Chapter 4

Phase diagram of a biaxial liquid crystal: A Monte Carlo study

"It seems that the Holy Grail of liquid-crystal science has at last been found." – G.R. Luckhurst [1]

4.1 Introduction

A biaxial nematic is a spatially homogenous liquid crystal with three distinct optical axes. This is to be contrasted to a simple nematic, which has a single preferred axis, around which the system is rotationally symmetric. The symmetric group of a biaxial nematic is $D_{2h}$, i.e. corresponding to a rectangular right parallelepiped, having three orthogonal $C_2$ axes and three orthogonal mirror planes. Biaxial nematic schematically can be visualized as a system comprising of platelets with $\vec{m}$ as the long axis, $\vec{e}$ and $\vec{e}_\perp$ as the minor axes.

Biaxiality was for the first time experimentally observed in lyotropic liquid crystals [2] [3]. Thermotropic biaxial liquid crystal was experimentally realized for the first time in nonlinear oxadiazole units [4]. A mixture of rods and discs showed a biaxial phase using experimental methods like polarized microscopy and conoscopy. However, efforts to observe a biaxial nematic ($N_B$) phase in two component melts of rod-like and disk-like liquid crystals have been unsuccessful [5] [6] [7]. There have been recent papers reporting the detection of biaxiality in tetrapodes using IR spectroscopy [8]. Experimental detection of biaxiality has always been rather difficult owing to the artifacts introduced in the detection itself [8], [9]. Using X-ray diffraction methods a biaxial nematic phase
was observed, which was in agreement with the calculation of the form factor of bent-core shaped molecules and the structure factor of the nematic phase [10].

Research in biaxial liquid crystal is of equal importance to both experimentalists as well to theoreticians. Computer simulations have made a great deal of mark in understanding biaxial liquid crystals. Based on two simple models of uniaxial liquid crystals, biaxial liquid crystal models have been developed. First, model based on the Gay – Berne potential which permits both translational and orientational degrees of freedom. A biaxial version of Gay-berne potential, originally used to model uniaxial anisotropic molecules was developed [11]. This biaxial model can be used to deal with molecules of different attractive and repulsive contributions along the three axes. This was further developed into a generalized potential describing interactions between two arbitrary, not necessarily identical, ellipsoidal particles [12]. Using these improvements, it is realized that a biaxial orthogonal smectic phase could also be observed in addition to the uniaxial and biaxial nematic phases [13]. When this model was extended to discotic particles, it was observed that a biaxial phase was seen when the well depth anisotropies have the same sign [14]. A molecular dynamics simulation was carried out to study the response of a bulk biaxial liquid crystal to an external field [15]. Application of this potential to investigate biaxial systems has been reviewed in detail recently [16].

Monte Carlo simulation using hard ellipsoids [17] was done to obtain the phase diagram of a system comprising of biaxial liquid crystal molecules [18]. Bent – core molecule were formed by joining two hard spherocylinders with chosen length – breadth ratio. Computer simulation and theoretical studies were carried out on these molecules [19]. Extending these spherocylinders by adding an ideal tail was studied using computer simulations. It was observed that a smectic A phase was formed with no presence of a biaxial nematic phase [20]. Some models that really influenced experimental studies were the modeling of bent-shaped molecules. Most known was the Monte Carlo simulation of a generic model to look for biaxiality in the bulk system [21]. Bent shaped molecules usually have core molecules in between due to which a biaxial phase can in principle be formed. Further
improvements of this model were effected by adding a bending potential to it. This helped to investigate the relationship between the flexibility of the bent-core molecule and inability to form a biaxial nematic phase [22].

Second model for studying the biaxial nematic liquid crystals is based on Lebwohl-Lasher model, which has only orientational degrees of freedom. A pair potential was developed using the complete set of Euler angles to describe the molecular orientations. This model uses the London-de Boer-Heller approximation for dispersive forces, and has a control parameter in the form of molecular biaxiality $\lambda$. Setting this parameter to 0.2, detailed computer simulation studies were done to investigate the order parameters [23]. Using mean field approximations, a pair-wise inter-molecular potential for an ensemble of particles with lower symmetry was developed. This model gave results very much in agreement with the experimental data [24]. With further developments, a pair-wise additive lattice model was proposed, and Monte Carlo simulations were done in order to compute the four order parameters (a brief introduction to these was previewed in chapter 1) [25]. This effort led to the determination of the phase diagram, with a triple point where a direct isotropic to biaxial nematic transition occurs. A more detailed study at this transition point showed that the $I - N_B$ transition is a second order transition [26]. For values of the biaxiality parameter lesser than $1/\sqrt{6}$, the molecules are mapped to prolate geometry, else oblate. Using this model a Monte Carlo study of defects [27], [28] was done with reference to the Schlieren textures gotten experimentally [29].

Monte Carlo simulation studies of an equal mixture of rod-like and disc-like liquid crystals [30] showed that at lower temperatures the system split into two phases of rod-like and disc-like uniaxial nematic, rather than forming a biaxial nematic [31]. The interaction between the rod – like and disc – like molecules was further changed in order to see if a biaxial order could be observed [32]. A computer experiment of hard spherocylinders to model a continuous mixture of rods and discs was attempted, demixing occurred in these system [33].

A real liquid crystal molecule is always inherently biaxial in its symmetry, even though
the appearance of macroscopic biaxiality comprising of such constituents is a rare phenomenon. Curiosity among the physicists rose as to why microscopic biaxiality does not get translated to macroscopic biaxial symmetry, almost as a rule. The formation of biaxial phases is mostly overtaken by other mechanisms like crystal formation or layering. Based on the theoretical studies and computer simulations done, molecular modeling of a biaxial liquid crystal was attempted [24], [34] in order to possibly determine microscopic criteria for fanning a realistic biaxial liquid crystal. In this context, it was found useful to define a molecular biaxiality parameter in terms of the length, breadth and width of the liquid crystal molecule. It is noted that unambiguous acceptance of an experimental finding of a biaxial phase could be a challenging question to be resolved [35]. A number of applications have already been envisaged for the biaxial nematic phase. For example, it is to be expected that rotation of the minor directors might be relatively rapid and possibly faster than the primary director \( \hat{n} \). Technological applications of biaxial particles are a very challenging.

