regime and figure 3.18 shows a typical presentation of the fitting of above equations into the experimental data. By fitting equations (4.9) with the experimental data, it is possible to subtract background effects from the dielectric spectrum in the low and high frequency region [21]. Therefore for the better results resistance of ITO should be as low as possible. This problem can be removed by the application of metal electrodes. However for liquid crystals it is necessary to use transparent electrodes which allow optical observations of measured structure at the same time. As mentioned, in our case the resistance of the ITO sheet is 10Ω/□ which allows the measurement up to 10 MHz.
3.3.4 Data Presentation

In the old literature the susceptibility for describing the contribution from any relaxation mode is given by:

\[ \Delta \chi = \chi_0 - \chi_\infty \]  

or

\[ \Delta \varepsilon = \varepsilon_0 - \varepsilon_\infty \]  

Many researchers introduced a shorthand version as “dielectric strength” which we should try to avoid because this is certainly a different thing and already well defined.

The dielectric strength is well defined in the field of dielectrics as the maximum field strength of a material that it can withstand before dielectric breakdown occurs. Therefore to avoid this confusion one can use dielectric contribution or relaxation strength instead of dielectric strength and represented by \( \delta \varepsilon \) [21]. In the present thesis \( \Delta \varepsilon \) will used to represent the dielectric anisotropy.
Figure 3.18 An example of the best theoretical fitting of equation (4.9) into the experimental data. The open legends are presenting the experimental data, while the solid line represents the best theoretical fit.

3.4 Optical Transmittance And Optical Anisotropy

The optical transmittance measurement has been done by placing the sample holders between two-crossed polarizers of polarizing microscope model (CENSICO 7626) fitted with a hot stage. The complete experimental arrangement for the optical transmittance measurement is shown in figure 3.19.

The most fascinating thing about this method is the visualization and clicking of sample texture during measurement by a digital camera (Cannon A95) fitted on one of the eyepieces of the microscope. The light intensity coming through one of the eyepieces has been measured by light dependent resistance (LDR). The two terminals of LDR are connected to a digital multimeter. Now the sample holder has been placed in the path of incident light, under the crossed polarizer-analyzer position. The variation of light intensity coming out through the sample can easily be read on Digital Multimeter in terms of LDR resistance (at various temperatures), which gives the value of optical transmittance. The 0% and 100% optical transmittance have also been measured for empty and black ink filled sample holder to calculate the percentage optical transmittance [23].
Examination of a sample through this reveals information about the alignment of the optic axis. As the sample is rotated, annihilation of light is observed when the optic axis is parallel to the polarizer or analyzer axis. At other orientations light is transmitted, the colour of which can give information about the birefringence and thickness of the sample. The transmitted light intensity \( I \) can be written as [24]

\[
I = I_0 \sin^2(2\chi) \sin^2\left(\frac{\pi \Delta n d}{\lambda}\right)
\]

Here \( I_0 \) is the incident intensity, \( \chi \) is the angle of the optic axis relative to the anisotropy

\[
\Delta n = n_e - n_0
\]

d is the sample thickness and \( \lambda \) is the wave length of the incident light [25].
The change in temperature of the thin layer of liquid crystal under crossed polarizer condition causes a significant change in optical texture due to the change in the intermolecular interaction field [25].

### 3.5 Mesophase Identification

In the course of research and commercial manufacturing, it is vitally important to be able to identify the types of liquid crystals phases that are exhibited by compound or a mixture of compounds [26-30].

The most widely used techniques of liquid crystal phase identification are optical polarizing microscopy, which reveals that each different liquid crystal phase has a distinct optical texture. However this identification of liquid crystal phases through optical polarizing microscopy is often difficult and requires a lot of experience.

Differential scanning calorimetry (DSC) is nearly always employed as a complementary tool to optical microscopy and reveals the presence of mesophases and liquid crystals phases by detecting the enthalpy change that is associated with a phase transition [26-39]. However this technique cannot identify the types of liquid crystals phase but the level of enthalpy change does give some information about the degree of molecular ordering within a mesophase.

However the ultimate technique for the identification and classification of mesophases is X-ray analysis. X-ray analysis of a liquid crystal will map the positions of the molecules within the phase and hence determine the phase structure and classification to which the particular phase belongs. However to maximize the information aligned samples are required. Miscibility study is another method of identifying the mesophase. The material with unknown mesophase is mixed with a known material that possesses mesophases that have already been identified. If a particular mesophase of the unknown material is
completely miscible with a known mesophase, then both the mesophases are identical. Other technique used to identify the structure of mesophase and liquid crystalline mesophase include neutron scattering and nuclear magnetic resonance.

### 3.5.1 Optical Polarising Microscopy

Everyone working in the field of liquid crystals will at some point need to use optical polarizing microscopy in the analysis of liquid crystals. The identification of mesophase through optical polarizing microscopy usually involves the magnified view of a thin sample of mesogenic material sandwiched between a glass microscope slide and glass cover slip [26]. Usually phase identification is carried out on glass slides that are not treated to obtain any particular alignment. Polarizers in the microscope are placed at 90° to each other, so no light passes through when isotropic liquid or no sample is analyzed [26-39]. But when birefringence material is present, optical textures appears that gives information relating to the arrangement of the molecules within the medium.

![Optical Polarizing Microscope and Optical Textures](image)

**Figure 3.20** (A) Optical Polarizing Microscope. (B) And (C) Optical textures of some Liquid Crystals.

Smectic phases that are generated by heating a sample from the crystal phase are often very difficult to identify unequivocally because their optical defect
textures retain characteristics of crystal phase. Therefore material is heated into the isotropic liquid phase and mesophases are identified from their defect textures generated on cooling.

### 3.5.2 Differential Scanning Calorimetry

DSC reveals the presence of phase transition in a material by detecting the enthalpy change associated with each phase transition [29]. Eventhough the precise identity of the phase cannot be obtained, but the level of enthalpy change at the phase transition does provide some identification of the types of phase involved. Therefore optical microscopy and DSC are used in conjunction with each other.

In general there are two types of phase transition- continuous (first order transition) and discontinuous (second order transition). If the entropy at phase transition shows a discontinuity, then a discontinuous first order transition has occurred. Most liquid crystal to liquid crystal transitions are discontinuous, but some such as SmC to SmA transition, are often continuous.

![Differential Scanning Calorimeter](image1)

![DSC Thermogram of well known Nematic Liquid Crystal (5CB)](image2)

Figure 3.21 (A) Differential Scanning Calorimeter. (B) DSC Thermogram of well known Nematic Liquid Crystal (5CB).
3.6 Response Time Measurement

There are two well known methods for the measurement of response time of the liquid crystals i.e. electrical and the optical method [1, 20]. We have used the optical switching method. The response time of nematics can be measured by the three in one analyser shown in figure 3.22. A square wave of frequency 1 Hz and amplitude of 20V peak to peak has been applied to the sample cell. The LDR is used to record optical response of molecules and the LDR response is fed to storage oscilloscope (HM 407). For the nematic, response time is defined as the time taken by the molecules to produce the change in transmission from 10 % to 90 % of its maximum value as shown in figure 3.23 [1, 20].

\[
\tau_{\text{rise}} = \tau_{90} - \tau_{10}
\]

\[
\tau_{\text{fall}} = \tau_{10} - \tau_{90}
\]

The total response time is given by \( \tau_{\text{total}} = \tau_{\text{rise}} + \tau_{\text{fall}} \).
3.7 Gamma Ray Modification Technique

The phenomenon of gamma radiation induced conductivity in solid insulators has been studied by several investigators. Most attention has been given to studies of organic insulators [30-32], and some have been made of inorganic insulators [33-35]. Up to now, only few reports were dedicated to radiation effects on physicochemical properties and on the conductivity of the liquid crystals materials [36]. Data regarding radiation effects on liquid crystal and organo-photonic material is almost non-existent [37].
Preliminary studies on some liquid crystals suggest that their physical and chemical properties are highly affected by radiation. Most of these suggest that the transition temperatures and the stability of various liquid crystalline mesophases are strongly affected by radiation [38]. Some of the electrical properties such as electrical conductivity and charge carrier mobility subjected by ionizing radiation have been studied very first in 1988 by Kovalchuk et al. [39]. Talor et al. first reported on the degradation of light transmission characteristics of a smectic C liquid crystal [40]. Graham et al. also reported on the effect of space radiation dose on the nematic liquid crystal variable retarders (LCVR) [41]. Such other radiation effects on the liquid crystal materials namely electron beam radiation, UV radiation, ion beam radiation has also been reported [42].

Absorption of gamma rays by liquid crystal may cause physical conformational changes due to thermal and thermo-mechanical effects. These physical changes may cause scattering of light, changes in transmission and reflection properties of filters and coatings. Early liquid crystal phase retarders were screened at Raytheon for radiation sensitivity circa 1989 under the AFRL Beam agility technique program (F33615-87-1507). Phase retarders were used as surrogates for optical phased arrays and subjected to increasing gamma ray dose from a cobalt-60 source, upto a total dose of 9.5 Mrad. It was the first known radiation testing of liquid crystal [43].

The contribution of ions in the electric properties of semi conductors, electrolytes and dielectric materials has been extensively investigated in the past both theoretically and experimentally [44, 45]. The dielectric characterization of a sample is usually done by applying a single frequency voltage (or current) to the electrodes and measuring the phase shifts and amplitude of resulting current at that frequency. The sample behaves as linear system when the amplitude of the measurement voltage is small with respect to the thermal voltage. When more than
one type of ions are present and the measurements are done in the linear region, one uses the superposition principle to add the contribution of each type of ions in the dielectric response of the sample. Here we have used gamma radiation technique to evaluate the dielectric and electro-optical enhancement by gamma ray with the liquid crystal molecules. The details are discuss in next chapters. We are thankful to BRNS India for financial assistance. We are also thankful to Mr. T.K. Srinivasan for his help in the gamma irradiation.

3.8 FTIR Study

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. FTIR has made dispersive infrared spectrometers all but obsolete (except sometimes in the near infrared), opening up new applications of infrared spectroscopy.

The term Fourier transform infrared spectroscopy originates from the fact that a Fourier transform (a mathematical process) is required to convert the raw data into the actual spectrum. The goal of any absorption spectroscopy (FTIR, ultraviolet-visible ("UV-Vis") spectroscopy, etc.) is to measure how well a sample absorbs light at each wavelength. The most straightforward way to do this, the "dispersive spectroscopy" technique, is to shine [46] a monochromatic light beam at a sample, measure how much of the light is absorbed, and repeat for each different wavelength. (This is how UV-Vis spectrometers work, for example.)

