



AN OVER VIEW ON THE ANISOTROPIC PROPERTIES OF LIQUID CRYSTALS

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ABSTRACT

Liquid crystals have found applications in modern display technology and other fields because of their some specific properties inherent to them. They exhibit anisotropic behavior in different properties e.g. dielectric, optical, elastic, magnetic etc. These properties have made them useful in different technological applications. In this article we have discussed these properties in some details and explained the origin these anisotropies. We have also discussed some physical parameters which are relevant in understanding the physical properties of liquid crystals.

Key words:

liquid crystal, order parameter, director, chiral pitch, optical anisotropy, dielectric anisotropy, magnetic anisotropy.

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INTRODUCTION

Liquid crystals have become an important field of research over the last several decades because of their potential applications in modern display technology and other fields. *Liquid Crystal* is a state of matter that is *intermediate* between the crystalline solid and the amorphous liquid. In this state, liquid crystals exhibit *anisotropic behavior* in some of their properties e.g. dielectric, optical, magnetic, electrical etc. These properties are inherent in crystals. At the same time they also exhibit some properties which are specific to liquids. As for example, they can flow, they have ability to form droplets etc. The liquid crystalline or *mesomorphic state* was discovered towards the end of the 19th century by Reinitzer [1] and Lehmann [2]. Now-a-days several thousand of organic compounds have been found to form liquid crystalline state [3,4]. It has been observed that the molecules of liquid crystals are geometrically anisotropic in shape. Actually they are either rod or disc shaped. Liquid crystals can be mainly classified into two categories: i) thermotropic, ii) lyotropic. Both the thermotropic and lyotropic liquid crystals are made of organic molecules. Thermotropic liquid crystals undergo a phase transition when temperature is changed. However lyotropic liquid crystals exhibit a phase transition when a solvent is added to them. Another kind of liquid crystal has been found, which is known as metallotropic liquid crystal. These liquid crystals are composed of both organic and inorganic molecules; their phase transition depends both on the temperature, concentration as well as on their organic-inorganic composition ratio.

Liquid crystals have found applications extensively both in modern technology and in natural world [5]. Modern electronic displays use liquid crystals. Lyotropic liquid crystals are found in living systems. For examples, many proteins and cell membranes are composed of liquid crystals. Other well known liquid crystals are solutions of soaps and various related detergents, as well as the tobacco mosaic virus etc.

It has been observed that most of the thermotropic liquid crystals consist of rod like molecules. They are mainly categorized into three types; i) nematic, ii) cholesteric and iii) smectic [5]. The above nomenclature was first proposed by Friedel [6].

Theoretical Approach and Discussion

First we shall introduce some important physical parameters of liquid crystals, which are found to be very helpful in discussing the different properties of liquid crystals.

Few Important Physical Parameters of Liquid Crystals

Director

It is known that nematic liquid crystals consist of rod-like molecules. The long axes of the neighbouring molecules are approximately parallel to each other. Hence in order to specify this anisotropic property, a *dimensionless unit vector* \hat{n} is introduced to represent the direction of *preferred orientation* of the molecules in the neighbourhood of any point within the liquid crystal. This unit vector \hat{n} is referred to as the *director* of the liquid crystal.

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Order parameter

Experimentally it has been found that liquid crystals are small ordered systems. There exist small ordered regions or domains within the liquid crystals. Hence in order to describe a liquid crystal, a physical parameter, called *order parameter* has been introduced. Generally, a second rank symmetric traceless tensor order parameter is used to describe the orientational order of a nematic liquid crystal. However, it is sufficient to use *a scalar order parameter* to describe a uniaxial liquid crystal. Order parameter (S) of a liquid crystal is quantitatively defined as the average of the second Legendre polynomial as follows:

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

Here θ is the angle between the liquid crystal molecular axis and the *local director* (which is the ‘preferred direction’ in a volume element of a liquid crystal). In equation (1) the brackets denote both a temporal and a spatial average. From this definition, it is clear that for a completely random and isotropic sample, $S = 0$, whereas for a perfectly aligned liquid crystal, $S = 1$. For a typical liquid crystal sample, S is of the order of 0.3 to 0.8. However it generally decreases as the temperature is increased. A sharp drop of the order parameter to 0 is observed when the system undergoes a phase transition from a liquid crystal state to an isotropic phase [7]. The order parameter of liquid crystals can be measured by experiments in different ways. As for example, diamagnetism, birefringence, Raman scattering, NMR and EPR methods are generally used to find the order parameter S by experiments [8, 9].

