STATISTICAL PHYSICS OF MODULATED PHASES
IN NEMATIC LIQUID CRYSTALS

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by

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CHAPTER 1

Introduction

It was long believed that matter exists in three states: solid, liquid and gas. This idea was proved to be wrong in 1888 after Reinitzer [1] found that some cholesterol derived organic compounds undergo a cascade of melting transitions on heating. In those pioneering experiments, he observed that a solid crystal melted into a cloudy liquid, after which it transformed into a transparent liquid. These intermediate phases between solid and liquid are called mesophases or liquid crystalline phases. The study of these liquid crystalline phases has now become one of the intriguing aspects of the theory of soft matter.

This chapter presents a basic theoretical description of the most common liquid crystalline phase: the conventional nematic phase, and then discusses the modulated chiral phase. We first develop the nematic orientational order parameter that arises due to the symmetry breaking transition from the high temperature disordered phase to the low temperature ordered phase. The orientational order parameter of the nematic phase is a tensor quantity that has a unique eigen vector called the director. The other two eigen vectors are degenerate. For the magnitude of the order parameter, we present the Landau-de Gennes theory of the isotropic-nematic transition [2, 3]. For the eigen vectors of the order, we construct the Frank free energy, and use this free energy to describe the modulated structure in nematic liquid crystals where molecular chirality plays an important role in forming this phase with micro-scaled one dimensional periodicity.
On the other hand, molecules that are achiral and polar also tend to form a periodic structure. Examples are banana-shaped molecules or pear-shaped molecules, or molecules that have large electric dipoles. These features reduce the molecular symmetry compared to that of a cylindrical rod. In this class of materials there is an important physical effect called the flexoelectric effect, discovered by R. B. Meyer in 1969 [4], in which the polar order is linearly coupled to the director gradients. Polarity driven modulation due to this flexoelectric effect is the central idea we will be putting forward in this dissertation. This chapter will conclude by discussing some computation techniques adopted to develop a simulation strategy for finding new physics discussed in this dissertation project.

1.1 Broken Symmetry and Order

Symmetry plays an important role in understanding the phases of a physical system. For a physical system we look for a specific symmetry that is preserved by the system. Knowing that symmetry we can determine how much the order is developed when symmetry breaks in some particular way. In liquids and crystals there are two key ideas regarding order and symmetry [2, 3]:

(1) Crystals have certain special positions called lattice sites (as a periodic array) where there is a maximum probability of finding an atom or center of mass of a molecule (crystals are nonuniform), but there is no special positions in liquid, all positions are equivalent (liquids are uniform). This difference can be understood experimentally when we study the properties of liquids and crystals using the x-ray diffraction technique. In this technique we can obtain the x-ray diffraction pattern which reveals the non uniformity of crystals by giving distinct peaks of x-ray intensity as a function of incident and diffraction angles for crystals. These peaks are called
Bragg peaks. For a liquid there are no Bragg peaks. For this reason, we say that
crystals have less symmetry than liquids because the perfect positional symmetry of
a liquid is broken in a crystal. In this terminology an order parameter arises due to
that broken symmetry in crystals.

(2) Crystals have certain special directions called the crystalline axes where there
is a maximum probability of finding a collection of atoms (crystals are anisotropic),
but there is no special direction in a liquid, all directions are equivalent (liquids are
isotropic). This difference can also be understood experimentally when we study the
macroscopic optical properties of liquids and crystals. For this reason, we say that
crystals have less symmetry than liquids because the perfect orientational symmetry
of a liquid is broken in a crystal. In this terminology an orientational order arises due
to that broken symmetry in crystals but not in liquids.

Liquid crystal phases or mesophases are intermediate between liquids and crystals
because they have partial order. In some liquid crystals only orientational order is
present, others have both orientational order and positional order (along one or two
space dimensions). But, it is impossible to have positional order without at least
some orientational order in liquid crystal materials. Positional order requires some
crystalline axes, which select certain directions in space. Moreover, in the field of
molecular crystals it is possible to have transitions among phases with different types
of orientational order. The basic concept behind only having orientational order
without positional order lies in the fact that the molecules forming the phase are not
spherically symmetric. So with these asymmetric shapes (such as rod-like molecules)
when they are aligned with their neighbors, the positions of the molecular centers of
mass can be random resulting in a long-range order in the orientation of molecular
alignment.

As an example, Fig. 1.1(a) shows an extensively studied organic molecule of 4-cyano-4'-pentylbiphenyl. In short, it is called 5CB. Most importantly, this molecule forms a liquid crystal phase. It has a longitudinal electric dipole moment due to the CN triple bond. Ignoring the details, a schematic representation of such a molecule can be shown by an arrow as depicted in Fig. 1.1(b). For a collection of such molecules one would want to study the molecular organization from a statistical physics perspective.

Fig. 1.2 shows three possible molecular orientations for a collection of 5CB molecules which have a permanent longitudinal dipole moment in them. At high temperature they form an isotropic phase of these molecules, with disorder in molecular axes where the arrows are equally likely to orient in any direction in 3D space as shown in Fig. 1.2 (a). As the temperature decreases they form a nematic phase, in which the axes of the molecules tend to align up or down along an axis. Suppose this axis is $\pm z$ as shown in Fig. 1.2 (c). Instead, if all the molecules on average tend to align along a particular direction, we would have a polar phase. From the symmetry and order perspective, the isotropic phase is the most symmetric because all directions are equivalent, and hence least order. On the other hand, the polar
Figure 1.2: Distribution of molecules in (a) isotropic phase (b) polar phase and (c) nematic phase
phase is the least symmetric because it has picked a special direction in 3D space, \( +z \) in the example shown in Fig. 1.2 (b), hence it has the most order. The nematic phase is in between because it has picked an axis (two special directions) in 3D space. It is more symmetric than polar but less symmetric than isotropic. Or in other words it has more order than isotropic but less order than the polar phase.

### 1.2 Order Parameter and Phase Transition

In order to construct the order parameter of different phases, we must calculate the ensemble average of the molecules constituting the phase. We look back at the symmetry and order argument from the last section where we stated that the isotropic phase has the least order, the polar phase has the most order, and the nematic phase has intermediate order. Since molecules are randomly oriented in 3D in an isotropic phase, the ensemble average will be zero in this phase. If we represent the orientation of each molecule as a unit vector \( \hat{l} \) and after taking ensemble average we get

\[
P_x = \langle \hat{l} \cdot \hat{x} \rangle \quad (1.1)
\]

Or if we generalize by calling the alignment direction \( \hat{n} \) instead of \( \hat{x} \), and allowing \( \hat{n} \) to vary slowly in space, \( P = \langle \hat{l} \cdot \hat{n} \rangle \) and \( P = P\hat{n} \). We understand that the quantity \( P \) is zero in the isotropic phase and non-zero in the polar phase. But, it does not respect the symmetry property of the nematic phase where \( -\hat{n} \) and \( \hat{n} \) are equivalent. So we can not take \( P \) as an order parameter for the nematic phase. but \( P \) could well be the order parameter for the polar phase. To construct the nematic order parameter we need some quantity that does respect the nematic symmetry property, and also becomes zero in the isotropic phase. A scalar order parameter might be \( \langle (\hat{l} \cdot \hat{n})^2 \rangle \),
but in the isotropic phase, the ensemble average is 1/3, so instead the scalar order parameter is

\[ S = 1/2 \left[ 3 \left( \langle \hat{l} \cdot \hat{n} \rangle^2 \right) - 1 \right] \]  

(1.2)

The factor of 1/2 is arbitrary, but it makes \( S = 1 \) for \( \hat{l} \) always parallel or anti-parallel to \( \hat{n} \). Including the directional aspect the complete order parameter becomes the traceless combination of \( \hat{n} \times \hat{n} \) and the identity tensor:

\[ Q_{\alpha\beta} = S \left[ \frac{3}{2} n_{\alpha} n_{\beta} - \frac{1}{2} \delta_{\alpha\beta} \right] \]  

(1.3)

The scalar order parameter gives the magnitude of the order present in different phases. It is zero in the isotropic phase and one in the perfectly aligned nematic phase. The second part \( \left[ \frac{3}{2} n_{\alpha} n_{\beta} - \frac{1}{2} \delta_{\alpha\beta} \right] \) describes the direction of the nematic order, where the unit vector \( \hat{n} \) is the local nematic director.

Notice that \( Q_{\alpha\beta} \) is symmetric and traceless. For a general second-rank tensor there are nine components. As \( Q_{\alpha\beta} \) is symmetric and traceless, the total degrees of freedom becomes five (9-(3+1)). Two of them are associated with the nematic director \( \hat{n} \), being a unit vector. Another is for the scalar order parameter. The remaining two are related to biaxiality of the phases; biaxial order and direction. In this case we need to consider one more special direction which is perpendicular to the main director \( \hat{n} \).

Now we will discuss a well established macroscopic theory of the isotropic-nematic phase transition called the Landau-de Gennes theory. The basic concept of this theory is to construct the free energy as a function of the tensor order parameter \( Q_{\alpha\beta} \). Assuming that the order parameter \( Q_{\alpha\beta} \) is small we can construct the free energy
density as a power series expansion in $Q_{\alpha\beta}$ as follows:

$$f = f_0 + \frac{1}{2}A Q_{\alpha\beta} Q_{\alpha\beta} + \frac{1}{3} B Q_{\alpha\beta} Q_{\alpha\gamma} Q_{\gamma\alpha} + \frac{1}{4} C (Q_{\alpha\beta} Q_{\alpha\beta})^2$$  \hspace{1cm} (1.4)$$

where we kept only first four terms in the expansion, and the coefficients $A$, $B$ and $C > 0$ are arbitrary. A list of 4 Q’s such as $Q_{\alpha\beta} Q_{\alpha\gamma} Q_{\gamma\delta} Q_{\delta\alpha}$ is not independent from the C term above. Here we have not included terms involving gradients of $Q_{\alpha\beta}$ such as $(\partial_{\alpha} Q_{\beta\gamma})(\partial_{\alpha} Q_{\beta\gamma})$. We will discuss these terms later.

We can simplify the terms in $f$ using the $Q_{\alpha\beta}$ tensor definition of Eq. (1.3). The result is

$$f = f_0 + \frac{1}{2}a S^2 + \frac{1}{3} b S^3 + \frac{1}{4} c S^4$$  \hspace{1cm} (1.5)$$

where $a = 3A/2$, $b = 3B/4$ and $c = 9C/4$.

For the free energy to be stable we must have $c > 0$. We eliminate the unphysical occurrence of a negative order parameter state by choosing $b$ to be negative, and we assume $a$ is a linearly increasing function of temperature. Figure 1.3 shows four plots of the free energy density as a function of $S$ for decreasing values of $a$, while $b$ and $c$ are fixed. At high temperature, the free energy has one minimum at $S = 0$, which corresponds to the isotropic phase as shown in Fig. 1.3(a). As temperature decreases, the free energy also gets a metastable nematic minimum for non-zero positive $S$ as shown in Fig. 1.3(b). If we decrease the temperature further we end up having two equally deep minima as shown in Fig. 1.3(c). This is a first order transition point from the isotropic phase to the nematic phase. If we decrease the temperature further we will get a stable minimum in the nematic phase $(S > 0)$, while there is also a metastable minimum at $(S = 0)$. When $a$ is negative there is a metastable
minimum for \((S < 0)\) and a stable minimum at \((S > 0)\).

