Chapter-I
Introduction
I. Introduction

1.1 Liquid Crystals

The three conventional states of matter namely solids, liquids and gases are characterized by certain, specific properties as described below:

(a) Packing Force

The nature and magnitude of intermolecular attraction present in matter makes it possible to differentiate the different states. Thus, in solid the molecules are constrained with respect to their relative position and orientation. In liquids, however, the translational motions are restricted while the rotational or sliding constraints are largely absent. In gases, the molecules are relatively free in all respect though a weak Van der Waal type of force still exists between the molecules [1-2].

(b) Long-Range and Short-Range Order

The molecular order is an alternative way of describing the states or phases. This description makes it possible to differentiate between crystalline and amorphous states in solids. In crystals, the long-range and short-range order persists to a considerable extent while in liquids the short-range order is predominant while the long-range order is present only nominally. In gases, both long-range and short-range orders are absent [3].

Between the orderly crystalline states, formed due to strong intermolecular binding, and liquid state, the existence of an intermediate phases is known for over a century [4, 5]. Substances e.g. Chloestaryl benzoate, para-azoxyanisole etc. do not directly pass from solid to isotropic liquid or vice-versa, but adopt structures which though flow like liquids yet possess a considerable long-range order similar to those in crystalline state [6]. On further heating at still higher temperature, this turbid condition is converted into a true isotropic liquid. Mixing of suitable solvents with some substances like sodium and potassium salts of higher fatty acids etc. also produces such intermediate phases that have structural order between the conventional solids and liquids. Due to such intermediate character which shows such properties are called mesogens and now commonly referred to as liquid crystals [7-9]. Thus, liquid crystalline substances may be defined as those which have rheological behaviour similar to an isotropic liquid and
optical behaviour similar to those of crystalline solids in a single phase (i.e., over a certain range of either temperature or concentration of solvent etc.) [10-12].

The study of such substances is of considerable interest because of their applications in display devices, from small watch displays to flat TV screen and computer panels [13-16]. There are many other applications in connection with information storage and possible elements to combine with other in creation of nanoscale devices [17-20].

1.2 Building Blocks of Liquid Crystals

The mesomorphic behaviour of liquid crystalline substances rests upon the typical aggregation of molecular clusters [21, 22]. The molecular property which causes such aggregation needs intense investigation. As, the molecular structures play an important role in determining the phases, phase transition temperatures, optical and electro optical properties of the liquid crystals, they are called building blocks of the liquid crystals [23-25].

(a) Basic Molecular Structures

For many liquid crystals, the chemical structure can be represented as

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   R    A    Z    B    X
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where R is called side chain group, A and B are called aromatic rings, Z is a linking group and X is a terminal group. R and X are short and partly flexible chains [26].

(b) Side Chain (R)

Three side chains are commonly used, alkyl group (C\(_n\)H\(_{2n+1}\)), alkoxy group (C\(_n\)H\(_{2n+1}\)O), alkenyl group (C\(_n\)H\(_{2n-1}\)); an alkyl group with a carbon-carbon double bond or alkenyloxy group (C\(_n\)H\(_{2n-1}\)O) are also used. The length and flexibility of the side chain affect the phase transition temperature and type of mesogenic phases [26].

(c) Aromatic Rings (A and B)

Most of the compounds exhibiting a mesogenic phase consist of one or more aromatic rings. These aromatic rings can be a totally saturated cyclohexane, cyclocyclo
hexane, an unsaturated phenyl, biphenyl, terphenyl or a combination of both. Usually, the longer the ring, higher will be the melting temperature. The saturated cyclohexane ring consists of purely \( \sigma \)-electrons, where as a phenyl ring consists of six-\( \pi \) electrons and several \( \sigma \)-electrons. Their contributions to the melting temperature, refractive indices and the viscosity of the liquid crystal are quite different [27].

(d) Linking Group

Linking group makes important contribution to the phase transition temperature and physical properties of liquid crystals. Several linking groups generally used are

(i) Saturated groups, such as ethylene (\( \text{C}_2\text{H}_4 \)), ester (\(-\text{C} - \text{O}-\))

(ii) Unsaturated groups containing double bonds, such as stilbene (\(-\text{CH} = \text{CH}\)), azoy (\(-\text{N}=\text{N}\)), and Schiff’s base (\(-\text{CH}=\text{N}\)) and

(iii) Unsaturated groups containing triple bond such as acetylene (\(-\text{C} \equiv \text{C}\)); and diacetylene (\(-\text{C} \equiv \text{C} \equiv \text{C}\)) [28-31].

If two separated phenyl rings are linked by an ester or an ethylene group, the electron clouds in both rings do not overlap. On the other hand, stillbene, azoy and acetylene and diacetylene are unsaturated linking groups. They contribute their \( \pi \)-electrons to the two phenyl rings on the side. Thus, the overall conjugation length is increased.

(e) Terminal Group

Terminal group makes the primary contribution to dielectric anisotropy, which in turn affects the threshold voltage in some of the switching devices. The terminal groups generally used are alkyl, alkoxy, cyano, isocyanate, sulphide and halides such as F, Cl, Br, I, CF\(_3\), and OCF\(_3\) groups. From electron conjugation point of view, alkyl group is a neutral group that does not contain any \( \pi \)-electron. Alkoxy group contains an oxygen atom; therefore its conjugation length gets increased. The cyano and isocyano groups contain several \( \pi \)-electrons. Their contribution to the conjugation length is more [27].
1.3 Classification of Liquid Crystals

Liquid crystals are classified into two types; viz., thermotropic liquid crystals and lyotropic liquid crystals. Polymer LC corresponds to high molecular weight LC, and cannot be in the same branch as the other kind of LC. The detail classifications of liquid crystals are shown in Table 1.1. The thermotropic liquid crystals are of interest from the standpoint of basic research and also for applications in electro optic displays, temperature and pressure sensors etc. [32-34]. The lyotropic liquid crystals are on the other hand, of a great interest in biology and appear to play an important role in living systems [35-37].

Polymer Based Liquid Crystals

Liquid crystalline polymers combine the self organization of the mesogenic groups into the ordered structure of liquid crystalline phases with some typical polymer properties, such as the freezing of the disorder polymer chain at glass transition temperature. It can be prepared by incorporating the anisotropic mesogenic groups into polymeric systems. The mesogenic groups can be linked to the polymer chain as side groups, to produce liquid crystal side group polymers. The mesogenic groups can be incorporated into the polymer chain, to obtain liquid crystal main chain polymers [38-41].

Lyotropic Liquid Crystals

The liquid crystalline substances which are exhibiting phases due to the influence of solvent concentration and temperature are called lyotropic liquid crystals. The molecules that make up lyotropic liquid crystals are surfactants consisting of two distinct parts: a polar (often ionic) head and a non-polar (often a hydrocarbon) tail. Following the rule of “like dissolves like”, the head is attached to water (or hydrophilic) and the tail is repelled by water (a hydrophobic). When dissolved in high enough concentrations, the molecules arrange themselves so that the polar heads are in contact with a polar solvent and/or the non-polar tails are in contact with a non-polar solvent [42-44].

Thermotropic Liquid Crystals

The term thermotropic arises because transitions involving these mesophases are most naturally effected by the change of temperature. Thermotropic liquid crystals in which the transitions takes place reversibly on both heating and cooling or the
Table 1.1. The classification of Liquid Crystals

- Thermotropic LCs
  - Sanidics LCs
  - Calamitic LCs
  - Bowlics LCs
  - Discotics LCs

- Lyotropic LCs
  - Soaps
  - Phospholipids

- Smectic LCs
- Nematic LCs
  - Non-Tilted
  - Tilted
  - Non-Chiral Smectics
  - Chiral Smectics

- Cholesteric LCs
- Nematic
- Columnar
- Chiral Nematic
Thermotropic liquid crystals which are stable at temperatures above the melting point of the compound are called enantiotropic. In certain cases, the phases are observed only on cooling or the liquid crystalline state is only stable at the temperature below the melting point. The phases of this kind are called monotropic. Thermochromic liquid crystals are thermotropic in origin and have chiral (twisted) structures [45, 46]. Thermotropic liquid crystals are broadly classified into four types. They are Sanidic LCs, Calamitic LCs, Bowlic LCs and Discotic LCs [47, 48].