Fourier transform spectroscopy is a less intuitive way to obtain the same information. Rather than shining a monochromatic beam of light at the sample,
this technique shines a beam containing many frequencies of light at once, and measures how much of that beam is absorbed by the sample. Next, the beam is modified to contain a different combination of frequencies, giving a second data point. This process is repeated many times. Afterwards, a computer takes all these data and works backwards to infer what the absorption is at each wavelength [46].

The beam described above is generated by starting with a broadband light source—one containing the full spectrum of wavelengths to be measured. The light shines into a Michelson interferometer—a certain configuration of mirrors, one of which is moved by a motor. As this mirror moves, each wavelength of light in the beam is periodically blocked, transmitted, blocked, transmitted, by the interferometer, due to wave interference. Different wavelengths are modulated at different rates, so that at each moment, the beam coming out of the interferometer has a different spectrum [46].

Here we have used the IRAffinity-1 (Shimadzu) Fourier Transform Infrared Spectrophotometer.
3.9 Temperature Controller

The accurate temperature measurement is very crucial point while studying the characteristics of any thermotropic liquid crystals. For the same purpose the INSTEC hot plate HCS 302 and Julabo temperature controller have been used in the present work.

3.9.1 Julabo F-25

A microprocessor based temperature controller (model Julabo F-25 HD) is used as shown in figure 3.25(a). It uses synthetic oils for maintaining the temperature of the sample holder. The oil circulates in a double walled jacket and a Pt-100 type sensor is placed in the jacket at the appropriate place to measure the temperature. With this temperature controller we can read a temperature variation of ±0.01°C.

Figure 3.24 (a) FTIR (b) IR spectra for a liquid crystalline sample.
3.9.2 Instec HCS 302

The INSTEC HCS 302 heating/cooling stage is an instrument of very high precession for the temperature control. This package includes heating/cooling stage HCS 302, 1/16 DIN temperature controller STC 200 and computer software WinTemp. The hot stage HCS 302 uses single heater located underneath the sample chamber shown in figure 3.25 (b).

The HCS 302 is equipped with ports for the cooling accessories, such as liquid Nitrogen (LN2) pumps as well as gas purging of the sample chamber and defrost of the top and bottom windows (to prevent condensation during below ambient operation), and frame cooling (to prevent excessive external temperature during the high temperature operations) [47, 48]. These features of hot stage provide flexibility to a user to operate it in the wide temperature range from -190 °C to 400 °C. This hot stage also provides easy handling by the specially designed swing open cover.
The STC 200 temperature controller is used to adjust the sample temperature for observation and their measurement. STC 200 is a very user friendly device which provides simple temperature operations using the four keys provided at the front panel. The simple isothermal setting can be achieved by up or down arrow keys on STC 200 CPU. The STC 200 temperature controller can be used in standalone mode as well as in remote mode with computer software WinTemp. The STC 200 can be interfaced with the computer simply by RS232 port or IEEE card and can be operated with the help of WinTemp software.

The WinTemp software provides easy single command or small program algorithms to operate STC 200 for different temperature operations. The list of commands is as follows:

- **HOLD:** used to hold the temperature
- **HOLD AT:** used to hold at a specified temperature
- **HOLD FOR (Time Interval min.):** used to hold for a particular time

---

**Figure 3.25** (a) Julabo F-25 Temperature Controller  (b) Instec HCS 302 heating/cooling stage (c) Instec STC 200 temperature controller.
HOLD AT (temperature) FOR (time interval): used to hold at a particular temperature for a particular time

RAMP TO (temperature) AT rate: used to ramp the temperature at a particular rate

STOP: used to stop the programme

BEEP: used as an indicator (to beep the speaker)

A small program algorithm is as follows-

RAMP TO 80.00 AT 0.50
HOLD AT 80.00 FOR 2
BEEP
BEEP
HOLD AT 80.00 FOR 10
BEEP
RAMP TO 70.00 AT 0.50
HOLD AT 70.00 FOR 2
BEEP
BEEP
HOLD AT 70.00 FOR 10
BEEP

The above program algorithm is a small part of the dielectric measurement program. The first command ramp the hot stage to 80 °C with the heating rate of 0.5 °C/min and after reaching at this temperature the second command holds the hot stage at the same temperature for 2 minutes so that sample can stabilize. After 2 minutes next command intimates us by the beeping alarm to start reading procedure of the HP 4194A which needs approximately 10 minutes to complete.
The next command used to hold hot stage at the same temperature for 10 minutes in which reading process completes. Again an intimating beep alarm becomes active and this intimates that the reading process is completed. The preceding commands follow the same steps discussed above for the next temperature i.e. 70 °C in the present case. Similar type of small program algorithm has been developed for different set of experiments and performed successfully.

*Table 3.1. Specification of the heating/cooling stage Instec HCS 302.*

<table>
<thead>
<tr>
<th>Features</th>
<th>HCS302</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature Range</td>
<td>-190 °C to 400 °C. Optional higher temperature limit available</td>
</tr>
<tr>
<td>Temperature Accuracy</td>
<td>0.5 °C to 100°C, + 1.0 °C to 200°C</td>
</tr>
<tr>
<td>Temperature Stability</td>
<td>0.1 °C at 100°C</td>
</tr>
<tr>
<td>Minimum Heating and Cooling Rate</td>
<td>0.1°C/Hour</td>
</tr>
<tr>
<td>Maximum Heating Rate</td>
<td>+ 100 °C/Min. at 37°C</td>
</tr>
<tr>
<td>Maximum Cooling Rate (Using LN2-P2F2)</td>
<td>- 100 °C/Min. at 37°C</td>
</tr>
<tr>
<td>Temperature Control Sensor</td>
<td>100 Q Platinum R TD</td>
</tr>
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<td>Control Method</td>
<td>Switching PID</td>
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<tr>
<td>Minimum Condenser Distance</td>
<td>10 mm</td>
</tr>
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<td>---------------------------</td>
<td>-------</td>
</tr>
<tr>
<td>Sample Area</td>
<td>38 mm x 50 mm</td>
</tr>
<tr>
<td>Chamber Height</td>
<td>2.0 mm, up to 12.5 mm when using optional spacers</td>
</tr>
<tr>
<td>Sample View Aperture</td>
<td>5 mm diameter (10 mm optional)</td>
</tr>
</tbody>
</table>
References

Dielectric Investigation on Newly Synthesized H-Shaped Liquid Crystalline Dimer
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References
4.1 Introduction

Liquid crystal possesses many unique physical and optical properties thus importance of liquid crystals lies in their extensive use in display devices, as well as many other scientific applications [1, 2]. However the use of liquid crystals in different devices depends on various dielectric as well as electro-optical parameters. A particular application of liquid crystals requires a particular set of parameters of liquid crystals in required range [3]. Researchers have made significant inroads into understanding the properties of liquid crystalline substances, but still the problem of predicting physical properties of liquid crystalline compounds based upon information on molecular shape and intermolecular interaction remains one of the most fundamental problems in the liquid crystal physics [4, 5]. The design of novel thermotropic liquid crystals involves suitable selection of a core fragment, linking group and terminal functionality. In 1907 Vorlander proposed a rule that the liquid crystalline state is obtained for the most linear of molecules. Later, an isometric rod like- or disk like-shape molecules used to be a fundamental requisite for conventional thermotropic liquid crystal formation because of steric packing considerations play an important role in this interesting state of soft matter [6, 7]. More recently, with the discovery of banana shaped liquid crystals, where bent molecules serve as core, interest in the incorporation of non linear units has gained importance from application point of view. A large number of bent core liquid crystal molecules have been synthesized and their analyses have been reported in the field of liquid crystal [8, 9].

Currently molecular topology and microsegregation have attracted much attention for producing unusual molecular structure such as supramolecular assemblies composed of super molecules i.e. oligomeric and dendritic liquid crystals [10, 11]. Recently dendritic liquid crystals have been investigated intensively, because functional dendrimers have rich super molecular chemistry and self assembling properties [12, 13]. The introduction of a bent shape in a molecular structure is another important strategy in the design of super molecules which exists in our liquid crystalline sample (discussed
Recently, liquid crystal dimers have been the focus and targets of many researchers because they exhibit remarkable and quite different phase transition properties to conventional liquid crystals; they can also be regarded as model compounds for main chain liquid crystals [14, 15]. A symmetrical or unsymmetrical dimer is formed when two chemically identical or non-identical anisometric segments, respectively, are connected covalently through a flexible spacer.

Lateral substitution at the centre of the mesogen increases the molar volume and decreases the liquid crystal packing density, thereby hindering their ability to form any kind of liquid crystalline phase if the mesogens is short, and smectic mesophases if the mesogen is more extended [16, 17].

Several factors influence the dielectric properties of liquid crystal materials. The value and the position of the dipole moment in the molecule, the ratio of the longitudinal to transverse dimensions of molecules, the lengths and flexibility of the terminal groups and the rigidity or an internal rotational freedom in the molecular cores seem to be the most important structural factors [17-19].

The present chapter reports the dielectric properties of unusual H-Shaped liquid crystal dimer exhibiting two meso phases (SmC and SmX). The dielectric spectroscopy method is very well suited to study the rotational dynamics of molecules in liquid crystalline phases if the constituting molecules posses a dipole moment. The dielectric results show that sample follow Cole-Cole type of relaxation. The different dielectric parameters have been evaluated by Cole-Cole plots. The temperature dependence of different dielectric parameters such as dielectric permittivity; dielectric loss has also been reported. In addition to this activation energy for the given sample has also been evaluated. The dynamics of the dielectric relaxation process in molecules, in which internal rotation is possible, has been of interest to several research workers in the past.
4.2 Experimental Procedure

4.2.1 Material Used

The sample under investigation is H-shaped mesogenic dimer: Bis[5-(4'-n-dodecyloxybenzoyloxy)-2-(4’-chlorophenylazo)phenyl]butylethers (12-Cl-H4), that has been prepared by the alkylation of 4-chloro-2’-hydroxy-4’-(4-n-alkoxybenzoyloxy) azobenzene with 1, 4-dibromo butane following the process reported in the literature. Energy-minimized balls and sticks model (MM2 models derived from CS Chem draw Ultra 7.0 software) of H-shaped liquid crystal (12-Cl-H4) is given in figure 4.1.