There has to be considerable amount of opposition in finding an experimental method to detect biaxiality in a liquid crystals system. Deuterium NMR has been known to be one of the most powerful methods to detect orientational order, particularly biaxiality, in a liquid crystal system [9]. The biaxial nematic phase was recently observed in different thermotropic liquid crystals, namely bent-core compounds, side-chain polymers, bent-core dimers, and organosiloxane tetrapodes [36]. A nuclear magnetic resonance NMR spectra are collected for a nematic organosiloxane tetrapode. The sample was continuously rotated around an axis perpendicular to the magnetic field. In conjunction with the analysis of a deuterium NMR experiment on the same system reported earlier has been discussed. The three principle components of any tensorial property are different for a biaxial nematic phase, refractive index being such a representative property, which can be measured readily. Using conoscopy, isogyres for a uniaxial phase are two dark lines forming a cross; however, if the phase is biaxial the isogyres open and do not cross in the center of the image. A definitive identification of the nematic phase as biaxial could not be confirmed since for thin films the surface can induce an optical biaxiality in the sample even if the bulk
phase is uniaxial is a problem. An alternative method, free from the influence of surface forces on the director orientation, needed to establish the symmetry of the nematic phase could be deuterium NMR spectroscopy. In the isotropic phase, the NMR spectrum of a sample containing a set of equivalent deuterons contains a single line. However, on entering the liquid crystal phase, it splits into a doublet because of the quadrapolar interaction of the deuteron under the presence of a long range orientation order. The magnitude of the splitting depends both on the (second rank) orientational order parameters of the medium and the orientation of the director with respect to the external magnetic field. If the nematic phase is biaxial the ratio of the splitting when the magnetic field is along \( n \) to that when it is parallel to \( l \) or \( m \) deviates from the ratio expected of a uniaxial medium, \( \text{viz.} \ 2 : 1 \). Therefore, it would be necessary to prepare a monodomain sample of the nematic and then change its orientation with respect to the magnetic field to establish the phase symmetry. In practice this can be difficult because one of the directors will always be aligned with the magnetic field of the spectrometer and so a competing electric field would be necessary to change its orientation. Possible detection of biaxiality through NMR measurements continues to be a challenging experimental problem.

A simple treatment to deal with an ensemble of biaxial particles using mean field methods was proposed [34] and is based on generalized Maier – Saupe theory for asymmetric molecules [37]. Four order parameters were found to be necessary to define the biaxial phase of liquid crystals. It was seen that there existed another second order transition, other than the uniaxial nematic to isotropic \((N_U - I)\) transition, at a much lower temperature from uniaxial nematic \(N_U\) to a biaxial nematic \(N_B\) [38].

Using the models of Straley [34], a simple pair-wise interactive model was proposed,
wherein every anisotropic molecule is considered to have uniaxial \((q)\) and biaxial \((b)\) components. Thus, anisotropic part of every molecular biaxial tensor has two traceless, orthogonal components, defined as

\[
q := m \otimes m - \frac{1}{3} I \quad \text{(4.1.1)}
\]

\[
b := e \otimes e - e_\perp \otimes e_\perp.
\]

Here, \(m\) is the long axis of the molecule, and \(e\) and \(e_\perp\) represent the other two axes. The \(q\) tensor is uniaxial around \(m\) and the other is biaxial. Considering two molecules, the interaction Hamiltonian between them is given as

\[
V = -U_o \{q . q' + \gamma (q . b' + q' . b) + \lambda (b . b') \} \quad \text{(4.1.2)}
\]

The incremental energy \(\delta V\), relative to the state of alignment of two molecules, when constrained to be positive definite restricts \((\gamma, \lambda)\) space to a fan-shaped plot (figure 4.1). On further restrictions applicable to calamitic molecules, with the long molecular axis \(\overrightarrow{m}\) harder to orient than the other two axes \(\overrightarrow{e}\) and \(\overrightarrow{e_\perp}\), only a part of the fan-shaped plot (the shaded triangle region in figure 4.1) is available for the parameter \((\gamma, \lambda)\). Dispersion forces approximation [25] [26] further restrict the space to a parabolic trajectory corresponding to \(\lambda = \gamma^2\), yielding a suitable set of parameters in the above potential (equation 4.1.2). A phase diagram was proposed using mean field methods when the second term was neglected \(i.e.\ \gamma = 0\) (figure 4.1). This plot showed the presence of a tri-critical and a triple point. A tri-critical point occurs at \(\lambda_C = 0.20\), where the \(N_B - N_U\) transition changes from second order to first order transition. A triple point is seen at \(\lambda_T = 0.22\), where the three phases (isotropic \(I\), uniaxial nematic \(N_U\) and biaxial nematic \(N_B\)) coexist. A more elaborate phase diagram was proposed by extending the variation of the parameter \(\lambda\) up to 1, keeping however, \(\gamma = 0\) [40]. By defining a criterion for a tri-critical point for a biaxial particles, another tri-critical point was shown to exist when the \(I - N_B\) transition changes from first order to second order for a higher value of \(\lambda\) (figure 4.2). The existence of the second tri-critical \(I - N_B\) point was also predicted using bifurcation analysis.
Monte Carlo simulations confirmed the appearance of these different phases, with changes in $\lambda$. These developments were further generalized to find a thermodynamically exact criterion that governing a biaxial phase [42]. It was shown that the complete phase diagram proposed is universal. A identical phase diagram was proposed using quadrupolar approximations [43]. A parameter $\rho = \frac{T_{N_B - N_U}}{T_{(N_U - I)}}$, is defined as ratio of transition temperature $N_B - N_U$ to $I - N_U$ [44]. It was found that $\rho$ was almost independent of the parameter $\gamma$, and interpreted as a quantitative indication that the term $\lambda$ is the dominant biaxial interaction (equation 4.1.2). Hence a tri-critical line could be drawn in figure 4.3 (the thick black line intersecting at C). This parameter is not defined beyond $\lambda = 0.22$, as a uniaxial nematic phase does not exist and a direct $I - N_B$ transition occurs. Hence a triple point line can be defined in the triangle that intersects at C (figure 4.3). Moving in the triangle along either $\gamma$ or $\lambda$ axis gave a understanding to the occurrence of tri – critical and triple point. Bifurcation analysis was done to obtain a profile of free energy using the equilibrium free energy for $\lambda=0.174$ and $\gamma=0.193$. Its seen that a definite first order transition occurred from isotropic to uniaxial nematic region. The order of uniaxial nematic to biaxial nematic did depend on the values of the parameters ($\lambda, \gamma$).

This present work attempts to study the biaxial lattice Hamiltonian by generating the phase diagram in the ($\gamma, \lambda$) space and tries to look for a criteria that stabilizes or otherwise, a biaxial phase. In our attempt to do this we have used a pair-wise interaction potential.
Figure 4.2: The phase diagram proposed with the parameter $\gamma = 0$ and varying $\lambda$ (reference [43] figure 6)

Figure 4.3: Contour map of the ratio $\rho := T_{N_B-N_U}/T(N_U - I)$ between the biaxial-uniaxial temperature and isotropic-uniaxial temperature as a function of the parameters $(\gamma, \lambda)$ restricted to the triangle. (reference [44] figure 3(a))
4.2 Model Used and Computational details.