**Calamitic Liquid Crystals**

The mesogens, which are having rod-like structure, are called calamitic liquid crystals. The most important phase structure of liquid crystals belonging to this class is **Nematics**.

The molecules possess long-range orientational order, i.e., the molecules tend to align parallel to each other. The nematic phase is fluid and there is no long-range correlation of the molecular centre of mass position. The main feature of the molecular organization of nematic is the orientational order along the long molecular axis. This orientational order allows us to define an average direction of the molecules called director, denoted by \( \hat{n} \). The direction of the principal axis \( \hat{n} \) (the director) is arbitrary in space. The material is still fluid, the molecules prefer to orient along \( \hat{n} \) (r). Thus, the material is anisotropic [47-50]. The other important variable in nematic liquid crystal is the order parameter, which measures how the molecules are aligned with the director. The usual measure of this order is,

\[
S = \frac{1}{2} < 3 \cos^2 \theta - 1 > 
\]

where S represents the thermal fluctuations of the individual molecular along long axis and the brackets\(< >\) denote a thermal averaging and \( \theta \) is the angle between each molecule (molecular long axis) and the director (\( \hat{n} \)). If the molecules are very well aligned with the director then \( S=1 \), and if the molecules are randomly oriented about \( \hat{n} \) (i.e.) isotropic, then \( S=0 \). In nematic phase, \( S \) generally increases from 0.3 (near to clearing temperature) to 0.6 or even 0.7 at low temperatures [51].
The parallelity of the molecular long axis makes the nematic phase to exhibit anisotropy in its physical properties, viz., optical properties (double refraction), viscosity, electrical and magnetic susceptibility, electrical and thermal conductivity etc. The parallelity of the molecules is not exact, and is strongly temperature dependent [52-54].

**Cholesteric Liquid Crystals**

Cholesterics are regarded as a special kind of nematics. These materials are extremely optically active much more than can be accounted for on the basis of rotatory power of the constituent molecules alone, and they have natural twisted structure. In this phase, the molecules prefer to lie next to each other in a slightly skewed orientation. This induces helical director configuration in which the director rotates through the material. However, in chiral nematic mesophases are composed of helical aggregation of the molecules. Such a structure may be envisaged as being composed of the sheets of molecules. Within each sheet, the molecules behave as nematic phase and have an average direction defined by a unit director $\hat{n}$. To quantify the degree of twist, the pitch length $P$ of the helix is defined by convention as longitudinal distance in which this director has made one complete $360^\circ$ revolution. Thus, each molecule is skewed at some average angle with respect to its neighbors in the sheets immediately above and below. Two such helical arrangements one right-handed, other left-handed are possible, but one will have a lower energy than the other [55-58].

**Smectic Liquid Crystals**

Smectic is the name coined by G.Friedel for certain mesophases with mechanical properties reminiscent of soaps. From a structural point of view, all smectics are layered structures, with a well defined inter-layer spacing, which can be measured by X-ray diffraction technique [59].

Smectic phases are characterized by both long-range orientational order as well as short-range positional order. With simple changes in mutual arrangement of the layers and with changes (in the state of order) inside the layers, a variety of smectic phases can be obtained [60-63]. The smectic polymorphism is subtle than nematic polymorphism. These are classified into different types:
Smectic-A ($S_A$)

The molecules align perpendicular to the layer planes and the director in each layer is parallel to the layer normal. Inside each layer, the centers of gravity show no long-range order; each layer is a 2D liquid. The system is optically uniaxial, the optical axis being normal to plane of layers [64, 65].

Smectic-B ($S_B$)

In smectic-B materials, the molecules in each layer form a hexatic structure and the layer appears to have the periodicity and rigidity of 2D solid. X-ray reflections corresponding to an order inside each layer are observed. The layers are not flexible under microscope [66-68].

Smectic-C ($S_C$)

Smectic-C is a tilted analogue of Smectic-A phase and the molecules are tilted with respect to layer normal. Tilt angles up to $45^\circ$ have been observed with the decrease of temperature in some compounds. Each layer is still a 2D liquid. The material is biaxial [69-72]. In some compounds, the tilt angle is temperature independent.

Smectic-D ($S_D$)

Only few compounds are known to exhibit this phase and the common variants observed are I-$S_D$-$S_C$ or I-$S_A$-$S_D$-$S_C$ [73]. Diele et al. [74] proposed a structural model for this phase with a cubic close packing of spherical units with each unit consisting of the several molecules. No characteristic texture could be obtained as this phase is found to be optically isotropic.

Smectic-E ($S_E$)

The smectic-E phase possesses high degree of molecular ordering in smectic layers with a distinctly non-hexagonal lattice. The orthogonal arrangement of molecules with respect to the layers form 3-D lattice. Both uniaxial and biaxial $S_E$ phase possesses an orthorhombic unit cell in layers with chevron like arrangement of molecular cross-sectional areas [75-77].
**Smectic-F (SF)**

The molecules are packed in layers with their long axes tilted with respect to the layer planes. Smectic-F phase possesses long-range tilt order and has a quasi two-dimensional structure, with poor correlation between layers i.e., a shift distortion of hexagonal net often occurs between layers. The layers are free to slide one over the other but not to rotate relative to one another, i.e., the phase has long range bond orientational ordering [78-81].

**Smectic-G (SG)**

The smectic-G phase is a C-centered monoclinic cell. The molecules possess pseudo-hexagonal close packing (in plane) at right angles to the tilt direction. This close packing arrangement is of hexagonal kind. The layers are well correlated giving a 3D structure. A considerable dynamic disorder of molecule is known to exist in SG phase [81].

**Smectic-H (SH)**

Sakagami *et al.* [82] have first differentiated smectic-G and smectic-H phases in the well studied liquid crystal terephalylidene bis – p-n-butyl aniline (TBBA) and in its higher homologues. The structure of this phase is equivalent to SE except that the molecules have their long axes tilted with respect to the normal of the layer planes [83].

**Smectic-I (SI)**

The smectic-I phase has a similar molecular structure as SF phase, but the difference being the tilt direction of pseudo-hexagonal molecular packing i.e., towards the edge in SF and towards apex of the hexagon in SI phase [66, 84].

**Smectic-J and Smectic-K (SJ and SK)**

These two phases are two disordered crystal phases and are related in structural characteristics of smectic-G and smectic-H phases respectively. They differ only in the direction of tilt. Both the phases have monoclinic symmetry (with b>a) and pseudo-hexagonal packing of molecules which are tilted towards apex of the hexagon, the distortion from the hexagonal packing is greater in the lower temperature phase [81].
Smectic-M (SM)

Heppke et al. [85] recently reported the existence of a new smectic phase, for which they have proposed the code letter SM. This new phase belongs to the group of tilted smectic phases with short-range positional order. Presumably SM belongs to group of hexatic phases exhibiting long range bond orientational order.

Smectic-O (SO)

The existence of smectic-O phase was established by Levelut et al. [86] in chiral as well as racemic 1-methyl heptyl-terephthalylidene-bis-amino-cinnamate (MHTAC). X-ray investigations showed that this phase has a tilted smectic structure without positional order within the layers. Conoscopic investigations on this compound indicated that the optical axis is parallel to the layer normal for the zero field state and tilted for the two other states induced by electric field. The synthesis of new materials exhibiting these phases and various experiments on these phases is progressing [87-90].

Smectic-Q (SQ)

Levelut et al. [86] discovered a new type of liquid crystalline phase, which occurs in chiral but not in racemic 1-methyl heptyl-terephthalylidene-bis-amino-cinnamate (MHTAC) which was also the source of the first Q phase [91]. Only recently other compounds exhibiting this phase are reported.