To find the analytical solution of the order parameter that minimizes the free energy we take the derivative of the free energy density and set it equal to zero.

\[
\frac{\partial f}{\partial S} = a(T)S + bS^2 + cS^3 = 0 \quad (1.6)
\]

The solutions to Eq. (1.6) are

\[
S = 0, \frac{-b + \sqrt{b^2 - 4ac}}{2c}, \frac{-b - \sqrt{b^2 - 4ac}}{2c} \quad (1.7)
\]

We evaluate the free energy at each solution and compare them to find which solution minimizes the free energy for each temperature. The temperature at which the isotropic-nematic transition takes place can be determined by equating the free energy of the isotropic phase\((S = 0)\) to that of the nematic phase\((S \neq 0)\) i.e.,

\[
f(S = 0, T = T_c) = f(S \neq 0, T = T_c) \\
0 = \frac{a(T_c)S^2}{2} + \frac{1}{3}bS^3 + \frac{1}{4}cS^4 \quad (1.8)
\]

Solving Eqs. (1.6) and (1.8), we have

\[
S(T_c) = 0, -\frac{2b}{3c} \quad (1.9)
\]

The corresponding transition temperature is
Figure 1.3: Plots of free energy density as a function of order parameter $S$ with different values of coefficient $a$, but coefficients $b$ and $c$ are held constant ($b = -1, c = 1$, ignoring units here which are not important in this context) (a) in the isotropic phase far away from isotropic-nematic transition (b) in the isotropic phase a little above transition (c) at the isotropic-nematic transition and (d) in the nematic phase below the isotropic-nematic phase transition.
\[ a(T_c) = \frac{2b^2}{9c} \quad (1.10) \]

We assume \( a \) varies linearly with temperature as \( a = a'(T - T_0) \), where \( T_0 \) is the super-cooling limit of the isotropic phase i.e. the metastable minimum of the isotropic phase exists down to temperature \( T_0 \). Hence eq. (1.10) becomes

\[ T_c = T_0 + \frac{2b^2}{9a'c} \quad (1.11) \]

Figure 1.4 shows the order parameter plot as a function of temperature, which shows that as the temperature decreases from high temperature, at transition temperature \( T_c \) the system goes to the ordered nematic phase. Below \( T_c \) the order parameter increases by following the second solution of eq.(1.7).

Besides the Landau-de Gennes macroscopic theory there are also microscopic theories namely, the Maier-Soupe [5] and Onsager [6] theories of the nematic-isotropic transition. Those will not be needed in this dissertation.

In the above we saw the Landau-de Gennes free energy density deals with the magnitude \( S \) of the nematic order and describes the isotropic-nematic phase transition of liquid crystals. But it does not determine the orientation \( \hat{n} \) of nematic order unless terms involving gradients of \( Q_{\alpha\beta} \) are included. The ground state of a nematic liquid crystal consists of the director \( \hat{n} \) pointing in the same direction everywhere. Any kind of local deviation from this direction is a deformation that involves a certain amount of elastic energy cost. As \( \hat{n}(r) \) varies in space, the free energy depends on the details of the vector field \( \hat{n}(r) \). With all its local variations a vector is known if we know its
Figure 1.4: Order parameter plot as function of quadratic coefficient $a$ while $b = -1$ and $c = 0.9$
divergence, $\nabla \cdot \hat{n}$, and curl, $\nabla \times \hat{n}$, everywhere. This spatial variation in $\hat{n}$ can be described with the Frank-Oseen elastic free energy of nematic liquid crystals

$$F = \frac{1}{2}K_1S^2 + \frac{1}{2}K_2T^2 + \frac{1}{2}K_3B^2$$

(1.12)

Here the vectors $S = \hat{n} (\nabla \cdot \hat{n})$ and $B = \hat{n} \times (\nabla \times \hat{n})$ represent splay and bend distortions respectively and the pseudo-scalar (it changes sign on reflection in a plane parallel to the twist axis or when we go from a right handed to a left-handed reference frame) $T = \hat{n} \cdot (\nabla \times \hat{n})$ represents twist distortions, which is the component of $\nabla \times \hat{n}$ along the director, whereas the bend is described by a vector with the component of $\nabla \times \hat{n}$ perpendicular to the director. Note that we write the splay vector as $S = \hat{n} (\nabla \cdot \hat{n})$ instead of splay scalar $S = \nabla \cdot \hat{n}$ because the scalar violates the symmetry $\hat{n} \leftrightarrow -\hat{n}$. In fact the elastic free energy was first derived by Oseen [7] in 1928 by invoking that symmetry and rederived thirty years later by Frank in a very influential paper [8].

The terms $(\partial_\alpha Q_\beta)(\partial_\alpha Q_\beta)$, $(\partial_\alpha Q_\alpha\beta)(\partial_\gamma Q_\gamma\beta)$, $(\partial_\alpha Q_\beta\gamma)(\partial_\beta Q_\alpha\gamma)$ that are possible in the Landau-de Gennes theory produce the three terms appearing in eqn. (1.12) as well as additional term: $\nabla \cdot (S + B), \nabla S \cdot S$ and $\nabla S \cdot B$. By Green’s theorem, the $\nabla \cdot (S + B)$ term in the free energy density depends on the normal component of $S$ and $B$ at the surface of the sample and therefore is called a surface elastic term. It can be neglected in this dissertation. Similarly $\nabla S$ has been found to be significant only near surfaces or defects, and we will neglect them. Finally, Landau-de Gennes theory requires higher order terms like $Q(\partial Q)(\partial Q)$ to obtain $K_1 \neq K_3$. 

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1.3 Modulated Phases in Nematic Liquid Crystals

So far we have dealt with liquid crystal molecules that are not chiral. Chirality means an object that is different from its mirror image i.e it cannot be superimposed on its mirror image through any rotation. Now we will consider chiral molecules and their resulting phase behavior. They pack together with a certain favored twist, and the mirror-partner packed together with the opposite favored twist. To understand this concept we can think of a collection of hard screws which are chiral objects, and hence they are different from their mirror images. When screws pack in the most possible compact way, their threads fit together. They are not parallel to their neighbors. Instead, they make a small twist angle with their neighbors. For a chiral liquid crystal, due to this favored twist the Frank free energy of eq.(1.12) can also have an extra term that is linear in twist ($T$). By completing the square with this linear term we can write the Frank free energy density as
\[ F = \frac{1}{2}K_1S^2 + \frac{1}{2}K_2(T - q)^2 + \frac{1}{2}K_3B^2 \]  \hspace{1cm} (1.13)

We can see from eq.(1.13) that the minimum free energy for a chiral liquid crystal has zero splay and bend \((S = B = 0)\), but non-zero twist \((T = q)\). The linear term breaks the symmetry between left-handed twist \((T > 0)\) and right-handed twist \((T < 0)\). If \(q > 0\) then left-handed twist is favored, and oppositely right-handed twist is favored when \(q < 0\).

The free energy structure is the one-dimensional modulated/periodic structure shown in Fig. 1.6 (called the cholesteric liquid crystal phase). The director field of these structures can be expressed mathematically as

\[ \hat{n} = \cos(qz) \, \mathbf{x} + \sin(qz) \, \mathbf{y} \]  \hspace{1cm} (1.14)

The periodicity of the modulation is defined by the wave vector \(q\). i. e. the periodicity is \(\frac{\pi}{q}\). It is half of the pitch \(\frac{2\pi}{q}\), because \(\hat{n}\) and \(-\hat{n}\) are equivalent. The cholesteric pitch changes with temperature. Because of this dependence, one application of cholesteric is for a thermometer, which changes its pitch, and hence its colored indicator when temperature changes.

The role of chirality in liquid crystals also allows for more complicated three-dimensional (3D) structures, called the blue phases. Chiral liquid crystals at a sufficiently low temperature form a thermodynamically stable cholesteric phase. However, experiments show that upon cooling from the isotropic phase, a system of highly chiral molecules undergoes a series of first order phase transitions before the cholesteric phase is reached. Those intermediate phases are the blue phases. Their origin is
attributed to a competition between an intermolecular twist induced by strong chirality and the fact that the molecules must fill the space. This competition results in the mesogens self-assembling into double-twisted cylindrical structures separated by disclination lines in the molecular orientation [9], producing three thermodynamically distinct blue phases, all of which appear typically in a narrow temperature range (typically $\nabla\leq 10^\circ C$). Recently new materials have been found that have a wide range of temperature for blue phases. Fig. 1.7 shows the two cases (blue phases I and II, or BPI and BPII). The disclination lines for the first case form body-centered (bcc), and in the second case they form simple cubic (sc) lattices. For both cases the lattice spacing is in the optical range [10, 11] giving rise to vivid colored Bragg-like reflection of visible light. The third blue phase, BPIII, is amorphous in nature.

### 1.4 Flexoelectric Effect in Nematic Liquid Crystals

We have seen in eq.(1.12) that the elastic free energy cost for any kind of director variations from the nematic ground state can be expressed in a quadratic form in
Figure 1.7: Visualization of the chiral blue phases. The red sphere represents the defect locations where the disinclination line intersects with the surface of a cubic cell, and the green boxes simply represent the molecules in a chiral liquid crystal system (a) BPI with bcc lattice defects (b) BPII with sc lattice defects.

three independent curvature deformations (splay, twist, and bend). In this section we will discuss whether these deformations can polarize the nematic in analogy with the piezoelectric effect, where an elastic deformation in the form of a mechanical stress can give rise to polarization for certain solid materials (such as some crystals, certain ceramics, DNA and various protein). The origin of this appearance of polarization is attributed to the absence of inversion symmetry. A material can not develop charges of opposite polarity at opposite ends of a line through its center if it has an inversion center. Looking at the deformations in fig.1.5, we can certainly say two of the three nematic distortions splay and bend do not have a center of symmetry. We know a cholesteric liquid crystal lacks a center of inversion because of it’s chiral symmetry breaking, discussed in section 1.3. Hence the twist deformation also lacks a center of symmetry. These symmetry arguments allow a local polarization to appear in
response to local deformations in the director field. We see from fig.1.5 that the splay deformation itself (not the splay term in eq.1.12) violates the \( \hat{\mathbf{n}} \leftrightarrow -\hat{\mathbf{n}} \) invariance, whereas twist and bend do not. Therefore a polarization may appear along \( \hat{\mathbf{n}} \) in the case of splay, but has to be perpendicular to \( \hat{\mathbf{n}} \) in the case of twist and bend. However, if we look at the fig.1.6, there are two-fold rotational symmetry along the director at the middle of a twist. Polarization will cancel out under those symmetry operations.

The local polarization density \( \mathbf{P} \) due to splay and bend deformations can be expressed as

\[
\mathbf{P} = e_s \mathbf{S} + e_b \mathbf{B}
\]

This phenomenon is called the flexoelectric effect. The coefficients \( e_s \), and \( e_b \) are the splay and bend flexoelectric coefficients. Thus the flexoelectric effect is a linear coupling between polar order and director deformations in nematic liquid crystals. An imposed deformation of the nematic director leads to an electrostatic polarization, and conversely, an applied electric field induces a deformation of the nematic director. Since the initial discovery by Meyer [4], this effect has drawn great interest due to its possible application in devices like displays, actuators, micropower generators, and transducers (electro-mechanical) for sensing or energy-harvesting uses. In general, the director deformation might be either splay or bend, but one would expect the bend flexoelectric effect to be dominant in bent-shaped liquid crystals, whereas the splay flexoelectric effect to be dominant in pear-shaped liquid crystals.

1.5 Computational Technique

Nowadays macroscopic observable properties of a complex liquid crystal system can be studied using computer simulations because of the rapid growth of computer
power. One of the simplest approaches is the lattice simulation. The starting point of this modelling technique is the original Lebwohl-Lasher model [15], where each molecule is represented by a 3D spin fixed at lattice points of a simple cubic lattice. The interaction potential between nearest neighbors can be represented as

\[ V_{ij} = -A(n_i \cdot n_j)^2 \]  

(1.16)

where \( n_i \) and \( n_j \) are the local molecular directors at nearest neighbor lattice sites \( i \) and \( j \) respectively, and \( A \) is the strength of the nematic interaction. This model has been successful in explaining many properties of the \( I \leftrightarrow N \) phase transition and the phases involved.