From this simple model 4.1.2 a Hamiltonian was derived where the orientations of the spins determine the interaction energy between two particles [39]. 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 $\mu$ and $\nu$, 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 $w_{\mu,k}$. Here, for a given j, $u_j$ and $v_j$ have the same functional dependence on $\omega_\mu$ and $\omega_\nu$, respectively. Let $\tilde{\Omega} = \Omega_{\mu\nu}$ denote the set of Euler angles defining the rotation transforming $u_i$ to $v_j$. Then we define,

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

(4.2.1)

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

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

(4.2.2)

Here $\epsilon$ denotes a positive constant setting the energy scales. The reduced temperature in turn is defined in terms of this energy scale as $T^* = k_B T/\epsilon$. $|\Gamma|$ and $|\Lambda|$ are often taken lesser than one. The parameters $\Gamma$ and $\Lambda$ in the equation 4.2.2 have a one – to – one mapping to the parameters $\gamma$ and $\lambda$ in the equation 4.1.2. Setting these two terms to zero of course corresponds to reducing the above potential to Lebwohl-Laser model. It was shown that a
biaxial phase does not appear when a simulation is done keeping the third term as zero, i.e. \( \Lambda = 0 \) [23]. An approximation proposed on equation 4.2.2, is the London-de Born-Heller approximation where, \( \Lambda = \Gamma^2 \).

Monte Carlo simulations using this model (equation 4.2.2) were carried out earlier in detail setting the parameter \( \Gamma = 0 \). Based on the mean field considerations it is argued that a second order uniaxial to biaxial transition occurs for \( 0 < \Lambda \lesssim 0.22 \), a first order transition for \( 0.20 < \Lambda \lesssim 0.22 \), and finally a direct transition from isotropic to biaxial nematic phase for \( \Lambda > 0.22 \) [39]. It was seen that for simulations within \( \Lambda = 0.24 \) did not show a direct transition from \( N_B \) to isotropic, but there was a uniaxial nematic present for a small range of temperature [45]. A direct transition from \( I - N_B \) did occur at \( \Lambda = 0.30 \). This simulation showed that there is one point of \( \Lambda \) where two transitions collapsed into one in the region \( 0.24 \leq \Lambda \leq 0.30 \) for \( \Gamma = 0 \).

In the light of these earlier prediction and simulations, we take up in this study a detailed simulation of the above model spanning the parameter space \((\Gamma, \Lambda)\), but without restricting the Hamiltonian to dispersive force approximation. In this context, we consider a \( 20 \times 20 \times 20 \) cubic lattice of biaxial molecules interacting through a pair-wise, restricted to a nearest neighbors, through the potential (equation 4.2.2) as mention above. Every lattice points is considered as biaxial molecule defined by a set of orientation vectors \((us, vs)\). These do not have the translational degrees of freedom. Each distinct system is characterized by the specifications of the values of \( \Gamma \) and \( \Lambda \). Metropolis algorithm with Boltzmann sampling is used to equilibrate this system, typically requiring 250,000 Monte Carlo lattice starting from an arbitrary initial condition of the orientation of different molecules. Equilibrium ensembles were collected over 250,000 microstates at every temperature. The temperature is varied from 4.0 to 0.05 in steps of 0.0395. The equilibrium ensemble is used to compute average of different relevant quantities, such as \( R_{00}^2, R_{02}^2, R_{20}^2 \) [46] [47] [17]. average energy and the specific heat (Details on the computation of these parameters is discussed in Chapter 2).
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Table 4.1: The values of all the Γ and Λ values used in equation 4.2.2. (4f system - system with Γ=0.3 Λ=0.5, second column refers to Γ values, columns a to k gives the Λ values)
4.3 Results and Discussion

The effect of the two parameters ($\Gamma$ and $\Lambda$) was studied by choosing systematically different values of them, and simulating the resulting systems. For the various systems in the table 4.1, the relevant physical parameters were computed as a function of temperature. The parameter $\Gamma$ was varied from 0 to 1 in steps of 0.1. For every $\Gamma$, $\Lambda$ was changed from 0 to 1 in steps of 0.1; a variation with a resolution of 0.01 was effective if necessary for a more detailed study. Table 4.1 gives the details of the variation of the two parameters along with the nomenclature followed to refer to a specific system of study.

4.3.1 Simulation details for $\Gamma = 0.0$

From the Table 4.1 for the value of $\Gamma = 0.0$, it is seen that $\Lambda$ is changed from 0.0 to 1.00. For $\Lambda = 0.0$ this system is just the LL model as in the Hamiltonian 4.2.2, the terms with the biaxial interactions being set to zero. Increasing the value of $\Lambda$ to 0.1, it is seen that there are two transitions occurring: first transition from uniaxial nematic ($N_U$) to a biaxial nematic phase ($N_B$) occurring at $T_{C1} = 0.6$, a second transition from a disordered phase to a uniaxial nematic phase $N_U$ at $T_{C2} = 1.1165$. Figure 4.4 gives the details of the various parameters obtained for this set of parameters $\Gamma = 0.0$ and $\Lambda = 0.1$ (Set 1b in Table 4.1). The biaxiality parameter $R^2_{22}$ for this set of parameter $\Gamma = 0.00$ and $\Lambda = 0.1$ has a maximum value of 0.65 at the low temperature indicating the least temperature phase is a biaxial nematic phase ($N_B$). For $\Lambda = 0.2$ it is seen that $T_{C1} = 1.119$ and $T_{C2} = 1.195$, the uniaxial nematic phase is still present though for a small range of temperature. For values of $\Lambda$ beyond 0.26, it is seen that there exits only one transition, a $I - N_B$. It is observed in figure 4.5, that there is just one peak in the specific heat, and both $R^2_{00}$ and $R^2_{22}$ become non-zero at this transition temperature. Plotting all the specific heat profiles corresponding to different $\Lambda$ values for $\Gamma = 0.0$, it is seen that for lower values of $\Lambda$ there are two transitions and for higher values of $\Lambda$ there is only one transition (figure 4.6). In the figure 4.7, plotting the transition temperatures $T_C$ values (obtained from the location of
Figure 4.4: Variation of (a) order parameter, (b) biaxiality parameter, (c) specific heat ($C_V$), (d) Energy, (e) $R_{02}$, (f) $R_{20}$ with temperature for a system with the parameter $\Gamma = 0.0$ and $\Lambda = 0.1$.

Figure 4.5: Variation of (a) order parameter, (b) biaxiality parameter, (c) specific heat ($C_V$), (d) Energy, (e) $R_{02}$, (f) $R_{20}$ with temperature for a system with the parameter $\Gamma = 0.0$ and $\Lambda = 0.8$. 
$C_V$ peaks) against $\Lambda$, a phase diagram at $\Gamma = 0.0$ is obtained. With the initial increase in 
$\Lambda$, there are two transitions present, first from a uniaxial nematic phase to a biaxial nematic 
phase, and the second from uniaxial nematic phase to the isotropic phase.

As the value of $\Lambda$ is increased, the specific heat peaks comes closer and collapses into 
a single peak at $\Lambda = 0.26$. When $\Lambda$ was increased beyond 0.26, a direct transition occurs 
from biaxial nematic ($N_B$) to isotropic phase ($I$). The phase diagram simulated here for 
$\Gamma = 0.00$, is in agreement to that obtained through mean filed consideration [43]. A direct 
$I - N_B$ transition occurred after $\Lambda$ was increased beyond 0.26, in agreement with reference 
[45]. It may be noted that in the earlier Monte Carlo simulations [45] also two transitions 
ocurred at $\Lambda = 0.24$, which is beyond the value predicted by mean filed studies. Our 
present results are in agreement with these simulation results.