Smectic-X (SX)

Brand and Cladis reported [92] a first truly ferroelectric liquid crystalline phase in the compound 8SI* and named it as smectic-X which has shown a net spontaneous polarization. The in-plane structure of this phase was predicted to be similar as a non helicoidal G or K phases. Chiral smectic phases are optically uniaxial, because of helix structure, where as the smectic-X phase turned out to be biaxial.

Discotic Liquid Crystals

Chandrasekhar discovered liquid crystalline phases in molecules of discotic shape [93]. The molecules of these classes are flat and disc-like in shape and able to be packed in different structures. In most cases, the disc-shaped molecules are packed one upon
another to form columns that constitute hexagonal arrangement, but the spacing between the discs in each column is irregular. Thus, the structure has translational periodicity in two dimensions but liquid like disorder in the third. This new state of matter is designated as disc-like mesophase. Within the columns, the molecules can have certain order or disorder. The columns itself are arranged in a two dimensional network leading to columnar phases with hexagonal, rectangular or oblique symmetry where by the tilted variants are possible. Similar to rod-shaped molecules, the disc-shaped molecules can also form a nematic phase characterized by a long-range orientational order, but no long range positional order with a director parallel to the disc normal. In chiral compounds, the discotic nematic exhibits a twisted structure [94-97].

**Sanidic Liquid Crystals**

The molecules with lath-like structure form sanidic liquid crystals. Depending on the relative size of main axes, these liquid crystals can be derived from rod-like or disc-like molecules. The structure of sanidic phases can be characterized by three translational periods (in accordance with length, breadth and thickness) of scattering maxima, which cause three molecular units by investigation with X-ray techniques [98].

**Bowllic Liquid Crystals**

Mesogens with bowl-like molecules forms the bowllic liquid crystal. They contain molecules, which are 3D in a physical sense, and can exhibit mesophases as the one-dimensional rod-like and two-dimensional disc-like compounds. Lin had first proposed mesophase of bowl-like molecules [99]. The compounds containing pyramidal-shaped, banana-shaped and cone-shaped are also reported [100, 101]. The banana liquid crystals are formed by macroscopic formation of the molecules in layers with banana-like structure. These are composed of bent molecules [102, 103].

**1.4 Theoretical Approach for Liquid Crystalline Properties**

Theoretical attempts to understand their behaviour started about 50 years ago [104] but a completely satisfactory method is yet to be established. Among the various types of liquid crystals, nematics are the simplest type having only a long-range orientational order of anistropic molecules. Though compounds with both rod-like and
disk-like molecules exhibit nematics phase, only the former type of compounds has been taken as model, and in the course of theoretical developments, a cylindrical symmetry for such compound have been assumed by most of the workers. In a few theoretical models, however, they are assumed to be biaxial objects although the shape of the molecules may not be simple [105].

**Earlier theoretical approach**

Of the two popular approaches for theoretical explanation of liquid crystallinity, the first one based on rigid rod features of the molecules developed by Onsager [104] assumes the configurational partition function as [105]

\[
Q_N = \frac{1}{N!} \sum_{\Omega} \int d\mathbf{R} \exp(-\beta U_N) \quad \text{-------- (1.2)}
\]

\[\Omega = \text{Orientation of the molecules}\]

where \( v_N = \sum_{i \neq j} v_{ij} \) is the potential energy of the system, \( \beta = \frac{1}{kT} \),

where \( k \) is the Boltzmann constant. \( v_{ij} = \infty \) if \( i \) and \( j \) overlap.

\( = 0 \) otherwise.

Onsager’s approximation is valid only for low densities and hence for very long rods. Zwanzig [107] could calculate higher virial coefficients by restricting the molecules to take three mutually perpendicular orientations. Flory and Ronca [108, 109] used a lattice model and were able to make calculations at relatively high densities. However, all these models are useful to describe the Nematic-Isotropic transitions (hence forth referred to as N-I transitions) only if the molecules have very large length to breadth ratios (~100). In the sealed particle theory (SPT) calculating the reversible work by interpolation, the phase transition is located by equating the Gibbs free energy as well as the pressure of the ordered and disordered phases. The calculated [106, 110] transition properties like Order parameter \( S_{NI} \), \( \Delta \rho_{NI}/\rho_N \), (\( \rho \) refers to density) etc. are in reasonable agreement with the experimental data on para-azoxyanisole (PAA) when length to breadth ratio \( \chi = 2.5 \).

Monte Carlo (MC) and molecular dynamic simulations [111, 112] have also shown that the SPT overestimates the pressure at higher densities. Attempts have been made to use the data for the isotropic phase from the computer simulations and extend the calculation
to the thermodynamic properties of the nematic phase [110, 113, 114] giving somewhat better agreement with experiments.

Density functional approach has been used to discuss the N-I transition in a system of hard ellipsoids by several authors [115-117]. A simple scaling arrangement has been proposed by Lee [118, 119] to write an Onsager type free energy for ensembles of both hard spherocylinders and ellipsoids of revolution. A very good agreement with the computer simulation results on the packing fraction at the N-I transition is obtained by this method. Frenkel et al. [120,121] have done Manto Carlo studies on the hard ellipsoid system. By computing the equations of state and free energies of different phases, they have constructed ‘phase diagram’ for hard ellipsoid of different axial ratios.

All the hard particle models are however ‘a thermal’. For instance, using measurements of the orientational order parameter as a function of both pressure and temperature, it is possible to calculate the quantity \( \gamma = (\partial \ln T / \partial \ln \rho)_s = \text{const.} \) which is a measure of the relative importance of the variation of the \( S \) near \( T_{NI} \). While experiments on para azoxy anisole [122] yield \( \gamma \approx 4 \), the hard particle models give \( \gamma = \infty \). Clearly, the attractive interactions between the molecules, which have been ignored, also have to be taken into account in the theory [105].

The second popular approach is based on the classic article of Maier and Saupe [123-125], which is an application of Landau’s mean field theory of LC. They assumed that the anisotropic dispersion forces are entirely responsible for the orientational order and ignored altogether the shape anisotropy of the molecules. The orientational energy of a molecule \( i \) is given by

\[
 u_i = -\frac{A}{V^2} P_2 < \cos \theta_i > \\
 A = \text{Constant} \\
-------(1.3)
\]

where \( P_2 < \cos \theta_i > \) is the second Legendre polynomial and the \( V^{-2} \) dependence is assumed as the potential arised from dispersion forces. Cotter [126], based on the idea of Widom [127], suggested that mean field model will be thermodynamically consistent if and only if \( u_i \propto V^{-1} \). Accordingly, the molar free energy is given by

\[
 F = NkT \left[ \frac{A}{2kTV} S(S+1) - \ln \int_0^1 \exp \left( \frac{3A}{2kTV} S \cos^2 \theta_i \right) d(\cos \theta_i) \right] \\
-------(1.4)
\]
where \( N \) is the Avogadro number. Free energy minimization yields the consistency condition as

\[
S = \langle P_2(\cos \theta_i) \rangle
\]

where averaging is done using Boltzmann distribution corresponding to the potential energy \( U_i \). First order NI transition appears at \( S_{NI} \approx 0.42 \) as a universal value \([128]\). Experimental values of \( S_{NI} \) varies in the range of 0.25 to 0.5 for different compounds. The potential can be generalized by including a term \( \alpha \langle P_4(\cos \theta_i) \rangle \) where \( P_4(\cos \theta_i) \) is the \( 4^{th} \) Legendre Polynomial \([129]\). A better agreement of \( S_{NI} \) with experimental data thereby is achieved \([130,131]\).