1.5.1 Metropolis Monte Carlo

Metropolis Monte Carlo is an efficient and reliable physical minimization procedure in which one searches for a global minimum of some function (e.g. free energy), called the fitness function, defined over some multivariate parameter space, analogous to physical degrees of freedom. The algorithm [16] proceeds by choosing an initial starting point and making random steps \( \delta x \). At each step the change in the fitness function (say, energy \( E(x) \)) is calculated. If \( \delta E = E(x + \delta x) - E(x) \) is negative the move is accepted. If \( \delta E \) is positive, then the move is accepted with a Boltzmann classical probability distribution \( \exp \left[ -\frac{\delta E(x)}{k_B T} \right] \), where \( k_B \) is the Boltzmann constant, and \( T \) plays the role of temperature. A random walk is then generated with the series of accepted steps which explore the parameter space, and at long times it follows a probability distribution

\[ P(x) = \frac{1}{Z} \exp \left[ -\frac{E}{k_B T} \right] \]  

(1.17)
where the partition function $Z$ is given by

$$Z = \sum_i \exp \left[ -\frac{E_i}{k_B T} \right]$$ (1.18)

### 1.5.2 Randomized Optimization Algorithm

Randomized Optimization is a popular method of obtaining the global optimum of the fitness function, $E(x)$ of a given problem. It works by iteratively moving to better solutions in the search-space which are sampled by following some distribution surrounding the current solution. There are various types of randomized optimization algorithms such as the Randomized Hill Climbing (RHC), Simulated Annealing (SA) [17], Genetic Algorithms (GA). In this study we used the simulated annealing technique which uses the Boltzmann classical probability distribution discussed above. The actual algorithm uses this probability distribution to decide in what direction it will search in order to find the global optimum of $E(x)$. In this method the temperature $T$ is decreased slowly, and the phase space volume shrinks (with non-negligible $P(x)$) until the system is eventually forced to “freeze” or “anneal” into the configuration of optimum $E(x)$. If the anneal is carried out slowly enough, the system will avoid getting trapped in local minima because the Boltzmann probability does allow steps which increase $E$ temporarily to get over a barrier into a new local(or global) minimum. By doing so it increases the probability of finding the global optimum by increasing the search space which the algorithm covers. So the algorithm often chooses paths that are initially worse solutions than the current point, but the probability of selecting the wrong path decreases slowly over time.
BIBLIOGRAPHY


CHAPTER 2

Theory and Simulation of the Twist-bend Phase in Bent-shaped Liquid Crystals

2.1 Introduction

Bent-core liquid crystals exhibit a rich variety of phases with different types of orientational order. At high temperature they form an isotropic phase, with disorder in all of the molecular axes. As the temperature decreases they form a nematic phase, in which the long axes of the molecules tend to align up or down along a director $\hat{n}$. The transverse orientations of the molecules can then have various types of order in the plane perpendicular to $\hat{n}$: they might be disordered (leading to a uniaxial nematic phase), or have nematic order (leading to a biaxial nematic phase), or have polar order (leading to a net polarization). A classic argument of Meyer [1] shows that polar order of the transverse directions couples to bend variations in the main director $\hat{n}$. As a result, it is particularly easy to induce polar order and director bend in bent-core liquid crystals, compared with analogous rod-like liquid crystals.

Recent research has found two remarkable physical phenomena arising from polar order and director bend in bent-core liquid crystals: flexoelectricity and modulated phases.

2.1.1 Flexoelectricity

The flexoelectric effect is a linear coupling between polar order and director deformations in the uniaxial or biaxial nematic phase. An imposed deformation of the
nematic director leads to an electrostatic polarization, and conversely, an applied electric field induces a deformation of the nematic director. Since the initial discovery by Meyer [1], this effect has drawn great interest due to its possible application in devices such as display panels, actuators, micropower generators, and electro-mechanical transducers for sensing or energy-harvesting uses. In general, the director deformation might be either splay or bend, but one would expect the bend flexoelectric effect to be dominant in bent-core liquid crystals. Indeed, recent experiments by Harden et al. [2, 3] have found that bent-core liquid crystals have a surprisingly large bend flexoelectric coefficient, up to 35 nC/m, roughly three orders of magnitude larger than the typical value of 3–20 pC/m in rod-like liquid crystals.

For flexoelectricity, the key theoretical question is how to explain the large effect found in bent-core liquid crystals, so that it can be exploited for technological application. In a previous article from our research group [4], Subas Dhakal and Jonathan Selinger conjectured that the large flexoelectric effect is a statistical phenomenon associated with nearby polar phase. Near a polar phase, a nematic liquid crystal is on the verge of developing spontaneous polar order, and hence any deformation of the director should induce a large polar response. In that article, they explored that concept by constructing a model for splay flexoelectricity in a system of pear-shaped molecules. It is still necessary to extend the model to the more complex but physically realistic case of bend flexoelectricity in bent-core liquid crystals.

We recognize that experimental measurements of flexoelectricity in bent-core liquid crystals are controversial [5, 6]. Regardless of the experimental flexoelectric coefficient in any particular material, we would like to understand what behavior is theoretically possible.
2.1.2 Modulated phases

Classic work by R. B. Meyer [7] and further studies by I. Dozov [8] predicted two possible structures, known as twist-bend and splay-bend from two different perspectives, the former inspired by the bend flexoelectric mechanism and the latter starting from purely elastic (and steric) considerations. A helical molecular arrangement was also seen in the molecular simulations of Memmer [9], who considered bent-core Gay-Berne molecules with no polar electrostatic interactions, though featuring an effective shape polarity. Dozov’s $N_{tb}$ theory requires a negative bend elastic constant. He noted that bent-core liquid crystals have a very low energy cost for bend in the director, and described this low energy cost by a very small bend elastic constant $K_3$. He then speculated that $K_3$ could actually become negative in some bent-core liquid crystals. (In this case, the free energy would need to be stabilized by higher-order terms in the bend.) Dozov showed theoretically that the uniform nematic phase would become unstable to the formation of a modulated phase, which could be either a twist-bend or a splay-bend phase. This theoretical prediction is now supported experimentally in bimesogens by optical observations of spontaneous periodic deformations [12], and by extensive studies of a liquid crystal dimer, which identify the twist-bend phase using a series of techniques including small-angle x-ray scattering, modulated differential scanning calorimetry, dielectric spectroscopy, and magnetic resonance [13], then by Freeze Fracture Transmission Electron Microscopy (FFTEM) [14], and lastly using transmission electron and optical microscopy [15].

For the twist-bend and splay-bend modulated phases, there are two important theoretical questions. First, how does the elastic constant $K_3$ become negative; what is the physical meaning of this negative value? Second, what happens to the polar...
order in these phases? The schematic illustrations in Dozov’s work [8] clearly show the presence of local polar order, but this polar order is not included in his theoretical formalism.

The purpose of this chapter is to develop a theory of polar order and director bend in bent-core liquid crystals, which can explain both flexoelectricity and modulated phases in these materials. For this work, we use both Landau theory and lattice simulations. In Landau theory, we construct a free energy functional in terms of director gradients and polarization. In the uniform nematic phase, we can minimize the free energy to find the optimal polarization for fixed bend, or conversely the optimal bend for fixed polarization (or applied electric field). This minimization gives the bend flexoelectric coefficient $e_3$, as well as the effective bend elastic constant and effective dielectric coefficient. In particular, it shows the difference between the bare elastic constant $K_3$ and the effective (or renormalized) elastic constant $K_3^{\text{eff}}$. As the temperature decreases toward a critical temperature, $e_3$ increases and $K_3^{\text{eff}}$ goes to zero. Below that critical temperature, the uniform nematic phase becomes unstable to the formation of a new phase which has both polar order and spontaneous bend, and hence must have a modulated structure. By minimizing the free energy over variational forms for the director and the polarization, we find that the director configuration is equivalent to Dozov’s twist-bend or splay-bend phase, and we also determine the accompanying polarization configuration.

In simulations, we construct a lattice Hamiltonian that generalizes the classic Lebwohl-Lasher model [16] for nematic liquid crystals by including two vectors on each site, which represent the long molecular axis and the transverse direction, respectively. This model is analogous to our previous lattice model for splay flexoelectricity [4], but
now extended to bend flexoelectricity. We run Monte Carlo simulations of this Hamiltonian in both the high-temperature uniform nematic phase and the low-temperature modulated polar phase. These simulations give results that are equivalent to Landau theory, but without the mean-field and variational assumptions of Landau theory. In the uniform nematic phase, they show the increasing flexoelectric coefficient as the temperature decreases. In the low temperature phase, they show the structure of the modulated phase, which may be twist-bend or splay-bend, depending on model parameters.

The plan of this chapter is as follows. In sections 2.2 and 2.3, we develop a theory for the flexoelectric effect in the uniform nematic phase, first using Landau theory and then lattice simulations. In sections 2.4 and 2.5, we extend the theory to the low-temperature modulated polar phase, now in the reverse sequence of lattice simulations and then Landau theory. In section 2.7 we discuss and summarize the conclusions of this chapter.

### 2.2 Flexoelectric effect: Landau theory

To describe the flexoelectric effect in a uniform nematic phase, we must construct the free energy density in terms of the nematic director $\hat{n}$ and the polarization $P$. We assume that gradients of $\hat{n}$ are small, and $P$ is also small, so that we can work to quadratic order in both of these quantities. (We will go to higher order in a later section, when discussing modulated phases.) The free energy has three parts:

a. The free energy of director gradients is just the standard Oseen-Frank free energy. It can be written as

$$F_{nn} = \frac{1}{2} K_1 S^2 + \frac{1}{2} K_2 T^2 + \frac{1}{2} K_3 B^2, \quad (2.1)$$
in terms of the splay vector $S = \hat{n}(\nabla \cdot \hat{n})$, the twist pseudoscalar $T = \hat{n} \cdot (\nabla \times \hat{n})$, and the bend vector $B = \hat{n} \times (\nabla \times \hat{n})$.

b. Polar order does not occur in the uniform nematic phase, and hence it must have a positive free energy cost. To lowest order, this cost can be written as

$$F_{pp} = \frac{1}{2} \mu P^2,$$  \hspace{1cm} (2.2)

where $\mu$ is an arbitrary coefficient. There may be several physical contributions to $\mu$. Entropy makes a positive contribution proportional to temperature $T$, and the electrostatic energy makes another positive contribution independent of $T$. Because we are modeling bent-core liquid crystals, we suppose that there are packing considerations that favor polar order, in competition with entropy and electrostatics. This packing energy can be modeled by a negative part of the free energy, proportional to $P^2$, independent of $T$. Hence, the combination of these effects gives a coefficient $\mu$ that varies with temperature, and can be written as $\mu = \mu'(T - T_0)$. Note that $T - T_0$ is positive in the uniform nematic phase.

c. Following the argument of Meyer [1], polar order is coupled to both splay and bend in the director. Splay flexoelectricity (hence the splay coupling) is already considered in subas dhakal’s work [4]. In this chapter we are concerned with bend flexoelectricity, and hence we consider the coupling

$$F_{np} = -\Lambda B \cdot P,$$  \hspace{1cm} (2.3)

which favors polar order along the bend direction, perpendicular to the director, and hence describes ordering of the transverse orientations of the molecules.
Putting these three pieces together, we obtain the total free energy density

\[ F = \frac{1}{2} K_1 S^2 + \frac{1}{2} K_2 T^2 + \frac{1}{2} K_3 B^2 + \frac{1}{2} \mu P^2 - \lambda B \cdot P \]  \hspace{1cm} (2.4)

to quadratic order in director gradients and polar order. Note that the last three terms are a quadratic form in \( B \) and \( P \). The uniform nematic phase is only stable if the quadratic form is positive-definite, which occurs if \( \lambda^2 < \mu K_3 \). This condition can be rewritten as

\[ \mu > \mu_c = \frac{\lambda^2}{K_3}, \]  \hspace{1cm} (2.5)

or equivalently as

\[ T > T_c = T_0 + \frac{\lambda^2}{\mu' K_3}. \]  \hspace{1cm} (2.6)

Below that critical temperature, the uniform nematic phase must become unstable to a phase with director gradients and polar order, which will be discussed in sections 2.4 and 2.5 below.