4.3.2 Simulation details for $\Gamma = 0.1$

Increasing $\Gamma$ to 0.1 indicates that the interaction between the uniaxial and biaxial terms in 
the Hamiltonian (Equation 4.2.2) increases. For lower values of $\Lambda$ it is seen that there are 
two transitions occurring, at the first the order parameter $R_{00}^2$ becomes non zero, and at the 
second $R_{22}^2$ also becomes non–zero value. Figure 4.9 gives the different order parameters 
that were computed for the systems with $\Gamma = 0.1$ with various values of $\Lambda$ (Table 4.1: 
systems 2a to 2k). It is seen that for lower values of $\Lambda$ there exists two transitions: first 
$T_{C1}$ from biaxial nematic $N_B$ to a uniaxial nematic $N_U$. The higher transition temperature 
$T_{C2}$ corresponds to the transition from uniaxial nematic to a isotropic phase (figure 4.10). 
Plotting the specific heat against temperature for different values of $\Lambda$, it is observed that 
in this case the range of $\Lambda$ values over which a direct transition from isotropic to biaxial 
phase reduces considerably (figure 4.11). With the increase in $\Lambda$ till 0.25, two transitions 
are observed. The two transitions collapsed to a single transition after $\Lambda = 0.25$, indicating 
a direct transition occurring from a isotropic phase to a biaxial nematic phase. Unlike 
$\Gamma = 0.0$, it is seen that there are again two transitions possible beyond $\Lambda = 0.5$, first from 
the isotropic to uniaxial nematic and then from uniaxial nematic to a biaxial nematic phase.
Figure 4.6: The specific heat with temperature at different $\Lambda$ values.

Figure 4.7: The phase diagram for $\Gamma=0.00$, taking the transition temperature from the peak position(s) of the specific heat data for every system by changing the $\Lambda$ value ($T_1$ – transition temperature from state $N_U$ to $N_B$ and $T_2$ – transition temperature from $N_U$ to isotropic phase).
Figure 4.8: $R_{00}^2$ and $R_{22}^2$ with variation in temperature for different values of $\Lambda$ keeping $\Gamma = 0.1$.
Figure 4.10: The specific heat with temperature at different $\Lambda$ values.

Figure 4.11: The phase diagram for $\Gamma=0.10$, taking the transition temperature from the peak position(s) of the specific heat data for every system by changing the $\Lambda$ value ($T_1$ – transition temperature from state $N_U$ to $N_B$ and $T_2$ – transition temperature from $N_U$ to isotropic phase).
### 4.3.3 Simulation details for $\Gamma = 0.2$

This section deals about the 11 systems studied by keeping the parameter $\Gamma = 0.2$ corresponding to the systems 3a to 3k in the Table 4.1. Keeping $\Gamma = 0.2$, $\Lambda$ was changed from 0 to 1.00. The specific heat plots against temperature for the different values of $\Lambda$ were plotted together to look for the different phases formed (figure 4.12). Considering the transition temperatures from the specific heat profiles a phase diagram was plotted for the different values of $\Lambda$ (figure 4.13). It is observed that beyond $\Lambda = 0.2$ there is only one transition, — a direct isotropic — biaxial nematic transition. A more detailed study was done around this point to determine more accurately the value of $\Lambda$ where the two transitions ($N_U - N_B$ and $I - N_U$) collapsed to one ($I - N_B$). Similarly for values of $\Lambda$ beyond 0.5, similar study with a finer variation in the value of $\Lambda$ was carried out to obtain an accurate estimate of $\Lambda$ value where the single transition splits into two. Figures 4.14 and 4.15 give the different parameters computed for two systems with the parameters ($\Gamma = 0.2$ and $\Lambda = 0.22$) and ($\Gamma = 0.2$ and $\Lambda = 0.23$), respectively. It is clear from these plots how the phases of the system change qualitatively with the change in $\Lambda$ for the specific value of $\Gamma$.

### 4.3.4 Simulation details for $\Gamma = 0.3$

Figure 4.16 gives the various physical parameters computed for the system with $\Gamma = 0.3$ and $\Lambda = 0.0$. It is seen that the biaxiality parameter is nearly negligible ($\sim 0$) at the lowest temperature. There is only one transition occurring at $T_{C_2} = 1.116$, and the order parameter $R_{00}^2$ becomes non-zero at this $T_{C_2}$. It is seen that $\Lambda$ is a very important for the formation of a biaxial phase, this is in agreement to the perviously done Monte Carlo studies [48] and theoretical studies [44]. A non-zero value of $\Lambda$ is necessary to observe a biaxial phase. By just increase the $\Lambda$ value by 0.1, a very stable biaxial phase is observed for $\Gamma = 0.3$ (figure 4.17). A phase diagram for the parameter $\Gamma = 0.3$ is plotted by considering the transition temperatures from peak positions of the specific heat plots (figure 4.18). The transition temperatures are plotted against the $\Lambda$ values for $\Gamma = 0.3$ (figure 4.19). It is evident from this plot there exist two triple points, where the three phases ($I$, $N_U$, $N_B$)
Figure 4.12: The specific heat with temperature for different $\Lambda$ values.

Figure 4.13: The phase diagram for $\Gamma=0.2$, considering the transition temperature from the specific heat for every system by changing the $\Lambda$ value.
Figure 4.14: Variation of (a) order parameter, (b) biaxiality parameter, (c) specific heat \( (C_V) \), (d) Energy, (e) \( R_{02}^2 \), (f) \( R_{20}^2 \) with temperature for a system with the parameter \( \Gamma = 0.2 \) and \( \Lambda = 0.22 \).

Figure 4.15: Variation of (a) order parameter, (b) biaxiality parameter, (c) specific heat \( (C_V) \), (d) Energy, (e) \( R_{02}^2 \), (f) \( R_{20}^2 \) with temperature for a system with the parameter \( \Gamma = 0.2 \) and \( \Lambda = 0.23 \).
Figure 4.16: Variation of (a) order parameter, (b) biaxiality parameter, (c) specific heat \( (C_V) \), (d) Energy, (e) \( R_{02}^2 \), (f) \( R_{20}^2 \) with temperature for a system with the parameter \( \Gamma = 0.3 \) and \( \Lambda = 0.00 \).

Figure 4.17: Variation of (a) order parameter, (b) biaxiality parameter, (c) specific heat \( (C_V) \), (d) Energy, (e) \( R_{02}^2 \), (f) \( R_{20}^2 \) with temperature for a system with the parameter \( \Gamma = 0.3 \) and \( \Lambda = 0.1 \).
coexist, first at $\Lambda_C = 0.25$ and the other at 0.3. In the intermediate range of $\Lambda$ a direct $I - N_B$ transition occurs, is evident from the specific heat profile. For a direct $I - N_B$ transition order parameters becoming non-zero at this transition temperature $T_C$.