Jeu et al. \([132]\) emphasized that realistic theory of the isotropic – nematic phase transition within the homologous series should explain (a) the odd-even alteration of \( T_{IN} \) within a homologous series, (b) an increase of \( T_{IN} \) with \( n \) for series with relatively low transition temperature where \( n \) is the number of carbon atoms in the end chain, and (c) a decrease of \( T_{IN} \) with \( n \) for series with higher transition temperatures. Mercelja \([133]\) added two more points, as (d) an increase of \( \Delta S_{IN} \) with \( n \) and (e) the odd-even alterations of \( \Delta S_{IN} \) within a homologous series. Considering the flexibility of the end alkyl chains, Marcelja incorporated the configurational statistics of the end chains in the theory of the nematic phase in a Flory type calculation. His calculation demonstrated the ‘Odd-Even’ effect of both \( T_{NI} \) and \( S_{NI} \) as a homologous series is ascended. The results are in broad agreement with the experimental trends. These calculations were later refined by Luckhurst \([134]\) and used to make successful calculations for compounds that have two rigid cyanobiphenyl moieties linked by flexible spacers in which the Odd-Even alteration is at \( T \sim 100^\circ C \).

Madhusudana \([135]\) has discussed the discrepancies of the mean field model in detail and pointed out that

(a) The mean field models generally overestimated the strength of the transition. For example, the predicted heat of transition is usually a few times higher that the experimental value. Further, the magnetic birefringence in the isotropic phase diverges as the N-I transition is
approached as if a second order transition point $T^*_N$ exists $\sim 1^\circ$ below the actual first order transition at $T_{NI} - T^*_N \sim 30^\circ - 40^\circ$ or $(T_{NI} - T^*_N)/T_{NI} \sim 0.9$. With some approximation [126-130], the free energy can be evaluated and the calculated value of $S_{NI} \sim 0.40$ and $(T_{NI} - T^*_N)/T_{NI} \sim 0.50$, the exact values depending on the lattice type. Later extensions [131-144] have improved the value further up to 0.01.

(b) Maier-Saupe theory assumes that the molecular interactions are cylindrically symmetric so that it is sufficient to define one order parameter S. In reality, most nematogens have lath shaped molecules which have a biaxial character. Straley [145] and Gelbart and Barby [146] worked out models using the biaxiality of the geometrical shape of the molecule while Luckhurst et al. [147] and Bergensen [148] have developed extensions of the Maier-Saupe Model using attractive potentials. The results are that (1) the biaxiality decreases the S value at the transition point which compares better with experimental results and (2) since different properties will in general have different types of biaxial anisotropies, the S values derived from different techniques may differ.

A rigorous molecular model of the nematic phase should, therefore, incorporate many different aspects (a) the hard rod feature should include deviation from cylindrical symmetry; (b) the attractive interactions including the influence of any permanent dipoles should be coupled to the excluded volume effects and (c) the flexibility of end chains, and short-range orientational correlations should be taken into account. Binary mixtures have been treated theoretically using extensions of the Maier-Saupe theory [149-150], lattice model of hard rods [151] and hybrid models [152].

Since curvature elasticity is a consequence of the orientational order in the medium, expressions for the elastic constants are believed to be derived using the statistical theories of nematics. In the Landau model [153,154], if the expansion in deformation energy is retained on up to quadratic terms in S, only two independent elastic constants ($K_{11}=K_{33}$ and $K_{22}$ where $K_{11}$, $K_{22}$ and $K_{33}$ are the splay, twist and bend elastic constants respectively) are obtained, and $K_{ii} \propto S^2$. 


Similar result is obtained by using MS theory [155, 156] in which the shape anisotropy is ignored. Further one gets [157] \( K_{22} > K_{11} = K_{33} \). A lattice model [158] in which near neighbour antiparallel correlations of polar molecules are included still gives \( K_{ii} \propto S^2 \). Priest [159], Staraley [160] and other [161, 162] showed that hard rod models can lead to the usually observed trend \( K_{33} > K_{11} > K_{22} \) but the models are strictly valid only for very long and thin rods and they usually predict too large a value for the ratio \( K_{33} / K_{22} \). There have been attempts to incorporate both hard rod features and attractive interactions in the calculations of elastic constants [163-166].

These have been many statistical models to account for the helical twist in the cholesteric phase [167-176]. It is clear that the interaction energy between the chiral molecules should have in addition to the nematic potential, extra terms which give rise to the helical arrangement of the director.

Smectic-A phase is characterized by a one-dimensional density wave and is subjected to the Landau-Pererls instability. It has no long range translational order in the thermodynamic limit [177]. Later, Mc-Millan [178] and Kobayashi [179,180] extended the Maier-Saupe theory of the nematic phase to include the one – dimensional translational order of the Smectic-A phase. Hosino et al. [181] developed a hard cylindrical model for smectic-A phase who used the technique of symmetrical breaking potential to calculate the phase diagram. Stroobants et al. [182, 183] demonstrated the occurrence of the smectic-A phase using computer simulation studies on a system of hard spherocylinders. The origin of the stability of the smectic-A phase in a system of hard cylinders has been discussed by Wen and Meyer [184]. In the nematic phase, the excluded volume is mainly contained in configurations in which the voids are adjacent to the end of the rods. In the Smectic-A phase, on the other hand, the layering prevents random lengthwise overlapping of rods and now the voids are distributed in the layers, reducing the lateral packing density of the layers. Excluded volume theory for both the smectic-A and columnar phases of a system of hard spherocylinders with full translational and a cell model for positionally ordered dimensions [185]. The density functional theory has been used to study the A-N transition in a system of parallel hard spherocylinders [186-188] as well as a system with orientational degree of freedom [189].
Several theories of the Smectic-C phase have been developed which take into account specific features of the molecules. A steric model proposed by Wulf [190] assumes a zig zag shape for the molecules and freezing of free rotation around the long axes to produce the tilted structure. Mc-Millan [191] developed a model in which the real physical mechanism for the smectic-A & smectic-C transition would be a freezing out of the rotation of the molecules about their long axes and a resulting dipolar ordering. NMR and other experiments clearly indicate that molecules are practically freely rotating about their long axes in the smectic-C phase in disagreement with assumptions of the both Wulf and Mc-Millan. Cabib and Bengnigni [192] tried to overcome this problem by postulating a special type of molecular structure in which only the longitudinal components of two symmetrically placed outboard dipoles are effective, although most compounds do not have such a structure. Some other models [193-199] have tried to overcome these difficulties but each of them has their own limitation. There have been discussions on the NAC point on the basis of Landau theory [200,201]. The Landau theory, however, does not speak on the physical origins of the tilt. But, it appears that the main role of the transverse dipole in compounds exhibiting the smectic-C phase is to build a strong enough quadrupole moment which can in turn lead to a tilting of the molecules in the layered phase. Osipov and Pikin [202,203] have developed a molecular model for smectic-C phase assuming that the chiral dipolar molecules have a banana shape. In particular, they calculate the flexoelectric part of the polarization which arises from the bend deformation [204] is present in a helical arrangement of tilted molecules. Zeks et al. [205,206] have given a microscopic model, which is consistent with the Landau expressions.

**Hard Rod Models**

It is clear from the above discussion that the development of the theories to explain liquid crystallinity had been, in general, need based. Model based on hard rod features included the excess free energy \( F \) relative to an ideal gas of a system of molecules having fixed orientations as

\[
\int dR \exp(-\beta U_N) = V^N \exp[-\beta \phi_N(\Omega)]
\]