To model the flexoelectric effect, we minimize the free energy of Eq. (2.4) over the polarization \( P \) for fixed bend \( B \) to obtain

\[ P = e_3 B, \]  \hspace{1cm} (2.7)

where the bend flexoelectric coefficient is given by

\[ e_3 = \frac{\lambda}{\mu} = \frac{\lambda}{\mu'(T - T_0)}. \]  \hspace{1cm} (2.8)

This coefficient increases toward a finite limit as the temperature decreases toward
the critical temperature $T_c$. Substituting the expression (2.7) for $\mathbf{P}$ back into Eq. (2.4) gives the effective free energy

$$F_{\text{eff}} = \frac{1}{2} K_1 S^2 + \frac{1}{2} K_2 T^2 + \frac{1}{2} K_3^{\text{eff}} B^2,$$

(2.9)

where the effective, renormalized bend elastic constant is given by

$$K_3^{\text{eff}} = K_3 - \frac{\lambda^2}{\mu} = K_3 - \frac{\lambda^2}{\mu'(T - T_0)}.$$

(2.10)

Note that there is an important physical distinction between the bare elastic coefficient $K_3$ and the renormalized coefficient $K_3^{\text{eff}}$: the bare coefficient $K_3$ gives the energy cost of a bend in a hypothetical experiment where the polarization is constrained to be zero, while the renormalized coefficient $K_3^{\text{eff}}$ gives the energy cost of a bend in an experiment where the polarization is free to relax to its lowest-free-energy value. This distinction is essentially the same as the distinction between the bend coefficient $K_3^D$ at constant electric displacement $\mathbf{D}$ compared with $K_3^E$ at constant electric field $\mathbf{E}$, as discussed by Castles et al. in the context of blue phase stability [17].

The renormalized coefficient is apparently the coefficient $K_3^{\text{eff}}$ calculated by Cestari et al. through molecular field theory with atomistic modeling, because their calculation involves averaging over molecular distributions that respond to bend [18]. The bare coefficient $K_3$ is always positive, while the renormalized coefficient $K_3^{\text{eff}}$ passes through zero as the temperature passes through $T_c$. In Sec. V below, we will discuss the behavior below $T_c$, and will show that $K_3^{\text{eff}}$ is the negative bend constant discussed by Dozov [8].

To model the converse flexoelectric effect, we add an electric field coupling to the
polarization into the free energy (2.4), which gives

\[ F = \frac{1}{2} K_1 S^2 + \frac{1}{2} K_2 T^2 + \frac{1}{2} K_3 B^2 + \frac{1}{2} \mu P^2 - \lambda B \cdot P - E \cdot P. \]  

(2.11)

We minimize this free energy over both bend \( B \) and polarization \( P \) for fixed electric field \( E \) to obtain

\[ B = \frac{\lambda E}{\mu K_3 - \lambda^2}, \quad (2.12a) \]
\[ P = \frac{K_3 E}{\mu K_3 - \lambda^2}. \quad (2.12b) \]

Equation (2.12a) shows that an electric field induces a bend through the converse flexoelectric effect, while Eq. (2.12b) shows that an electric field induces a polarization. The latter equation can be compared with the standard expression for the induced polarization in a dielectric material, \( P = \varepsilon_0 (\varepsilon - 1) E \). This comparison shows that the effective dielectric constant is

\[ \varepsilon_{\text{eff}} = 1 + \frac{1}{\varepsilon_0 (\mu - \lambda^2 / K_3)}. \]  

(2.13)

Hence, the effective dielectric constant is renormalized upward by the coupling between polarization and bend, compared with the value \( \varepsilon = 1 + 1/(\varepsilon_0 \mu) \) without this coupling. At the critical temperature \( T_c \) where the uniform nematic phase becomes unstable, the effective dielectric constant diverges.

Here, we should emphasize which quantities diverge and which remain finite at the critical point \( T_c \). When we apply an electric field in the converse flexoelectric effect, the induced bend and polarization are given by susceptibilities multiplying the field.
These susceptibilities both diverge as $T \rightarrow T_c$, as usual for susceptibilities at a second-order phase transition. Likewise, if we were to apply a torque that couples directly to the bend, the induced bend and polarization would be given by susceptibilities multiplying the torque, and those susceptibilities would also diverge as $T \rightarrow T_c$. However, the flexoelectric coefficient $e_3$ is not exactly a susceptibility; rather, it is the ratio between bend and polarization, which both diverge at the transition. This ratio does not diverge, but approaches the finite maximum value $e_3^{\text{max}} = K_3/\lambda$. By comparing this maximum value with the bend elastic constant and dielectric constant as $T \rightarrow T_c$, we see that

$$(e_3^{\text{max}})^2 = K_3\epsilon_0(\epsilon - 1) = K_3^{\text{eff}}\epsilon_0^{\text{eff}}(\epsilon^{\text{eff}} - 1).$$

(2.14)

This equation for the maximum flexoelectric coefficient is approximately the same as the limit derived by Castles et al. [5]. However, they derive the limit based on arguments about the conservation of energy. We would not say that it is related to energy conservation, but rather that it is the limit of stability of the uniform nematic phase. Beyond that point, the uniform nematic phase becomes unstable to the formation of a modulated phase, as will be discussed in later sections.

### 2.3 Flexoelectric Effect: Lattice Model

In the previous section, we developed a Landau theory for the bend flexoelectric effect near a transition to an incipient polar phase. In this section, we develop a lattice simulation model to describe the same effect. This model is an extension of the lattice model for splay flexoelectricity of our previous group member Subas Dhakal’s work [4]. In order to have the coherency of our discussion, in this section I compile his work
Figure 2.1: Lattice model for neighboring bent-core liquid crystal molecules, showing possible orientations of two neighboring molecules under a bend deformation.

on lattice model of bend flexoelectricity. Because this lattice simulations will provide clear visualizations of the types of molecular order that occur in the flexoelectric effect. They will also allow us to avoid the standard limitations of Landau theory, which neglects correlated fluctuations and applies only over a limited temperature interval.

We consider a simple cubic lattice with a bent-core liquid crystal molecule on each site. The orientation of each molecule is characterized by two orthogonal unit vectors, as shown in Fig. 2.1. The vector \( \hat{n}_i \) represents the long molecular axis, while the vector \( \hat{b}_i \) represents the transverse dipole of the molecule at site \( i \). In the uniaxial nematic phase without any bend, the \( \hat{n} \) vectors are ordered but the \( \hat{b} \) vectors are disordered. We would like to model how a bend in \( \hat{n} \) induces polar order in \( \hat{b} \), or conversely, how an electric field applied to \( \hat{b} \) induces bend in \( \hat{n} \).

For the lattice interaction between molecules on neighboring sites \( i \) and \( j \), we must
consider several terms. First, we need the standard Lebwohl-Lasher [16] interaction $-A(\hat{n}_i \cdot \hat{n}_j)^2$, which favors nematic order of the molecules. Second, to describe a bent-core liquid crystal with incipient polar order, we need an interaction of the form $-B_1 \hat{b}_i \cdot \hat{b}_j$. This term favors polar order of the transverse dipoles, driven by packing energy or any other mechanism. Third, there may also be a higher-order interaction of the form $-B_2 (\hat{b}_i \cdot \hat{b}_j)^2$, which favors nematic order of the transverse dipoles, perpendicular to the main nematic axis. This term gives the possibility of a biaxial nematic phase, as in the model of Straley [19]. Fourth, there must be an interaction $-E \cdot \hat{b}_i$ between each dipole and the applied electric field.

Finally, we need a coupling of $\hat{b}$ with the local bend in $\hat{n}$. Following the argument of Ref. [4], a lattice version of the bend vector between sites $i$ and $j$ can be written as

$$[\hat{n} \times (\nabla \times \hat{n})]_{ij} = \frac{1}{2} \left[ \hat{n}_i (\hat{r}_{ij} \cdot \hat{n}_i) - \hat{n}_j (\hat{r}_{ij} \cdot \hat{n}_j) + \hat{n}_i (\hat{n}_i \cdot \hat{n}_j) (\hat{r}_{ij} \cdot \hat{n}_i) - \hat{n}_j (\hat{n}_i \cdot \hat{n}_j) (\hat{r}_{ij} \cdot \hat{n}_i) \right]$$

(2.15)

where $\hat{r}_{ij} = (\vec{r}_j - \vec{r}_i)/|\vec{r}_j - \vec{r}_i|$ is the unit vector from site $i$ to $j$ on the lattice. Note that this expression is invariant under the symmetry operations $i \leftrightarrow j$, $\hat{n}_i \to -\hat{n}_i$, and $\hat{n}_j \to -\hat{n}_j$. This expression for the local bend can be coupled with the local
polar order, averaged over sites $i$ and $j$, to give

$$V_{\text{bend}} = C [\hat{n}_i \times (\nabla \times \hat{n}_i)]_{ij} \cdot \frac{\hat{b}_i + \hat{b}_j}{2}$$

$$= \frac{C}{4} \left[ (\hat{b}_j \cdot \hat{n}_i) [\hat{r}_{ij} \cdot \{ \hat{n}_i + \hat{n}_j (\hat{n}_i \cdot \hat{n}_j) \}] \right.$$ 

$$- (\hat{b}_i \cdot \hat{n}_j) [\hat{r}_{ij} \cdot \{ \hat{n}_j + \hat{n}_i (\hat{n}_i \cdot \hat{n}_j) \}] \right]. \quad (2.16)$$

Combining all the terms, our final expression for the lattice Hamiltonian is

$$H = -\sum_{(i,j)} \left[ A(\hat{n}_i \cdot \hat{n}_j)^2 + B_1 \hat{b}_i \cdot \hat{b}_j + B_2 (\hat{b}_i \cdot \hat{b}_j)^2 
\right.$$

$$\left. - \frac{C}{4} \left[ (\hat{b}_j \cdot \hat{n}_i) [\hat{r}_{ij} \cdot \{ \hat{n}_i + \hat{n}_j (\hat{n}_i \cdot \hat{n}_j) \}] \right. \right.$$ 

$$\left. - (\hat{b}_i \cdot \hat{n}_j) [\hat{r}_{ij} \cdot \{ \hat{n}_j + \hat{n}_i (\hat{n}_i \cdot \hat{n}_j) \}] \right] \right]$$

$$- \sum_i E \cdot \hat{b}_i. \quad (2.17)$$

This expression is analogous to the lattice Hamiltonian in Ref. [4], except that it has two orthogonal unit vectors on each site instead of just one, so that it can describe bend instead of splay flexoelectricity.

We carry out Monte Carlo simulations of a system of bent-core molecules interacting with the Hamiltonian of Eq. (2.17) on a simple cubic lattice of size $16 \times 16 \times 16$. When an electric field is applied, it is in the $Z$-direction. The simulation box has periodic boundary conditions in $Z$, but the boundaries in $X$ and $Y$ are free so that the system can form bend across those directions. In each Monte Carlo step, a molecule is chosen randomly and it is slightly rotated about a random axis. The change in energy $\Delta E$ is calculated, and the step is accepted or rejected following the Metropolis algorithm. Starting from a high-temperature isotropic state, the system is cooled down
slowly with temperature steps of $\Delta T = 0.01$. The final configuration at each temperature is taken as the initial configuration for the next lower temperature. Typical runs take about $10^5$ steps to come to equilibrium, while runs near phase transitions take about $6 \times 10^5$ steps.