### 4.3.5 Simulation details for $\Gamma = 0.4$

With the increase in $\Gamma$ to 0.4, it is observed that the range of $\Lambda$ values over which a direct transition occurs from a isotropic to biaxial nematic phase are decreases. Figure 4.20 gives the specific heat computed with a temperature variation for different values of $\Lambda$ keeping $\Gamma = 0.4$. Initially for the lower values of $\Lambda$ two transitions are visible, $T_{C1}$ a $N_B - N_U$ transition and the second $T_{C2}$ a $I - N_U$ transition. There are values around $\Lambda = 0.2$ where a direct transition occurs $I - N_B$. For $\Lambda = 0.2$, a direct transition is observed from isotropic phase $I$ to a biaxial nematic phases $N_B$. This direct transition is confirmed by both the order parameters $R_{00}^2$ and $R_{22}^2$ becoming non-zero at the transition temperature $T_C = 1.156$ (figure 4.22). From these simulations there is a narrow range of $\Lambda$ values (0.19 – 0.21)where a direct transition occurs $I - N_B$ (for $\Gamma = 0.4$). It is observed that with the increase in $\Gamma$ from 0.1 to 0.4 the two triple points come closer, shrinking gradually the range of $\Lambda$ over which a direct $N_B$ phase is possible starting with the isotropic phase. It may be noted that under dispersion approximation, a direct transition is possible only for a specific value of $\Lambda$ ($1/\sqrt{6} \sim 0.416$) [25].

### 4.3.6 Simulation details for $\Gamma = 0.5$

Increasing $\Gamma$ value to 0.5, two transitions were observed when the specific heat with temperature was plotted for different values of $\Lambda$ (figure 4.23). The triple points observed for $\Gamma = 0.4$, do not appear any more on further increasing the $\Gamma$ value beyond 0.4. The phase diagram for $\Gamma = 0.5$ was plotted by considering the transition temperatures from the specific heat profiles (figures 4.23, 4.24). Plotting order parameters $R_{02}^2$ and $R_{20}^2$ against temperature, the signatures for the two transitions is observed (figure 4.25). Figure 4.25 (a) and (b) give the order parameter $R_{00}^2$ and biaxiality parameter $R_{22}^2$ for the system with
Figure 4.18: The specific heat with temperature at different \( \Lambda \) values.

Figure 4.19: The phase diagram for \( \Gamma = 0.3 \), taking the transition temperature from the peak position(s) of the specific heat data for every system by changing the \( \Lambda \) value (\( T_1 \) – transition temperature from state \( N_U \) to \( N_B \) and \( T_2 \) – transition temperature from \( N_U \) to isotropic phase).
Figure 4.20: The specific heat with temperature at different $\Lambda$ values.

Figure 4.21: The phase diagram for $\Gamma=0.4$, taking the transition temperature from the peak position(s) of the specific heat data for every system by changing the $\Lambda$ value ($T_1$ – transition temperature from state $N_U$ to $N_B$ and $T_2$ – transition temperature from $N_U$ to isotropic phase).
Figure 4.22: Variation of (a) order parameter, (b) biaxiality parameter, (c) specific heat ($C_V$), (d) Energy, (e) $R_{02}^2$, (f) $R_{20}^2$ with temperature for a system with the parameter $\Gamma = 0.4$ and $\Lambda = 0.2$.

parameters $\Gamma = 0.5$ and $\Lambda = 0.9$.

4.3.7 Simulation details for $\Gamma = 0.6$

For $\Gamma = 0.6$ similar to $\Gamma = 0.5$, it is observed that there is always a uniaxial nematic phase present for every $\Lambda$ value. The lowest temperature phase can be reached through uniaxial nematic phase, i.e. the phase sequence is always $I \rightarrow N_U \rightarrow N_B$. It is seen that on increasing $\Gamma$ the interaction between uniaxial part and biaxial part increases, leading to more stable biaxial phases. The phase diagram for $\Gamma = 0.6$ was plotted by considering the transition temperatures from the specific heat profiles (figures 4.26, 4.27). On increasing $\Lambda$, it is observed that the uniaxial phase becomes more stable too for a particular value of $\Gamma$. The order parameter $R_{00}^2$ and the biaxiality parameter $R_{22}^2$ become non-zero at a higher temperature with the increase in $\Lambda$ (figure 4.28) i.e. the transition temperatures $T_{C1}$ and $T_{C2}$ increase with the increase in $\Lambda$ value. The order contributed to along the $Z$ direction due to the biaxiality at the molecular level $R_{02}^2$ and the phase biaxiality parameter are also
Figure 4.23: The specific heat with temperature at different $\Lambda$ values.

Figure 4.24: The phase diagram for $\Gamma=0.5$, taking the transition temperature from the peak position(s) of the specific heat data for every system by changing the $\Lambda$ value ($T1$ – transition temperature from state $N_U$ to $N_B$ and $T2$ – transition temperature from $N_U$ to isotropic phase).
Figure 4.25: Variation of (a) order parameter, (b) biaxiality parameter, (c) specific heat ($C_V$), (d) Energy, (e) $R_{02}^2$, (f) $R_{20}^2$ with temperature for a system with the parameter $\Gamma = 0.5$ and $\Lambda = 0.9$

plotted as a function of temperature for different values of $\Lambda$ at $\Gamma = 0.6$.

4.3.8 Simulation details for $\Gamma = 0.7$

When the $\Lambda = 0.7$, it is seen that a biaxial phase is not observable (figure 4.30). The biaxiality parameter is negligible at the least temperature, there is only one transition observed at $T_C = 1.077$. These results are in agreement with the earlier Monte Carlo studies, and also predictions based on mean – filed considerations. These point out the dominant value of the term in the Hamiltonian in the formation of biaxial phase. This phenomenon is observed for all $\Gamma$ with $\Lambda = 0.0$. The phase diagram showed that a very stable uniaxial nematic phase is present for all the values of $\Lambda$. It is seen that increasing the value of $\Gamma$ from 0.5 to 0.7, a more stable uniaxial nematic phase forms. Figures 4.31 and 4.32 give the specific heat profiles with temperature for different values of $\Lambda$ and the phase diagram obtained for $\Gamma = 0.7$, respectively.

4.3.9 Simulation details for $\Gamma = 0.8$

Considering the different values of $\Lambda$ from the Table 4.1 for $\Gamma = 0.8$, a phase diagram was plotted by considering the transition temperatures from the specific heat profiles (figures 4.33, 4.34). The uniaxial nematic phase becomes stable with the increase in $\Lambda$. The
Figure 4.26: The specific heat with temperature at different $\Lambda$ values.