![Energy-Minimized Balls and Sticks Model (MM2 Models Derived From CS Chem Draw Ultra 7.0 Software) Of H-Shaped Liquid Crystal (12-Cl-H4)](image)

Figure 4.1 Energy-Minimized Balls and Sticks Model (MM2 Models Derived From CS Chem Draw Ultra 7.0 Software) Of H-Shaped Liquid Crystal (12-Cl-H4)

The phase transition scheme for the sample (12-Cl-H4) is given below:-

\[
\text{Cr} \quad \rightarrow \quad \text{SmC} \quad \rightarrow \quad \text{SmX} \quad \rightarrow \quad \text{Cr}
\]

(87°C) (66°C) (55°C)

4.2.2 Preparation of Cell

Two similar cells having active area 49 mm², (sheet resistance and the visible light transmission are 10Ω/mm² and more than 90%, respectively) were prepared by using transparent and highly conducting ITO-coated (Indium Tin Oxide), optically flat glass substrates used as electrodes. These electrodes provide a base to align the liquid crystal sample. The preparation of sample cells with planar alignment has been discussed in chapter 3.
4.2.3 Dielectric Permittivity Study

The dielectric behavior of the material has been studied by using a computer-controlled impedance/gain phase analyzer Hewlett Packard (HP 4194 A) [20-23]. The dielectric parameters were measured as a function of frequency and temperature. In order to vary the temperature a microprocessor-based heating device (Julabo – F25) has been used. The experiment was performed at very slow heating rate, and temperature was measured and controlled with accuracy of ±0.01°C. The experimental details has been already discussed in chapter 3.

4.3 Result and Discussion

We have determined the different dielectric parameters of the sample using the Cole-Cole [24] dispersion equation given by

\[ \varepsilon^* = \varepsilon'_\infty + \frac{\delta \varepsilon'}{1 + (j\omega\tau)^{1-\alpha}} \]  

(4.1)

Here \( \delta \varepsilon' \) is the dielectric strength of the material, \( \varepsilon'_\infty \) is the high frequency limit of the dielectric permittivity, \( \omega (=2\pi f) \) is the angular frequency, \( \tau \) is the relaxation time and \( \alpha \) is the distribution parameter. If the value of \( \alpha \) is small and approaches zero, the above equation will satisfy the Debye type of relaxation phenomena, but for values more than 0.5, the above equation suggests the existence of more than one relaxation process.

The sample cell geometry introduces errors in the data in both the low and high ends of the frequency range investigated. Therefore, the experimental results required a low- and high-frequency correction. On separating real and imaginary parts of the equation (4.1) and adding high- and low-frequency correction parameters, we find

\[ \varepsilon' = \varepsilon'_\infty f^{-\alpha} + \varepsilon'_\infty + \frac{\delta \varepsilon'[1+(2\pi\tau)^{1-\alpha})\sin(\alpha\pi/2)]}{1+(2\pi\tau)^{2(1-\alpha)} + 2(2\pi\tau)^{(1-\alpha)}\sin(\alpha\pi/2)} \]  

(4.2)

and
\[ \varepsilon'' = \frac{\sigma_{dc}}{\varepsilon_0 2\pi f} + \frac{\delta \varepsilon'(f\tau)^{(1-n)} \cos(\alpha \pi / 2)}{1 + (2\pi f \tau)^{(1-n)} + 2(2\pi f \tau)^{(1-n)} \sin(\alpha \pi / 2)} + Af^m \]  

(4.3)

Where \( \sigma_{dc} \) is the ionic conductance, \( \varepsilon_0 \) is the free space permittivity and \( f \) is the frequency, while \( n, m \) and \( k \) are the fitting parameters. The terms \( \sigma_{dc}, f^n \) and \( \sigma_{dc} / \varepsilon_0 2\pi f^k \) are added in equations (4.2) and (4.3) to correct for electrode polarization, capacitance, and ionic conductance at low frequencies. Term \( Af^m \) is added in equation (4.3) for high frequencies to correct for the ITO sheet resistance and lead inductance of the cell. By a least square fitting of the above equations using experimental data, we have removed the low and high frequency errors.

\[ (A) \]

Figure 4.2 (A) Cole Cole Plot Showing Dual Smectic Phases (B) Fitted Cole Cole Plot

The Cole-Cole plot of the sample, while it is in the dual smectic phases, has been drawn at specific temperature 75°C as shown in figure 4.2(A). Figure 4.2(B), has been obtained from best theoretical fitting of the Cole-Cole equation with the data, black circles represent experimental data while solid red line shows best theoretical fitting data. Using such plots, values of dielectric parameters, such as the relaxation frequency, dielectric permittivity, activation energy and many more have been evaluated.
Figure 4.3 Variation In Relaxation Frequency With Temperature

Figure 4.3 shows the variation in relaxation frequency with temperature. Such relaxation studies provide information about the molecular reorientation of the molecules. The observations suggest that the relaxation peak gradually increases with increase in temperature. The reason for this is the distortion in the shape of the molecules and thus relaxation processes exhibited may be correlated to the rotation of the side chain of the molecule. To explain it a topological molecular arrangement presented in figure 4.4.

Figure 4.4 Shows the Two Different Possible Conformers in H Shaped Liquid Crystal

In this model there are two possible conformers called Species1 (rod1) and Species2 (rod2) having two most preferred alignment directions of molecule. With increase in temperature the rotation of molecules produces polarization which is in
opposite direction vanishes and becomes minimum. Due to this reason relaxation peak shifted toward higher side by presence of conformer’s rotation in such a manner.

![Figure 4.5 Variation In Dielectric Permittivity With Temperature](image)

**Figure 4.5 Variation In Dielectric Permittivity With Temperature**

The observed dielectric permittivity with variation in temperature has been shown in figure 4.5. Figure suggest that the dielectric permittivity increases up to a definite temperature than decreases at the clearing point or isotropic temperature, because in isotropic state molecule does not experience any force. Value of effective dielectric permittivity increases for the sample, shows slight change near crystal to SmX phase transition at 55°C. Further increase in temperature, occurred and after 66°C sample enters in SmC phase, the reason which can be attributed behind this trend could be (the rotation of the side chains of molecules), the coupling between the orientational and conformational order, which is due to the influence of flexible spacer. This also effects interlayer permeation of chain of molecules (the shorter tails and the longer tails co-exists along with a flexible spacer) causing correlation between cores in adjacent layers in SmC and SmX phase which is influenced by the dimeric property of unusual shape of the liquid crystal molecule.
Relaxation strength as a function of temperature for the sample has been plotted in figure 4.6. The observed relaxation strength for the sample increases with increase in temperature. The relaxation strength of the sample slightly decreases at higher temperature due to zig-zag shape of molecule which may result in the rotational freezing of the molecule resulting in slight tilting of the molecule at higher temperatures.

![Graph](image)

**Figure 4.6 Relaxation Strength with Variation in Temperature**

In our case oxygen atom links the terminal chains to the core units in series, and addition of oxygen atom tends to bend the terminal chains away from the long axis of the central part of the molecule. Thus the molecule exhibits the zig-zag picture; this unusual detailed investigation on single mesogen molecule reveals that (zig-zag molecules can pack tightly into layers, but only if parts of the molecules are tilted relative to a line perpendicular to the layers).
Figure 4.7 Behaviour Of Dielectric Permittivity with Variation in Frequency

Figure 4.7 shows the variation in dielectric permittivity with frequency, initially; at lower frequency the trend is same as observe in many liquid crystal samples and this is maintained due to “tumbling” motion -which can be co-related with the molecular rotation around the short molecular axis (LF process). Such motion are referred to as molecular “tumbling” where as when frequency is increased in SmC phase the same constant trend is observed but this time molecular rotation around the long molecular axis (HF process). Such motions are referred as spinning. This constancy in trend has been obtained due to the spacer attached between the two rod like molecules (species 1 and 2) which plays a vital role in maintaing constancy at higher and lower frequencies (flexible spacer group and length in A^0, is represented in structure).
Figure 4.8 Behaviour of Dielectric Loss with Variation in Frequency

Figure 4.8 represents the dielectric loss with variation in frequency. The dielectric loss curve has been plotted for both phases SmX and SmC. Dielectric loss of the sample has been examined the loss in the sample is due to the mutual interaction between the permanent and the induced dipoles of the molecular sites, (lateral component in the molecule is essential to exhibit SmC phase), thus during the phase transition dipole moment (permanent and induced) plays a vital role and results in loss, exhibiting such a trend.

The Arrhenius equation describes the behavior for a process from one state to another separated by a potential barrier (Such as for example a double wall potential) the height of the barrier translate to the activation energy. In liquid crystal devices the relaxation time is of extreme importance which further depends on the cell gap, the degree of molecular alignment and many other parameters. When a high voltage is applied to the sample cell it affects relaxation time and all these properties depend on the activation energy, which plays a crucial role in many applications.
Therefore activation energy has been calculated by using Arrhenius plot of the relaxation time Figure 4.9.

\[ \tau = \tau_o \exp \left( \frac{W_b}{kT} \right) \]  

(4.4)

Where \( W_b \) is the activation energy, \( k \) is Boltzmann’s constant and \( \tau \) is the relaxation time. The activation energy for this sample is 15.15 meV in SmC phase and 27.20 meV SmX phase.

As we are aware of the fact that liquid crystal sample suffers from several defects one of them is splay.

The Maier Saupe theory assumes that the force between liquid crystal molecules is a dispersion force. The dispersion force arises between two molecules that posses no permanent electric dipoles but posses induced electric dipoles. In fact, we have observed that the average force experienced by a single molecule, due to other molecule can be derived using more forces than just the dispersion force because in our case molecules are not perfect rods and complete structure of the molecule are taken in to account. Thus, splay defect suffered by many liquid crystalline systems can be minimized by utilizing the specific molecule which is subject of this study.
Thus, on the basis of the proposed topological molecular model we predict that the average force on each molecule is inversely proportional to the magnitude of the splay defect. For a sample the rotation of side chain, the interlayer permeation of tails producing a correlation between cores in adjacent layers and with spacer, the unusual structure and most importantly, the relatively high average force experienced by each molecule in a bulk sample, all result in reducing the splay defect. Thus, we predict that the average force on each molecule is inversely proportional to the magnitude of splay defect (in our case this average force is large as compared with other liquid crystal molecules.) To overcome splay defect, molecules are arranged in a usual manner due to which average force experienced by the molecule help in reducing splay defect. Thus this material could trigger a revolution in liquid crystalline devices.
References

Enhancement in dielectric properties of nematic liquid crystal by gamma-irradiation
5.1 Introduction

5.2 Experimental Details
   5.2.1 Material
   5.2.2 Preparation Of Cell
   5.2.3 Gamma Ray Treatment
   5.2.4 Dielectric Permittivity Study

5.3 Results And Discussion

5.4 Conclusion

References
5.1 Introduction

Nematic liquid crystals (NLCs) consist of asymmetric molecules that tend to align in a common local direction described by the director. Smectic liquid crystals usually do not respond to applied electric and magnetic fields as easily as NLCs and so attempts are continuously being made to enhance the properties these liquid crystals from application point of view [1-3]. In addition to this nematic Liquid crystals have long-range orientational order, which gives rise to many properties important for liquid crystal displays [4-8]. It is known that dielectric studies of liquid crystalline materials are a valuable source of information on their molecular arrangement, molecular dynamics and specific intermolecular interactions, in both mesomorphic and isotropic phases [9, 10].