Figure 2.2 shows snapshots of the molecular configuration in four phases at zero electric field. At high temperature, the system is in an isotropic ($I$) phase, with disorder in both $\hat{n}$ and $\hat{b}$. As the temperature decreases, it forms a uniaxial nematic ($N_U$) phase, with nematic order in $\hat{n}$ but disorder in $\hat{b}$ vectors, which are uniformly distributed in the plane perpendicular to the average director. At lower temperature, it forms a biaxial nematic ($N_B$) phase, with nematic order in both $\hat{n}$ and $\hat{b}$. In the $N_B$ phase, the $\hat{b}$ vectors have two favored orientations perpendicular to the average director. At the lowest temperature, it forms a polar ($P$) phase, with nematic order in $\hat{n}$ and polar order in $\hat{b}$ vectors, which now have one favored orientation perpendicular to the average director. In this case, the polar order induces bend in the director. (At longer length scales more complex modulated structures are seen, as discussed in the following section.)

A key feature of our model is that bend in $\hat{n}$ is coupled to polar order in $\hat{b}$. For that reason, we expect nonzero bend to occur spontaneously as the system moves into the polar phase, even under zero applied electric field. This can be seen in Fig. 4 of Ref [22], where the average bend calculated from Eq. (2.15) is plotted against temperature and coupling coefficients. Note that this spontaneous bend is zero in the isotropic, uniaxial nematic, and biaxial nematic phases, and becomes nonzero in the polar phase.
Figure 2.2: Equilibrium configurations from Monte Carlo simulations showing (a) isotropic phase, (b) uniaxial nematic phase, (c) biaxial nematic phase, and (d) polar phase. Cross sections through the $XZ$-plane are shown, and the color on each molecule represents the orientation of its short axis $\hat{b}$ with respect to the laboratory $Z$-axis.
Figure 2.3: Phase diagram of the model system as a function of (a) $T$ and $B_2$, for fixed $B_1 = 0.03$. (b) $T$ and $B_1$, for fixed $B_2 = 0.45$. In all cases $A = 1.0$, $C = 0.3$, and $E = 0$.

Figure 2.3 shows two cross-sections through the phase diagram. Note that increasing $B_2$ enhances the stability of the biaxial nematic phase at the expense of the uniaxial nematic and isotropic phases, but does not affect the polar phase. By comparison, increasing $B_1$ enhances the stability of the polar phase at the expense of all the other phases.

We can simulate the converse flexoelectric effect by applying an electric field $E$ along the $Z$-axis. As expected, the dipole direction $\hat{b}$ aligns parallel to the field, while the director $\hat{n}$ bends across the system, as a function of $X$ or $Y$. We can calculate this induced bend from Eq. (2.15) as a function of temperature, electric field, and coupling coefficients. The results are shown in Fig. 6 of Ref. [22]. Note that the bend increases as the field increases, as the bend-polarization coupling $C$ increases, and as the temperature decreases. In particular, as the temperature decreases toward the transition into the polar phase, the bend responds sensitively to any applied field. The temperature dependence of the bend is sharpest for very low fields, and it is rounded.
off for larger fields. This behavior is similar regardless of whether the system passes through the biaxial nematic phase or goes directly from uniaxial nematic to polar. These trends are the normal behavior of an induced order parameter in the presence of a symmetry-breaking field above a second-order phase transition. They are consistent with the Landau theory presented in the previous section, which suggests that the flexoelectric and converse flexoelectric effects become large near an incipient polar phase, where the uniform nematic phase is almost unstable and the system is most sensitive to any symmetry-breaking perturbation.

2.4 Modulated phases: Lattice model

As noted in the previous section, when the system cools into a polar phase with spontaneous polar order, it also acquires spontaneous bend. A simple example of the spontaneous bend is illustrated in Fig. 2.2(d), which shows a gradual bend across the system, between the free boundaries. However, this simple configuration cannot be extended to give the molecular orientation across a larger system. In general, it is impossible to fill space with pure uniform bend. Rather, the system must form a more complex modulated phase, which might have a regular array of defect walls, or might have a mixture of bend with splay or twist in the director. Indeed the problem of filling space with bend in a polar liquid-crystal phase is quite analogous to the problem of filling space with twist in a chiral liquid-crystal phase, as discussed in Ref. [23].

To determine the modulated structure of the polar phase, we repeat the simulations of the previous section with three modifications: we use periodic boundary conditions in all three directions, we use a slightly larger lattice of size $20 \times 20 \times 20$, and we increase the bend-polarization coupling coefficient $C$ to increase the bend,
Figure 2.4: Equilibrium configuration in a Monte Carlo simulation of the twist-bend phase, for model parameters $A = 2$, $B_1 = 0.5$, $B_2 = 0.4$, $C = -2.0$, and $T = 0.5$. (a) Top view. (b) Side view.

i. e. reduce the wavelength of the modulated structure, so that a full wavelength will fit in the simulation box. In these simulations no electric field is applied, so the only polarization is spontaneous order. We begin the simulations in the high-temperature isotropic phase and gradually cool into the low-temperature polar phase. In this way, the system is free to select its own modulated structure.

In these simulations, two distinct types of modulated structures form, depending on the model parameters. The first structure, shown in Fig. 2.4, is equivalent to the twist-bend phase proposed by Dozov [8]. In this structure, the director $\hat{n}$ has a helical modulation, which is randomly right- or left-handed. The director is not perpendicular to the helical axis, as in a cholesteric liquid crystal. Rather, it precesses...
in a cone about the helical axis, with a fixed cone angle between 0° and 90°. As a result, the director deformation is a mixture of twist and bend, unlike a cholesteric liquid crystal which has pure twist. The dipole direction $\hat{b}$ also precesses about the helical axis, while remaining perpendicular to $\hat{n}$ and perpendicular to the helical axis. This structure is spatially homogeneous, in that every position is equivalent to every other position with a twist. Hence, every position has the same energy, and there are no defects.

The second structure, shown in Fig. 2.5, is equivalent to the splay-bend phase proposed by Dozov [8]. Here, the director $\hat{n}$ goes back and forth within the plane of the figure. As a result, the director deformation is a mixture of splay and bend. Note that different regions are not equivalent to each other—some regions have almost pure bend, and other regions have almost zero bend. In this structure, the local polar order varies in both magnitude and direction. In the pure-bend regions the $\hat{b}$ vectors are very well aligned, and hence the polar order parameter has a large magnitude. These regions are indicated by the labels $P > 0$ and $P < 0$ in the figure. By contrast, in the zero-bend regions, the $\hat{b}$ vectors are disordered, and hence the polar order parameter averages to zero. These regions are indicated by the label $P = 0$ in the figure. The zero-bend regions have a higher energy than the pure-bend regions, so they can be regarded as defect walls.

The simple example of Fig. 2.2(d) can be understood as one pure-bend region going across the finite simulation cell. The splay-bend structure of Fig. 2.5 shows how this structure can fill space with a periodic alternation of pure-bend “defect-free” regions and zero-bend “defect walls.”

When we say that the structures of Figs. 2.4 and 2.5 are equivalent to Dozov’s
Figure 2.5: Equilibrium configuration in a Monte Carlo simulation of the splay-bend phase, for model parameters $A = 3$, $B_1 = 0.15$, $B_2 = 0.4$, $C = -2.0$, and $T = 0.3$. The director and polar order are both in the plane of the figure. The labels indicate the local polarization along the vertical axis.
twist-bend and splay-bend phases, we mean that the director modulations are the same as what he proposed. His chapter does not explicitly consider the polarization modulation, although his sketches suggest a variation in the polarization direction that is similar to our simulation results. The twist-bend phase has also been visualized in a simulation by Memmer [9].

2.5 Modulated phases: Landau theory

To understand the modulated phases better, we return to the Landau theory of Sec. II. These phases occur for temperatures below the critical temperature of Eq. (2.6), where the quadratic form in the free energy of Eq. (2.4) is not positive-definite. Hence, we must add further terms to stabilize the free energy. First, there must be a term of $\frac{1}{4} \nu \mathbf{P}^4$, which keeps the magnitude of the polar order from increasing without limit. Second, there must be a term of $\frac{1}{2} \kappa (\nabla \mathbf{P})^2$, which penalizes gradients in the magnitude and direction of polar order. (In terms of tensor indices, we interpret this gradient term as $\frac{1}{2} \kappa (\partial_i P_j)(\partial_i P_j)$. There could be other tensor contractions, but they do not matter for our analysis.) With these new terms, the Landau free energy becomes

$$
F = \frac{1}{2} K_1 S^2 + \frac{1}{2} K_2 T^2 + \frac{1}{2} K_3 B^2 - \lambda \mathbf{B} \cdot \mathbf{P} \\
+ \frac{1}{2} \mu'(T - T_0) \mathbf{P}^2 + \frac{1}{4} \nu \mathbf{P}^4 + \frac{1}{2} \frac{1}{\kappa} (\nabla \mathbf{P})^2.
$$

(2.18)

To model the twist-bend phase, we make the variational ansatz for $\mathbf{n}(x)$ and $\mathbf{P}(x)$
inspired by the simulation results of Fig. 2.4,

\[
\hat{n}(x) = (1 - a^2)^{1/2}\hat{x} + a\sin(qx)\hat{y} + a\cos(qx)\hat{z},
\]

\[
P(x) = -p\cos(qx)\hat{y} + p\sin(qx)\hat{z}.
\]

(2.19)

This ansatz has three variational parameters: \(a\) is the sine of the cone angle for the director, \(p\) is the magnitude of the local polar order, and \(q\) is the wavevector of the modulation. In terms of these parameters, the splay, twist, and bend become

\[
S(x) = \hat{n}(\nabla \cdot \hat{n}) = 0,
\]

\[
T(x) = \hat{n} \cdot (\nabla \times \hat{n}) = a^2 q,
\]

\[
B(x) = \hat{n} \times (\nabla \times \hat{n})
\]

\[
= a(1 - a^2)^{1/2}q[-\cos(qx)\hat{y} + \sin(qx)\hat{z}].
\]

(2.20)

Note that the splay is zero, as it should be for the twist-bend deformation. The twist and the bend magnitude are constants, while the bend direction precesses in a helix.