---------(1.6)
where $U_N = \sum_{i \in i \in j \in j} U_{ij}$ is the potential energy of the system. $\beta = 1/kT$ where $k$ is the Boltzmann constant. The intermolecular pair energy for hard particles $U_{ij} = \infty$ if $i$ and $j$ overlap and $=0$ otherwise. In Maier and Saupe approach the orientational energy of a molecule $i$ is given by $u_i = -A/V^2 SP_2 \cos \theta_i$ where $P_2(\cos \theta_i)$ is the second Legendre polynomial and the $V^{-2}$ dependence is assumed as the potential arises from dispersion forces. Clearly, selectiveness of $P_2$ towards alignment around $\theta^0$ or $180^0$ is imposed in the design of the potential $V^{-2}$ dependence. Attempts to improve the theories have been made by adding terms to intermolecular pair potential while retaining the mean field framework [207-211]. At the expense of one or more additional adjustment parameters, the fit to experiments could indeed be improved. Cotter [212] assumed the pseudo-potential as

$$\Psi(\Omega, \rho) = -\nu_0 \rho - \nu_2 \rho \eta \rho_2(\cos \theta)$$

where $\rho$ is the number density, $\nu_0$ and $\nu_2$ are positive constants, and $\eta_2$ is the traditional nematic order parameter. In this approach, $\nu_0$ and $\nu_2$ are treated as adjustable parameters. The linear dependence of $\Psi$ on $\rho$ is required for statistical mechanical self-consistency [213]. In generalized van der Waals (GVDW) theory of nematics, the average attractive energy is derived by using the expression

$$U_N = \frac{1}{2V} \sum_i \sum_j \tilde{N}_i \tilde{N}_j \int dR \gamma_{ij}^{(2)}(R)u_a(R, \Omega_i, \Omega_j)$$

where $\gamma_{ij}^{(2)}(R)$ is the pair correction function between 2 molecules with fixed orientation $\Omega_i$ and $\Omega_j$ and is calculated using the hard rod potential

$$\gamma_{ij}^{(2)}(R) \equiv \exp[-\beta u_{ij}(R, \Omega_i, \Omega_j)]$$

where $u_{ij}$ is the repulsive potential. In the theory of nematic mixture, Palffy-Muhray et al. [214] have taken the pair potential of the form

$$u_i(\cos \theta_i) = \gamma^0 - \nu_2 \rho SP_2(\cos \theta_i) + 1/2 \nu_2 \rho S^2$$
in which $\gamma^0$ is the isotropic part, and the last term which is independent of the angle $\theta$ is added to the potential itself so that the free energy expression may be simplified as

$$F = -kT \ln Q = N \left\{ \gamma^0 + kT \ln \rho + 1/2 \nu_2 S^2 - KT \int_0^1 \exp \{\beta \nu_2 SP_2(\cos \theta)\} \, d \cos \theta \right\}$$

---------(1.11)

Similarly, in their theory of cholesteric phase, van der Meer et al. [215, 216] argued that in the simplest approximation, the interaction energy between two chiral molecules can be assumed to be of the form

$$u_{ij} = -J(\vec{a}_i \cdot \vec{a}_j) - k(\vec{a}_i \cdot \vec{a}_j)(\vec{a}_i \times \vec{a}_j \cdot \vec{a}_j)$$

---------(1.12)

where $\vec{a}_i$ is the unit vector along the long axis of the $i^{th}$ molecule, and $\vec{a}_j$ is that along the line joining the centers of the $i^{th}$ and $j^{th}$ molecules. The first term is the MS potential and the second term is the chiral interaction which can arise from the dipole-quadrupole part of the dispersion interaction. For smectic-C phase, van der Meer and Vertogen [217] used a chiral interaction term of the form

$$u_{chiral} = -uI(\vec{a}_i \cdot \vec{a}_j)(\vec{a}_i \times \vec{a}_j \cdot \vec{a}_j) - u3(\vec{a}_i \cdot \vec{a}_j)(\vec{a}_i \times \vec{a}_j \cdot \vec{a}_j)$$

---------(1.13)

Zeks used the simple particle potential for the $(\vec{a}_i \times \vec{a}_j \times \vec{a}_j)$ rotation of a molecule around its long axis as

$$u(\Psi) = -a_1\omega \cos \Psi - a_2\omega^2 \cos^2 \Psi$$

---------(1.14)

where $\Psi$ describes the transverse orientation of a molecule made by the transverse dipole with reference to a direction perpendicular to the tilt. Goossens used the quadrupolar interaction energy between two molecules $i$ and $j$ as

$$V^i_q V^j_q = \frac{1}{u} q_{\alpha \beta} q_{\delta \gamma} \frac{\partial}{\partial R^i_\alpha} \frac{\partial}{\partial R^j_\beta} \frac{\partial}{\partial R^i_\gamma} \frac{\partial}{\partial R^j_\delta} (1/R)$$

---------(1.15)

where $R^i_\alpha$ is the $\alpha^{th}$ component of the radius vector $R^i$, $R$ is the intermolecular separation and $q_{\alpha \beta}$ the quadrupole moment tensor, Mc-Millan, while dealing the smectic A phase wrote the simple particle potential as

$$u_i(Z_i, \cos \theta_i) = -v_0 \left[ S + \sigma \alpha \cos(2\pi z_i/a) \right] (3\cos^2 \theta_i - 1)/2$$

---------(1.16)
where \( a \) is the layer thickness. The Mc-Millan parameter \( \alpha \) is given by
\[
\alpha = 2 \exp\left[-\pi r_0^2/a^2\right]
\]
in which ‘range’ of the dispersion interaction, \( r_0 \) is of the order of the length of the rigid core of the molecules. \( S \) is the usual orientation order parameter, and \( \sigma \) an order parameter, which couples translational and orientational order.

1.5 Behaviour of Liquid Crystals at Molecular Level

Understanding of the behaviour of liquid crystals at the molecular level has been considerably enhanced by computer simulation studies. With help of computer one can easily generate molecular structure based on crystallographic and other experimental evidences. Also, one can introduce minor modifications in the molecule without actually synthesizing them on the basis of the available data on similar molecules. Since the nature of intermolecular forces is not completely understood, one can freely choose from the intermolecular potentials proposed by various workers and visualize the details of variation in structure or molecular arrangements. One can also generate experimental conditions through computer like change in physical parameters such as temperature, pressure, density, etc. A suitable optimization procedure enables the workers to study the behaviour of the system under varying conditions as mentioned above. However, the right choice of intermolecular potential is the key of success for such investigation. Indeed, this determines whether the system even forms liquid crystal phases or not. Since the essential requirement is an anisotropy in the potential, the constituent particles are often represented, somewhat idealistically, by geometric shapes, such as ellipsoids of revolution or by sphero-cylinders, with cylindrical symmetry. With dominant hard core repulsion in the pair potential, a variety of mesophases have been identified in such systems of idealized particle [218-223]. Theoretical methods using hard particle models as reference systems and introducing attractive terms through a perturbation approach [224] provide a basic understanding of the underlying physics of the interactions. Phenomenological descriptions have provided a valuable source of potentials. Such models describe both repulsive and attractive contributions to the potential. Further, they can be fine-tuned to agree with experiment by means of a set of adjustable parameters. One such potential with a simple site interaction was proposed by Corner [225]. The
intermolecular interaction was chosen to be a function of the distance between two centers, scaled by a suitable range parameter $\sigma(\Omega)$:

$$U_{\text{corner}} = \varepsilon(\Omega)f\left\{r/\sigma(\Omega)\right\} \quad \text{(1.17)}$$

The strength and range parameters $\varepsilon(\Omega)$ and $\sigma(\Omega)$ are both dependent upon the orientation $\Omega$ of the molecules and the intermolecular vector. Berne and Pechukas [226] used a Gaussian overlap model to obtain functional forms for $\varepsilon(\Omega)$ and $\sigma(\Omega)$. In this approach, the overlap $S(\mathbf{u}_1, \mathbf{u}_2, \hat{r})$ between two terms ellipsoidal Gaussian distribution was evaluated and found the take the analytical form:

$$S(\mathbf{u}_1, \mathbf{u}_2, \hat{r}) = \varepsilon_0 \varepsilon_1(\mathbf{u}_1, \mathbf{u}_2) \exp\left[-r^2/\sigma^2(\mathbf{u}_1, \mathbf{u}_2, \hat{r})\right] \quad \text{(1.18)}$$

