

Chapter 1

A Brief Introduction to Liquid crystal Physics

A liquid that is interesting due to the order present in it. - A liquid crystal, an oxymoron.

The term *liquid crystal* signifies a state of aggregation that is intermediate between the crystalline solid and amorphous liquid. Liquid crystalline phases appear in the so-called mesogens which are composed of molecules having an anisotropic shape and interacting with each other. In the most disordered condensed phase - the isotropic phase - each molecule uniformly explores positions and orientations throughout the whole available space by diffusion mechanisms. In contrast, in the most ordered crystalline phase, the positions of the molecules are fixed in a lattice as are their orientations with respect to this lattice. The simplest example of a mesophase is the nematic phase which appears in systems of elongated molecules tending to orient parallel to each other while showing no positional order, which gives this phase its liquid character.

The first subsection of this chapter contains a brief introduction to liquid crystal (LC) physics, which includes an introduction to different types of ordering and their quantification. Also introduced are the possible interaction among molecules with biaxial symmetry, and their consequences leading to a new (biaxial) phase. The next subsection gives a brief introduction to surface physics and confinement. The last subsection describes the different models used in the Monte Carlo studies which have been elaborated upon in the later chapters of the thesis.

1.1 Phases of Liquid crystal

It was only in the end of the year 1888 that the word 'liquid crystal' was coined, although for many generations people used them without knowing that as such. In daily life, liquid crystals come across in many forms viz. soap, lubricants, TV displays and more recently, calculator and computer displays. The study of liquid crystals has drawn considerable attention from all branches of science and technology [1]. While the technological applications of liquid crystals is of significant interest, liquid crystal physics continues to provide excitement and challenges to condensed matter and soft material scientists due to the wide variety of physical phenomenon that it encompasses [2] [3] [4] [5].

Liquid crystals are mesophases - a state in-between solids and liquids. They flow like a liquid but have properties like birefringence as in crystalline solids. These anisotropic properties arise due to the anisotropic molecular structures. These could be rods, discs or even combinations. This thesis is concerned with rod like molecules. Structurally, liquid crystals are long organic molecules of the size of 10-15 Å in length, and about 5 Å in breadth. The characteristic feature of a medium comprised of such molecules is the presence of long range orientational order - they align along the long axis of the molecules. The order in these liquid crystals is mainly controlled by temperature - *thermotropic liquid crystals*, or by the concentration of the liquid-crystalline material in the solution - *lyotropic liquid crystal*. All the studies discussed in this thesis are concerned with thermotropic liquid crystals.

With variation of temperature, thermotropic liquid crystals can be characterized into different phases depending on the order developed in them [6]. At high temperatures the liquid crystal is in an isotropic phase, which is the most symmetrical phase and the orientational order in this phase is expected to be zero due to the inherent spherical symmetry of the molecules. With decrease in temperature a (weak first order) transition occurs signalling the onset of orientational order and breaking the spherical symmetry. The nematic liquid crystal can have a high degree of long - range orientational order of molecules, but no

translational order. The molecules are spontaneously oriented with their long axes approximately parallel to each other. The preferred direction usually varies across a macroscopic medium, but a homogenous aligned specimen is optically uniaxial and strongly birefringent. The mesophase owes its fluidity to the ease with which the molecules slide past one another while still retaining their parallelism. The average preferred direction of a nematic liquid crystal is called a director, \hat{n} .

The cholesteric mesophase is a nematic type of liquid crystal except that it is composed of optically active molecules. These molecules form a helical structure. The molecules are aligned perpendicular to the axis of the spiral. Optically inactive molecules or racemic mixtures result in a helix of infinite pitch which corresponds to a true nematic. Thermodynamically, the cholesteric is very similar to the nematic as the energy of the twist forms only a minute part of the total energy associated with the parallel alignment of the molecules.

With further decrease in temperature more ordered mesophases are formed - the Smectic phases. In the smectic phase translational order is present in addition to the orientational order. Smectic phases can be differentiated from one another depending on the orientation of the molecules in every layer. In smectic A, the molecules are upright with respect to the layer planes, whereas in smectic C the molecules are tilted at an angle. These liquid crystals typically crystallize with further cooling.

A liquid crystal is said to be biaxial when the three axis are distinct unlike a uniaxial liquid crystal which has a preferred axis, around which the system is rotationally symmetric (figure 1.1). When such molecules constitute the medium the nematic phase can in principle show up which is no longer cylindrically symmetric (uniaxial) and can exhibit a biaxial order. The characteristic physical parameter that differentiates the above various phases in a liquid crystal is the order parameter.

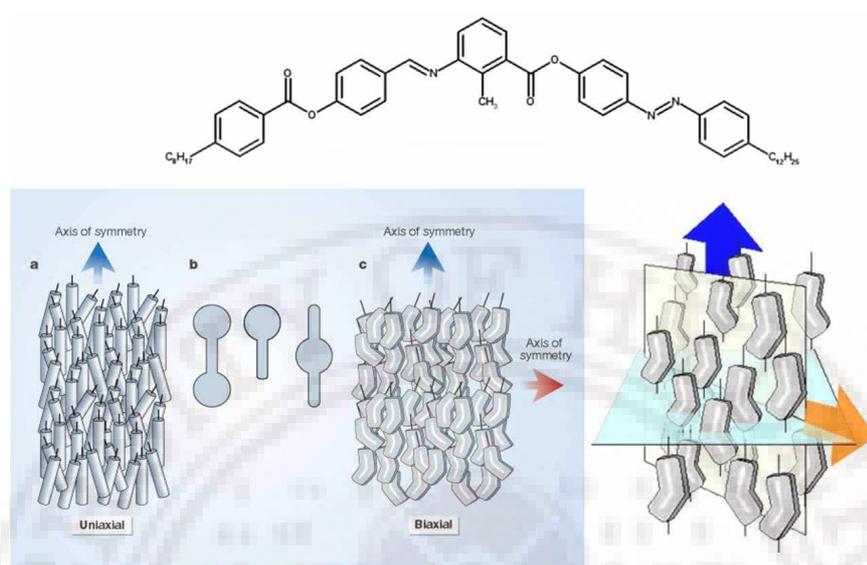


Figure 1.1: An illustrative picture of a biaxial molecules and biaxial nematic phase.

1.2 Order Parameter

The order parameter is a normalized parameter that indicates the amount of order present in the system. It is normally defined for convenience in such a way that it is zero in one phase, say above the transition temperature and non-zero below. Proven to be very convenient to define an appropriate order parameter to facilitate unambiguous quantification of the symmetry of the medium for its experimental observation and subsequent interpretation through suitable theoretical formulations.

In order to identify appropriate order parameters of the nematic LC system, it is important to note that it is the probability distribution of the orientations of the constituent molecules that undergoes qualitative changes due to changes in the symmetry of the system, and therefore any measure of such loss of symmetry should be derivable from the features of the distribution function. Formation of layered structures (like in smectic phases) decreases the symmetry of the medium further with respect to the homogeneities

of the density, and such order parameter hence should be obtained from probability distribution of the molecular positions. The order parameters in liquid crystals are very transparently formulated starting with appropriate distributions, as indicated below [7].

Consider a system with ' N ' molecules in a certain state of aggregation [8]. Assuming that these particles are classical and fixed at a position specified by the vector \mathbf{r} , and are specific in their orientation Ω with respect to a laboratory frame. The orientation of the molecule Ω is given in terms of the Euler angles (α, β, γ) . Now, let us assume that a molecule is formed of a collection of connected rigid rotors, if \mathbf{r} gives its position and Ω the orientation of one rigid fragment and another set of variables, Φ specifies the orientation of the other fragments with respect to the first (conformational variable). With only one rotor, $\Phi = \phi$ specifies the conformational state. $P(r, \Omega, \Phi)$ gives the probability of a particle to have a position $(r + dr)$, orientation $(\Omega + d\Omega)$, and internal state $(\Phi + d\Phi)$. The average of any quantity $\langle A(r, \Omega, \Phi) \rangle$ is given as

$$\begin{aligned} \langle A \rangle &= \langle A(r, \Omega, \Phi) \rangle \\ &= \int dr d\Omega d\Phi A(r, \Omega, \Phi) P(r, \Omega, \Phi). \end{aligned} \quad (1.2.1)$$

Here the volume elements dr , $d\Omega$ are $dx dy dz$ and $d\alpha \sin\beta d\beta d\gamma$ respectively, and for one rotor $d\Phi = d\phi$. The normalization of the distribution $f(r, \Omega, \Phi)$, is

$$\int dr d\Omega d\Phi P(r, \Omega, \Phi) = 1. \quad (1.2.2)$$

This singlet distribution f contains all the information necessary to calculate one particle properties.

$$f(r, \Omega, \Phi) = \langle \delta(r - r') \delta(\Omega - \Omega') \delta(\Phi - \Phi') \rangle \quad (1.2.3)$$

where $\delta(a - a')$ is the dirac delta function, a counting device since it is different from zero only when the primed value equals the desired. The distribution function is obtained by counting all of the particles that have the position-orientation-internal variables equal to the desired value in the given configuration and then averaging over the equilibrium configurations. Generalization of the distribution for n variables is a general multiplet

distributions. The singlet distribution function can be written in terms of Fourier integral representation of the positional delta function

$$\delta(r - r') = (2\pi)^{-3} \int dk \exp(i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')). \quad (1.2.4)$$