Plugging those quantities into the free energy gives

\[
F_{TB} = \frac{1}{2}K_2a^4q^2 + \frac{1}{2}K_3a^2(1 - a^2)q^2 - \lambda apq(1 - a^2)^{1/2}
\]

\[
+ \frac{1}{2}\mu'(T - T_0)p^2 + \frac{1}{4}\nu p^4 + \frac{1}{2}\kappa p^2 q^2.
\]

(2.21)

Minimizing the free energy over the variational parameters \(a, p,\) and \(q\) then gives the
behavior near the transition, for $T < T_c$,

\[
a = \frac{K_3}{2\lambda} \left( \frac{\mu'}{K_2} \right)^{1/2} (T_c - T)^{1/2},
\]

\[
p = \frac{K_3^2 \mu'}{4\lambda^2} \left( \frac{3}{2K_2\kappa} \right)^{1/2} (T_c - T),
\]

\[
q = \frac{1}{2} \left( \frac{3\mu'}{2\kappa} \right)^{1/2} (T_c - T)^{1/2}.
\]

(2.22)

Also, the free energy of the twist-bend phase just below the transition is

\[
F_{TB} = -\frac{K_3^4 \mu^3}{64K_2\kappa\lambda^4} (T_c - T)^3.
\]

(2.23)

By comparison, to model the splay-bend phase, we make the variational ansatz inspired by the simulation results of Fig. 2.5,

\[
\hat{n}(x) = \cos \phi(x) \hat{x} + \sin \phi(x) \hat{z},
\]

\[
P(x) = \frac{1}{2} p \cos(qx) \sin 2\phi(x) \hat{x} - p \cos(qx) \cos \phi(x) \hat{z},
\]

(2.24)

where $\phi(x) = \alpha \sin(qx)$. This ansatz also has three variational parameters: $\alpha$ is the amplitude of the director modulation, $p$ is the amplitude of the polarization modulation, and $q$ is the modulation wavevector. For this state, the splay, twist, and bend become

\[
S(x) = -\frac{1}{2} q\alpha \cos(qx) \sin 2\phi(x) \hat{x} - q\alpha \cos(qx) \sin \phi(x) \hat{z},
\]

\[
T(x) = 0,
\]

(2.25)

\[
B(x) = \frac{1}{2} q\alpha \cos(qx) \sin 2\phi(x) \hat{x} - q\alpha \cos(qx) \cos \phi(x) \hat{z}.
\]
Here the twist is zero, as it should be for the splay-bend deformation. The splay and bend both vary periodically through the modulated structure. Plugging these quantities into Eq. (2.18) gives a free energy density that also varies periodically through the modulated structure. We average the free energy density over the full modulation, and then minimize the average free energy over the variational parameters \( \alpha, p, \) and \( q \). This minimization gives the behavior near the transition,

\[
\alpha = \frac{K_3}{\lambda} \left( \frac{\mu'}{K_1} \right)^{1/2} (T_c - T)^{1/2},
\]
\[
p = \frac{7K_3^2 \mu'}{8\lambda^2} \left( \frac{1}{2K_1\kappa} \right)^{1/2} (T_c - T),
\]
\[
q = \frac{7}{8} \left( \frac{\mu'}{2\kappa} \right)^{1/2} (T_c - T)^{1/2}.
\]

Furthermore, the free energy of the splay-bend phase just below the transition is

\[
F_{SB} = -\frac{K_3^4 \mu^3}{32K_1\kappa\lambda^4} (T_c - T)^3.
\]

From these results, we see that the uniform nematic phase can become unstable to the formation of either the twist-bend phase or the splay-bend phase at the critical temperature \( T_c \). We can then ask which of these modulated phases is more stable. Comparison of the free energies (2.23) and (2.27) shows that the twist-bend phase is more stable if \( K_1 > 2K_2 \), while the splay-bend phase is more stable if \( K_1 < 2K_2 \). Interestingly, this is exactly the same criterion for the relative stability of the phases calculated by Dozov [8]. This criterion is reasonable, because the elastic constants \( K_1 \) and \( K_2 \) give the energetic costs of splay and twist deformations, which are required in the splay-bend and twist-bend phases, respectively.
2.6 First order transition

In the preceding sections we have presented a simulation of TB modulated phases in nematics, and provided continuum elastic theory-based mathematical modeling. In particular, we have predicted a second order transition from the regular nematic to a 1D modulated twist-bend (TB) nematic phase. Chapter 4 will further develop the second order transition. But various experimental groups[10, 11] have observed the transition from nematic to twist-bend phase to be first order in nature in some material.

In this section we have extended our model to capture the first order transition that shows up in some experiments. In order to do that, we have considered a positive sixth order term in the free energy density, and also put a negative sign before the fourth order term.

Including the higher order term the free energy density can be written as

\[
F = \frac{1}{2}K_1 S^2 + \frac{1}{2}K_2 T^2 + \frac{1}{2}K_3 B^2 - \lambda B \cdot P \\
+ \frac{1}{2}\mu P^2 - \frac{1}{4}\nu P^4 + \frac{1}{6}\omega P^6 + \frac{1}{2}\kappa (\nabla P)^2 + \eta (n \cdot P)^2
\]  

(2.28)

where the splay vector \( S = n(\nabla \cdot n) \), the twist pseudoscalar \( T = n \cdot (\nabla \times n) \), and the bend vector \( B = n \times (\nabla \times n) \). Also \( K_1, K_2, \) and \( K_3 \) are the Frank elastic constants for splay, twist, and bend distortions of the director. The coefficient \( \mu = \mu_0(T - T_0) \) is the temperature-dependent Landau coefficient for the polarization \( P \) (\( \mu_0 \) being a constant), while \( \nu > 0 \) and \( \omega > 0 \) are higher-order, temperature-independent Landau coefficients. The elastic constant \( \kappa \) penalizes spatial distortions in \( P \). The last term (not considered in the second order transition model) with \( \eta > 0 \), favors polarization...
perpendicular to the nematic director (bend flexoelectricity), and with \( \eta < 0 \), favors polarization parallel to the nematic director (splay flexoelectricity).

Plugging the ansatz for \( \mathbf{n} \) and \( \mathbf{P} \) from eqn. (2.19) into the free energy eqn (2.28) yields

\[
F = \frac{1}{2} K_2 a^4 q^2 + \frac{1}{2} K_3 a^2 q^2 - \frac{1}{2} K_3 a^4 q^2 - \lambda a \sqrt{1 - a^2 p q} \\
+ \frac{1}{2} \mu p^2 - \frac{1}{4} \nu p^4 + \frac{1}{6} \omega p^6 + \frac{1}{2} \kappa p^2 q^2 
\] (2.29)

Because of the higher order term in \( p \), we can not minimize this free energy analytically to get the equilibrium solutions for \( (a, p, q) \). To do that we first minimize over \( q \) to get the expression,

\[
q = \frac{a(1 - a^2)^{1/2} p \lambda}{a^4 K_2 + a^2 (1 - a^2) K_3 + p^2 \kappa} 
\] (2.30)

Now we put this solution for \( q \) back in to the free energy Eq. (2.29) to get free energy as functions of two variational parameters \( (a, p) \), and other model parameters. Then, we minimize this effective free energy density \( F(a, p) \) with respect to \( a \) to get the expression,

\[
a^2 = -\frac{\kappa p^2}{K_2} + \sqrt{\frac{\kappa p^2}{K_2} \left( 1 + \frac{\kappa p^2}{K_2} \right)}. 
\] (2.31)

Putting this solution for \( a^2 \) into \( F(a, p) \) to get the final effective free energy density \( F(p) \), which we will have to minimize numerically over \( p \), the only variational parameter left. For the free energy to be stable we must have \( \omega \) positive. In the case of a second order transition (calculation will be presented in chapter 4) there will be no
Figure 2.6: Plot of free energy vs polarization order parameter (p) at different temperatures for dimensionless model parameters $\omega = 1.2, \kappa = 0.01, \nu = 0.39, K_2 = 0.2, K_3 = 0.5$. 
\( \omega \) term, and \( p \) can be solved for analytically.

The free energy density \( F(p(\mu)) \) is plotted as a function of polarization order parameter \( p \) as shown in Fig.(2.6), for various values of \( \mu \). Obviously, at very high temperature, the free energy has one minimum at \( p=0 \). But, we are considering here the nematic to twist-bend nematic transition where close to the transition (red line in Fig. (2.6)) \( p=0 \) is still an energy minimum solution in the nematic phase. If we decrease the temperature further we end up having two equally deep minima at the transition (green line in Fig. (2.6)). It is a first order transition point from nematic to twist-bend nematic phase. Further decreasing the temperature gives a stable minimum in the twist-bend phase \((p \neq 0)\), and a metastable minimum at \( p = 0 \).

We also plot these order parameters vs the temperature. These plots show a jump in order parameters at the transition, a signature of a first order phase transition as shown in figure 2.7. The phase diagram of the model in \( \mu - \lambda \) space is given in figure 2.8.

### 2.7 Discussion

In this chapter, we have presented a theory for orientational order in bent-core liquid crystals. The theory combines three parts: the Oseen-Frank free energy for director gradients, a tendency toward polar order perpendicular to the director, and a coupling between polar order and director bend. In Landau theory, the Oseen-Frank free energy is represented by the \( K \) terms, the tendency toward polar order by the \( \mu \) term, and the coupling by the \( \lambda \) term. In the lattice model, the Oseen-Frank free energy is represented by \( A \), the tendency toward polar order by \( B_1 \), and the coupling by \( C \). Either way, the physical conclusions are the same: In the uniform nematic
Figure 2.7: Plot of variational parameters vs temperature (a) Sine of cone angle vs temperature (b) Polar order vs temperature (c) Pitch vs temperature for dimensionless model parameters $\omega = 1.5, \kappa = 0.1, \nu = 3.9, K_2 = 0.02, K_3 = 0.1$. 
Figure 2.8: Phase diagram in the first-order transition model for dimensionless model parameters: $\omega = 1.5, \kappa = 0.1, \nu = 3.9, K_2 = 0.02, K_3 = 0.1.$
phase, there is a flexoelectric effect, where an imposed bend leads to a polarization, and conversely an applied electric field leads to a bend. This flexoelectric effect increases as the temperature decreases toward a polar phase. At the critical point, the response to an applied field diverges, and there is a second-order transition from the uniform nematic phase into a modulated polar phase. The modulation may have the twist-bend or splay-bend structure, depending on the relative values of $K_1$ and $K_2$.

To compare our theory with the previous work by Dozov [8], note that two phenomena occur at the critical temperature $T_c$: the system transitions from the uniform nematic phase to the polar phase, and the renormalized bend elastic constant $K_{3}^{\text{eff}}$ of Eq. (2.10) changes sign from $K_{3}^{\text{eff}} > 0$ for $T > T_c$ to $K_{3}^{\text{eff}} < 0$ for $T < T_c$. Dozov would say that the modulated phase is caused by the negative elastic constant $K_{3}^{\text{eff}}$. By contrast, we would say that the modulated phase and the negative $K_{3}^{\text{eff}}$ are both caused by the bend-polarization coupling together with the tendency toward polar order. Of course, there is no contradiction between these two theories; they are just different ways of expressing the same physical concept.

Our theoretical results can be compared with recent experiments. For the flexoelectric effect, the most relevant comparison is with the experiments of Harden et al. [2, 3], which found a surprisingly large bend flexoelectric coefficient in bent-core liquid crystals, about three orders of magnitude larger than the typical value in rod-like liquid crystals. This observation is at least qualitatively consistent with our concept that bent-core liquid crystals are near an incipient polar phase, and hence are very sensitive to any slight polar perturbations. However, one aspect of this comparison is confusing. In our theory, it is easy to understand why the polarization and
bend induced by an applied electric field or an applied torque should be very large in bent-core liquid crystals, because these quantities diverge at the critical point. By comparison, it is not easy to understand why the ratio between induced polarization and induced bend should be very large, because this ratio does not diverge at the critical point. (The ratio increases as \( T \to T_c \), but only toward a finite limit.) Even so, that ratio is the standard definition of the flexoelectric coefficient, which Harden et al. found to be surprisingly large. One possible explanation of this discrepancy might be that the experiment involves local smectic order, which is not included in the theory; perhaps this smectic order increases the ratio of polarization to bend. An alternative explanation might be that the experiment is somehow measuring one of the response coefficients that diverges at the critical point and is not actually measuring the ratio of polarization to bend. Yet another possibility might be that the experiment is actually in a modulated polar phase that has not yet been identified.

For the modulated polar phases, the most relevant comparison is with recent experiments that find nonuniform nematic phases in systems of bimesogens [12, 13, 14, 15]. These experiments provide good evidence that the observed modulation is a twist-bend structure, which is an encouraging consistency between theory and experiment.