Heavy ions of various energies are being used for material modifications. These induced modifications depend on defect in the material during interaction of ions with the target material [11]. Absorption of gamma rays by liquid crystal may cause physical conformational changes due to thermal and thermo-mechanical effects. These physical changes may cause scattering of light, changes in transmission and reflection properties of filters and coatings. Early liquid crystal phase retarders were screened at Raytheon for radiation sensitivity circa 1989 under the AFRL Beam agility technique program (F33615-87-1507). Phase retarders were used as surrogates for optical phased arrays and subjected to increasing gamma ray dose from a cobalt-60 source, upto a total dose of 9.5 Mrad. It was the first known radiation testing of liquid crystal [12, 13].

Dielectric studies of the liquid crystals are important as they provide useful information about molecular structure, molecular dynamics, phase transition and display performance of liquid crystals [14]. Most of the dielectric studies on liquid crystals are concentrated in the nematic phase and usually examine the nematic -Isotropic phase transition. The optical characteristics, threshold voltages and switching times of liquid crystals are strongly dependent on the absolute value of their dielectric permittivity. Dielectric relaxation studies provide one of the few techniques for finding the nature of molecular reorientation within a system. Dielectric studies of a large number of
thermotropic liquid crystalline substances have been conducted and thus dielectric spectroscopy is found to be one of the best techniques for measuring dielectric permittivity and dielectric losses with high accuracy and sensitivity [15-17].

Therefore to observe the effect of gamma radiation on nematic liquid crystal materials, we have applied Gamma- irradiation technique. This is a powerful technique for investigations of condensed matter. Relaxation of different physical origin, such as molecular reorientation, dynamics of collective or surface polarization modes, and conductivity can be investigated in different liquid crystal systems. Detailed qualitative and quantitative information characterizing these processes has been obtained by this technique. In fact we have attempted to investigate how this irradiation affects in the alignment of the sample and consequently how it affects the dielectric parameters.

5.2 Experimental details

5.2.1 Material

The liquid crystal sample under investigation is a rod shaped molecule contains a cyano group at its one end, which makes it a highly polar molecule. The nematic liquid crystal is 5CB and its transition scheme with its molecular structure is given in the figure 5.1.

![Chemical structure of 5CB]

Figure 5.1 Chemical structure of 5CB

5.2.2 Preparation of cell
Two similar cells having active areas 25 mm$^2$, (sheet resistance and the visible light transmission is 10Ω/mm$^2$ and more than 90% respectively) were prepared by using transparent and highly conducting ITO (Indium Tin Oxide) (Diamonds Coating UK) coated optically flat glass substrates used as electrodes. These electrodes give a base to the liquid crystal sample to align. Planar alignment is obtained by treating both adhesion promoter and polymer (Nylon 6/6) and then rubbed unidirectional with a velvet cloth. The thickness of the cell was maintained at 5 μm by means of mylar spacer. The complete preparations of cell have been given in chapter 3. The correct and proper alignment of the liquid crystal molecules is extremely important, for precise measurement of electrical properties and which in turn influences dielectric parameters and thus plays an extremely important role in molecular geometry [18].

5.2.3 Gamma Ray treatment

We irradiated the 5CB liquid crystal as well as blank planar cell. The irradiation used a $^{60}$Co source, at the dose rate of 2.9kGy/h, up to a total dose for 34.5 h is 100 kGy.

5.2.4 Dielectric permittivity study

The dielectric behavior of the material has been studied by using a computer controlled impedance/ gain phase analyzer Hewlett Packard (HP 4194 A). The dielectric parameters have been measured as a function of temperature and frequency. In order to vary the temperature of the sample holder a microprocessor based heating device Instec hot plate (HCS-302) with an accuracy of ± 0.1$^0$C has been used. Before taking measurements the sample was left for 15 minutes at a particular temperature. The detail discussion about the experimental procedure has been given in chapter 3.

5.3 Results and Discussion

The live capacitance value of empty irradiated planar cell was measured and it was found to be flippantly lower (approximately 2%) than that of the unirradiated empty sample cell. The difference of live capacitance is very small for gamma irradiated and unirradiated cell within the scope of experimental error. It is not expected to affect the dielectric properties of the liquid crystal material. The dielectric data have been analyzed by well known Cole-Cole dispersion equation \((1)\) given by:

\[
\varepsilon^* = \varepsilon'(\infty) + \frac{\delta \varepsilon'}{1 + (j \omega \tau)^{(1-\alpha)}}
\]

Here \(\delta \varepsilon'\) is the dielectric strength of the material, \(\varepsilon'(\infty)\) is the high frequency limit of dielectric permittivity, \(\omega (= 2\pi f)\) is the angular frequency, \(\tau\) is the relaxation time and \(\alpha\) is the distribution parameter. The value of distribution parameter more than 0.5 suggests the existence of more than one relaxation process.

The Cole-Cole plot of the sample, which exhibits nematic phase, has been drawn for both gamma irradiated and unirradiated sample cell, filled with 5CB, at specific temperature 29°C as shown in figure 5.2, black legend shows experimental data while solid red line shows best theoretical fitting of Cole-Cole equation into experimental data. Using such plots dielectric parameters such as relaxation frequency, relaxation strength was calculated and their temperature dependence has been discussed in the later part of the chapter.
Figure 5.2 Cole-Cole plot for gamma irradiated and unirradiated 5CB

On separating real and imaginary part of the equation (1) one may get after adding high and low frequency correction parameters

\[
\varepsilon'(\omega) = \varepsilon'(dc)f^{-n} + \varepsilon'(\infty) + \frac{\delta\varepsilon'[1 + (\omega \tau)^{(1-\alpha)} \sin(\alpha \pi / 2)]}{1 + (\omega \tau)^{2(1-\alpha)} + 2(\omega \tau)^{(1-\alpha)} \sin(\alpha \pi / 2)}
\]  

(2)

And

\[
\varepsilon''(\omega) = \frac{\sigma(d\varepsilon)}{\varepsilon_o \omega^k} + \frac{\delta\varepsilon'(f\tau)^{(1-\alpha)} \cos(\alpha \pi / 2)}{1 + (\omega \tau)^{2(1-\alpha)} + 2(\omega \tau)^{(1-\alpha)} \sin(\alpha \pi / 2)} + Af^m
\]  

(3)

Where \(\sigma(d\varepsilon)\) is the ionic conductance and \(\varepsilon_o\) is the free space permittivity and \(f\) is the frequency while \(n, m\) and \(k\) are the fitting parameters. The term \(\varepsilon'(dc)f^{-n}\) and \(\sigma(d\varepsilon)/\varepsilon_o2\pi f^k\) are added in equations for low frequency effect due to the electrode polarization, capacitance and ionic conductance. The term \(Af^m\) is added in equation (3) for high frequency effect due to the ITO sheet resistance and lead inductance of the cell. By the least square fitting of above equation into experimental data we have removed the low and high frequency errors. After adding correction terms the complex dielectric permittivity has been plotted against natural log of frequency as shown in the figure 5.3.
Figure 5.3 Complex dielectric permittivity with respect to natural log of frequency for gamma irradiated and unirradiated 5CB

The observed value of complex dielectric permittivity for both irradiated and unirradiated 5CB sample, nature of variation with frequency is same [19], but the values have increased for gamma irradiated 5CB sample. This increment in the values of dielectric permittivity for gamma irradiated sample could be explained on the basis of physicochemical [20] change in the liquid crystals. Actually irradiation causes a chemical change in liquid crystals, it may include cross linking, chain scission, formation of alkyl groups, depletion of hetero atoms. Effect of gamma irradiation or such other ionizing radiation is primarily chain scission. Therefore many physical and chemical properties can show modification with gamma irradiation. Radiation mainly affects in two basic ways, both resulting with excitation or ionization of atoms. In this fashion ionic conductivity of liquid crystal material has also been investigated. The ionic conductivity
for irradiated 5CB is comparatively higher than that of unirradiated 5CB sample. This increment in ionic conductivity between irradiated and unirradiated sample has been shown with variation of temperature in figure 5.4. When filled 5CB cell is gamma irradiated, the irradiation causes a chemical change in the 5CB, which results in the generation of new ions. The influence of the ions on the dielectric properties of nematic liquid crystals has been well explained by many authors because of their technological importance. The theoretical analysis of the problem is usually contains only a group of cations and anions, with equal or different diffusion coefficients. The extension of theory to the case where several groups of ions are dissolved in nematic liquid crystal is important from the practical point of view, because more than one type of impurities is, usually, present in the nematic liquid crystals, which intern affects the creation of ions that are responsible for the electrical parameter. These ions play an important role in the formation of charge carriers in the nematic liquid crystal. The presence of positive ions due to gamma irradiation cause the change in the conductivity of liquid crystal cell. It can be said that such a trend in the dielectric permittivity is resulted due to the modification in 5CB molecule as well as substrate due to high energy gamma irradiation. This increase in permittivity for irradiated sample has also been observed at all temperatures under investigation as shown in figure 5.5.
Figure 5.4 Ionic conductivity with respect to temperature for gamma irradiated and unirradiated 5CB

Figure 5.5 Dielectric permittivity with respect to temperature for gamma irradiated and unirradiated 5CB
Variation of different dielectric parameters (Distribution Parameter, Relaxation Time, Relaxation Strength) for gamma irradiated and unirradiated 5CB sample at constant temperature 29°C has been presented in Table 1. The value of relaxation time and relaxation strength is increased while value of distribution parameter is decreased for gamma irradiated sample as compared to unirradiated sample.

Table 1. Variation of different dielectric parameters for gamma irradiated and unirradiated 5CB sample at constant temperature (29°C)

<table>
<thead>
<tr>
<th>Sample (5CB)</th>
<th>Distribution Parameter (α)</th>
<th>Relaxation Time (τ in Second)</th>
<th>Relaxation Strength (δε)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irradiated</td>
<td>0.00721</td>
<td>5.37E-07</td>
<td>6.10605</td>
</tr>
<tr>
<td>Unirradiated</td>
<td>0.00866</td>
<td>3.42E-07</td>
<td>3.3358</td>
</tr>
</tbody>
</table>

Another important dielectric parameter on which we have concentrated is relaxation frequency with variation in temperature shown in figure 5.6. The relaxation frequency has been extracted from the theoretical fittings of the Cole- Cole equation to experimental results and its temperature dependence has been plotted, for both irradiated and unirradiated samples. It is clear from the figure that the relaxation frequency shifts towards the lower side for the gamma irradiated sample and this relevant decrease occurring in the nematic phase and the relaxation process can be interpreted in the terms of gamma irradiation effect on the sample. As discussed earlier that as soon as the cell is irradiated –this results in creation of ions that are responsible for currents through the liquid crystals. The presence of positive ions in 5CB which govern conductivity in the liquid crystal cell –gradually affects the molecular reorientations. Due to this reason each molecule move in time as a sequence of small angular steps caused by collisions with its surroundings and, under the influence of a potential of mean- torque set up by these molecules, decrease the relaxation frequency. Figure 5.7 shows variation of relaxation.
strength with temperature for both gamma irradiated and unirradiated 5CB sample. From the figure we can see that after gamma irradiation on 5CB the value of relaxation strength increases as compared to the unirradiated 5CB sample. The reason is same as earlier discussion of relaxation frequency with variation in frequency.