The expansion of angular delta function is either in generalized spherical harmonics or Wigner rotation matrices $D_{m,n}^L$

$$\delta(\Omega - \Omega') = \sum_{L=0}^{\infty} \sum_{m=-L}^L \sum_{n=-L}^L \{(2L+1)/8\pi^2\} D_{m,n}^L(\Omega) D_{m,n}^{L*}(\Omega'). \quad (1.2.5)$$

The functions $D_{m,n}^L$ with the integers L, m, n ($L \geq 0, -L \leq m \leq L, -L \leq n \leq L$) constitute a convenient set in the space of variables, and indeed represent physically the presence of different types of symmetries with respect to the angular variables. Let $\Psi_\lambda(\Phi)$ be a basis set for the internal variables and representing as delta function gives

$$\int d\Phi \Psi_\lambda(\Phi) \Psi_{\lambda'}^*(\Phi) = k_\lambda \delta(\lambda - \lambda'). \quad (1.2.6)$$

1.2.1 Orientational Order

For a nematic medium, it is sufficient to consider a distribution function independent of translation, i.e, this particle is independent of the position vector \mathbf{r} . In a nematic liquid crystal the position of the molecules does not play an important role. A isotropic-nematic transition is distinguished by the building up of a orientational order. This thesis deals mainly with nematic-isotropic transition although positional ordering is important to study a nematic-smectic transitions. If the molecules are considered to be rigid and the system is uniform, only the orientational degrees of freedom are relevant so $f(\mathbf{r}, \Omega, \Phi)$ reduces to $f(\Omega)$

$$f(\Omega) = \sum_{L,m,n} p_{L,m,n} D_{m,n}^L(\Omega). \quad (1.2.7)$$

Assuming the axis of cylindrical symmetry, the director is along the laboratory Z axis. Thus rotating the sample about Z no observable property will change. The probability of a molecule in the sample having a orientation (α, β, γ) should be the same whatever be the angle α , m must be zero in $D_{m,n}^L$ and $f(\Omega) = f(\beta, \gamma)$.

In addition, if a uniaxial mesophase has a plane perpendicular to the director ($D_{\infty h}$), i.e. \hat{n} and $-\hat{n}$ are not distinguishable then only terms with even L can appear. Considering molecules are cylindrically symmetric, the rotation about the molecular axis will not modify the distribution $f(\Omega)$. The value of γ does not change the distribution function $f(\Omega)$, then $n = 0$ in $D_{m,n}^L$. Accordingly, we have $f(\beta) = f(\Omega)/4\pi$.

Consider a cylindrical particle with the director parallel to the laboratory Z axis.

$$f(\Omega) = f(\beta) = \sum f_L D_{0,0}^L \quad (1.2.8)$$

$$D_{0,0}^L = P_L(\cos\beta) \quad (1.2.9)$$

$$f(\beta) = \sum_{i=1}^{\infty} f_L P_L(\cos\beta) \quad (1.2.10)$$

where $P_L(x)$ are the Legendre polynomials and $f_L = (2L + 1)\Omega^{-1} \int d\Omega f(\beta) P_L(\cos\beta)$. $f_L \equiv 0$ for odd parameters of L as $\hat{n} = -\hat{n}$, so f_L s are non-zero for even L . The first nonzero order parameter is

$$f_0 = 1 \quad (1.2.11)$$

$$\begin{aligned} f_2 &= \frac{5}{\Omega} \int d\Omega f(\beta) P_2(\cos\beta) = 5 \left\langle P_2(\cos\beta) \right\rangle \\ &= 5 \left\langle \frac{1}{2} (3\cos^2\beta - 1) \right\rangle \equiv 5S \end{aligned} \quad (1.2.12)$$

where S is a scalar order parameter which describes the degree of uniaxial orientational order of the molecules about the director. The value of S is in the interval $[-\frac{1}{2}, 1]$: in a perfect nematic phase $\beta = 0$ for all molecules, so $S = 1$. When the orientations of the molecules are perfectly random $\langle \cos^2\beta \rangle = \frac{1}{3}$ and $S = 0$. The minimum value of order parameter corresponds to when all the molecules align perpendicular to the director. The first non-trivial term of the distribution function is

$$\begin{aligned} f(\beta) &= 1 + 5S P_2(\cos\beta) = 1 + 5S \frac{1}{2} (3\cos^2\beta - 1) \\ &= 1 + 5S \frac{1}{2} (3(\hat{n} \cdot \hat{a})^2 - 1) = 1 + 5S \frac{1}{2} [3(n_i a_i)(n_i a_i) - 1] \\ &= 1 + 5S \frac{1}{2} [3(n_i a_i)(n_i a_i) - \delta_{ij} a_i a_j] = 1 + 5S \frac{1}{2} [3(n_i n_j) - \delta_{ij}] a_i a_j \\ &= 1 + 5S \frac{1}{2} [3(\hat{n} \otimes \hat{n}) - I_{ij}] a_i a_j = 1 + 5(Q)_{ij} a_i a_j \end{aligned} \quad (1.2.13)$$

and

$$Q = \frac{1}{2}S(3\hat{n} \otimes \hat{n} - I) \quad (1.2.14)$$

is the tensorial order parameter of the nematic liquid crystal, which represents the quadrupole moment of the distribution i.e. the deviation from the perfect sphere. Here, I is the second rank unit tensor.

The order parameter is a second order tensor that has 9 degrees of freedom. Due to symmetry $Q_{ij} = Q_{ji}$, the degrees of freedom are reduced by 3. Also, $tr(Q) = 0$ reduces the degrees of freedom further by one. Hence, there are only 5 degrees of freedom. The symmetric traceless tensor order parameter has five independent components degrees of freedom. The five degrees of freedom considered here are the two angles that determine the direction of the director, the scalar order parameter, the angle specifying the secondary director and the biaxiality parameter. With respect to the 5 base tensors of the symmetrical traceless tensor the parametrization of the order parameter can be given as

$$\begin{aligned} T_0 &= \frac{3\hat{n} \otimes \hat{n} - I}{\sqrt{6}} \\ T_1 &= \frac{\hat{e}_1 \otimes \hat{e}_1 - \hat{e}_2 \otimes \hat{e}_2}{\sqrt{2}} \\ T_{-1} &= \frac{\hat{e}_1 \otimes \hat{e}_2 - \hat{e}_2 \otimes \hat{e}_1}{\sqrt{2}} \\ T_2 &= \frac{\hat{e}_1 \otimes \hat{n} + \hat{n} \otimes \hat{e}_1}{\sqrt{2}} \\ T_{-2} &= \frac{\hat{e}_2 \otimes \hat{n} - \hat{n} \otimes \hat{e}_2}{\sqrt{2}}. \end{aligned} \quad (1.2.15)$$

The above tensors are traceless and they are orthogonal with respect to the metric T_n : $T_m = tr(T_n T_m) = \delta_{nm}$. The order parameter can be given as

$$Q = \sum_{m=-2}^2 q_m T_m \quad (1.2.16)$$

where $q_m = tr(Q T_m)$. The multiplicative constants are set so that the amplitude q_0 represents the scalar order parameter. The parameters $q_{\pm 1}$ are non-zeros if the order is biaxial and parameters $q_{\pm 2}$ represent the deviations in the orientations of the director with respect to the assumed director \hat{n} .

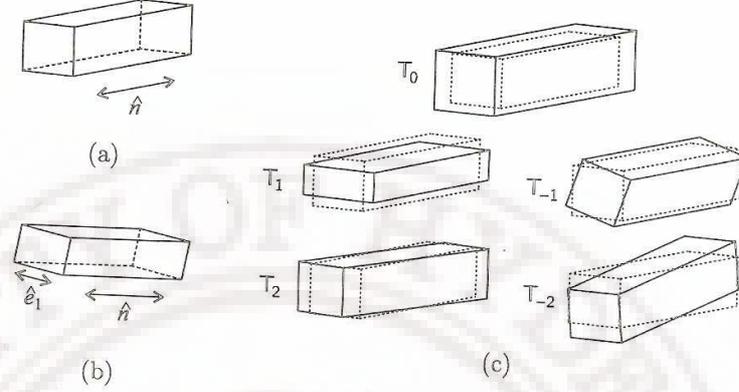


Figure 1.2: A visualization of the basis vector of order parameter (courtesy [9])

When the molecules are non-cylindrical then an extra angle γ is needed to define their orientation with respect to the laboratory frame. γ gives the extra angle of rotation needed around the molecular z -axis, and hence integer n has a non-zero value in $D_{m,n}^L$, thus making $f(\Omega) = f(\beta, \gamma)$

$$f(\Omega) = f(\beta, \gamma) = \sum_{L,n} f_{L,n} D_{0,n}^L(\beta, \gamma). \quad (1.2.17)$$