As a final point, we note that the modulated polar phases are locally ferroelectric; they have spontaneous polar order which leads to electrostatic polarization. This local polarization is modulated in a helix for the twist-bend phase or a planar wave for the splay-bend phase, and hence it averages to zero globally. For that reason, it might be difficult to observe in an experiment. In this respect, the modulated polar phases are similar to ferroelectric smectic-C* liquid crystals, which also have local
polar order that is modulated in a helix and averages to zero globally. By analogy with ferroelectric smectic-C* liquid crystals, there might be ways to unwind the helix of the twist-bend phase (or eliminate the wave modulation in a splay-bend phase) to obtain a structure with long-range polar order. For example, strong surface anchoring might give a surface-stabilized ferroelectric nematic phase. This surface stabilization could be another topic for future research.
BIBLIOGRAPHY


CHAPTER 3

Higher Dimensional Modulation: Polar Blue Phases

3.1 Introduction

Nematic liquid crystals exhibit couplings between polar order and gradients in the director field. These couplings lead to the flexoelectric effect, in which bend or splay of the director induces a net polarization, and the converse flexoelectric effect, in which an applied electric field induces bend and splay [1]. When the couplings become strong enough, the uniform nematic phase can become unstable to the formation of a modulated polar phase. The polar order may be electrostatic, magnetic, or steric, i.e. an ordering of the shape of the molecules. The question is then: What is the structure of the modulated polar phase? Classic work by Meyer [2] and further studies by other investigators [3, 4, 5, 6] predicted two possible structures, known as twist-bend and splay-bend. One of these predictions, the twist-bend phase, has recently been identified in experiments on bimesogens, and it is now recognized as a remarkable experimental discovery of a liquid-crystal phase with a new type of order.

The purpose of this chapter is to investigate whether liquid crystals can form modulated polar phases with other structures, different from twist-bend and splay-bend. This study is motivated by an analogy between polarity and chirality. The twist-bend phase of polar liquid crystals is similar to the cholesteric phase of chiral liquid crystals; both are helical phases induced by molecular asymmetry. Apart from the cholesteric phase, chiral liquid crystals also form blue phases, with complex three-dimensional (3D) modulations of the director [11]. We would like to consider
whether polar liquid crystals can form analogous blue phases. To explore this question, we use both lattice simulations and Landau theory. For lattice simulations, we use generalized Lebwohl-Lasher models, which was constructed in previous studies of splay flexoelectricity [12] by our research group member Subas Dhakal and bend Lebwohl-Lasher model for flexoelectricity was presented in chapter 2. For Landau theory, we generalize earlier theories of chiral blue phases, which represent the liquid-crystal order tensor as a series of plane waves and minimize the free energy over the Fourier coefficients [13, 14].

Both of our approaches demonstrate that the system can form polar blue phases. One polar blue phase is a 3D body-centered-cubic (bcc) lattice, resembling a lattice of micelles, which is dominated by splay in the director. Another such phase is a 2D hexagonal lattice, dominated by bend in the director. These results can be compared with experimental studies of complex modulated phases in supramolecular liquid crystals [15].

Our results can be contrasted with other theories of modulated phases in liquid crystals. In the theory of Alexander and Yeomans [16], an applied electric field can induce a flexoelectric blue phase, with uniform polar order and modulated director. Our work considers polar order that forms spontaneously, not induced by a field, and hence the system forms a more complex modulation in the polar order as well as the director. In the theory of Castles et al. [17], flexoelectric couplings help to stabilize chiral blue phases, thus increasing the blue-phase temperature range in chiral liquid crystals. Our work finds a new type of blue phase even without chirality. In the theory of Hinshaw et al. [18], the director and polar order are both modulated within the layers of ferroelectric smectic liquid crystals. We find similar modulations in nematic
Figure 3.1: (Color online) Equilibrium configurations from Monte Carlo simulations. On each lattice site, the red rod represents the director, and the green arrow represents the polar order. (a) Splay model with parameters $A = 1.25$, $B = 0.01$, $C = 3.0$, and temperature $T = 0.35$, simulated on a $20 \times 20 \times 20$ lattice with periodic boundary conditions. The resulting structure is approximately bcc. For clarity, only the sites on the surfaces are shown. (b) Bend model with $A = 2.5$, $B_1 = 0.4$, $B_2 = 0.5$, $C = -3.0$, $T = 0.45$, simulated on a $48 \times 48 \times 3$ lattice. The resulting structure is approximately hexagonal. For both models, several simulation volumes and aspect ratios were used, with similar results.

phases, without smectic layers. In the theory of Lorman and Mettout [19], the polar order is modulated in a series of plane waves, but there is no explicit nematic order. We consider waves in both polar and nematic order, so that we can model a liquid crystal that is mainly nematic with slight polar order.
3.2 Lattice Simulation

In simulations, we generalize the classic Lebwohl-Lasher model of nematic liquid crystals [20], where each lattice site has a spin representing the orientation of the director, obeying the nematic symmetry $\hat{n}_i \rightarrow -\hat{n}_i$. To construct a lattice Hamiltonian for splay flexoelectricity, applicable for pear-shaped molecules, we relax that nematic symmetry condition to capture the longitudinal polarity of the molecules. As shown in our previous study of splay flexoelectricity [12], the total lattice Hamiltonian can be written as

$$H = -\sum_{\langle i,j \rangle} \left[ A(\hat{n}_i \cdot \hat{n}_j)^2 + B(\hat{n}_i \cdot \hat{n}_j) + C \left( \frac{1 + \hat{n}_i \cdot \hat{n}_j}{2} \right)^2 \hat{r}_{ij} \cdot (\hat{n}_j - \hat{n}_i) \right].$$  \hspace{1cm} (3.1)

Here, the $A$ term favors nematic order, the $B$ term favors polar order, and the $C$ term represents the interaction between splay and polar order. Our previous research group member Subas Dhakal’s study showed that this model has three phases, isotropic, nematic, and polar, but did not examine the structure of the polar phase. Now, we run Monte Carlo simulations in the low-temperature polar phase to determine the equilibrium structure. These simulations show that the structure is a lattice of hedgehog defects, or micelles, as shown in Fig. 3.1(a). As the flexoelectric coupling $C$ increases, the lattice constant decreases. We cannot determine the structure precisely because the periodic boundary conditions interfere with the natural periodicity, but the symmetry is approximately bcc.
Similarly, the lattice Hamiltonian for bend flexoelectricity can be written as [5]

\[
H = -\sum_{(i,j)} \left[ A(\hat{n}_i \cdot \hat{n}_j)^2 + B_1 \hat{b}_i \cdot \hat{b}_j + B_2 (\hat{b}_i \cdot \hat{b}_j)^2 \\
- \frac{C}{4} \left[ (\hat{b}_j \cdot \hat{n}_i)[\hat{r}_{ij} \cdot \{\hat{n}_i + \hat{n}_j(\hat{n}_i \cdot \hat{n}_j)\}] \\
- (\hat{b}_i \cdot \hat{n}_j)[\hat{r}_{ij} \cdot \{\hat{n}_j + \hat{n}_i(\hat{n}_i \cdot \hat{n}_j)\}] \right] \right],
\]

where \( \hat{n}_i \) represents the long molecular axis and \( \hat{b}_i \) the transverse molecular dipole at site \( i \). In this Hamiltonian, the \( A \) term favors nematic order of the long axes, the \( B_1 \) term favors polar order of the transverse dipoles, the \( B_2 \) term favors nematic order of the transverse dipoles, and the \( C \) term represents the interaction between bend and polar order. Our previous research group member Subas Dhakal’s study showed that this model has several phases: isotropic, uniaxial nematic, biaxial nematic, twist-bend, and splay-bend. We now run further Monte Carlo simulations in the low-temperature polar regime. In addition to the twist-bend and splay-bend phases with 1D modulation, we also find a new phase with 2D modulation. This phase consists of a lattice of vortices, as shown in Fig. 3.1(b), with 3D animation in Supplemental Material. Each vortex involves bend of the director and splay of the polarization vector. At each antivortex, the magnitude of the polarization is reduced. This structure is similar to the prediction for modulated smectic layers by Hinshaw et al. [18], and to the polarization-modulated smectic phases found experimentally by Coleman et al. [21], but without smectic order. Again, we cannot determine the structure precisely because of the periodic boundary conditions, but it is approximately a 2D hexagonal lattice. We do not see any indication of a 3D modulated phase in this model.
3.3 Landau Theory

To understand polar blue phases further, we develop an analytic Landau theory. In this theory, we follow the approach developed for chiral blue phases in the “high chirality” limit [11, 13, 14]. For chiral blue phases, those theories expand the nematic order tensor field $Q_{\alpha\beta}(r)$ as a series of plane waves, with wavevectors corresponding to reciprocal lattice vectors of the proposed lattice. They then insert the tensor field into a free energy functional that represents the chirality of the phase, and minimize over the Fourier coefficients to determine the optimal structure. To describe polar rather than chiral blue phases, we must modify the theory in two ways. First, we must expand both the nematic order tensor field $Q_{\alpha\beta}(r)$ and the polarization vector field $P_{\alpha}(r)$ as series of plane waves, using appropriate spherical-harmonic modes. Second, we must use a free energy that represents the coupling between polarity and director gradients, without chirality.

In general, the nematic order tensor field $Q_{\alpha\beta}(r)$ can be expressed as a Fourier series with five modes at each wavevector $q$. In standard spherical-harmonic notation, these modes are $l = 2$ and $m = 0, \pm 1, \pm 2$ at each $q \neq 0$. The $m = \pm 2$ modes represent right- and left-handed cholesteric helices; these modes are used in the theory of chiral blue phases because they are the most chiral. The $m = \pm 1$ modes represent right- and left-handed tilted conical helices, as in the twist-bend and splay-bend phases. The $m = 0$ mode represents a modulation of the nematic order parameter with no twist; we will use that mode to describe polar blue phases. Hence, for each single wavevector $q$, we write

$$Q_{\alpha\beta}^{q}(r) = a_{q} \left( \frac{3}{2} q_{\alpha} q_{\beta} - \frac{1}{2} \delta_{\alpha\beta} \right) \cos (q \cdot r + \theta_{q}).$$

(3.3)
Here, \( a_q \) is the amplitude of the mode, \( \theta_q \) is the phase, and \( \hat{q} = q/|q| \) is a unit vector.

Similarly, the polarization vector field \( \mathbf{P}(r) \) can be expressed in terms of three modes at each wavevector \( q \). In spherical-harmonic notation, they are \( l = 1 \) and \( m = 0 \) or \( \pm 1 \) at each \( q \neq 0 \). The transverse \( m = \pm 1 \) modes represent right- and left-handed helices, which describe polar order in the twist-bend and splay-bend phases. The longitudinal \( m = 0 \) mode represents a modulation in the magnitude of polar order, and we will use it for polar blue phases. For each single wavevector \( q \) we write

\[
\mathbf{P}^q(r) = b_q \hat{q} \cos (\mathbf{q} \cdot \mathbf{r} + \phi_q),
\]

where \( b_q \) is the amplitude and \( \phi_q \) the phase of the mode.

To describe a polar blue phase with any particular symmetry, we must sum both \( Q_{\alpha\beta}(r) \) and \( \mathbf{P}(r) \) over wavevectors \( q \) in the reciprocal lattice,

\[
Q_{\alpha\beta}(r) = \sum_q Q^q_{\alpha\beta}(r), \quad \mathbf{P}(r) = \sum_q \mathbf{P}^q(r),
\]

using at least all the reciprocal lattice vectors with the smallest magnitude. For bcc symmetry, we sum over six wavevectors in the fcc reciprocal lattice,

\[
q = \left( \frac{q}{\sqrt{2}}, \pm \frac{q}{\sqrt{2}}, 0 \right), \left( 0, \frac{q}{\sqrt{2}}, \pm \frac{q}{\sqrt{2}} \right), \left( \pm \frac{q}{\sqrt{2}}, 0, \frac{q}{\sqrt{2}} \right).
\]

Each of these modes must have the same amplitude \( a \), but they may have different phases \( \theta_q \) and \( \phi_q \). Three linear combinations of the phases are arbitrary, corresponding to uniform translations in \( x, y, \) or \( z \). All other linear combinations affect the structure, and must be determined by minimizing the free energy.