Figure 4.27: The phase diagram for $\Gamma=0.6$, taking the transition temperature from the peak position(s) of the specific heat data for every system by changing the $\Lambda$ value ($T_1$ – transition temperature from state $N_U$ to $N_B$ and $T_2$ – transition temperature from $N_U$ to isotropic phase).
Figure 4.28: $R^2_{100}$ and $R^2_{22}$ with variation in temperature for different values of $\Lambda$ keeping $\Gamma = 0.6$

Figure 4.29: $R^2_{20}$ and $R^2_{20}$ with variation in temperature for different values of $\Lambda$ keeping $\Gamma = 0.6$
Figure 4.30: Variation of (a) order parameter, (b) biaxiality parameter, (c) specific heat ($C_V$), (d) energy, (e) $R_{02}$, (f) $R_{20}$ with temperature for a system with the parameter $\Gamma = 0.7$ and $\Lambda = 0.0$.
Figure 4.31: The specific heat with temperature at different $\Lambda$ values.

Figure 4.32: The phase diagram for $\Gamma=0.7$, taking the transition temperature from the peak position(s) of the specific heat data for every system by changing the $\Lambda$ value ($T_1$ – transition temperature from state $N_U$ to $N_B$ and $T_2$ – transition temperature from $N_U$ to isotropic phase).
Figure 4.33: The specific heat with temperature at different $\Lambda$ values.

Figure 4.34: The phase diagram for $\Gamma=0.8$, taking the transition temperature from the peak position(s) of the specific heat data for every system by changing the $\Lambda$ value ($T_1$ – transition temperature from state $N_U$ to $N_B$ and $T_2$ – transition temperature from $N_U$ to isotropic phase).
\( R_{00}^2, R_{02}^2, R_{20}^2 \) and \( R_{22}^2 \) are plotted against temperature for different values of \( \Lambda \) for \( \Gamma = 0.8 \) (figures 4.35, 4.36).

4.3.10 Simulation details for \( \Gamma = 0.9 \)

For this particular value of \( \Gamma = 0.9 \), \( \Lambda \) values are varied from 0.0 to 1.00 in steps of 0.1 (systems 10a to 10k). For these different values of \( \Lambda \) specific heat was plotted against temperature. It is observed that there were always two transitions present. The first one occurs at a lower temperature \( T_{C1} \) - a transition from \( N_U - N_B \). The second transition occurs at a higher temperature \( T_{C2} \) a transition from isotropic phase to a \( N_U \) phase. The lower transition in some cases is seen only as shoulder in the specific heat profile, but can be readily confirmed by the variation of the biaxiality parameter \( R_{22}^2 \). Figure 4.39 shows the plots of the different parameters obtained for the system 10g in the Table 4.1. Signatures of the first transition \( (T_{C1}) \) are seen in the order \( R_{02}^2 \) and \( R_{20}^2 \) order parameters also.

4.3.11 Simulation details for \( \Gamma = 1.0 \)

For \( \Gamma = 1.00 \), similar to the lower values of \( \Gamma \) all the parameters were computed. In the Hamiltonian 4.2.2, considering \( \Gamma = 1 \), is considering the interaction between the uniaxial and biaxial terms between the neighboring particles on equal terms as the interaction between the uniaxial terms (the energy being always measured in units of \( \epsilon \)). The biaxial phase is observed as a very stable phase for all values of \( \Lambda > 0 \). The biaxial order parameter \( R_{22}^2 \) reaches a value of \( \sim 0.6 \) for the least temperature. The system order parameter becomes non - zero at the \( T_{C2} \), indicating the onset of a nematic phase. The other two order parameters \( R_{02}^2 \) and \( R_{20}^2 \) give a clear evidence of the phases (figure 4.40). Figures 4.42 gives the phase diagram for \( \Gamma = 1.00 \) by considering the transition temperatures from the specific heat profiles for the different \( \Lambda \) values (figure 4.41).
Figure 4.35: $R_{00}^2$ and $R_{22}^2$ with variation in temperature for different values of $\Lambda$ keeping $\Gamma = 0.8$.

Figure 4.36: $R_{20}^2$ and $R_{20}^2$ with variation in temperature for different values of $\Lambda$ keeping $\Gamma = 0.8$. 

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Figure 4.37: The specific heat with temperature at different \( \Lambda \) values.

Figure 4.38: The phase diagram for \( \Gamma = 0.9 \), taking the transition temperature from the peak position(s) of the specific heat data for every system by changing the \( \Lambda \) value (\( T1 \) – transition temperature from state \( N_U \) to \( N_B \) and \( T2 \) – transition temperature from \( N_U \) to isotropic phase).
Figure 4.39: Variation of (a) order parameter, (b) biaxiality parameter, (c) specific heat \((C_V)\), (d) Energy, (e) \(R_{02}\), (f) \(R_{20}\) with temperature for a system with the parameter \(\Gamma = 0.9\) and \(\Lambda = 0.6\)
Figure 4.40: Variation of (a) order parameter, (b) biaxiality parameter, (c) specific heat ($C_V$), (d) Energy, (e) $R_{02}^2$, (f) $R_{20}^2$ with temperature for a system with the parameter $\Gamma = 1.00$ and $\Lambda = 0.3$
Figure 4.41: The specific heat with temperature at different $\Lambda$ values.

Figure 4.42: The phase diagram for $\Gamma=1.00$, taking the transition temperature from the peak position(s) of the specific heat data for every system by changing the $\Lambda$ value ($T_1$ – transition temperature from state $N_U$ to $N_B$ and $T_2$ – transition temperature from $N_U$ to isotropic phase).
4.4 Conclusions

With the change in $\Gamma$ it was observed there were subtle changes in the phase diagrams obtained. For $\Gamma = 0.00$ and lower values of $\Lambda$ two transitions were observed, first a transition $N_U - N_B$ and then a higher temperature transition from $I - N_B$. It is realized that with the further increase in $\Lambda$ beyond 0.6 only a direct isotropic to a $N_B$ transition is observed. Increasing $\Gamma$ to 0.1 (Figure 4.11, 4.10), two triple points are observed when the phase diagram was plotted with $\Lambda$ variation, first at $\Lambda = 0.25$ and other at $\Lambda = 0.5$. It is seen that there is line of $\Lambda$ values where a direct transition occurs from biaxial nematic ($N_B$) to an isotropic phase. For the lower and the higher values of $\Lambda$, there was a uniaxial nematic phase present between a isotropic and a biaxial nematic phase. Further increasing $\Gamma$ to 0.2, two triple points are observed at $\Lambda = 0.25$ and $\Lambda = 0.4$ (Figure 4.19, 4.18). The phase diagram for $\Gamma = 0.3$ (Figure 4.19, 4.18) showed two triple points appearing at $\Lambda = 0.24$ and $\Lambda = 0.30$ in a similar way as $\Gamma = 0.2$. Increasing the $\Gamma$ parameter, the two triple points come closer to each other. The range of $\Lambda$ values for which a direct transition from $N_B$ to $I$ occurs decreases. With the increase in $\Gamma$ the two peaks ($N_U - N_B$ and $I - N_U$) come closer. Further for $\Gamma$ to 0.4 it is seen that there exists much lesser values of $\Lambda$ for which a direct $I - N_B$ transition occurs (Figure 4.21, 4.20). Further increasing $\Lambda$ beyond 0.21 for $\Gamma = 0.4$, no direct $I - N_B$ transition is observed. For $\Gamma = 0.5$ (Figure 4.24, 4.23) the phase diagram was plotted by considering the transition temperatures from the specific heat plots (Figure 4.23). It was observed that there were no values of $\Lambda$ for which a direct $I - N_B$ transition occurred. With further increase in $\Gamma$ the uniaxial nematic phase became more stable. There are always two transitions occurring first an $I - N_U$ and a $N_U - N_B$ with a temperature variation for every value of $\Lambda$. For $\Gamma = 0.6$ (Figure 4.27, 4.26), it is realized from the plot of the phase diagram that the uniaxial nematic phase is stable over a larger range of temperature compared to the plot of $\Gamma = 0.5$. A similar phenomenon is observed for $\Gamma = 0.6, 0.7, 0.8, 0.9, 1.0$ (Figures 4.27, 4.32 4.34, 4.38, 4.42) that a stable biaxial phase is present with the change in temperature, and occurs as a transition from a
uniaxial nematic phase. For $\Gamma = 1$ (Figure 4.42), the uniaxial phase becomes more stable, i.e. exists over a larger range of temperature. A stable biaxial phase is observed for higher values of $\Gamma$, but can be approached only from a uniaxial nematic phase.