![Figure 5.6 Relaxation Frequency with respect to temperature for gamma irradiated and unirradiated 5CB Liquid Crystal](image)

*Figure 5.6 Relaxation Frequency with respect to temperature for gamma irradiated and unirradiated 5CB Liquid Crystal*
Figure 5.7 Relaxation Strength with respect to temperature for gamma irradiated and unirradiated 5CB Liquid Crystal

5.4 Conclusion

The changes due to gamma irradiation on nematic liquid crystal have been investigated using dielectric spectroscopy technique. Some of the dielectric parameters like complex dielectric permittivity, relaxation frequency have been evaluated for the gamma irradiated sample and compared with the unirradiated sample. We observe that the nature of variation of dielectric permittivity with frequency and temperature remains same for both the gamma irradiated and the unirradiated 5CB samples, but the value of dielectric permittivity for the gamma irradiated sample is higher as compared to the unirradiated 5CB sample. This increment in the gamma irradiated sample can be explained on the basis of physicochemical change in the 5CB molecules due to irradiation. The relaxation frequency for gamma irradiated sample is shifted towards the
lower side than the unirradiated sample. The value of dielectric strength for gamma irradiated sample is found to be higher than the unirradiated sample.
Chapter 5: Enhancement in dielectric properties of nematic liquid crystal by gamma irradiation

References

Modification in nematic liquid crystal made by gamma irradiation: Biasing voltage and electro-optical study
6.1 Introduction

6.2 Experimental Details

6.2.1 Material

6.2.2 Preparation Of Cell

6.2.3 Gamma Ray Treatment

6.2.4 Bias Voltage Study

6.2.5 Electro-Optical Study

6.3 Result And Discussion

6.4 Conclusion

References
6.1 Introduction

The role of surface polarization of nematic layers was first recognized in connection with some electro structural transitions, notably flexo electric ones. Along with the surface polarization an important factor is the surface electric field, it may appear as a result of the ions over the substrates confining the liquid crystal layers [1-5]. During last forty years a lot of research and development has been done in the field of liquid crystal for their use in display applications. The key features required for the display application are flatness, low power consumption, compactness, low weight and high color capability [6]. The simplest liquid crystal phase is nematic, characterizing with the molecules that have no positional order but tend to point in the same direction (director). As such, weak electrical potentials are enough to change the alignment, which can be used to produce large electro optical effects [7, 8]. Smectic liquid crystals usually do not respond to applied electric and magnetic field as easily as nematic liquid crystal, it made to enhance these liquid crystals from application point of view [9]. For high resolution devices liquid crystal molecular orientation is defined not only by surface alignment, but also by the anchoring effect on polymeric walls. When the electrode spacing approaches the pixel size, the electric field distribution in the anisotropic liquid crystal medium becomes complicated and numerical techniques are required to model the electro optical properties of the devices [10].

The contribution of ions in the electric properties of semi conductors, electrolytes and dielectric materials have been theoretically and experimentally investigated in the past [11]. The dielectric characterization of a sample is usually done by applying a single frequency voltage (or current) to the electrodes and measuring the phase shifts and amplitude of resulting current at that frequency. The sample behaves as linear system when the amplitude of the measuring voltage is small with respect to the thermal voltage. When more than one type of ions are present and the measurements are done in the linear
region, one can use the superposition principle to add the contribution of each type of ions in the dielectric response of the sample [12].

Therefore to observe the effect of gamma radiation on nematic liquid crystal materials, we have applied Gamma- irradiation technique [13-17]. This is a powerful technique for investigations of condensed matter. In fact we have attempted to investigate how this irradiation affects the dielectric as well as the electro-optical parameters for nematic liquid crystals.

6.2 Experimental details

6.2.1 Material

The liquid crystal sample under investigation is a rod shaped molecule having a cyano group at its one end, which makes it a highly polar molecule. The Nematic liquid crystal is 5CB and its transition scheme and molecular structure is shown in figure 6.1.

\[
\text{C}_5\text{H}_11 - \text{CN}
\]

4-Cyano-4'-pentylibiphenyl

\[
\text{Cr} \quad 22.5^\circ\text{C} (N) \quad 35.3^\circ\text{C} (I)
\]

Figure 6.1 Chemical structure of 5CB

6.2.2 Preparation of cell

Two similar cells having active area 25 mm\(^2\), (sheet resistance and the visible light transmission is 10Ω/mm\(^2\) and more than 90%) were prepared by using transparent and highly conducting ITO (Indium Tin Oxide)(Diamonds Coating UK) coated optically
flat glass substrates used as electrodes. These electrodes give a base to the liquid crystal sample to align. Planar alignment is achieved by treating with adhesion promoter and polymer (Nylon 6/6; Sigma Aldrich) and then rubbed unidirectional with a velvet cloth. Although the homeotropic cell has been prepared by applying lecithin on the ITO coated surface. The thickness of the cell was maintained at 5 μm by means of Mylar spacer [18, 19]. The preparation of cell has been already discussed in chapter 3.

6.2.3 Gamma Ray treatment

We irradiated the 5CB liquid crystal using a $^{60}$Co source, at the dose rate of 2.9 kGy/h, up to a total does for 34.5 h is 100 kGy.

6.2.4 Bias voltage study

The Threshold voltage measurement has been done by using a computer controlled impedance/ gain phase analyzer Hewlett Packard (HP 4194 A). The dielectric permittivity has been measured as a function of voltage. A microprocessor based heating device Instec hot plate (HCS-302) maintained with an accuracy of ± 0.01°C has been used. Before taking measurement the sample was left for 15 minutes at a particular temperature. Dielectric permittivity is very sensitive to impurities as reported by Murakami and Naito [20], so measurement was made using fresh sample.

6.2.5 Electro-Optical study

The response time of nematic liquid crystal has been measured by the optical switching method [21, 22]. In this method a square wave of frequency 1Hz and amplitude 20Vpp has been applied to the planar sample cell. The optical response of molecule observed by the detector is fed to a storage oscilloscope (Tektronics TDS 2024C) in
electrical form. The output waveform is now used to determine the response time. The response time of nematic liquid crystal has been evaluated using the formula \( \tau_0 = \tau_{0N} + \tau_{0FF} \) where \( \tau_{0N} = \tau_{10} - \tau_{90} \) and \( \tau_{0FF} = \tau_{90} - \tau_{10} \) [21]. Here \( \tau_{90} \) and \( \tau_{10} \) are the time taken by the output waveform to reach 90% and 10% of maximum of the output waveform for rise and fall of reference square wave signal. The setup used for measuring response time and threshold voltage is shown in figure 6.2.

\[
\begin{align*}
\tau_0 &= \tau_{0N} + \tau_{0FF} \\
\tau_{0N} &= \tau_{10} - \tau_{90} \\
\tau_{0FF} &= \tau_{90} - \tau_{10}
\end{align*}
\]

\[\text{Figure 6.2 The experimental arrangement for the measurement of electro-optical parameters}\]

\section{6.3 Result and Discussion}

The components of dielectric permittivity, i.e. constant and loss, of the liquid crystal material has been measured as a function of frequency ranging from 100 Hz to 10MHz, at different amplitude of the field is shown in figure 6.3(a, b). As expected, permittivity is sensitive to both amplitude and frequency of the electric field. The dielectric permittivity data has been analyzed using Debye model, which addresses the frequency dependence of the dielectric function. One can see that the gamma irradiation
essentially changes the dielectric spectra of 5CB. The changes caused by the gamma irradiation at the different voltages can be detailed in the following: as the irradiation affect the liquid crystal sample, the dielectric relaxation peak becomes broader and deceases. The dielectric relaxation behavior, namely the shifting of relaxation peak with increasing bias voltage was also observed in the irradiated 5CB sample.

Figure 6.3 (a) Dielectric permittivity and (b) dielectric loss with respect to natural log of frequency for unirradiated and gamma irradiated 5CB nematic liquid crystal

Figure 6.4 (a) Dielectric permittivity and (b) relaxation frequency with variation in voltage for unirradiated and gamma irradiated 5CB nematic liquid crystal
The variation in the dielectric permittivity with applied electric field has been shown in above figure 6.4(a). The variation in amplitude of dielectric permittivity can be defined on the basis of physicochemical change caused by the gamma irradiation. With the help of this figure the threshold voltage \( V_{th} \) has been identified; at which liquid crystal directors begin to align along with applied electric field. The observation suggest that the threshold voltage \( V_{th} \) is almost unaffected by gamma irradiation. The dielectric relaxation frequency with variation in applied electric field has also been evaluated, shown in the figure 6.4(b). As the field is increased above \( V_{th} \), sufficiently large number of liquid crystal molecules aligns with the field. For sufficiently high values of the electric field, the external field may overcome the surface anchoring forces and then most of the liquid crystal directors will aligned along the direction of the applied electric field. Because of the initial alignment of the liquid crystal molecules, these forces align the liquid crystal molecules parallel to the glass surface i.e. perpendicular to the direction of the external applied electric field. Therefore the trend has been observed.