Orthogonality of the basis set immediately permits identifying the coefficient $f_{L,n}$

$$f(\beta, \gamma) = \frac{1}{4\pi} \sum_{L=0}^{\infty} \sum_{n=-L}^L (2L+1) \langle D_{0,n}^{L,*} \rangle \langle D_{0n}^L \rangle (\beta, \gamma). \quad (1.2.18)$$

Biaxial molecules have molecular frame axis along the C_2 axes [10]. For such molecules with C_{2h} group, the symmetry operation gives the restriction

$$\langle D_{m,n}^L \rangle = (-)^m \langle D_{m,n}^L \rangle = (-)^{L+m} \langle D_{m,n}^L \rangle. \quad (1.2.19)$$

This implies L and m have to be even. The relevant order parameters are

$$\langle D_{0,n}^2 \rangle; \quad (1.2.20)$$

$$\langle D_{2,n}^2 \rangle = (-)^n \langle D_{-2,n}^{2,*} \rangle \quad (1.2.21)$$

If the particles constituting the phase are cylindrically symmetric, then there are two independent orders, which include phase biaxiality also. If the constituent molecules of the

biaxial phase are themselves biaxial, then the different order parameters are

$$\begin{aligned}
& \langle D_{0,0}^2 \rangle \\
& \langle D_{0,2}^2 \rangle = \langle D_{0,-2}^2 \rangle \\
& \langle D_{2,0}^2 \rangle = \langle D_{-2,0}^2 \rangle \\
& \langle D_{2,2}^2 \rangle = \langle D_{-2,2}^2 \rangle = \langle D_{2,-2}^2 \rangle = \langle D_{-2,-2}^2 \rangle .
\end{aligned} \tag{1.2.22}$$

Another approach considers how to extract these same order parameters from tensors, or dyadics, constructed from the vectors $\mathbf{e}_z^{(i)}$, $\mathbf{e}_x^{(i)}$ and $\mathbf{e}_y^{(i)}$. A vector \mathbf{u} can be represented as a column matrix $U = [\mathbf{u}_x, \mathbf{u}_y, \mathbf{u}_z]^T$ in the basis E_x, E_y, E_z . The vector \mathbf{u} can be represented as

$$\mathbf{u} = \mathbf{u}_x E_x + \mathbf{u}_y E_y + \mathbf{u}_z E_z. \tag{1.2.23}$$

The dyadic $\mathbf{u} \otimes \mathbf{u}$ is then represented by the matrix UU^T . The dyadic Q^{zz} can be given in two stages: initially P^{zz} , constructed from the vectors $\mathbf{e}_z^{(i)}$.

$$P^{zz} = \frac{1}{N} \left(\sum_{i=1}^N \mathbf{e}_z^{(i)} \otimes \mathbf{e}_z^{(i)} \right) \equiv \langle \mathbf{e}_z^{(i)} \otimes \mathbf{e}_z^{(i)} \rangle. \tag{1.2.24}$$

Secondly, the Saupe order tensor is defined as

$$Q^{zz} = (3P^{zz} - I)/2 \tag{1.2.25}$$

Similarly, P^{xx} and P^{yy} and hence the corresponding Q^{xx} and Q^{yy} are obtained by replacing z by x or y in 1.2.25.

P and Q dyadics have the same eigenvectors, though their eigen vectors differ: if v is an eigenvector of P with eigenvalue λ , then it is an eigenvector of Q with eigenvalue $(3\lambda - 1)/2$. It may be noted that the sum of eigen values of a Q dyadics is zero by construction.

The eigenvector associated with the dominant eigenvalue of Q^{zz} is the system director by convention, and the corresponding eigenvalue gives a measure (S) of the orientational order along the major director. The size and sign of S give how well the molecular long axes are organized (aligned), and the orientation of their average ordering direction with respect to the reference direction chosen. If the system's properties are invariant with respect to

arbitrary rotation about the director, the system is said to be uniaxial. Otherwise, the system is said to be biaxial. To quantify this, the axes of the molecules are projected on to the plane orthogonal to the major director. If the axes of the molecules are equally likely to point in any one of those directions, then the system has no biaxiality; on the other hand, if projections show a preferred direction, then the system does display biaxiality called phase biaxiality. To give some measure of this, diagonalize the matrix Q_{zz} ; in other words, we find its components in a basis built out of its eigenvectors. This gives a matrix of the form

$$\begin{pmatrix} q_x & 0 & 0 \\ 0 & q_y & 0 \\ 0 & 0 & q_z \end{pmatrix}$$

where $|q_z| \geq |q_y| \geq |q_x|$ by choice. Since S is related to q_z as $S = 1.5q_z$ and $q_x + q_y + q_z = 0$, one has for the ordering matrix of the major axis of the molecules in its principle system:

$$\begin{pmatrix} -S/2 - \xi & 0 & 0 \\ 0 & -S/2 + \xi & 0 \\ 0 & 0 & S \end{pmatrix}$$

So ξ , which is given by half the difference between the smaller eigenvalues of Q_{zz} measures the extent to which it is possible to distinguish a direction in the plane orthogonal to the director. If $\xi = 0$, then the system is unchanged by a rotation about the director; if ξ is non-zero, there is a preferred direction orthogonal to the director, and we have a phase biaxial system. We regard the density of molecular long axes as determining an ellipsoid in space. Then the major axis of this ellipsoid lies along the system director, and its magnitude determines the order parameter. The difference between the minor axes is a measure of the extent to which the molecule directors are not equally scattered in all directions perpendicular to the system director, and gives the phase biaxiality parameter.

1.3 Phenomenological free energy and Maier Saupe Theory

1.3.1 Landau's theory of Phase transition

A phenomenological description of a phase transition is possible using Landau theory, as has been treated in many well written books [11] [12]. An order parameter is defined to describe the change in symmetry, accompanying a phase transition. Typically the system is expected to undergo a transition from high temperature phase to a low temperature less symmetric phase. Taking the specific example of the transition from an isotropic to the nematic phase on cooling, the order parameter is defined as a tensor which becomes zero in the more symmetrical phase. The thermodynamic quantities of the less symmetric phase can be obtained by expanding the thermodynamic potential at the transition point. This procedure, originally was developed for continuous transitions, is extended to cover first order transition also suitably, and for weak first order $I - N$ transition. Landau description certainly provides a convenient basis to understand the qualitative characteristics of this phenomenon.

An extension to phase transitions in liquid crystal was suggested by De Gennes [13]. The nematic phase is described by a symmetric tensorial (second rank) order parameter \tilde{Q} with zero trace. Expansion of the thermodynamic potential up to the 4th order in the tensor order parameter \tilde{Q} has been found sufficient to describe satisfactorily the nematic-isotropic phase transition. Following [11], Gibbs free energy per unit volume at constant pressure and temperature is:

$$G = G_{iso} + \frac{1}{2}A_{\alpha\beta\gamma\delta}Q_{\alpha\beta}Q_{\gamma\delta} - \frac{1}{3}B_{\alpha\beta\gamma\delta\mu\nu}Q_{\alpha\beta}Q_{\gamma\delta}Q_{\mu\nu} + \frac{1}{4}C_{\alpha\beta\gamma\delta\mu\nu\rho\sigma}Q_{\alpha\beta}Q_{\gamma\delta}Q_{\mu\nu}Q_{\rho\sigma} \quad (1.3.1)$$

$$Q_{\alpha\beta} = S(N_{\alpha\beta} - \frac{1}{3}\delta_{\alpha\beta}). \quad (1.3.2)$$

For capturing the essential features, it is more convenient to deal with the case of a uniaxial nematic phase requiring only one order parameter. Then the above potential can be written

in terms of scalar order parameter S as

$$G = G_{iso} + \frac{1}{2}A(T)S^2 - \frac{1}{3}BS^3 + \frac{1}{4}CS^4 \quad (1.3.3)$$

$$A(T) = A_0(T - T^*). \quad (1.3.4)$$

G and G_{iso} represent the Gibbs free energy in the nematic and the isotropic phases, respectively. A linear term in the order parameter is not considered since this would mean that the free energy per unit volume of the nematic phase would be less than the free energy of the isotropic phase at all temperatures. The negative sign before B is taken as per convention. A_0 and T^* are constants, T^* is a temperature slightly lower than the transition temperature T_C , A_0 is independent of temperature. Near the phase transition the temperature dependencies of B and C are neglected. C must be greater than zero, as a negative value of C would not allow G to have a minimum for a finite value of S . If there were to be a stable nematic phase at a certain value of S , then G must have a minimum at this value of S . The equilibrium value of S is obtained by minimizing the free energy density with respect to S . Taking the derivative of equation 1.3.3, the solutions are

$$S_{\pm} = \frac{B}{4C} \left\{ 1 \pm \left[1 - \frac{24aC(T - T^*)}{B^2} \right]^{1/2} \right\} \quad (1.3.5)$$

$S = 0$ represents a phase with no order – an isotropic phase. The other two values of S represent the local maximum and the local minimum for the non – zero values of S . If S is the local minimum, then the solution containing the negative sign must be either the local maximum or the local minimum solution, and the positive sign being the other. At T_C both $S = 0$ and $S > 0$ must have local minima with the same value of free energy per unit volume G_{iso} . Setting the two values to zero and combining the requirements we get

$$\begin{aligned} S_c = 0, \quad T_c = T_c^* \\ S_c = \frac{B}{3C} \quad T_c = T_c^* + \frac{B^2}{27A_0C}. \end{aligned} \quad (1.3.6)$$

S_+ is a stable solution, as this gives a solution $S_c = B/(3C)$ at T^* . The solution (1.3.5)

determines a third temperature T_c^{**}

$$T_c^{**} = T_c + \frac{B^2}{24A_0C}. \quad (1.3.7)$$

If $T = T_c^{**}$ the solutions S_- and S_+ do not hold good because of their imaginary values.