Comparing the Monte Carlo study with the mean field work [39] and the bifurcation analysis [44] done, there are some new results obtained by doing a Monte Carlo simulations of a lattice model for biaxial liquid crystal systems. It is seen in figure 4.3 that a uniaxial nematic and a biaxial nematic phases are formed with the change in $\Lambda$ for different $\Gamma$. It is observed that there are $\Lambda$ values for which a direct $I - N_B$ transition occurs, which is not mentioned in the perviously done studies. These Monte Carlo simulations are in agreement with reference [48], where two transitions occur for $\Lambda = 0.24$ (model B1 in [48] [45]) and a $I - N_B$ transition for $\Lambda = 0.30$ (B2 model in [48] [45]). After a certain $\Lambda$ it is seen for a given $\Gamma$ there is a direct $I - N_B$ transition. Initially for lower values of $\Gamma$, say for $\Gamma = 0.1$ two transitions occur first $I - N_U$, then $N_U - N_B$, these are in agreement to what has been observed using simulations. From figure 4.3, an $I - N_B$ occurs at $\Lambda = 0.22$ for $\Lambda = 0.1$, whereas in the Monte Carlo simulation $\Lambda_{I-N_B} = 0.25$. Our simulations show that only until $\Gamma = 0.4$, there is at least a value of $\Lambda$ for which an $I - N_B$ can occur. For $\Gamma$ greater than 0.4 a uniaxial nematic phase is always present and becomes stable with increase in $\Gamma$. The bifurcation analysis studies dealt with the values of $\Gamma$ and $\Lambda$ that lay in the triangle $(0 \geq \lambda \geq 0.33$ and $0 \geq \gamma \geq 0.25)$. Both the parameters $\Gamma$ and $\Lambda$ are equally important to decide the kind of transitions occurring in a biaxial liquid crystal system. This study indicates that there exists a range of $(\Gamma, \Lambda)$ parameter where the biaxial phase cannot be reached directly from isotropic phase. In real systems a biaxial phase has not been realized in principle due to the competing mechanisms stabilizing other phases (like layered phases) after the onset of $N_U$ phase.

Monte Carlo simulations are carried out based on the Hamiltonian (equation 4.2.2) covering systematically useful range of the model parameter $[\Gamma, \Lambda]$. Resultant phase diagrams are presented for the biaxial systems. This simulation shows a triple point occurring for $\Gamma=0.0$, two triple points for $\Gamma=0.1, 0.2, 0.3$ that move closer with increase in $\Gamma$. Increasing
$\Gamma = 0.4$, only one triple point is observed. With further increase of $\Gamma$ there always exists two transitions, $I \rightarrow N_U$ and $N_U \rightarrow N_B$. This simulation shows that both the parameters are important in mediating the transitions occurring in a biaxial nematic system.

Further study of this system can be undertaken with a more improved non-Boltzmann sampling methods. Due to the many degrees of freedom present, obtaining a density of states becomes a difficult task. Using these advanced techniques the order of the transitions and the exact transition temperature can be obtained from the free energy profiles.
Bibliography


Chapter 5

Structures and transitions in hybrid films of biaxial molecules

5.1 Introduction

A thin film of liquid crystal when confined between two substrates (with larger surface dimension than the thickness) with antagonistic boundary conditions is a hybrid film. In a typical hybrid planar film nematic order is induced by the two substrates in mutually perpendicular directions along, say laboratory $z$ – axis, one in the homeotropic direction at $z = d$ (thickness of the film) and the other in the lateral (planar) direction at $z = 0$. Here we consider such thin film of biaxial liquid crystal molecules, confined in such a geometry. Monte Carlo simulations are carried out to look for details of director structures, and possible orientational transitions, as the sample is cooled from its isotropic phase.

Biaxial nematic phases continue to attract considerable attention [1] [2] both from theoretical [3] [4] [5] and experimental [6] [7] [8], points of view. Interest in biaxial liquid crystals led to many models being proposed, and these were investigated using computer simulations [9] [10]. Biaxial liquid crystals deviate from cylindrical symmetry, usually being broad-like in structure. Besides the usual ordering of long axes of the molecules (along the primary director, say) orientational ordering of the remaining axes of the molecules (leading to secondary directors, say) is an interesting possibility. This leads to an in principle possibility of using switching of the secondary direction for effecting changes in the optical properties of the medium. It is expected that rotation of the minor directors might be relatively rapid and possibly faster than for the director $\hat{n}$. This could possibly lead to
a display with a fast response and based on in-plane switching [2]. Thus, confined biaxial liquid crystals are fascinating objects of study in liquid crystal research. Such confinement effects can be mimicked in computer simulations by introducing suitable anchoring conditions at the surfaces. One such confined system recently studied is a biaxial nematic droplet [11]. The optical textures of this droplet were studied, looking for defects that can be formed in such systems. One of the well known and well investigated confined systems of liquid crystal is the hybrid film.

Interest in confined liquid crystal research is shown by both experimentalists and theoreticians. Theoretical studies using mean field methods, minimization of Franks free’s energy were studied in detail to understand the different transitions and structures that are formed [12]. Experimentalists have used different methods to understand such systems in more detail [13] [14]. Detailed investigation were also carried out by using computer simulations methods, wherein liquid crystals were modeled by lattice based models like LL model [15] or off – lattice models like Gay – Berne [16] models [17] [13] [18]. Other models used were hard spherocylinders to understand the effects of different types of substrates on liquid crystal film. Attempts were made to understand the effect of confinement comparing their differences from bulk systems. Optical textures of confined systems were simulated for both uniaxial and biaxial particles [19] [20] [21].