![Figure 6.5 Variation in dielectric anisotropy with temperature for unirradiated and gamma irradiated 5CB nematic liquid crystal](image)

**Figure 6.5 Variation in dielectric anisotropy with temperature for unirradiated and gamma irradiated 5CB nematic liquid crystal**
In the present study we have also evaluated dielectric anisotropy using two components $\Delta \varepsilon$ i.e. $\varepsilon_{II}$ and $\varepsilon_{\perp}$ and the variation of $\Delta \varepsilon$ (dielectric anisotropy) with the temperature has been shown in figure 6.5. As the temperature increases the dielectric anisotropy decreases and become minimum. This type of dielectric anisotropy behavior can be explained on the basis of Maier and Meir theory (Maier & Sharpe, 1960), which gives,

$$\Delta \varepsilon = \left( \frac{NFR}{\varepsilon_0} \right) \left[ \Delta \alpha + \frac{F\mu^2}{2kT} (3 \cos^2 \beta - 1) \right] S$$  \hspace{1cm} (1)

Here the symbols have their usual meaning. The positive dielectric anisotropy of the sample suggest that the angle Beta is lesser than 54.70. Maier and Meir theory also predicts that the temperature dependence of $\Delta \varepsilon$ roughly follows the order parameter $S$ and temperature factor contributes only to a limited temperature range. The perpendicular component of the dielectric permittivity increases with increasing temperature suggest that the molecular dipolar contribute more towards perpendicular component of dielectric permittivity at the higher temperatures. Another reason behind this behavior is the physicochemical change in liquid crystal by gamma irradiation. Influence in the alignment of liquid crystal by gamma irradiation affects the origin of ions. This plays an important role in the formation of charge carriers in nematic liquid crystal. This effect increase dielectric permittivity for irradiated sample as observed at all temperatures under investigation shown in figure 6.6. The above nature of dielectric anisotropy also concludes that the transverse component of the dipole moment $\mu_t$ is less efficient than the longitudinal component of dipole moment $\mu_l$. Therefore the numerical value of dielectric anisotropy for gamma irradiated nematic liquid crystal goes down as compared unirradiated 5CB nematic liquid crystal. This can be easily seen by experimental results.
Chapter 6: Modification in nematic liquid crystal made by gamma irradiation: Biasing voltage and electro-optical study

This chapter has been published in the form of paper in Radiation Effects and Defects in Solids, Volume 168, Issue 4, April 2013, pages 297-307.

Figure 6.6 Behavior of dielectric permittivity behavior with variation in temperature for unirradiated and gamma irradiated 5CB nematic liquid crystal

Figure 6.7 Variation in splay elastic constant with temperature for unirradiated and gamma irradiated 5CB nematic liquid crystal

Rotational viscosity has been evaluated for unirradiated and gamma irradiated 5CB sample using the formula:

$$\gamma = \frac{\tau_0 K_{11} \pi^2}{d^2}$$

(2)
Here $\gamma$ is the rotational viscosity of the sample, $K_{11}$ is splay elastic constant and $d$ is the cell gap. In the same way splay elastic constant, shown in figure 6.7, has also been measured using the formula:

$$K_{11} = \left(\frac{V_{th}}{\pi}\right)^2 \Delta \varepsilon \varepsilon_0$$

(3)

The nature of variation in rotational viscosity is same for both unirradiated and gamma irradiated liquid crystal material, shown in figure 6.8. But the magnitude of gamma irradiated 5CB liquid crystal decreases. This might indicate a change of the boundary conditions in the liquid crystal and polymeric layers, i.e, a change in cohesion of the liquid crystal molecules with alignment layer, as reported by Graham on degraded alignment layer [16].

![Variation in rotational viscosity with temperature for unirradiated and gamma irradiated 5CB nematic liquid crystal](image)

*Figure 6.8 Variation in rotational viscosity with temperature for unirradiated and gamma irradiated 5CB nematic liquid crystal*
Chapter 6: Modification in nematic liquid crystal made by gamma irradiation: Biasing voltage and electro-optical study

This chapter has been published in the form of paper in Radiation Effects and Defects in Solids, Volume 168, Issue 4, April 2013, pages 297-307.

Figure 6.9 Electrical response curve for (a) unirradiated and (b) gamma irradiated 5CB nematic liquid crystal

Figure 6.9 shows the electrical curve of switching for unirradiated and gamma irradiated 5CB nematic liquid crystal. The drive voltage pulse was varied from 0.5V to 20V. The X-axis represents time scale while Y-axis represents the voltage. The rise time and the fall time treated separately as-

\[ \tau_{\text{rise}} = \frac{\gamma_1 d^2}{\varepsilon_0 \Delta \varepsilon (V-V_{th})^2} \]  \hspace{1cm} (4)

\[ \tau_{\text{fall}} = \frac{\gamma_d d^2}{\pi^2 k_{11}} \]  \hspace{1cm} (5)

In this way the response time behavior with respect to temperature for both unirradiated and irradiated 5CB nematic liquid crystal material has been shown in figure 6.10. Observations suggest that the response time decreases after the gamma irradiation on 5CB. When filled 5CB cell is gamma irradiated, the irradiation causes a chemical change in the 5CB, which results the generation of new ions. The influence of the ions on the dielectric properties of nematic liquid crystals has been well explained by many authors because of their technological importance [23]. The extension of theory to the case where several groups of ions are dissolved in nematic liquid crystal is important.
from the practical point of view, because more than one type of impurities, usually, present in the nematic liquid crystals, which also in turn affects creation of the new ions that are responsible for the electrical parameter [24]. These ions in 5CB nematic liquid crystal are responsible for the current through the liquid crystal sample. The presence of the positive ions [25-28] in 5CB, which governs the conductivity in the liquid crystal cell, gradually effects the molecular reorientations. Due to this reason each molecule move in time as a sequence of small angular steps under the influence of a potential of mean torque setup by these molecules, decreases the response time as shown in figure 6.10.

![Graph showing variation of response time with temperature for unirradiated and gamma irradiated 5CB nematic liquid crystal](image)

**Figure 6.10 Variation of response time with temperature for unirradiated and gamma irradiated 5CB nematic liquid crystal**

**6.4 Conclusion**

The changes caused by gamma irradiation in nematic liquid crystal have investigated using the electro-optical method and biasing voltage method. We observe that the nature of the variation in dielectric anisotropy for unirradiated and irradiated sample is same and discussed, but the response time for the gamma irradiated liquid
crystal decreases. The reason has been discussed in terms of the physicochemical change caused by the gamma irradiation. Observations have also been made for the dielectric permittivity with respect to both temperature and voltage. The reason behind this influence in the alignment of liquid crystal by gamma irradiation that is responsible for the origin of ions plays an important role in the formation of charge carriers in nematic liquid crystal. This effect increases the dielectric permittivity for gamma irradiated 5CB sample with respect to temperature.
References


Chapter 7

Gamma Induced Augmentation in EBHA: A Dielectric and Electro-Optical Study
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7.1 Introduction

The modification in dielectric and electro optical properties of liquid crystal caused by ion beam radiation is a new field of research. Ionizing particles like electrons, photons and laser and gamma particles have been used to modify the physical and chemical properties of the liquid crystal in the recent years [1-5]. These modifications are the result of superimposition of several mechanisms including the interaction of the incident particle with matter causing initiation of different secondary reactions [6]. Due to many advantages the radiation technology is preferred over other conventional methods. The radiation process differs from chemical initiation process because in radiation processing no catalyst or additives were required to initiate the reaction [7].

Preliminary studies on some liquid crystals suggest that their physical and chemical properties are highly affected by radiation [8-10]. Most of these suggest that the transition temperatures and the stability of various liquid crystalline mesophases are strongly affected by radiation [11]. Some of the electrical properties such as electrical conductivity and charge carrier mobility subjected by ionizing radiation have been studied very first in 1988 by Kovalchuk et al. [12]. After that a lot of experiments have been performed to evaluate the physicochemical change in liquid crystal by ionic radiation.

In addition to the dielectric properties [13-16], the electro-optical properties have also been measured for both gamma irradiated and unirradiated EBHA NLC. The investigation has been done for both gamma irradiated and unirradiated EBHA samples with the variation in temperature and voltage. Dielectric permittivity and threshold voltage for both irradiated and unirradiated EBHA NLC samples have been evaluated from dielectric data. In addition to this the optical response time has also been investigated using electro-optical data for irradiated and unirradiated EBHA NLC sample.
7.2 Experimental details

7.2.1 Material

The liquid crystal sample under investigation is a rod shaped NLC molecule. The structure and its phase transition behavior are given in the figure 7.1.

![Chemical structure of EBHA NLC](image)

**Figure 7.1 Chemical structure of EBHA NLC**

7.2.2 Preparation of cell

Two similar cells having active areas 25 mm$^2$, (sheet resistance and the visible light transmission is 10Ω/mm$^2$ and more than 90% respectively) were prepared by using transparent and highly conducting ITO (Indium Tin Oxide) (Diamonds Coating UK) coated optically flat glass substrates used as electrodes. These electrodes give a base to the liquid crystal sample to align. Planar alignment is obtained by treating both adhesion promoter and polymer (Nylon 6/6) and then rubbed unidirectional with a velvet cloth. Although the homeotropic cell has been prepared by applying lecithin on the ITO coated surface. The thickness of the cell was maintained at 5 μm by means of Mylar spacer [17]. The complete preparation of cell has been given in Chapter 3.
7.2.3 Gamma Ray treatment

We have irradiated the EBHA NLC. The irradiation used a $^{60}$Co source, at the dose rate of 2.9 kGy/h, up to a total dose for 34.5 h is 100 kGy.

7.2.4 Dielectric study

The dielectric behavior of the material has been studied by using a computer controlled impedance/ gain phase analyzer Hewlett Packard (HP 4194 A). The dielectric parameters have been measured as a function of temperature and frequency. In order to vary the temperature of the sample holder a microprocessor based heating device Instec hot plate (HCS-302) with an accuracy of ± 0.01°C has been used. Before taking measurements the sample was left for 15 minutes at a particular temperature.

The Threshold voltage measurement has also been done by using the same computer controlled impedance/ gain phase analyzer Hewlett Packard (HP 4194 A). The dielectric permittivity has been measured as a function of voltage. The experimental details has been already discussed in chapter 3.