Landau de-Gennes theory distinguishes four different temperature regions.

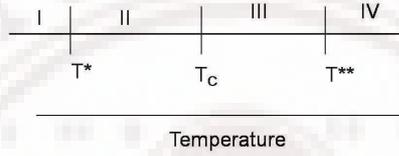


Figure 1.3: Schematic representation of the different temperature regions and the available phases.

- Phase IV (figure 1.3): $T > T_c^{**}$: Only solution $S = 0$, i.e. the isotropic phase exists and is stable.
- Phase III (figure 1.3): $T_c < T < T_c^{**}$: The minimum of the free energy still gives $S = 0$, i.e. the isotropic phase in the thermodynamic stable state. An energy density barrier of height $f_n(S_-) - f_n(S_+)$ exists between the two minima $S = 0$ and $S = S_+$. At T_c^{**} the height of the barrier becomes zero, for $S_+(T_c^{**}) = S_-(T_c^{**}) = B/4C$ and this corresponding point in free energy density curve is a point of inflection. The temperature T_c^\dagger corresponds to super heating temperature.
- Phase II (figure 1.3): $T_c^* < T < T_c$: Here $S = S_+$ gives a lowest free energy and $S = 0$ is relative minimum. The nematic phase is a stable state in this range of temperature. The $S = S_-$ corresponds to a relative maximum of the free energy density. The free energy height barrier is $f_n(S_-) - f_i$. At T_c^* the height becomes zero, because $S_- = 0$. This implies that the isotropic phase, which can be obtained by super cooling, is metastable in the temperature region between T_c^* and the clearing point T_c .

- Phase I (figure 1.3): $T < T_c^*$: The nematic phase is the thermodynamically stable phase as S_+ gives the lowest free energy density, S_- a relative minimum and $S = 0$ a relative maximum. The S_- describes a phase where the molecules orient perpendicular to the uniaxial phase. T_C^* is the super cooling temperature.

Figure 1.4 shows the discontinuity in the free energy at the transition temperature with the variation in S for different temperatures.

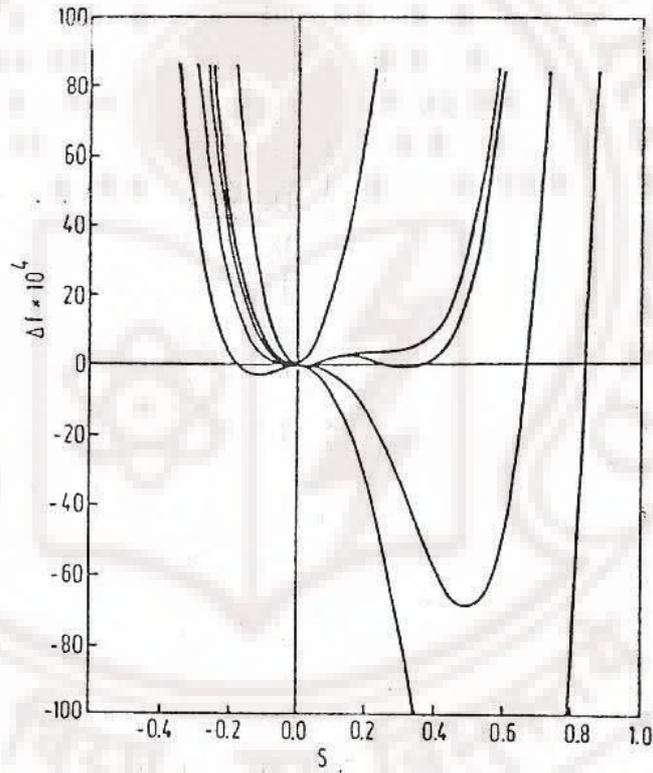


Figure 1.4: The free energy density plots for different temperatures with the change in order parameter [11]

1.3.2 Maier-Saupe Theory

Maier Saupe [14] [6] [11] [12] theory is a molecular theory that starts with the behavior of one molecule in the “field” of other molecules and determines the characteristics of a macroscopic phase. This approach that has proved to be extremely useful in developing a

theory of spontaneous long range orientational order and the related properties of the nematic phase, is a molecular field method. Each molecule is assumed to be in an average orienting field due to its environment, but otherwise uncorrelated with its neighbors. A macroscopic sample contains a huge number of molecules and it's not predictable to account for all possible interactions among all molecules. As a result approximations and simplifications are necessary, and result in a simplified treatment.

Maier-Saupe theory uses the concept of orientational order in the nematic phase. Each molecules is assumed to experience an average attractive potential $U(\theta)$ given by

$$U(\theta) = -\varepsilon \langle P_2(\cos \theta) \rangle P_2(\cos \theta) \quad (1.3.8)$$

where ε is the strength of the potential. The distribution function is related to the potential by

$$f(\theta) = Z^{-1} \exp \left[\frac{-U(\theta)}{k_B T} \right] \quad (1.3.9)$$

where Z serves to normalize the $f(\theta)$. In its original form Maier and Saupe considered anisotropic Van de Waal forces between the molecules. Every molecule possesses an anisotropic polarizability determined by α_l (lateral component) and α_t (transverse component) or alternatively by $\bar{\alpha} = (\alpha_l + 2\alpha_t)/3$ and $\delta\alpha = \alpha_l - \alpha_t$. In a perturbation expansion this leads to three types of contributions, which are proportional to the quantities

$$\alpha \cdot \alpha, \quad \alpha \cdot \delta\alpha \quad \text{and} \quad \delta\alpha \cdot \delta\alpha \quad (1.3.10)$$

In spite of the anisotropy, a spherical average was assumed. In this consequence, only the last term contributes to the anisotropic part of the free energy and thus to ε , stabilizing under appropriate conditions the nematic phase. For such averages, any contributions from the first two terms is zero. The extreme point in the Maier-saupe theory is the existence of a nematic phase due to the presence of the anisotropic part of the dispersion interaction energy between the molecules. This interaction energy originates from the intermolecular electrostatic interactions, which is taken into account by means of perturbation theory, called the dispersion energy. The simple expression for interaction of a single molecule

in a sea of molecules under the above simplifying condition is given as

$$U_i(\theta_i) = -\frac{A}{V^2}S\left(\frac{3}{2}\cos^2\theta_i - \frac{1}{2}\right) \quad (1.3.11)$$

where θ_i is the angle between the long axis of the molecule and the director. A is a constant that is independent of temperature, V is the volume of the sample. Few approximations were made in this context regarding the electrostatic interactions and the properties of the molecules.

1. As long as long range order is assumed the permanent dipoles can be neglected. This means that the interaction between the molecules is due to induced dipoles only. A momentary dipole moment of one molecule induces a dipole moment on other molecule resulting in attractive interaction.
2. Molecules are considered as rotationally symmetric with respect to the long axis of the molecule - molecules are perfect cylinders. The interaction between the molecules can depend only on the angle between them.
3. For a given molecule the distribution of the centers of mass of the remaining molecules may be assumed to be spherically symmetric.
4. The degree of orientational order of the molecules enters into the mean-field potential in a linear way.

The Maier – Saupe theory thus tends to ignore the short range forces and have contributions from the long range forces only. One of the major criticisms on Maier Saupe theory is the complete negligence of short range forces which should be important for elongated molecules forming nematics [15]. The success of this theory however lies in the generalization of the Van de Waal interactions, and it does provide a qualitative insight into the factors that contribute to the orientational ordering [16].

1.4 Effect of Confinement

Liquid crystals are part of soft matter whose physical properties are fairly difficult to predict from their atomic or molecular constituents. Soft matter self-organizes into mesoscopic physical structures with length scales that are much larger than the microscopic scale, and yet could be much smaller than the macroscopic (overall) scale of the material. Another important feature of soft matter is that all predominant physical behavior occurs at an energy scale comparable to thermal energy at room temperature.

Liquid crystals find wide use in liquid crystal displays, which rely on the optical properties in the presence or otherwise of external (electric) fields. Liquid crystalline materials confined to different geometries attracted considerable attention due to their novel electro-optic properties and their rich physical phenomena. Surface effects on liquid crystal have thus become very important for both theoretical and experimental investigators, and play crucial role in technological applications like displays.