Here $\mathbf{u}_1$ and $\mathbf{u}_2$ are unit vectors giving the orientation of ellipsoid 1 and 2, while $\hat{r}$ is the unit vector between their centers. The range parameter $\sigma(\Omega)$ was taken to the term scaling the interparticle distance $r_1$ and the strength parameter $\varepsilon(\Omega)$ as that which scales $S(\mathbf{u}_1, \mathbf{u}_2, \hat{r})$:

$$\sigma(\mathbf{u}_1, \mathbf{u}_2, \hat{r}) = \sigma_0 \left[1 - \left(\chi^2/2\right)\left\{\left(\mathbf{u}_1 \cdot \hat{r} + \mathbf{u}_2 \cdot \hat{r}\right)^2 + \left(\mathbf{u}_1 \cdot \hat{r} - \mathbf{u}_2 \cdot \hat{r}\right)^2\right\} \left(1 + \chi(\mathbf{u}_1 \cdot \mathbf{u}_2)\right) \left(1 - \chi(\mathbf{u}_1 \cdot \mathbf{u}_2)\right)\right]^{-3/2} \quad \text{(1.19)}$$

and $\varepsilon_1(\mathbf{u}_1, \mathbf{u}_2) = \left[1 - \chi^2(\mathbf{u}_1, \mathbf{u}_2)^2\right]^{3/2}$

where $\chi = \left[\left(\sigma_e/\sigma_s\right)^2 - 1\right]/\left[\left(\sigma_e/\sigma_s\right)^2 + 1\right]$

$\sigma_e$ and $\sigma_s$ represent the range parameter for the end-to-end and side-by-side orientations, respectively. The ratio $\sigma_e/\sigma_s$ is equal to $\sigma_i/\sigma_b$, where $\sigma_i$ and $\sigma_b$ are the semi-axes of the ellipsoidal Gaussians considered, the constant $\sigma_0$ is given by $\sqrt{2}\sigma_s$. It is interesting to note that in this definition, both $\varepsilon_1(\mathbf{u}_1, \mathbf{u}_2)$ and $S(\mathbf{u}_1, \mathbf{u}_2, \hat{r})$ are dependent upon the same parameter $\sigma_e/\sigma_s$, and that these are directly related to the shape of the ellipsoidal Gaussian. The model was first applied to study of liquid crystalline system by Kushick and Berne [227]. The single site intermolecular potential was chosen to take 6-12 Lennard Jones potential of the form:
and the calculations indicate that a system of prolate Berne-Pechukas Kushick (BPK) Centres exhibit a nematic $\rightarrow$ isotropic transition.

This model, however, possesses a number of deficiencies (a) the strength parameter $\varepsilon (\vec{u}_1, \vec{u}_2)$ is independent of the intermolecular unit vector $\hat{r}$. This results in the unrealistic characteristics of the end-to-end and side-by-side orientations possessing equal well depths, and (b) As a consequence of the distance scaling with respect to $\sigma (\vec{u}_1, \vec{u}_2, \hat{r})$, the well width varies with orientations [228]. When $\sigma (\vec{u}_1, \vec{u}_2, \hat{r})$ is large (i.e. end-to-end configuration of prolate molecules), the well width is proportionally large and vice versa. A number of modifications have been suggested that seek to overcome these unphysical features [229-231]. The functions proposed include an additional term in the strength parameter expression:

$$
\varepsilon(\vec{u}_1, \vec{u}_2, \hat{r}) = \varepsilon_0 \varepsilon_1(\vec{u}_1, \vec{u}_2) \varepsilon_2(\vec{u}_1, \vec{u}_2, \hat{r})
$$

where $\varepsilon_2(\vec{u}_1, \vec{u}_2, \hat{r})$ is chosen to take the form of $\left[ \frac{\sigma_0}{\sigma(\vec{u}_1, \vec{u}_2, \hat{r})} \right]^2$, and therefore depends on the relative orientation of particles with respect to the intermolecular vector. The exponents $\nu$ and $\mu$ have varied with each modification. Tsykalo and Bagmet [229] used the form of the strength parameter given above with $\nu = 1, \mu = 1$ in their molecular dynamics study of nematic liquid crystals; this parameterization decreases the well depth of the end-to-end and T configuration relative to the BPK model. Simulation results showed good agreement for the temperature dependence of the second rank orientational order parameter with the experimental data obtained for 4, 4'-dimethyloxy benzene. The modification suggested by Walmsley [230] corresponds to $\nu = 2, \mu = 1/2$, significantly reducing the well depths of the T configurations. The Gay-Berne Potential [231] included additional modifications where a shifted rather than scaled functional form was chosen for the potential:

$$
U(\vec{u}_1, \vec{u}_2, \hat{r}) = 4\varepsilon(\vec{u}_1, \vec{u}_2, \hat{r}) \left\{ \left[ r - \sigma(\vec{u}_1, \vec{u}_2, \hat{r}) + 1 \right]^{-12} - \left[ r - \sigma(\vec{u}_1, \vec{u}_2, \hat{r}) + 1 \right]^{-6} \right\}
$$

------- (1.22)
as first suggested by the Stone [228]. This has the advantage that the well depth is now insensitive to particle orientation. \( \sigma(\vec{u}_1, \vec{u}_2, \hat{r}) \) takes the BPK form, \( \varepsilon(\vec{u}_1, \vec{u}_2, \hat{r}) \) is given with \( \nu=1 \) and \( \mu=2 \) but \( \varepsilon_2(\vec{u}_1, \vec{u}_2, \hat{r}) \) takes the form:

\[
\varepsilon_2(\vec{u}_1, \vec{u}_2, \hat{r}) = 1 - \frac{\chi'}{2} \left[ \frac{(\vec{u}_1 \cdot \hat{r} + \vec{u}_2 \cdot \hat{r})^2}{1 + \chi'(u_1 \cdot u_2)} + \frac{(\vec{u}_1 \cdot \hat{r} - \vec{u}_2 \cdot \hat{r})^2}{1 - \chi'(u_1 \cdot u_2)} \right]
\]

\[\text{--------(1.23)}\]

where \( \chi' \) replaces \( \chi \) and \( \chi' = \left[ 1 - \left( \frac{\varepsilon_e}{\varepsilon_s} \right)^{\nu\mu} \right]^{\frac{1}{1 + \left( \frac{\varepsilon_e}{\varepsilon_s} \right)^{\nu\mu}}} \)

and \( \varepsilon_e/\varepsilon_s \) is the ratio of the strength parameters corresponding to side-by-side and end-to-end configurations. The values of \( \nu=1 \) and \( \mu=2 \) were chosen by fitting the potential form to that of a linear array of four Lennard-Jones centers placed \( 2\sigma/3 \) apart. In this way a length-to-breadth ratio \( \sigma_s/\sigma_e \) of 3 and a well depths anisotropy \( \varepsilon_s/\varepsilon_e \) of 5 was chosen.

In turn the Gay-Berne overlap model (GBOM) has been subjected to a number of modifications and simplifications [231]. Kabadi [232] has introduced a parameter \( \text{div}\sigma_0 \) into the potential energy equation allowing control over the well width of the potential:

\[
U(\vec{u}_1, \vec{u}_2, \hat{r}) = 6\varepsilon(\vec{u}_1, \vec{u}_2, \hat{r}) \left\{ \left[ \frac{\text{div}\sigma_0}{r - \sigma(\vec{u}_1, \vec{u}_2, \hat{r})} + \text{div}\sigma_0 \right]^{12} - \left[ \frac{\text{div}\sigma_0}{r - \sigma(\vec{u}_1, \vec{u}_2, \hat{r})} + \text{div}\sigma_0 \right]^{6} \right\}
\]

\[\text{--------(1.24)}\]

Inclusion of \( \sigma_0 \) in the equation also avoids the dimensionally ambiguous form of the earlier equation. However, this form of potential is found to be less sensitive (within 5% of an exact choice of \( \text{div} \)). Hence, to a good approximation, \( \text{div} \) can be taken as unity for prolate particles. Sediawan et al. [233] used the shifted potential form in their molecular dynamics calculations of benzene and naphthalene. However \( \chi' \) was set equal to \( \chi \), with \( \nu=-1 \) and \( \mu=2 \). This is analogous to the modification of the BPK model suggested by Tsykalo and Bagment [229] (\( \nu=1, \mu=1 \)) and Walmsley [230] (\( \nu=2, \mu=1/2 \)). The parameterization proposed by Sediawan et al [233] favour cross \((\vec{U}_1 \cdot \hat{r} = 0, \vec{U}_2 \cdot \hat{r} = 0, \vec{U}_1 \cdot \vec{U}_2 = 0) \).
\[ \mathbf{T}(\mathbf{U}_1 \cdot \hat{r} = 0, \mathbf{U}_2 \cdot \hat{r} = 0, \mathbf{U}_1 \cdot \mathbf{U}_2 = 0) \] orientations compared with the GBOM. The cross orientation is always favoured over the side-by-side and T configurations. This is unrealistic for non-polar molecules (even for quadrpolar particles the T orientation is energetically favoured over the cross configuration). Luckhurst et al. [234] have used the GBOM, but with \( n = 2 \) and \( \mu = 1 \) in their molecular dynamics calculations of prolate particles. In comparison with the original GBOM, configurations expected to favour orientational order are lowered in energy, relative to disordering cross and T configurations.