7.2.5 Electro-Optical study

The response time of NLC has been measured by the optical switching method. In this method a square wave of frequency 1Hz and amplitude 20V peak to peak has been applied to the planar aligned sample cell. The optical response of molecule observed by the detector is fed to a storage oscilloscope (Tektronics TDS 2024C) in electrical form. The output waveform use to determine the response time. The response time of NLC has been evaluated using the formula $\tau_0 = \tau_{ON} + \tau_{OFF}$ where $\tau_{ON} = \tau_{10} - \tau_{90}$ and $\tau_{OFF} = \tau_{90} - \tau_{10}$ [18], here $\tau_{90}$ and $\tau_{10}$ are the time taken by the output waveform to reach 90% and 10% of maximum of the output waveform for rise and fall of reference square wave signal. The setup used for measuring response time is shown in figure 7.2.
7.3 Result and Discussion

The dielectric data for unirradiated EBHA and gamma irradiated EBHA NLC samples has been measured by varying in frequency and voltage. The dielectric data has been analyzed by using the well known Cole –Cole dispersion equation (1) given below:

\[
\varepsilon^* = \varepsilon'(\infty) + \frac{\delta\varepsilon'}{1 + (j\omega\tau)^{(1-\alpha)}}
\]  

(1)

Here \(\delta\varepsilon'\) is the dielectric strength of the material, \(\varepsilon'(\infty)\) is the high frequency limit of dielectric permittivity, \(\omega(=2\pi f)\) is the angular frequency, \(\tau\) is the relaxation time and \(\alpha\) is the distribution parameter. The Cole-Cole plot of the sample, which exhibits nematic phase, has been drawn for both gamma irradiated and unirradiated sample cell, filled with EBHA, at specific temperature of 65°C as shown in figure 7.3. The black legend shows experimental data while solid red line shows the best theoretical fitting of Cole-Cole equation into experimental data. Using such plots dielectric parameters such as relaxation frequency, relaxation strength have been evaluated. The temperature dependence of dielectric parameters have been discussed in the later part of the chapter.
On separating real and imaginary part of the equation (1) and on adding high and low frequency correction parameters

$$
\varepsilon'(\omega) = \varepsilon'(dc) f^{-n} + \varepsilon'(\infty) + \frac{\delta\varepsilon'[1 + (\omega \tau)^{(1-\alpha)} \sin(\alpha\pi / 2)]}{1 + (\omega \tau)^{(2(1-\alpha))} + 2(\omega \tau)^{(1-\alpha)} \sin(\alpha\pi / 2)}
$$

(2)

And

$$
\varepsilon''(\omega) = \frac{\sigma(dc)}{\varepsilon_0 \omega^k} + \frac{\delta\varepsilon'(\infty) \cos(\alpha\pi / 2)}{1 + (\omega)^{(2(1-\alpha))} + 2(\omega)^{(1-\alpha)} \sin(\alpha\pi / 2)} + Af^m
$$

(3)

Where $\sigma (dc)$ is the ionic conductance and $\varepsilon_0$ is the free space permittivity and $f$ is the frequency while $n$, $m$ and $k$ are the fitting parameters. The term $\varepsilon'(dc)f^{-n}$ and $\sigma(dc)/\varepsilon_0 2\pi f^k$ are added in equations for low frequency effect due to the electrode polarization, capacitance and ionic conductance. The term $Af^m$ is added in equation (3) for high frequency effect due to the ITO sheet resistance and lead inductance of the cell. By the least square fitting of the above equation into experimental data the low and high frequency errors have been removed. After adding correction terms the dielectric...
permittivity has been plotted against natural log of frequency as shown in the figure 7.4. This type of permittivity behavior has been reported earlier by our group [19-21].

![Figure 7.4 Variation in dielectric permittivity with respect to natural log of frequency](image)

The observed value of dielectric permittivity for both unirradiated and gamma irradiated EBHA NLC sample, nature of variation with frequency is same, but the values have increased for gamma irradiated EBHA NLC sample. This increment in the values of dielectric permittivity for gamma irradiated sample could be explained on the basis of physicochemical change in the liquid crystals. Radiation mainly affects in two basic ways, both resulting with excitation or ionization of atoms. In this fashion ionic conductivity of liquid crystal material has also been investigated. The ionic conductivity for irradiated EBHA is comparatively higher than that of unirradiated EBHA NLC sample. This increment in ionic conductivity between irradiated and unirradiated sample
has been shown with variation of temperature in Figure 7.5. When filled EBHA NLC cell is gamma irradiated, the irradiation causes a chemical change in the EBHA, which results is the generation of new. The extension of theory to the case where several groups of ions are dissolved in NLC, because more than one type of impurities, usually, present in the NLCs, which also in turn affects creation of the new ions after gamma radiation. These ions play an important role in the formation of charge carriers in the NLC. The presence of positive ions generated by the spontaneous dissociation of EBHA cell due to gamma irradiation cause the change in the conductivity of liquid crystal cell. It can be said that such a trend in the dielectric permittivity is resulted due to the modification in EBHA NLC molecule as well as substrate due to high energy gamma irradiation. This increase in permittivity for irradiated sample has also been observed at all temperatures under investigation as shown in Figure 7.6.

![Figure 7.5 Electric conductivity with variation in temperature](image)

*Figure 7.5 Electric conductivity with variation in temperature*
Figure 7.6 Variation in dielectric permittivity with respect to temperature

Figure 7.7 shows the behavior of dielectric permittivity with variation in voltage. With the help of this figure the threshold voltage $V_{th}$ has been identified; at which liquid crystal directors begin to align along with applied electric field. The observation suggest that the threshold voltage $V_{th}$ is almost unaffected by gamma irradiation. As the field is increased above $V_{th}$, sufficiently large number of liquid crystal molecules aligns with the field. For sufficiently high values of the electric field, the external field may overcome the surface anchoring forces and then most of the liquid crystal directors will aligned along the direction of the applied electric field. Because of the initial alignment of the liquid crystal molecules, these forces align the liquid crystal molecules parallel to the glass surface i.e. perpendicular to the direction of the external applied electric field. Therefore the trend has been observed.
The measurement of dielectric anisotropy for the EBHA NLC sample in both irradiated and unirradiated state shows that, the order parameter in the nematic phase manifest itself in the anisotropy of the dielectric constant. In the uniaxial nematic phase there are two principle dielectric constants $\varepsilon_{||}$ and $\varepsilon_{\perp}$ (parallel and perpendicular to the director), the difference between the two is referred as the dielectric anisotropy. It is clear a decrease in the nematic order parameter say by trans and cis isomeraization, should decease the dielectric anisotropy to become zero in the isotropic phase. The material used for this study has a positive dielectric anisotropy and hence during the nematic to isotropic transition $\varepsilon_{\perp}$ should increase while $\varepsilon_{||}$ should decrease. The temperature dependence of dielectric anisotropy i.e. the difference of $\varepsilon_{||}$ and $\varepsilon_{\perp}$, in both unirradiated and the irradiated states are shown in figure 7.8. The important feature to be notice is after irradiation, the magnitude of $\varepsilon_{||}$ and $\varepsilon_{\perp}$ decreases. Which may results
an increment in $T_{NI}-T$. This is to be expected for efficiency of the trans and cis conversation by a given intensity of radiation should decrease.

![Dielectric and Electro-Optical Study](image)

**Figure 7.8** Parallel and perpendicular component of dielectric constant with variation in temperature
In the same manner, the response time of the EBHA liquid crystal sample has been calculated for both irradiated and unirradiated states. The electrical response curves for both EBHA irradiated and unirradiated samples are shown in figure 7.10. Observations suggest that the response time decreases after the gamma irradiation on EBHA. When filled EBHA cell is gamma irradiated, the irradiation causes a chemical change in the EBHA, which results the generation of new ions. Also one type of impurities, usually, present in the NLCs, which also in turn affects creation of the new ions after irradiation that are responsible for the electrical parameter [22]. These ions in EBHA NLC are responsible for the current through the liquid crystal sample. These ions are responsible for the conductivity in the liquid crystal cell, gradually effects the molecular reorientations. Therefore fast response of molecule has been observed. The response time

**Figure 7.9 Dielectric anisotropic with variation in temperature**
curve for unirradiated and gamma irradiated EBHA sample has been shown in figure 7.11.

Figure 7.10 Electrical response curve for (a) unirradiated and (b) gamma irradiated 5CB nematic liquid crystal

Figure 7.11 Variation of response curve as a function of temperature
7.4 Conclusion

The changes due to gamma irradiation in NLC material have been investigated using dielectric spectroscopy and electro-optical techniques. Some of the dielectric parameters such as dielectric permittivity, dielectric anisotropy have been evaluated for the gamma irradiated sample and has been compared with the unirradiated EBHA NLC sample. It has been observed that the nature of variation of dielectric permittivity with frequency and temperature remains same for both the gamma irradiated and the unirradiated EBHA samples, but the value of dielectric permittivity for the gamma irradiated sample is higher as compared to the unirradiated EBHA sample. This increment in the magnitude of dielectric permittivity for gamma irradiated sample can be explained on the basis of physicochemical change in the EBHA molecules due to irradiation. The response time for gamma irradiated sample is lower than the unirradiated sample.
Chapter 7: Gamma Induced Augmentation in EBHA: A Dielectric and Electro-Optical Study

References


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Chapter 8

Final Conclusion
And
Future prospect
In the end of the thesis I would like to draw some final conclusions on the basis of experimental and theoretical study performed during the entire course of work.

Since, the discovery of liquid crystals considerable work has done to understand the relationship of the liquid crystal properties with the molecular structure. Despite this there exists only a poor understanding of how changes in molecular structure affect material properties. For liquid crystals this is complicated by several factors. Firstly, liquid crystal phases are formed by materials from the whole spectrum of chemical classes: organic, organometallic, and biological molecules can all form liquid crystal phases. Secondly, mesogenic molecules are generally quite large. Liquid crystals tend to be flexible. This inhibits crystallization, preventing the direct transition from an isotropic liquid to a crystalline solid. It also leads to a large degree of conformational freedom, so properties are generally determined by more than just the equilibrium structure. Finally liquid crystal molecules often contain disparate parts (such as alkyl and perfluoroalkyl chains) that can have a large effect on the phase behaviour. Investigation of these factors by experimental or theoretical means should hopefully lead to a better understanding of structure-property relationships in liquid crystals.

In the chapter 4, the structure property relationship has been concluded using the dielectric spectroscopy. In our case oxygen atom links the terminal chains to the core units in series, and addition of oxygen atom tends to bend the terminal chains away from the long axis of the central part of the molecule. Thus the molecule exhibits the zig-zag picture; this unusual detailed investigation on single mesogen molecule reveals that (Zig-zag molecules can pack tightly into layers, but only if parts of the molecules are tilted relative to a line perpendicular to the layers).

Also topological model has been proposed to overcome one of the defect splay defect. Thus, on the basis of the proposed topological molecular model we
predict that the average force on each molecule is inversely proportional to the magnitude of splay defect. To overcome splay defect, molecules are arranged in a usual manner due to which average force experienced by the molecule help in reducing splay defect. Thus this material could trigger a revolution in liquid crystalline devices.

We have also tried to provide the new concept of gamma ray irradiation technique to enhance the dielectric and electro-optical properties of liquid crystalline substances. Here we have used dielectric spectroscopy, electro-optical method and bias voltage method to evaluate the enhancement in the properties of nematic liquid crystalline materials. Dielectric properties of the irradiated nematic liquid crystals also show clear change in comparison to the unirradiated nematic liquid crystals.