Experimentally it is known that there are different methods of aligning a liquid crystal on a substrate. Two of these methods that are commonly known and used widely are rubbing and photo alignment. Depending on the substrate used different alignments are achieved, but it is still not known as to why some substrates align whereas some do not. Different methods of alignment effective for different substrates are reviewed very comprehensively [17]. The commonly known liquid crystalline director alignments near a solid substrate are homeotropic, planar and titled orientations.

LC develops an order in the direction of the easy axis of the substrate on which it is confined [18] [19] [20]. The aligning action of the polymer layer proceeds to the 'first molecular layer' via the anisotropic Van der Waal interaction and the excluded volume effects due to the topology of the interface. The LC aligns through the nematic interactions at the shear plane; the LC's anchorage is fairly weak and defines a slippery surface. Further into the bulk, the orientational order is transmitted via intermolecular forces that are responsible for the orientational order in the LC. In the absence of any other orienting field

(electric or magnetic field, flow, other surface, etc) this orientation is imposed on the bulk molecules via the elastic forces which tend to orient all the molecules parallel to each other. This phenomenon of orientation of a liquid crystal by a surface, called anchoring, is very similar to the epitaxy of solids on substrates.

Both orientational and positional orders are induced into the LC due to the surface. There is a first layer of molecules that transmits the aligning action of the surface into the bulk. This aligning action is transmitted through the medium by the elastic properties of the LC. Liquid crystals are known to have very small elastic constants in the range of $\sim 10^{-7}$ units. The positional order that is unstable in bulk nematic decays within the smectic correlation length from the surface whereas the orientational order is relatively long ranged. In a macroscopic picture, a confining homogenous surface aligns a nematic liquid crystal because it represents a state of spontaneously broken continuous rotational symmetry and corresponds to the minimization of the free energy.

Under these conditions, theoretical calculations of the surface energy with the bulk LC energy showed that the liquid crystals tend to align along the direction of the groove more readily than perpendicular to the groove. Grooves are produced by rubbing, unidirectional polishing, tangential evaporation or by the formation of grating on the substrate. The resulting model is based on the elastic continuum theory of nematic liquid crystal and the liquid crystal alignment is a result of the minimum of free energy of the system. In this picture, the effect of confining surface can be considered as the coupling of a spatially homogenous potential to the excitation modes in the nematic. Those modes that are unstable, decay from the surface and give rise to different orders, LC layers near the surface with a thickness of correlation length.

1.4.1 Anchoring Energy and Extrapolation length

Deep in the nematic phase, the variation in scalar order parameter does not play an important role. The main contributions to the elasticity are due to the elastic deformation of the

director field which contributes to the free energy density.

$$F = \frac{1}{2} \{ K_{11} (\nabla \cdot \hat{n})^2 + K_{22} [\hat{n} \cdot (\nabla \times \hat{n})]^2 + K_{33} [\hat{n} \times (\nabla \times \hat{n})]^2 \}. \quad (1.4.1)$$

The first three terms correspond to the three deformations of the director field, *viz.* splay, twist and bend deformations, respectively. This free energy density is invariant with respect to rotations of the system as a whole, space inversions and the transformation $\hat{n} \rightarrow -\hat{n}$. The relative elastic anisotropy of a typical nematic is usually not more than 50%, so it is reasonable to assume, for simplification that $K_{11} = K_{22} = K_{33} = k$. Consider a twist deformed nematic place between two solid substrates. Let axes x (easy axis of lower substrate direction) and t (easy axis of substrate 2) be energetically preferable directions of the nematic orientations near the solid walls. Due to the twist deformation in the bulk of the sample, the director in the areas adjacent to the wall deviate from x and t by, say angles ϕ_1 and $\tau - \phi_2$, respectively. So extra terms are needed to be added to account for the free energy density due to the excess surface energy. In the coordinate representation of the director $\mathbf{n}(\cos\phi, \sin\phi, 0)$, these terms can be written as

$$\begin{aligned} F_{1S} &= F_{1s}^a + F_{1s}^i = \frac{1}{2} W_1 \phi_1^2 + F_{1s}^i \\ F_{2S} &= F_{2s}^a + F_{2s}^i = \frac{1}{2} W_2 (\tau - \phi_2)^2 + F_{2s}^i. \end{aligned} \quad (1.4.2)$$

Here F_{1s}^i and F_{2s}^i are the densities of the isotropic surface energy of the nematic, the functions F_{1s}^a and F_{2s}^a are the angle-dependent anisotropic parts of the surface energy and the coefficients W_1 and W_2 are the so-called anchoring energies of the nematic liquid crystal. The physical meaning of W_1 and W_2 is evident as they are the energies required for maximum deviation of the director in the wall-adjacent areas from the easy orientation. There are usually two types of anchoring, connected with the azimuthal angle θ , W_θ and the other connect to the polar angle ϕ , W_ϕ . Considering only W_ϕ , the total free energy of the nematic is:

$$F = F_0 + \frac{1}{2} k \int_0^d \left(\frac{d\phi}{dz} \right)^2 dz + \frac{1}{2} W_1 \phi_1^2 + \frac{1}{2} W_2 (\tau - \phi_2)^2. \quad (1.4.3)$$

Here the isotropic energy F_0 includes both surface and bulk parts, d is the film thickness, and $k = K_{22}$ (twist deformed LC). In equilibrium state the free energy is minimal and its variation δF is zero:

$$\delta F = \left[k \frac{d\phi}{dz} - W_2(\tau - \phi) \right] \delta\phi|_{z=d} + \left[-k \frac{d\phi}{dz} + W_1\phi \right] \delta\phi|_{z=0} - k \int_0^d \frac{d^2\phi}{dz^2} \delta\phi dz = 0. \quad (1.4.4)$$

since $\delta\phi$ is arbitrary. The condition $\delta F = 0$ is satisfied by initializing

$$\begin{aligned} \frac{d^2\phi}{dz^2} &= 0 \\ -k \frac{d\phi}{dz} + W_1\phi &= 0, \quad z = 0, \\ k \frac{d\phi}{dz} - W_2(\tau - \phi) &= 0 \quad z = d. \end{aligned} \quad (1.4.5)$$

The first equation reflects the equilibrium distribution of the director in the bulk of a sample, while the rest are boundary conditions. Hence the solution of equation 1.4.5 is

$$\phi = az + b \quad (1.4.6)$$

using the boundary conditions

$$\phi = \frac{W_2\tau}{k(1 + W_2/W_1) + W_2d} (z + k/W_1). \quad (1.4.7)$$

When the anchoring is the same at both the surfaces *i.e.* $W = W_1 = W_2$ then,

$$\phi = \frac{W\tau}{2k + Wd} (z + k/W). \quad (1.4.8)$$

Hence the director deviations at the substrates are

$$\begin{aligned} \phi_1 &= \tau \frac{k}{2k + Wd}, \\ \phi_2 &= \tau \frac{k + Wd}{2k + Wd}. \end{aligned} \quad (1.4.9)$$

When the nematic director is strongly fixed at the surfaces, $W \rightarrow \infty$, $\phi_1 \rightarrow 0$ and $\phi_2 \rightarrow \tau$, *i.e.* the director near the walls coincides with the easy axis of the substrates.

If W is finite, the angle ϕ is zero when $z = -k/W$. The parameter

$$b = |z| = \frac{k}{W}, \quad (1.4.10)$$

having the dimension of length, is usually called the extrapolation length. The anchoring strength is measured in terms of extrapolation length which denotes the length on which the director field would relax to the one preferred by the substrate. It is the measure for the relevance of the competing elastic distortion vs. violating substrate order.

1. When the interaction energy of the nematic molecules with the substrate F_s^a is of the same magnitude as the mesophase interaction F , $F_s^a \sim F$. Then $b \sim a$, the molecular length is comparable to molecular size, this case is so called strong anchoring.
2. When interaction of substrate with the liquid crystal is very much less than the mesophase interaction, $F_s^a \ll F$. The extrapolation length is much greater than the molecular lengths, $b \gg a$. This condition is called weak anchoring.

Confined nematics exhibit peculiar physical phenomena connected to fundamental liquid crystal properties and lead to various important applications [21] [22]. The confining surfaces, for instance curved and/or possibly with antagonistic boundary conditions, can result in general in frustration of systems, leading possibly to observable transitions between a variety of thermally driven non-trivial equilibrium structures [22]. This is conveniently visualized as a resulting free energy profile in the appropriate parameter space exhibiting rugged features, manifesting as richness in the stable director space. The overall effect on the director field is difficult to predict, as in confined systems a competition exists between the effects due to the boundary conditions, the ordering interactions inside the LC system, and the disordering effects due to the temperature [23]. The study of confined liquid crystals thus is interesting from the point of observation of new stable structures that can be formed by appropriate external conditions and the transitions among these structures thereof [24] [25].

Consider the case of a second-order transition between an ordered and a disordered phase. When such a transition is approached from the disordered phase (in which the order parameter of the transition is zero) chosen to be, fluctuations of this order parameter appear in the bulk with a correlation length ξ which diverge at the transition. If the system is in

contact with an interface favoring the ordered phase, the correlation length at the surface will become infinite in a direction parallel to the surface plane. This creates an ordered layer at the surface in which the order parameter decreases exponentially from a non-zero value at the surface to zero in the bulk over a penetration length ξ_s ; ξ_s is equal to the correlation length ξ and thus diverges at the transition. This phenomenon is called critical adsorption.