Chiral pitch

Let us now discuss what we mean by chiral pitch. The *chirality* (handedness) property is exhibited by *chiral nematic liquid crystals*. This phase is often called the *cholesteric phase* because it was first observed in cholesterol derivatives. The chirality induces a finite azimuthal twist from one layer to the next, producing a spiral twisting of the molecular axis along the layer normal. The *chiral pitch*, p , is defined as the distance over which the liquid molecules undergo a full 360° twist. The pitch, p , is generally changed as the temperature is altered or other molecules are doped to the liquid crystal host.

Some Anisotropic Physical Properties of Liquid Crystals

Liquid crystals show anisotropy in many of their physical properties, e.g. elastic, magnetic, dielectric, optical etc. The origin of these anisotropies results due to the *molecular anisotropy* observed in these mesogenic materials. Because of the existence of these anisotropies, a number of phenomena are observed in liquid crystals which are absent in isotropic liquid phase. We give below a brief description of some of these anisotropic properties.

Optical Anisotropy: Refractive index

The optical anisotropic property is very important for application of a mixture of liquid crystals in optical display technology. It is well known that the liquid crystals are anisotropic; hence the speed of light is not the same in all directions. Rather the speed of propagation of light waves depends upon both direction and polarization of the light waves traversing through the liquid crystals. As a result, a liquid crystalline phase has different refractive indices in different directions. The behaviour of the uniaxial liquid

crystals (e.g. N_u, S_A, \dots) is almost the same as the *uniaxial crystal* and thus they are described as *birefringent* or *doubly refracting*. Consequently, the uniaxial liquid crystals possess two refractive indices, namely *extraordinary refractive index* n_e and the *ordinary refractive index* n_o . The ordinary refractive index n_o is observed when the electric field vector of a light wave vibrates perpendicularly to the optic axis of the material. On the other hand, extraordinary refractive index n_e results when the electric field vector of a linearly polarized light wave vibrates parallel to the optic axis. The optic axis of a uniaxial liquid crystal is given by director of the mesophase (Fig.1) [10].

The *optical anisotropy* or *birefringence* depends both on temperature and wave length and is defined as

$$\Delta n = n_e - n_o = n_{\parallel} - n_{\perp} \quad (2)$$

Where n_{\parallel} and n_{\perp} are the components of refractive index parallel and perpendicular to the director respectively. It is observed that $n_{\parallel} > n_{\perp}$ for rod like molecules; hence optical anisotropy Δn is positive and its value is found to be 0.02 to 0.4. However, for discotic molecules, $n_{\parallel} < n_{\perp}$ and thus Δn is negative for discotic nematic or columnar phases. For chiral nematics, the optic axis is identical with the helix axis which is perpendicular to the local director; $n_e = n_{\perp}$.

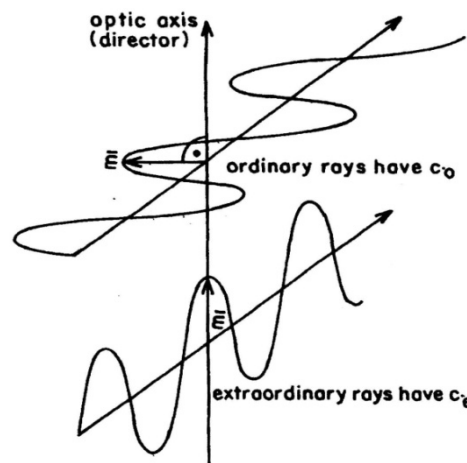


Fig 1 Birefringence for a N_u phase possessing positive optical anisotropy $\Delta n > 0$

In this case, n_o is a function of both n_{\parallel} and n_{\perp} and depends also on the relative magnitude of the wave length with respect to the pitch. When the wave length of the light is much larger than the pitch of the chiral nematic, then one gets,

$$n_o = \left[\frac{1}{2} (n_{\parallel}^2 + n_{\perp}^2) \right]^{\frac{1}{2}} \quad (3)$$

$$n_e = n_{\perp}$$

The above equation holds good for chiral nematics.

Dielectric Anisotropy: The Dielectric permittivity

When an electric field \vec{E} is applied to a dielectric material, an electric polarization is induced, which is related to the electric field as

$$\vec{P} = \vec{D} - \epsilon_0 \vec{E} \quad (4)$$

Where \vec{D} is the *electric displacement vector* and ϵ_0 is the permittivity of the vacuum. If the applied field is small, then \vec{P} is proportional to \vec{E} :

$$P_\alpha = \epsilon_0 \chi_{\alpha\beta}^e E_\beta, \quad \alpha, \beta = x, y, z \quad (5)$$

Where $\chi_{\alpha\beta}^e$ is an element of the electric susceptibility tensor χ^e . The permittivity tensor is related to the susceptibility tensor by the following relationship:

$$\epsilon_{\alpha\beta} = \delta_{\alpha\beta} + \chi_{\alpha\beta}^e \quad (6)$$