Radiation mainly affects in two basic ways, both resulting with excitation or ionization of atoms. In this fashion ionic conductivity of liquid crystal material has also been investigated. The ionic conductivity for irradiated 5CB is comparatively higher than that of unirradiated 5CB sample. When filled 5CB cell is gamma irradiated, the irradiation causes a chemical change in the 5CB, which results in the generation of new ions. The theoretical analysis of the problem is usually contains only a group of cations and anions, with equal or different diffusion coefficients. The extension of theory to the case where several groups of ions are dissolved in nematic liquid crystal is important from the practical point of view, because more than one type of impurities is, usually, present in the nematic liquid crystals, which in turn affects the creation of ions that are responsible for the electrical parameter. These ions play an important role in the formation of charge carriers in the nematic liquid crystal. The presence of positive ions due to gamma irradiation cause the change in the conductivity of liquid crystal cell. It can be said that such a trend in the dielectric permittivity is resulted due to the modification in 5CB molecule as well as substrate due to high energy gamma irradiation.
Ionization in the nematic liquid crystal molecules caused by gamma irradiation changes the values of relative permittivity. The positive ions governs the conductivity of nematic liquid crystal. From the present work it can be concluded that the gamma ray modification technique is a strong tool to enhance the dielectric properties of a nematic liquid crystal material.

In addition to this, the difference of live capacitance is also evaluated for both gamma irradiated and unirradiated planar cells. The evaluated value of live capacitance is found very small for gamma irradiated and unirradiated cell within the scope of experimental error. It is not expected to affect the dielectric properties of the liquid crystal material.

In the chapter 6, the biasing voltage and electro-optical parameters are evaluated for the same (5CB) sample. Variation in the conductivity of nematic liquid crystalline material makes this important. The changes caused by gamma irradiation in nematic liquid crystal have investigated using the electro-optical method and biasing voltage method. We observe that the nature of the variation in dielectric anisotropy for unirradiated and irradiated sample is same, but the response time for the gamma irradiated liquid crystal decreases. Observations have also been made for the dielectric permittivity with respect to both temperature and voltage. The reason behind this influence in the alignment of liquid crystal by gamma irradiation that is responsible for the origin of ions plays an important role in the formation of charge carriers in nematic liquid crystal. This effect increases the dielectric permittivity for gamma irradiated 5CB sample with respect to temperature.

The modification in dielectric and electro optical properties of liquid crystal caused by ion beam radiation is a new field of research. Therefore the dielectric and electro-optical behaviour of the EBHA NLC sample has been reported in the chapter 7. The changes due to gamma irradiation in EBHA NLC material have been investigated using dielectric spectroscopy and electro-optical techniques. Some of the dielectric parameters such as dielectric permittivity, dielectric
anisotropy have been evaluated for the gamma irradiated sample and has been compared with the unirradiated EBHA NLC sample. It has been observed that the nature of variation of dielectric permittivity with frequency and temperature remains same for both the gamma irradiated and the unirradiated EBHA samples, but the value of dielectric permittivity for the gamma irradiated sample is higher as compared to the unirradiated EBHA sample. This increment in the magnitude of dielectric permittivity for gamma irradiated sample can be explained on the basis of physicochemical change in the EBHA molecules due to irradiation. The response time for gamma irradiated sample is lower than the unirradiated sample. That makes it very important for the application point of view.

Therefore it can be conclude that, all of the vital properties show enhancement for the irradiated nematic liquid crystal than the unirradiated one. Thus it becomes very important from application point of view.

The nature of the research work is such as to always open new questions and so the work seems to be never finished and the aim never fulfilled. On my way to prepare this thesis, many new interesting aspects of gamma irradiated liquid crystals were raised; some results have presented in this work, and some of them will be investigated in future. However, this is what makes the research works interesting and what gives the assurance that there will be always something new to work on. Working on this thesis help in driving or becoming familiar with certain theories, techniques and models to describe physical phenomenon of gamma irradiated liquid crystals and provided some basic conceptual characteristic for gamma irradiated liquid crystals.
Liquid Crystals: a Dielectric and Electro-optical Study

Summary
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**Summary**

Liquid crystals were accidentally discovered by Austrian botanist Friedrich Reinitzer in 19th century. Study of this phase spread to all the continents, although very slowly in the beginning and then there was an explosive growth during 1970’s and 1980’s. Theories for the liquid crystal phases added a new dimension of study and the invention of liquid crystal displays gave the field, a practical dimension. Scientific studies of liquid crystals involve both the chemistry and physics of this state, being concerned with liquid crystal synthesis and investigation of structure-property relationships.

Liquid-crystal physics, although a field in itself, is often included in the larger area called ‘soft condensed matter’, which includes polymers, colloids and surfactant solutions, all of which are highly deformable materials. This property leads to many unique and exciting phenomena not seen in the ordinary condensed phases, having possibilities of novel technological applications.

The subject of liquid crystal is multidisciplinary and has for years impinged upon chemistry, physics, biology and mathematics and more recently, as consequence of the applications of liquid crystals upon applied chemistry, applied physics, electrical and electronic engineering and
Success in these areas has however arisen only through the collaborations among different disciplines of science. The reason liquid crystal research is an important and active field of science has changed over the last twelve years. New substances showed new properties, and the new theoretical ideas necessary to understand these properties has implications beyond the area of liquid crystals. In addition, the market for lightweight and low power computer displays was growing exponentially, fueling a boom in the application of liquid crystals to displays. In the 1990s, the rate at which discoveries concerning liquid crystals Nematic liquid crystals are the most simplest and the fascinating phase of liquid crystals. Their properties make them applicable for displays. Even though Ferroelectric liquid crystals have fast response and memory effect yet they are not being used in displays because of low contrast and small vision angle.

Liquid crystals have many wide and varied applications apart from high profile uses in displays. In such a short amount of time between its discovery and application in industrial field they become very popular because liquid crystals have technological importance. This is due to the fact that liquid crystal offers a unique and delicate collection of phase of matter that are precariously balanced between the organized solid state
and the amorphous liquid, and which can be accessed by the all type of material and not just organic compounds.

In 1907 Vorlander proposed his rule that “the liquid crystalline state is obtained for the most linear of the molecules”, but in the last few years, details of their molecular structure and micro-segregation have attracted much attention for producing novel, self-organizing systems. These types of molecular topology and their ability to form mesophases are fundamental topics in the investigation of molecular assembly, as these new molecular architectures can be important in critical applications as they widen the temperature range of functionality.

In the present thesis, along with gamma ray modification technique on nematic liquid crystals, newly synthesized H-Shaped dimeric liquid crystal has been analyzed. For H-Shaped dimeric liquid crystal, influences on the molecular orientation have been studied with the help of dielectric spectroscopy. The dielectric parameter have been analyzed thoroughly and there practical applications have also been mentioned. The gamma irradiation induced transformational changes in nematic liquid crystals have also studied in the present thesis. The variation in the dielectric and electro-optical properties in different nematic liquid crystals have been analyzed and well explained in this thesis. To examine the effect of applied
electric field on the dielectric properties the bias voltage study has also done for nematic liquid crystals.

The molecular structure and the phase transition scheme of the liquid crystal material used in the present thesis is given below:

Bis[5-(4'-n-dodecyl oxybenzoyloxy)-2-(4”-chlorophenylazo)phenyl]butylethers (12-Cl-H4)

Cr------(55°C)------SmX------(66°C)------SmC------(87°C)------Iso

4'-n-Pentyl-4-cyanobiphenyl (5CB)

Cr------(22.5°C)------Nematic------(35.3°C)------Iso
Chapter 1 basically deals with the introduction to the family of liquid crystals. History of the liquid crystals and recent development has been introduced in the chapter. The basic classification scheme has also been discussed. The chapter ends with the application of liquid crystals and their importance in various fields.

Chapter 2 is an introduction to the theoretical background of liquid crystalline phase. The brief discussion about basic terms related with liquid crystals such as director, order parameter, anisotropy etc, have been given in this chapter. The elastic properties including viscosity, elasticity, response time etc. have also been discussed in the mid of the chapter. The chapter also includes the broad discussion about the dielectric spectroscopy. The phase transition theories of liquid crystals such as Landau-deGennes theory, Maier-Saupe theory etc have also been discussed. In the last the description about the gamma ray modification technique has also given.
Chapter 3 is an introduction to the experimental techniques used in the present thesis. Sample holder preparation is the most important part of the investigation. The complete fabrication technique and precautions related with each step has been discussed extensively. Two basic alignment techniques have been given in this chapter. Different dielectric methods are also given in this chapter.

In the chapter 4, we analyze the dielectric behaviour of unusual H-Shaped liquid crystal dimer named Bis[5-(4'-n-dodecyloxybenzoyloxy)-2-(4”-chlorophenylazo)phenyl]butylethers (12-Cl-H4). The observations suggest that relaxation mode observed in MHz region for the sample. The relaxation mode follows Cole-Cole theory. Various dielectric parameters such as relaxation frequency, effective dielectric permittivity, distribution parameter, activation energy for the sample (12-Cl-H4) using Cole-Cole plot. The dielectric study for the given sample has been done with variation in both temperature and frequency. Also a strong theoretical background has been given, to minimize one of the liquid crystal defects - splay defect with this new molecular topology. Thus, this new molecular topology could trigger a revolution in liquid crystalline devices and could be used in future from application point of view.

The chapter 5 reports comparative dielectric study of gamma irradiated and unirradiated nematic liquid crystal. This study is an
attempt to see the irradiation effect in the alignment and dielectric parameters of nematic liquid crystal. The dielectric measurements have been done with the temperature variation in the frequency range 100 Hz to 10 MHz. The dielectric data show relaxation modes which follow Cole-Cole theory. The Cole-Cole plots have been used to determine the dielectric parameters such as relaxation frequency and relaxation strength. The dielectric permittivity is found to increase for gamma irradiated sample as compared to the unirradiated sample with variation in temperature and frequency and well explained in this chapter.

In the chapter 6 dielectric as well as electro optical parameters have been investigated for unirradiated 4-Cyano-4′-pentylbiphenyl (5CB) along with gamma radiated 5CB, as a function of temperature and voltage. The sample exhibits a strong positive dielectric anisotropy due to the presence of a large dipole moment along with the major molecular axis. The dielectric anisotropy $\Delta\varepsilon$ decreases for the irradiated 5CB sample as a result of gamma radiation. Some electro-optical parameters such as rotational viscosity, response time have also been determined and compared with the unirradiated 5CB samples.

Chapter 7 reports the comparative study of dielectric and electrot-optical properties of unirradiated EBHA nematic liquid crystal (NLC) with gamma irradiated EBHA NLC. The dielectric measurement has been
performed with the variation in voltage and temperature within the frequency range 100 Hz to 10 MHz. Variation in response time for both gamma irradiated and unirradiated samples have also been measured and well explained in the present chapter.

In the end I conclude that our experimental findings backed by theoretical model and explanations presented in the thesis provides a broad information about the modification techniques as well as the gamma ray modification technique, their consequences on the dielectric and electro-optical properties of liquid crystalline materials. Chapter 8 reports the final conclusions drawn from the experimental findings and some crucial suggestions.