When the transition between two phases I and II is approached, say from phase I, a layer of phase II can form at the surface: phase II is said to wet the surface. If the thickness of the phase II layer becomes infinite at coexistence, wetting is complete; if the thickness remains finite at coexistence wetting is partial. Another useful parameter of the wetting transition is the contact angle θ , between the surface and the phase I – phase II interface (between phase – I and phase – II) taken in phase I. When $\theta = 0$, phase I completely wets the interface between phase II and the other phase. When $0 < \theta < \pi$, phase I partially wets the interface. With such a definition, partial wetting by phase I or by phase II are equivalent.

Studies of confinement of liquid crystals have been carried out by using experimental techniques, theoretical methods and computer simulations in the recent past. Experimental studies have been done, mainly on the preparations on substrates that align the LC in particular desired direction [17]. Theoretical studies focussed on mean field methods and phenomenological studies [26]. In the latter approach the free energy is considered by adding relevant surface energy terms. Minimization of this free energy yields the director configuration in the system consistent with the boundary conditions. Relatively, computer simulations methods of more recent origin, and both Monte Carlo and Molecular Dynamics simulations have been quite successful in investigating the confined LC systems in the perspective.

The simplest perturbation can arise from symmetry breaking induced by the surface: the nematic phase is characterized by a translation invariance which is broken by the presence of a surface. As a result the center of mass of the molecules nearest to the surface may have a tendency to be located in a plane parallel to the surface, *i.e.* a layer of molecules tends

to form at the surface. Due to the intermolecular forces present the existence of this layer favors the formation of a second one, and so on. The presence of a surface is thus likely to induce a positional order of the molecules at the interface between the nematic liquid crystal and the other phase.

Surface layering may be obtained at the interface due to solid substrates, arising from the molecule-substrate interactions. This type of ordering has been revealed by scanning tunneling microscopy used to obtain the images of the first monolayer of mesogenic molecules in contact with the substrate. Another method which has been used to investigate nematic-substrate interface and also monolayers of nematogens is optical second harmonic generation. This method yields detailed information about the orientation of the molecules: mean tilt with respect to the surface normal, distribution of azimuthal orientation in the plane of the surface and the existence of dipolar anchoring. Several methods have been used to measure the surface order parameter: pretransitional birefringence measurements in the isotropic phase, refractive index measurements, optical reflectivity measurements, ellipsometry, evanescent-wave ellipsometry, and electrically induced surface twist measurements.

The main issue concerning the anchoring of nematic liquid crystals is to relate the observed anchorings with the structure of the interfaces and to find the microscopic interactions responsible for the orientation of these phases by surfaces. It is thus impossible to predict from a microscopic basis which type of anchoring a given interface should induce. Phenomenological approaches based on a macroscopic point of view consider only the orientation of the nematic phase and the dependence of the interfacial energy on this orientation, without considering the detailed structure of the interface. Anchoring transitions also appear in the same way as phase transitions. Anchoring transition can be defined as change from one anchoring state to another, obtained by varying suitable control parameters determining the interface structure. Such a transition can be continuous or discontinuous, and can separate anchorings of the same type or of different types.

These confined systems can be studied using computer simulations which has certain

practical advantages for example, imposition of complex boundary conditions can be mimicked in simulation experiments more. There are situations where phenomenological calculations proceed to be too difficult to give interesting predictions, whereas computer simulations yielded with relative ease, some of the essential features in the systems due to confinement under such complex bounding conditions [9] [27]. To understand these systems, all the desired parameters can be computed and plotted with respect to the variable. This thesis in this context reports Monte Carlo simulations of confined liquid crystals, mainly hybridly confined liquid crystal films and droplets. The properties of confined systems are examined by computing different macroscopic physical observables as a function of external variables, with a view to focussing on subtle changes in director structures. The next chapter provides a brief introduction to Monte Carlo technique, with the algorithms used for the study of these different systems.

1.5 Models studied

Computer simulation of liquid crystals has become a widely used tool to study the dynamics and the different structures in condensed matter systems [28] [29] [30] [31] [32] [33] [34] [35]. This is a tool that lies midway between experimental and theoretical (analytical) techniques. In simulations, the system is analyzed over long periods of time or a statistical average over a large ensemble is taken. In real sense simulation is a bridge between experiments and analytical theory. Structural and dynamical data can be obtained that can be compared to the available experimental data. Stability of different models to interpret the experimental observations can be explained using simulation techniques [36].

Different models have been proposed for liquid crystals using mean-field methods and phenomenological methods. One model widely used is due to Gay-Berne [37] model, and is not confined to a lattice. As a rule, such off – lattice models are on hand more realistic and offer flexibility in investigating complex phase diagrams involving layer structures. On the other hand, due to the more additional degrees of freedom introduced in this model, the

simulations are more computer intensive, requiring almost an order of magnitude more effort to obtain reliable predictions. To study the nematic – isotropic transition the lattice spin model is most convenient as it captures simply the physical nature of interaction leading to this transition. Thus, the present work relies exclusively on lattice models.

Computer simulations of lattice spin models for liquid crystal have been giving interesting opportunities to study anisotropic medium. In particular these models are easy to study the nematic-isotropic transition where the orientation of the spins gives rise to a transition. By adding different terms to the existing model new aspects of liquid crystals arising from subtle changes in the symmetry of the system can be studied. Three lattice models of liquid crystals that are used in this work are given in some detail below. Monte Carlo simulations were carried out by modeling droplets, hybrid films and different kind of substrates percolating various orders into the medium [38].

1.5.1 Lebwohl Lasher Model

A simple prototype lattice Hamiltonian which has the required symmetry of nematic liquid crystals was proposed by Lebwohl and Lasher (LL) [39]. Nematic liquid crystals are usually found with uniaxial symmetry, and this model captures this property when applied to bulk systems. Considering this symmetry, every molecule can be represented as a headless spin at every lattice point of an $L \times L \times L$ cubic lattice with periodic boundary conditions. Every spin is fixed in its position but has infinite degrees of freedom in its orientation. With respect to a three dimensional laboratory frame, every spin is represented by a unit vector having a specific orientation. The interaction between any two such spins is represented by a pair potential of the form

$$E = -\epsilon_{ij} \left(\frac{3}{2} \cos^2 \theta_{ij} - \frac{1}{2} \right) \quad (1.5.1)$$

where ϵ_{ij} is a positive constant, ϵ , for nearest neighbor spins i and j and zero otherwise. P_2 is the second order Legendre polynomial and θ_{ij} is the angle between two molecules.

This interaction tends to bring molecules parallel to one another and embeds the symmetry $\hat{n} = -\hat{n}$. LL model is widely used to study the orientational dynamics and different physical properties at the nematic-isotropic transition. When the focus is exclusively on the orientational degree of freedom, uncoupled from the translational degrees. It represents the lattice version of Maier and Saupe theory. The above potential (equation 1.5.1) was investigated based on Monte Carlo techniques with the Metropolis algorithm. This lattice was found to undergo a transition at $kT/\epsilon = 1.1234 \pm 0.0006$ with a spontaneous order of $\langle P_2(\cos(\theta)) \rangle = 0.33 \pm 0.04$ at the transition.

Utility of the LL model was well demonstrated by numerical simulations that were carried out, both on bulk and confined systems. This model provides the right kind of first order nature observed in real systems, and has been shown to be a very useful prototype model for the study of isotropic-nematic transition, much like the Ising and Heisenberg model for magnetics.

1.5.2 Biaxial Liquid Crystal Model

Most molecular theories of nematic liquid crystals assume that the constituent molecules are cylindrically symmetric. In real systems, the molecules are rarely cylindrically symmetric, and hence the molecular structures is in principle expected to play a very important role. Molecules that are not symmetric about their long axes, are known as biaxial liquid crystals. A general expansion of the pair-wise intermolecular potential together with the molecular field approximation, was developed for an ensemble of such particles [40].