An alternative approach is to construct a realistic total pair potential using a sum of Lennard-Jones site-site terms. For typical mesogenic molecules, the number of sites required in such a model is large. Several calculations have been performed using site total potentials [235-238]. Luckhurst and Simmonds [239] constructed the total potential for the molecules p-terphenyl defined as the sum of Lennard-Jones site-site terms, each particle containing 32 sites. Using this definition, the biaxial component of the total potential can be projected out by performing Boltzmann weighted average of the form:

\[
U_{\text{av}}(\mathbf{U}_1, \mathbf{U}_2, \hat{r}) = \frac{\int \int U_{ij} \exp(-U_{ij}/kT) d\alpha_1 d\alpha_2}{\int \int \exp(-U_{ij}/kT) d\alpha_1 d\alpha_2} \]  

\[ \text{------(1.25)} \]

where \( U_{ij} \) is given by

\[
U_{ij} = \sum_{i=1,n} \sum_{j=1,n} \left\{ 4\varepsilon_{ij} \left[ (\sigma_{ij}/r_{ij})^2 - (\sigma_{ij}/r_{ij})^6 \right] \right\}
\]

\( \alpha_1 \) and \( \alpha_2 \) are rotation angles about the molecular long axes of molecules 1 and 2, and \( n \) is the number of site per molecule. For a given particle separation, it is clear that some molecular orientations will be energetically favoured over others; the Boltzmann weighting \( \exp(-U_{ij}/kT) \) is included to take some account of this in the averages.

The Lennard-Jones parameter values used in the 32 site model of p-terphenyl were \( \varepsilon_{cc}/k = 51.2K \), \( \sigma_{cc} = 3.35A^0 \), \( \varepsilon_{HH}/k = 8.6K \), \( \sigma_{HH} = 2.81A^0 \), \( \varepsilon_{CH}/k = 21.0K \) and \( \sigma_{CH} = 3.08A^0 \); the values given by Allen and Tildesley[240]. Luckhurst and Simmonds
obtained a new set of parameters to fit into Gay-Berne potential as $\nu = 0.74$, $\mu = 0.8$, $\sigma_0 = 3.65\text{Å}$, $\varepsilon_0/k = 4302\text{K}$, $\sigma_e/\sigma_s = 4.4$ and $\varepsilon_e/\varepsilon_s = 39.6$. This new parameterization exhibited isotropic, nematic and smectic phases. The results indicated that the phase behaviour is strongly dependent upon the number density used; the structure of the nematic and isotropic phases being dominated by short-range interaction. In later papers of Luckhurst, this method was applied to the study of disordered liquid crystals [241] but they did not adopt the parameters set by Luckhurst and Simmonds [239]. It is, therefore, clear that attempts to obtain a simplified potential through parameterization have provided success in particular cases but such attempts have not been able to provide a simple potential which could be uniformly applicable to all types of mesophases. Although, the increasing complexity due to large size of molecules places practical difficulties before the computer simulation, it seems that for understanding of the physics of mesophase formation a much more detailed procedure unavoidable.

Computer simulation of dipolar liquid crystal phases reported by Houssa et al., [242]. They presented a computer simulation study on the influence of dipolar interactions on the formation of mesophases.

The long-range behaviour in liquid crystals by computer simulation was studied by Allen [243]. Computer simulation provides a method of linking the microscopic details of molecular interactions with the much larger scale phenomena of interest in bulk phases. Much of the interesting and useful behaviour takes place in a regime which is reasonably well described by continuum theories, but consideration of molecular details is important, for example, in the vicinity of solid surfaces. This paper reviews recent work in which simulations have been used to study bulk liquid crystal phase diagrams, large-scale fluctuations near phase transitions, and elastic deformation near surfaces, making links with the appropriate theories.

Modelling of nematohydrodynamics in liquid crystal devices based on a lattice Boltzmann algorithm which solves the hydrodynamic equations of motion for nematic liquid crystals was formulated by Toth et al. [244]. The applicability of the approach is demonstrated by presenting results for two liquid crystal devices where flow has an important role to play in the switching.
Computational modelling of multi-phase equilibria of mesogenic mixtures was reported by Das et al., [245]. Their work deals with a computational study of phase equilibrium and phase diagrams of binary mixtures involving nematic liquid crystals and flexible polymers or monomeric solvents is performed using classical numerical integration schemes, and classical liquid crystalline thermodynamic models. A unique characteristic of these mixtures is the presence of isotropic–isotropic, isotropic–nematic, and/or nematic–nematic phase equilibrium. In addition, mixtures of nematic polymers and monomeric solvents are characterized by the ubiquitous bi-phasic chimney in the phase diagram. Also, the order parameter in the nematic phase is a highly non-linear function of temperature and concentration. The impact of integration schemes and asymptotic models on all these features is quantitatively determined. It is found that low order numerical quadrature schemes lead to poor order parameter predictions, which in turn lead to inaccurate phase diagrams. It is also found that the classical Landau-de Gennes asymptotic expansion model fails to predict important phase equilibrium features, such as the above-mentioned bi-phasic chimney, and nematic–nematic phase coexistence. This paper establishes computational modelling guidelines on integration schemes and thermodynamic models of liquid crystalline materials that ensure a high accuracy in the predicted phase diagrams.

Matsushita et al. [246] studied the structures and intermolecular interaction energies of ten dimers, included in the mesogenic core structures of typical liquid crystalline (LC) compounds, are studied. The results suggest an explicit linear relationship between the interaction energies and viscosities of these ten dimers. Application of a generalized thermodynamic model to study the ferroelectric properties of DOBAMBC and DOBA-1-MPC was reported by Singh and Singh [115]. The study includes the temperature variations of tilt angle, spontaneous polarisation, helical pitch, Goldstone mode rotational viscosity and twist elastic constant of the ferroelectric smectic C (SmC*) phase near the smectic A (SmA)-SmC* transition of the ferroic mesogens DOBAMBC and DOBA-1-MPC using a thermodynamic model based on an extended Landau expansion of the free-energy density. The model free-energy density of the system is written in terms of order parameters (tilt vector $\xi$, polarisation $P$ and wavevector $q$ of helical pitch) involving eleven mean-field coefficients including bilinear,
biquadratic and flexoelectric couplings between $\xi$ and $P$ and coefficients due to coupling between $\xi$ and $q$. The values of these coefficients were determined by fitting the results of calculation with the experimental data for the pitch, tilt angle and spontaneous polarisation. A detailed analysis of the relative contribution of each individual term appearing in the free-energy density expansion is presented. Taking these values of parameters, in addition to tilt angle, spontaneous polarisation and pitch, they calculated the Goldstone mode rotational viscosity and twist elastic constant as a function of temperature. The theoretical results agree well with the experimental data for both mesogens.