Generally, $\epsilon_{\alpha\beta}$ is dependent on frequency and wave vector of the applied field. Let us consider the director along the z-axis, then ϵ will be diagonal. Then we have the following relationship between the refractive indices and the elements of the permittivity tensor in the optical frequency range:

$$n_{\parallel}^2 = \epsilon_{zz}, \quad n_{\perp}^2 = \epsilon_{xx} = \epsilon_{yy} \quad (7)$$

If we fill a capacitor with a dielectric material having relative dielectric permittivity ϵ , it is observed that the capacitance of the capacitor increases from a value C to a value ϵC which is due to the polarization of the material by the electric field \vec{E} . In case of an anisotropic material, the resulting polarization per unit volume is given by equation (5). Using equation (6), we get

$$P_\alpha = \epsilon_0 (\epsilon_{\alpha\beta} - \delta_{\alpha\beta}) E_\beta \quad (8)$$

In a material consisting of non-polar molecules, only induced polarization occurs by the application of static electric fields. In this case, the polarization consists two parts: i) the *electronic polarization* (which is also present at optical frequencies) and ii) the *ionic polarization*. However, in materials with polar molecules, in addition to the induced polarization, an orientational polarization takes place, which arises due to the alignment of the permanent dipole moments of the polar molecules along the direction of the applied electric field. In case of isotropic fluids, the permittivity is isotropic, i.e. $\epsilon_{\alpha\beta} = \epsilon \delta_{\alpha\beta}$. In solids, the permittivity is usually anisotropic, and the contribution of the orientational polarization is less important because of the rather fixed positions of the molecules. However in liquid crystals consisting of polar molecules, the orientational polarization may contribute significantly to the anisotropic permittivity.

We consider a uniaxial liquid crystal phase and choose the z-axis along the director of the mesophase. The principal elements of the relative permittivity tensor ϵ are then given by $\epsilon_{zz} = \epsilon_{\parallel}$ and $\epsilon_{xx} = \epsilon_{yy} = \epsilon_{\perp}$. The *anisotropy of the dielectric permittivity* is defined as

$$\Delta \epsilon = \epsilon_{\parallel} - \epsilon_{\perp} \quad (9)$$

The mean dielectric permittivity $\bar{\epsilon}$ (N_u phase) is then given by

$$\bar{\epsilon} = \frac{1}{3} (\epsilon_{\parallel} + 2\epsilon_{\perp}) \quad (10)$$

The dielectric permittivity is also dependent on temperature and frequency of the applied electric field. We have investigated the dielectric anisotropy or dielectric strength of Antiferro- electric Liquid Crystals (AFLCs) (11) and Polymer Doped Antiferroelectric Liquid Crystals (PDAFLCs) (12).

Diamagnetic Anisotropy: The Magnetic susceptibility

The liquid crystals are diamagnetic like most of the organic materials. They are very sensitive to the external magnetic field. With the application of an external magnetic field to a nematic liquid crystal, a magnetization \vec{M} results in the system, which is defined by,

$$\vec{M} = \mu_0^{-1} \vec{B} - \vec{H} \quad (11)$$

Where \vec{B} is the magnetic induction and \vec{H} is the magnetic field intensity and μ_0 is the permeability of the free space. The magnetic susceptibility of a system is the response of the system under the action of an external field of magnetic induction \vec{B} . For small values of the external field, the response is linear and can be expressed as

$$M_\alpha = \mu_0^{-1} \chi_{\alpha\beta} B_\beta; \quad \alpha, \beta = x, y, z \quad (12)$$

Where $\chi_{\alpha\beta}$ is an element of the *magnetic susceptibility tensor* χ . χ is always negative for diamagnetic material and independent of the field strength, mostly dependent of temperature. For most of the organic materials, χ is found to be of the order of 10^{-5} (SI units).

The diamagnetic properties of uniaxial liquid crystals can be described by susceptibilities χ_{\parallel} and χ_{\perp} ; these are the susceptibilities corresponding to the external magnetic field applied parallel and perpendicular to the director of the mesophase respectively. The *diamagnetic susceptibility anisotropy* is defined as

$$\Delta \chi = \chi_{\parallel} - \chi_{\perp} \quad (13)$$

The diamagnetic anisotropy of all liquid crystals having an aromatic ring has been found to be positive and is of the order of 10^{-7} (SI units). A negative anisotropy is observed in purely cycloaliphatic liquid crystals.

CONCLUSION

In this article we have reviewed the various anisotropic properties of liquid crystals. Liquid crystals are mainly composed of organic molecules. The molecules are highly geometrically anisotropic in shape. This molecular anisotropy is the cause of all anisotropic properties exhibited by liquid crystals. We have explored different anisotropic properties. Of them optical anisotropy is very important in constructing modern liquid crystal devices.

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