The model used here is a pair-wise interaction lattice model [41] based on a mean field work . From this model equation

$$V = -U_o \{q \cdot q' + \gamma (q \cdot b' + q' \cdot b) + \lambda (b \cdot b')\} \quad (1.5.2)$$

a Hamiltonian was derived where the orientations of the molecules are used to compute the interaction energy between two particles. Consider classical, identical particles, possessing

D_{2h} symmetry, whose centers of mass are associated with a three-dimensional (simple-cubic) lattice N^3 ; let $x_\mu \in N^3$ denote the coordinate vectors of their centers of mass. The interaction potential will be isotropic in orientation space, and restricted to nearest neighbors, involving particles or sites labeled by μ and ν , respectively. The orientation of each particle can be specified via an orthonormal triplet of 3-component vectors (e.g. eigenvectors of its inertia tensor), say $\{w_{\mu,j}, j = 1, 2, 3\}$; in turn these are defined by an ordered triplet of Euler angles $\omega_\mu = \{\phi_\mu, \theta_\mu, \psi_\mu\}$; particle orientations are defined with respect to a common, but otherwise arbitrary, Cartesian frame. The two molecules can be represented as u_j for $w_{\mu,j}$ and v_k for $w_{\nu,k}$. Here, for j , u_j and v_j has the same functional dependence on ω_μ and ω_ν , respectively. Let $\tilde{\Omega} = \Omega_{\mu\nu}$ denote the set of Euler angles defining the rotation transforming u_i to v_j . Then,

$$f_{jk} = (u_j \cdot v_k), \quad G_{jk} = P_2(f_{jk}) \quad (1.5.3)$$

where P_2 denotes the second Legendre polynomial. The continuous interaction potentials used for this study are defined by appropriate linear combinations of terms G_{jk} , which can be cast in the form,

$$U = -\epsilon \{G_{33} - \Gamma [G_{11} - G_{22}] + \Lambda [2(G_{11} + G_{22}) - G_{33}]\}. \quad (1.5.4)$$

Here ϵ denotes a positive constant setting the temperature and the energy scales, $T^* = k_B T / \epsilon$. $|\Gamma|$ and $|\Lambda|$ are often taken lesser than one; setting these two terms to zero makes equation 1.5.4 converges to Lebwohl-Laser model. It was shown using MC simulation that a biaxial phase does not result even with the above model as long as the third term is neglected *i.e.* $\Lambda=0$ [42]. Many different approximations were proposed for equation 1.5.4, one of the most known being the London-de Born-Heller approximation, where $\Lambda = \Gamma^2$.

In this approximation, the above experiments can be conveniently recast in terms of relative orientation of the neighboring spins as [43].

$$U(\omega_{ij}) = -\epsilon_{ij} \{P_2(\cos\beta_\mu) + 2\lambda [R_{02}^2(\omega_\mu) + R_{20}^2(\omega_\mu)] + 4\lambda^2 R_{22}^2(\omega_\mu)\} \quad (1.5.5)$$

with the biaxial molecules or spins fixed to lattice sites of a three-dimensional lattice. ϵ_{ij} is the coupling parameter, taken as constant when nearest neighbors, λ the biaxiality parameter accounting for the deviation from cylindrical symmetry. The relative orientation of a molecular pair is considered in terms of ω_μ . This in a Cartesian frame can be expanded as

$$U_{ij} = -\epsilon\left(\frac{3}{2}V_{33} - \lambda\sqrt{6}(V_{11} - V_{22}) + \lambda^2(V_{11} + V_{22} - V_{12} - V_{21}) - \frac{1}{2}\right). \quad (1.5.6)$$

where $V_{ij} = (u_i \cdot v_j)^2$, and is related to direction cosines for the molecular pair. A phase diagram was proposed for this potential, where for a particular value of λ the so called Landau point is observed. A detailed Monte Carlo study at this point proved this to be a second order type of transition [44].

Based on mean-field considerations [41] a pair-wise lattice model was proposed which is more general and is not restricted to London's approximation. In this model two parameters (Γ and Λ) were considered as controlling the biaxiality of the medium and Monte Carlo simulations were done for a particular choice of these biaxiality parameters [45]. This model is a more generalized form of the equation 1.5.6. Latter chapters in this thesis deals with a detailed study on these models and interesting consequences of the variation of the parameters of the Hamiltonian.

1.5.3 Luckhurst Elastic Model

When studying confined systems where the elastic properties would play an important role due to the boundary conditions, a more information and relevant model can also be considered. A lattice based Hamiltonian which explicitly takes into account the elastic properties of the medium via the three elastic coefficients (splay (K_1), twist (K_2), and bend (K_3)) elastic constants is discussed here with this objective. This interaction is derived within the approximation of confine it to nearest neighbor lattice elements. Its application to Schadt – Helfrich cell was demonstrated through detailed Monte Carlo simulations [46].

The director configuration of a system with a given geometry and boundary conditions is determined by minimizing the elastic free energy of the sample in the continuum limit.

The corresponding energy density in the nematic phase is expressed in terms of powers of the gradient of the director \mathbf{n} , restricting to only the quadratic terms, as

$$\Psi = \frac{1}{2} \{ K_1 (\nabla \cdot \mathbf{n})^2 + K_2 [\mathbf{n} \cdot (\nabla \times \mathbf{n})]^2 + K_3 [\mathbf{n} \times (\nabla \times \mathbf{n})]^2 \}. \quad (1.5.7)$$

Only very simple systems permit an analytical solution of the above equation, and very often, in practice, free energy is calculated through numerical procedures. An alternative method is to assume a lattice model of pair-wise interacting nearest neighbors elements stipulated by a model Hamiltonian, and construct an equilibrium ensemble at different reduced temperatures (measured in units of the interaction strength introduced in the Hamiltonian), employing the usual Markov chain Monte Carlo methods [47] based on Metropolis algorithm. Earlier work on these droplets based on this methodology using Lebwohl-Lasher model was limited by the fact that the interaction energy depends only on the relative orientation of the two particles but not their relative positions, and hence cannot distinguish between the different deformations. This potential thus corresponds to an assumption of equal elastic constants (spherical approximation).

An alternative approach, initiated by Gruhn and Hess [48], and later developed by Romano and Luckhurst [49], involves derivation of a model potential for a pair-wise additive interaction between local directors, which approximately reproduces the elastic free energy density of the system. This is achieved by mapping the above equation onto a suitable expansion of the interaction potential. In this scheme, the space is discretized to a cubic lattice, each site representing a director. The free energy of the system is defined as the sum of pairwise additive interactions between nearest neighboring sites. An expression, with appropriate multiplicative and additive constants chosen to scale the isotropic average of the energy to be zero, is then derived to be used as model potential for Monte Carlo simulations. These naturally are defined through specific combinations of the three elastic coefficients, thereby making the model rich and useful so as to make them applicable to real systems with differing elastic constants. Derivation of the potential used in this work is briefly outlined below, in order to introduce the notation.

The pair potential between two directors located at two neighboring sites, say j and k , is expanded in terms of a complete set of basis functions depending on the orientation of the two directors \mathbf{n}_j and \mathbf{n}_k and the orientation of the vector joining them \mathbf{r} . The S -functions [46] $S_{L_j, L_k, J}(\mathbf{n}_j, \mathbf{n}_k, \mathbf{r})$ were found to be suitable for this purpose. Here the index L_j refers to the j -th director, L_k to the k -th director and J corresponds to the inter-director vector taking the values from $(L_j + L_k)$ to $|L_j - L_k|$. In this particular application it was found that the S -functions depend only on the scalar invariants associated with the vectors in their argument, viz. $a_j = \mathbf{n}_j \cdot \mathbf{r}$, $a_k = \mathbf{n}_k \cdot \mathbf{r}$, $b_{jk} = \mathbf{n}_j \cdot \mathbf{n}_k$ and $c_{jk} = \mathbf{n}_j \cdot (\mathbf{n}_k \times \mathbf{r})$. The symmetry of the nematic phase requiring that $\mathbf{n} = -\mathbf{n}$ demands that the total rank, $(L_j + L_k + J)$, of the S -function be even, thereby eliminating the factors c_{jk} . Thus the pair potential between two neighboring sites j and k is expanded in terms of S -functions restricted to terms of even total rank, with suitable coefficients, as [50] [46]

$$\Phi_{jk} = \sum_{L_j, L_k, J} \varphi_{L_j, L_k, J} S_{L_j, L_k, J}(a_j, a_k, b_{jk}). \quad (1.5.8)$$

This pair potential is then mapped onto the expression for the free energy density, assuming small angular displacements of the director so as to replace the gradients by finite increments. Finally certain well-defined deformations are considered in both the pair potential and the initial free energy density (approximated for small deviations), so as to derive relation between the coefficients of expansion in the pair potential and the elastic constants. The final expression for the pair potential $\Phi_{L_j, L_k, J}$ is given by

$$\begin{aligned} \Phi_{jk} = & \lambda [P_2(a_j) + P_2(a_k)] + \mu \left(a_j a_k b_{jk} - \frac{1}{9} \right) + \\ & \nu P_2(b_{jk}) + \rho [P_2(a_j) + P_2(a_k)] P_2(b_{jk}). \end{aligned} \quad (1.5.9)$$

Here, P_2 is the second rank Legendre polynomial. The coefficients of expansion are related to the elastic constants through the following relations, involving the chosen linear

dimension Λ of the volume element in the cubic lattice to represent their local directors:

$$\begin{aligned}\lambda &= \frac{1}{3}\Lambda (2K_1 - 3K_2 + K_3) \\ \mu &= 3\Lambda (K_2 - K_1) \\ \nu &= \frac{1}{3}\Lambda (K_1 - 3K_2 + K_3) \\ \rho &= \frac{1}{3}\Lambda (K_1 - K_3).\end{aligned}\tag{1.5.10}$$

An interesting feature of this potential is that Λ , enters as a length scale over which the director gradient is discretized and defines the lattice parameter corresponding to the distance between the neighboring sites. By setting all the elastic constants equal to each other, say K , the above potential is reduced to the form of the Lebwohl-Lasher potential,

$$\Phi_{jk}^{LL} = -\epsilon P_2 [\cos(\mathbf{n}_j \cdot \mathbf{n}_k)].\tag{1.5.11}$$

Under these special conditions, the energy scale parameter ϵ , is equal to ΛK for the present model. In general, the total free energy of the system is then given by

$$\Psi = \frac{1}{2} \sum_{j=1}^N \sum_{k=1}^6 \Phi_{jk},\tag{1.5.12}$$

where N is the number of sites. Following the procedure adopted earlier, the scaled potential for use in simulations is obtained by dividing equation 1.5.9 by $|\nu|$. This leads to a scaled temperature, to be used in the Monte Carlo scheme, given by

$$T^* = k_B T / |\nu| = 3k_B T / (\Lambda |K_1 - 3K_2 - K_3|).\tag{1.5.13}$$

With one elastic constant approximation *i.e.* $K_1 = K_2 = K_3 = K$ this equation 1.5.9 reduces to the LL model (equation 1.5.1). A Monte Carlo simulation of this model was investigated by simulating the three Freedericksz transitions as well as that of the Schadt - Helfrich cell [46]. An extension of this model was proposed to mimic a chiral nematic liquid crystal [51]. This model is used in the later chapters of the thesis to model a polymer dispersed liquid crystal [23].