Computational modeling of nematic phase ordering by film and droplet growth over heterogeneous substrates was done by Wincure and Rey [247]. This work deals with a computational study of defect nucleation associated with the kinetics of the isotropic-to-nematic phase ordering transition over heterogeneous substrates, as it occurs in new liquid crystal biosensor devices, based on the Landau-de Gennes model for rod-like thermotropic nematic liquid crystals. Two regimes are identified due to interfacial tension inequalities: (i) nematic surface film nucleation and growth normal to the heterogeneous substrate, and (ii) nematic surface droplet nucleation and growth. The former, known as wetting regime, leads to interfacial defect shedding at the moving nematic-isotropic interface. The latter droplet regime, involves a moving contact line, and exhibits two texturing mechanisms that also lead to interfacial defect shedding: (a) small and large contact angles of drops spreading over a heterogeneous substrate, and (b) small drops with large curvature growing over homogeneous patches of the substrate. The numerical results are consistent with qualitative defect nucleation models based on the kinematics of the isotropic-nematic interface and the substrate-nematic-isotropic contact line. The results extend current understanding of phase ordering over heterogeneous substrates by elucidating generic defect nucleation processes at moving interfaces and moving contact lines.

Monte Carlo simulations of a variety of hard-particle liquids and liquid mixtures have been conducted in the isotropic liquid region of the phase diagram by Cheung et al. [248]. The position- and orientation-dependent pairwise structure is computed and the results are compared with integral equation theories, allowing us to examine the closure
relations, and evaluate their accuracy, in a direct fashion. A simple molecular theory of smectic-C liquid crystals has been reported by Govind and Madhusudhana [249].

1.6 Experimental Approach for Liquid Crystalline Properties

The effects of terminal substituents on mesomorphic properties were studied by Matsunaga et al. [250]. Nematic-Isotropic transition temperature was determined for 4-(4-X-benzylidene amino) phenyl 4-Y-benzoates, where X and Y were chosen from methoxy, nitro, chloro, bromo, dimethyl amino, methyl, fluoro, trifluoro methyl groups. The order of group (X or Y) efficiency in promoting the nematic-isotropic transition temperature is found to be markedly affected by the nature of group (Y or X) located at the other end. The methoxy and methyl series give NO$_2$>CH$_3$O>N(CH$_3$)$_2$>Cl=Br>CH$_3$>F>CF$_3$, where as the trifluoro methyl series gives N(CH$_3$)$_2$>CH$_3$O>CH$_3$>Cl=Br>NO$_2$>F, suggesting that the dipole-dipole interaction contributes significantly to the stabilization of nematic phase. Matsunaga et al. [251] also studied 3-pyridyl 4-(4-propoxy benzylidene amino) benzoates. They observed that both nematic and smectic thermal stabilities decrease as the terminal alkyl chain length increases. The similar changes in the mesomorphic properties by the replacement are recorded for N-(4-(4-alkoxy bezoyloxy) benzylidene) anilines and other isomeric compounds.

Okamoto et al. [252] describes the synthesis and effect of a long alkoxy group on the mesomorphic properties of 4-(4-alkoxy phenoxy carbonyl) phenyl 3- alkoxy -4-cyano benzoates. The ethoxy and propoxy groups at the adjacent position of the cyano one are unfavourable for the formation of a smectic-A phase and the long alkoxy groups (such as butoxy, pentyloxy, and hexyloxy ones) facilitate the formation of a smectic-C Phase. The characterization and molecular arrangement of the smectic-C phase are made by a differential scanning calorimetry, microscopic observation and small-angle X-ray diffraction studies. The role of alkoxy group at the adjacent position of cyano group on the mesomorphic properties is discussed.

Yu and Lee esterified the hydroquinone with 4-alkoxy benzoic acid at one end and 3, 4-dialkyloxy benzoic acid at the other end [253]. Narrow nematic and smectic-C phases are observed for the homologues as compared to those of di (4-alkyloxy) benzoic acid esters. This is attributed to the substitution at the 3-position of the benzoic moiety.
The influence of the directions of two ester linkage in crystal structure is discussed by Tamura et al. [254]. In order to make clear the influence of two or more polar groups on packing modes of molecules, the crystal structures are determined for isomeric mesogens with different directions of two ester linkages \( C_{8}H_{17}O-C_{6}H_{4}XC_{6}H_{4}Y-C_{6}H_{4}OC_{8}H_{17} \) where \( X=\text{COO} \) and \( Y=\text{OOC} \) for I and \( X=\text{OOC} \) and \( Y=\text{COO} \) for II. In crystal I, molecules are found to be arranged so that moieties conjugate from C=O to an alkoxy O atom via a benzene ring that has an antiparallel arrangement, resulting in an imprecated structure. Crystal II has a lamellar structure with a small tilt, in which ester linkages of adjacent molecules come close to each other. The crystal structures are closely related to the phase sequences, smectic-C, nematic for I, smectic-C, smectic-A, and nematic for II.

Series of novel thermotropic liquid crystalline compounds that serve as models for mesogenic diols have been synthesized by Sudhakar et al. [255]. The mesogen molecules are constructed from 1, 4-disubstituted benzene rings through ester and azomethine units. Based on number of phenyl rings, a tetrad or pentad classification has been assigned to the core molecule. The structures of these compounds are established by FTIR and NMR spectroscopy, while the mesomorphic behaviour is confirmed using polarizing microscopy and DSC. All the compounds of the homologous series are found to be mesomorphic in nature. The lower members of the series are nematogenic while the higher members exhibit both nematic and smectic character with high melting points and wide mesophase range.

The experimental report of Tasaka et al. [256] describes the effect of alkyl and alkoxy chain lengths on thermal properties of four isomeric systems: 4-R-phenyl 4-(4-octyloxy benzoyloxy)benzoates (1), 4-Octyloxy phenyl 4-(4-R-benzoyloxy) benzoates (2), 4(4-R-benzoyloxy) phenyl 4-octyloxy benzoates (3) and 4-R-phenyl 4-octyloxy phenyl terephalates (4). (R= alkoxy, alkyl). The smectic properties for 1 and 2 are fairly different when both terminal alkyl and alkoxy groups are short, while both have the same liquid crystalline core. The homologue of 3 exhibits only a smectic-C phase even in the higher homologous. The homologue of 4 preferentially exhibits smectic-A and smectic-C phases. The difference in smectic properties is discussed in terms of their molecular characteristics.
The effect of alkyl and alkoxy chain lengths on the layer structures of smectic-A and three smectic phases has been examined by X-ray diffraction measurements on three isomeric systems: 4-alkoxy-phenyl acid 4-n-alkyl phenyl 4(4-(octyloxy phenyl) carbonyloxy) benzoates (1); 4-octyloxyphenyl 4-(4-Octyloxy phenyl)carbonyloxy) benzoates (2); 4-octyloxy phenyl, 4-alkoxy phenyl and 4-n-alkyl phenyl terephthalates (3); and p- phenylene 4-octyloxy benzoates, 4-alkoxy benzoate and 4-n-alkyl benzoate (4). Tasaka et al. [257] concluded that although all derivatives exhibit smectic-A and/or smectic-C phases with monolayer arrangement of the molecules, the layer spacing is considerably affected by alternation of ester linkages. The results are discussed in terms of a subtle change in the molecular structure due to replacement of the ester group.

The smectic layer structure has been examined by X-ray diffraction for four isomeric systems: viz., 1) the 4-nitrophenyl 4-(4-alkoxy benzoyloxy) benzoates, 2) the 4-alkoxyphenyl 4(4-nitrobenzoyloxy) benzoates, 3) 4-(4-alkoxy benzoyloxy) phenyl 4-nitro benzoates, and 4) 4-alkoxyphenyl 4-nitrophenyl terephthalates, by Tasaka et al. [258]. The phase transition behaviour and layer structure of the smectic-A phases are found notably influenced by the relative orientation of the two ester groups to the terminal groups by alkoxy chain length and temperature. The smectic-A phase for compounds 1 and 3 has mainly ‘monolayer’ arrangement where the layer spacing is 2-5 Å longer than the molecular length. The smectic-A phase for compounds 2 and 4 consists of a mixed layer structure with monolayer, bilayer and partially bilayer arrangements. The distribution is found to depend on the relative orientation of the ester groups, the alkoxy chain length and temperature. It is supposed that the diversity of smectic-A phase is related to the polar interaction around the nitro or the nitrobenzene moieties through the smectic layers. The reversal of the ester group is found to cause subtle changes in the entire molecular shape.
References