5.2 Hybrid film of Uniaxial Molecules

The stability of different structures of a nematic liquid crystal in a planar hybrid film was examined within the framework of a Gaussian description of order fluctuations [22] [23]. In a very thin film the director field is not bent smoothly between the two orientations induced at the two substrates, but exhibits a step-like change if the anchorings at the confining substrates are strong and comparable in magnitude. A (dis)continuous structural transition to the bent-director state, which occurs with increasing film thickness or decreasing temperature, is governed by the lowest bending director fluctuation mode. The (dis)continuity
of the structural transition depends on the temperature and film thickness. The analysis of nematic liquid crystals confined to highly constrained hybrid films with a biaxial structure has revealed a soft-mode or soft-mode-like dynamics in the vicinity of the structural transition toward hybridly aligned (bent-director) structure.

With this backdrop, Monte Carlo simulations were earlier preformed using the LL [15] lattice model. A hybrid film of liquid crystal (10 layers) was studied [24]. The existence of a biaxial phase was observed when the temperature is decreased from the isotropic phase. With further decrease in the temperature a bent-like structure is formed, that remains stable, a structural transition from biaxial-bent phases. This biaxial phase is stable only for a small range of temperature. The structural transition was monitored both by the change in order parameters and by the fluctuations in energy. These films were also investigated as a function of their thickness, and the findings are constant with prediction from phenomenological studies. To get a better understanding of this system a deeper study was undertaken using JSM modified Wang Landau algorithm [25] (Chapter 3 of the thesis). A clearer picture of the system was obtained by computing the bulk and the layer-wise order parameter at the transition. The layer-wise director angles (φ) were plotted with temperature change to map out the different structures that were formed. The exact transition temperature was confirmed by examining the features of the free energy profiles. This work is discussed in detail in the previous chapter of this thesis (Chapter 3). A similar study of a thin film of liquid crystal confined between two cylindrical hybrid film was carried out based on canonical Monte Carlo sampling methods (as reported in Chapter 3 earlier) [26]. A biaxial phase was realized for specific chosen anchoring strengths of the substrates in an intermediate range or temperatures.

The main interest in the present study lies in understanding a confined biaxial system and this was studied in detail keeping in mind the different structures seen in a hybrid film of uniaxial molecules. The objective is to look for possible effects on the self-organization of the biaxial molecules in a thin planar geometry, when subjected to a competing boundary conditions at the two surfaces. Such a film was studied based on canonical Monte
Carlo methods, as a function of temperature. All the relevant order parameters and their fluctuations were examined to look for signatures of possible intermediate stable structures which are direct consequence of hybrid boundary conditions. The motivation for this is qualitatively similar to the study of confined planar hybrid films. These simulations on biaxial systems were augmented by extending these simulation to film with variable relative anchoring strength.

5.3 Model Used and System studied

The system studied here is a planar geometry hybrid film of biaxial molecules. A hybrid film is built by inducing order into the liquid crystal system in perpendicular directions. Let us assume that \( X\ Y\ Z\ ) represent the laboratory frame and \( x\ y\ z\ ) represent the molecular frame. In order to get a hybrid nature in the liquid crystal system, the molecules of the first \((k = 1)\) and the last layer \((k = nz)\) of a cuboid are assumed as substrates or as ghost layers. The molecules at \( k = 1 \) layer are all fixed along the laboratory frame i.e. \( x \) is along \( X \), \( y \) along \( Y \) and \( z \) along \( Z \). The molecules on the substrate at \( k = nz \) are all fixed at orientations obtained by rotating the direction of the molecules on the ghost layer \( k = 1 \) by \( \pi \) about the \( X \) axis, i.e. \( x \) is along \( X \), \( y \) along \( -Z \) and \( z \) along \( Y \) (figure 5.1). The molecules on these two substrates of course do not participate in the Monte Carlo steps. Periodic boundary conditions are considered along the \( X \) and \( Y \) directions, in order to minimize the finite size effects. The system considered here is of the size \( 15 \times 15 \times 8 \ (X \times Y \times Z) \). The anchoring strengths of the two substrates are represented as \( \epsilon_1 \) and \( \epsilon_{nz} \). As usual, we represent the energy of the system in units of the coupling constant in LL potential, thereby representing the temperature of the system by a convenient dimensionless variable \( T^* \). The anchoring strength at the substrates which is the interaction constant between LC and substrate molecules is then also measured in the same units as \( T^* \).

A pairwise additive lattice Hamiltonian is used for this study [27]. The model chosen here is a lattice based Hamiltonian which has contributions from both the biaxial terms,
but requires only a simple parameter $\lambda$ for simplification. This corresponds to dispersion approximation, and has a phase diagram with a Landau point, is given as

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

$\epsilon, \lambda$ are positive constants, with $\epsilon$ being set to unity as mentioned above. $\lambda$ is the biaxiality parameter, and defines the amount of molecular biaxiality in the system. In this problem the study is done by considering the biaxiality parameter as $\lambda = 0.35$. Below the tri-critical point the molecules are known to be prolate in shape. Considering the biaxiality parameter as 0.35 has a certain significance, at this value of $\lambda$ the two transitions were clearly apart, with a range of temperature having a biaxial phase (figure 5.2).

This model was preferred over other that proposed by Romano [29] for the ease of computation and, is based on the Born-de-London’s approximation. This model was earlier studied in detail using Monte Carlo methods and mean field methods [28] [27]. It is known from the previously done Monte Carlo studies that the molecules are known to be prolate in shape for values of $\lambda$ below the tri – critical point ($\lambda = 1/\sqrt{6}$) and oblate else. Using the above mentioned Hamiltonian a droplet was studied using Monte Carlo simulations [11].

A hybrid film of biaxial molecules was studied using Markov Chain Monte Carlo methods with Metropolis algorithm (Chapter2 of the thesis for the details). This system was equilibrated for half a million Monte Carlo runs and a productions run of half a million
Biaxial Hybrid film

Figure 5.2: Phase diagram proposed for the hamiltonian 5.3 [28]

runs also. The average energy and the fluctuations in energy (specific heat) were computed for the system. Different order parameters $R_{00}, R_{02}, R_{20}, R_{22}$ were computed along with their fluctuations for the system [30]. The way these parameters are computed is given in detail in Chapter 2 of this thesis and Chapter 1 of this thesis contains the physical meaning of every parameter.

5.4 Results and Discussions

A planar thin film with dimensions $15 \times 15 \times 8$ in lattice units is considered for the present study, with periodic boundary conditions being imposed in the $x$ and $y$ directions. A layer of liquid crystals are placed at the two bounding surfaces in the $Z$ – direction, called the ghost layers to represent the effect of substrates. These substrate molecules are oriented suitably to induce boundary conditions of choice and are held fixed throughout the simulation (figure 5.1). The initial configuration of the LC system is taken as random i.e. all the liquid crystal molecules are initialized in random directions. The system is simulated at different temperatures (reduced units) 2.00 to 0.01, in steps of 0.005, yielding 400 data sets to investigate temperature dependencies. The system was equilibrated for 50,000 Monte