Bibliography

- [1] G.Durand and J.D.Lister. Recent advances in liquid crystals. *Ann. Rev. Mate. Sci.*, 23:269, 1973.
- [2] S.Chandrashekar and N.V.Madhusudana. Liquid crystals. *Ann. Rev. Mate. Sci.*, 10:133–135, 1980.
- [3] Michael J. Stephen and J.P.Straley. Physics of liquid crystals. *Reviews of Modern Physics*, 64:617, 1974.
- [4] M.Carme Calderer. Mathematical study of liquid crystal. 2004.
- [5] Zhengping Zhang, Amitabha Chakrabarti, Ole G Mouritsen, and Martin J. Zuckermann. Substrate-induced bulk alignment of liquid crystals. *Phys. Rev. E*, 53:2461 – 2465, 1996.
- [6] S.Chandrashekar. *Liquid crystals*. Cambridge University Press, 1977.
- [7] C.Zannoni. *Molecular Physics of Liquid Crystals*. Academic Press, 1979.
- [8] C. Zannoni. *Nuclear Magnetic Resonance in Liquid Crystals*. D.Reidel Publishing Company, Dordrecht, 1983.
- [9] Andreja sarlah. *Effect of the confining substrates on nematic order-fluctuations in liquid crystals*. PhD thesis, School of Mathematics and physics, University of Ljubljana, 2001.
- [10] C. Zannoni. *The Molecular Dynamics of Liquid Crystals*. D.Reidel Publishing Company, Dordrecht, 1989.

- [11] G. Vertogen and W.H. de Jeu. *Thermotropic Liquid crystals, Fundamentals*. Springer-Verlag, Berlin, 1988.
- [12] Peter J. Collings and Michael Hird. *Introduction to Liquid Crystals Chemistry and Physics*. Taylor and Francis, 1998.
- [13] P.D. de Gennes and J. Prost. *The Physics of Liquid Crystals*. Oxford University Press, 1995.
- [14] G.R. Luckhurst. *Molecular Physics of Liquid Crystals*. Academic Press, 1979.
- [15] G. R. Luckhurst and C. Zannoni. Why is the maier-saupe theory of nematic liquid crystals so successful? *Nature*, 267:412, 1977.
- [16] W. H. de Jeu. *Phase Transitions in Liquid Crystal*. Plenum Press; NATO Scientific Affairs Division, 1992.
- [17] J. Cognard. Alignment of nematic liquid crystals and their mixtures. *Mol. Cryst. Liq. Cryst. Suppl. 1*, 1982.
- [18] B. Jerome. Surface effects and anchoring in liquid crystals. *Rep. Prog. Phys.*, 54:391, 1991.
- [19] B. Jerome. Interfacial structural transitions in nematic liquid crystals. *J. Phys: Condens. Matter*, 6:A269–A273, 1994.
- [20] B. Jerome. Nematic liquid crystals at interfaces. *Mol. Cryst. Liq. Cryst.*, 212:21–32, 1992.
- [21] G P Crawford and S Zumer, editors. *Liquid Crystals In Complex Geometries*. Routledge, UK.
- [22] Theo Rasing. *Surfaces and Interfaces of Liquid Crystals*. Springer-Verlag New York, LLC, 2004.

- [23] P. Pasini, C. Chiccoli, and C. Zannoni. *Advances in the Computer Simulations of Liquid Crystals*. Kluwer, Dordrecht, 2000.
- [24] Eugene C Gartland. Structures and structural phase transitions in confined liquid crystal system.
- [25] J.Evans. Fluids adsorbed in narrow pores: phase equilibria and structure. *J.Phys: Condens. Matter*, 2:8989–9007, 1990.
- [26] A.Poniewierski and A.Samborski. Anchoring of nematic liquid crystals at a solid substrate. *Phys.Rev. E*, 53:2436, 1996.
- [27] Gregor Skacej. *Modeling of strongly confined liquid crystalline systems*. PhD thesis, University of Ljubljana, 2002.
- [28] Michael P. Allen. Liquid crystal systems. *Computational Soft Matter: From Synthetic Polymers to Proteins*, 23:289–320, 2004.
- [29] Michael P. Allen. Introduction to molecular dynamics simulations. *Computational Soft Matter: From Synthetic Polymers to Proteins*, 23:1–28, 2004.
- [30] C M Care and D J Cleaver. Computer simulation of liquid crystals. *Reports On Progress in Physics*, 68:2665, 2005.
- [31] Greg D.Wall and Douglas J. Cleaver. Computer simulation studies of confined liquid-crystal films. *Phys. Rev. E*, 56:4306, 1997.
- [32] N.V.Priezev, G.Skacej, R.A.Pelcovits, and S.Zumer. External and intrinsic anchoring in nematic liquid crystals: A monte carlo study. *Phys. Rev. E*, 68:041709, 2003.
- [33] M.P.Allen. *Mol. Phys.*, 96:1391–1397, 1999.
- [34] M.P.Allen. Molecular simulation and theory of the isotropicnematic interface. *Jour. of chem. Phys.*, 112:5447, 2000.

- [35] M.P.Allen and Mark A.Wilen. Simulation of structure and dynamics near the isotropic-nematic transition. *Phys Rev. Lett.*, 78:1291, 1997.
- [36] Martin A. Bates. Testing experimental analysis techniques for liquid crystal using computer simulations. *Liquid Crystal*, 32:1365–1377, 2005.
- [37] J. G. Gay and B. J. Berne. Modification of the overlap potential to mimic a linear sitesite potential. *J. Chem. Phys.*, 74:3316, 1981.
- [38] D.J.Cheung and F.Schmid. *arxiv:cond-mat*, 0522298v1.
- [39] P.A. Lebwohl and G. Lasher. Nematic liquid crystal order - a monte carlo calculation. *Phys. Rev. A*, 6:426, 1972.
- [40] G. R. Luckhurst, C. Zannoni, P. L. Nordio, and U. Segre. Molecular field theory for uniaxial nematic liquid crystals formed by noncylindrically symmetric molecules. *MP*, 30:1345, 1975.
- [41] A.M.Sonnet, E.G.Virga, and G.E.Durand. Dielectric shape dispersion and biaxial transitions in nematic liquid crystals. *Phys. Rev. E*, 67:061701, 2003.
- [42] G. R. Luckhurst and S. Romano. Computer simulation studies of anisotropic systems uniaxial and biaxial nematics formed by noncylindrically symmetric molecules. *Mol. Phys.*, 40:129, 1980.
- [43] F. Biscarini, C. Chiccoli, P. Pasini, F. Semeria, and C. Zannoni. Phase diagram and orientational order in a biaxial lattice model. a monte carlo study. *Phys. Rev. Lett.*, 75:1803–1806, 1995.
- [44] C. Chiccoli, P. Pasini, F. Semeria, and C. Zannoni. A detailed monte carlo investigation of the tricritical region of a biaxial liquid crystal systems. *Int. J. Mod. Phys. C*, 10:469–476, 1999.

- [45] Silvano Romano. Computer simulation of a biaxial nematogenic model on a three-dimensional lattice and based on a recently proposed interaction potential. *Physica A*, 337:505–519, 2004.
- [46] P.J. Le Masurier, G.R. Luckhurst, and G. Saielli. *Liq. Cryst.*, 28:769, 2001.
- [47] K. P. N. Murthy. *Monte Carlo methods in Statistical Physics*. Universities Press, 2003.
- [48] T. Gruhn and S. Hess. *Z. Naturforsch.*, A51:1, 1996.
- [49] G.R. Luckhurst, , and S. Romano. *Liq. Cryst.*, 26:871, 1999.
- [50] S. Romano. *Int. J. Mod. Phys. B*, 12:2305, 1998.
- [51] G. R. Luckhurst and G. Saielli. A pairwise additive potential for the elastic interaction energy of a chiral nematic. *Mol. Cryst. Liq. Cryst.*, 395:183–192, 2003.