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Likewise, for 2D hexagonal symmetry, we sum over three wavevectors in the hexagonal reciprocal lattice,

\[ \mathbf{q} = (q, 0, 0), \left( -\frac{q}{2}, \pm \frac{\sqrt{3}q}{2}, 0 \right). \]  

(3.7)

Here, two linear combinations of the phases are arbitrary, corresponding to uniform translations in \( x \) or \( y \). All other linear combinations affect the structure, and must be determined by minimizing the free energy.

We write the general free energy density for a liquid crystal of polar molecules as

\[
F = \frac{1}{2} A (Q_{\alpha\beta} Q_{\alpha\beta}) + \frac{1}{3} B (Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha}) + \frac{1}{4} C (Q_{\alpha\beta} Q_{\alpha\beta})^2 + \frac{1}{2} L_1 (\partial_\alpha Q_{\beta\gamma} \partial_\alpha Q_{\beta\gamma}) \\
+ \frac{1}{2} L_2 (\partial_\alpha Q_{\alpha\gamma} \partial_\beta Q_{\beta\gamma}) + \frac{1}{2} \mu |\mathbf{P}|^2 + \frac{1}{4} \nu |\mathbf{P}|^4 \\
+ \frac{1}{2} \kappa (\nabla \mathbf{P})^2 - \lambda P_\alpha \partial_\beta Q_{\alpha\beta} + \eta P_\alpha Q_{\alpha\beta} P_\beta.
\]

(3.8)

This expression is similar to the free energy given in previous chapter, but expressed in terms of the nematic order tensor \( Q_{\alpha\beta} \) instead of the director. Here, the \( A, B, \) and \( C \) terms are the standard Landau-de Gennes free energy expansion in powers of \( Q_{\alpha\beta} \). The \( L_1 \) and \( L_2 \) terms are the lowest-order terms in the Frank free energy, expressed in terms of \( Q_{\alpha\beta} \). The \( \mu, \nu, \) and \( \kappa \) terms are the Ginzburg-Landau expansion in powers of the polar order parameter \( \mathbf{P} \). The \( \lambda \) term is the flexoelectric coupling between \( \mathbf{P} \) and gradients in \( Q_{\alpha\beta} \), which may be either splay or bend. Finally, the \( \eta \) term favors alignment of \( \mathbf{P} \) with respect to \( Q_{\alpha\beta} \). If \( \eta < 0 \), the favored polarization is parallel to the director, leading to splay flexoelectricity. If \( \eta > 0 \), the favored polarization is
Figure 3.2: Visualization of polar blue phases obtained from Landau theory. (a) 3D bcc lattice, with black dots indicating the centers of the hedgehogs. (b) 2D hexagonal structure, in a cross section through the \((x, y)\) plane. In each case, the nematic order is represented by red boxes corresponding to the three eigenvalues and eigenvectors of \(Q_{\alpha\beta}(r)\), and the polar order is represented by green arrows with the magnitude and direction of \(P(r)\).

We can now determine the free energies of the bcc and hexagonal structures. For each structure, we insert the Fourier series expressions for \(Q_{\alpha\beta}(r)\) and \(P(r)\) into the free energy density of Eq. (3.8), and average over a full unit cell, to obtain the free energy as a function of amplitudes \(a\) and \(b\), phases \(\theta_q\) and \(\phi_q\), and the wavevector magnitude \(q\). First, we minimize over the phases, which enter only into the cubic and quartic terms of the free energy. This minimization gives the bcc and hexagonal structures shown in Figs. 3.2(a) and 3.2(b). Note that these structures are similar to the simulation results of Figs. 3.1(a) and 3.1(b). The bcc structure
Figure 3.3: Numerical phase diagram in terms of the two quadratic coefficients $A$ and $\mu$, which are expected to vary with temperature, for fixed parameters $\lambda = 1.5$, $B = -2.4$, $\eta = -0.18$, $C = L_1 = L_2 = \kappa = \nu = 1$. For these parameters, all transitions are first-order.

is a 3D lattice of hedgehogs, with splay in both $\mathbf{P}(\mathbf{r})$ and the main eigenvector of $Q_{\alpha\beta}(\mathbf{r})$. The hexagonal structure is a 2D lattice with splay in $\mathbf{P}(\mathbf{r})$ and bend in the main eigenvector of $Q_{\alpha\beta}(\mathbf{r})$. In both cases, $Q_{\alpha\beta}(\mathbf{r})$ is highly biaxial in much of the structure, as should be expected when it is represented by a small number of Fourier modes.

Next, we minimize the free energy of each structure, bcc and hexagonal, over the variational parameters $a$, $b$, and $q$. We then compare the free energies of these two structures, as well as the isotropic phase (with $Q_{\alpha\beta} = 0$ and $\mathbf{P} = 0$), nematic phase
(with uniform $Q_{\alpha\beta} \neq 0$ and $P = 0$), twist-bend and splay-bend phases (described with $m = \pm 1$ spherical harmonic modes for $Q_{\alpha\beta}(r)$ and $P(r)$ plus a uniform $Q_{\alpha\beta}$ mode), and 3D simple cubic and 2D square lattices (described with $m = 0$ spherical harmonic modes analogous to bcc and hexagonal). We obtain the numerical phase diagram shown in Fig. 3.3. This phase diagram is expressed in terms of the two quadratic coefficients $A$ and $\mu$ in the free energy, which are both expected to vary with temperature; the other model parameters are held fixed ($B, C, L_1, L_2, \nu, \kappa, \lambda$, and $\eta$). Reducing $A$ favors nematic order, while reducing $\mu$ favors polar order. Hence, the lower left of the phase diagram represents low temperature, and the upper right represents high temperature.

The phase diagram shows regions of the isotropic, nematic, twist-bend, bcc, and 2D hexagonal phases. Each of these phases is stable for some set of numerical parameters. We have not found any parameters for which the splay-bend, simple cubic, or 2D square phases are stable. Indeed, we would not expect the simple cubic or 2D square phases to be stable in this model, because the free energy includes cubic terms ($BQ_{\alpha\beta}Q_{\gamma\delta}Q_{\alpha\gamma} \text{ and } \eta P_{\alpha}Q_{\alpha\beta}P_{\beta}$). These terms can be negative for the bcc and 2D hexagonal structures, but they are zero for the simple cubic and 2D square structures (assuming that only the lowest-order reciprocal lattice vectors contribute to the modulations). Of course, we recognize that our predicted phase diagram is limited in several ways: we have only explored a limited range of numerical parameters; the free energy could include higher-order terms; and the system could form modulations with different lattice symmetries or different spherical-harmonic indices $m$ than we have considered. Nevertheless, the phase diagram gives an indication of the phases and phase sequences that can be found in a simple model.
As noted in the introduction, the twist-bend phase has recently been observed in experiments on bimesogens [7, 8, 9, 10]. The polar blue phases have not yet been reported in bimesogens, although future experiments might look for those phases. To our knowledge, the best experimental realization of polar blue phases is the work on supramolecular liquid crystals by Ungar et al. [15]. These materials are composed of dendrons, with the shapes of cones or flat wedges (like pizza slices). The cone shape should favor splay flexoelectricity, while the flat wedge shape should favor a combination of splay flexoelectricity and biaxiality. Indeed, experiments show that these systems form phases with complex 3D modulated structures, including a bcc lattice and a more complex tetragonal structure. These results have previously been modeled through geometric arguments [22] and molecular simulation [23]. Here, we emphasize that these structures can be regarded as polar blue phases, with local nematic and polar order parameters that are modulated in periodic lattices. These order parameters can be described by plane waves with appropriate spherical-harmonic modes, just as in chiral blue phases.

In conclusion, this chapter has explored a general analogy between chirality and polarity in liquid crystals. Just as chirality induces a spontaneous twist of the director, polarity induces spontaneous splay and bend. The spontaneous twist of chiral liquid crystals most commonly leads to a cholesteric phase, but it can also lead to more complex blue phases. Similarly, experiments have already shown that the spontaneous bend of polar liquid crystals leads to a twist-bend phase, and we now argue that it can also lead to polar blue phases. This argument provides a way to interpret modulated structures in supramolecular liquid crystals, and it predicts that similar structures may form in bimesogens.
BIBLIOGRAPHY


CHAPTER 4

Coarse-grained Description of TB-forming materials

4.1 Introduction

In previous two chapters [1, 2] we have presented simulation of various modulated
phases, and analyzed the equilibrium behavior of TB-forming nematic liquid crystals
using continuum elastic theory-based mathematical modeling, where the transition
between nematic and $N_{TB}$ could be either first or second order. In this chapter we
will study the coarse-grain description of TB nematic phase, and compare the results
with our collaborator’s recent dynamic light scattering experiments (DLS) [5].

We note that the first order transition model might be useful for analyzing the
$N - N_{TB}$ transition in other systems. But, the DLS data from our collaborator gives
no indication of a first-order transition, we will stick to the second order transition
model presented in chapter 2 [1] with slight modification of $\mathbf{P}$ vector formulation
in accordance with DLS experiment. Here it is convenient to use a dimensionless
form for the order parameter, $\mathbf{P} = P/P_{sat}$, where $P_{sat}$ corresponds to the saturated
polarization at low temperature.

The free energy density expanded in terms of the fields $\hat{n}$ and $\mathbf{P}$ reads

$$F_{NTB} = \frac{K_1}{2} (\nabla \cdot \hat{n})^2 + \frac{K_2}{2} (\hat{n} \cdot \nabla \times \hat{n})^2$$

$$+ \frac{K_3}{2} [\hat{n} \times (\nabla \times \hat{n})]^2 + \frac{\mu}{2} |\mathbf{P}|^2 + \frac{\nu}{4} |\mathbf{P}|^4$$

$$+ \frac{\kappa}{2} (\nabla \mathbf{P})^2 - \lambda [\hat{n} \times (\nabla \times \hat{n})] \cdot \mathbf{P} + \eta (\hat{n} \cdot \mathbf{P})^2.$$
Here, $K_1$, $K_2$, and $K_3$ are the Frank elastic constants for splay, twist, and bend distortions of the director $\hat{n}$. The coefficient $\mu = \mu_0(T - T_0)$ is the temperature-dependent Landau coefficient for the polarization $P$, while $\nu > 0$ is a higher-order, temperature-independent Landau coefficient. The elastic constant $\kappa$ penalizes spatial distortions in $P$, and the coefficient $\lambda$ couples $P$ with bend distortions. The last term (not included in chapter 2 [1]), with $\eta > 0$, favors polarization perpendicular to the nematic director and is consistent with bend flexoelectricity. Because $P$ is defined to be dimensionless, the Landau coefficients $\mu$ and $\nu$ carry the same units, and $\kappa$ has the same units as the Frank constants.

In the $N_{TB}$ phase, the director field has the heliconical modulation as shown in fig 4.1.

$$\hat{n} = \hat{z}(1 - a^2)^{1/2} + \hat{x}a \cos(q_0 z) + \hat{y}a \sin(q_0 z),$$

(4.2)
with pitch wavenumber \( q_0 \) and sine of cone angle \( a \). Likewise, the polarization field has the helical modulation

\[
p = \hat{x}p_0 \sin(q_0 z) - \hat{y}p_0 \cos(q_0 z),
\]

(4.3)

with magnitude \( p_0 \), perpendicular to \( \hat{n} \) and to the pitch axis \( \hat{z} \). In the nematic phase, \( a \) and \( p_0 \) are both zero while \( q_0 \) is undefined; in the \( N_{TB} \) phase, these quantities all become non-zero.

To find the ground state, as in chapter 2 we must insert Eqs. (4.2) and (4.3) into Eq. (4.1) for \( F_{NTB} \) and then minimize with respect to \( q_0 \), \( a \), and \( p_0 \). Here we repeat the calculation of chapter 2 [1] and generalize it to the case of weak polar elastic constant \( \kappa \), which will turn out to be physically relevant. First, minimization with respect to \( q_0 \) gives

\[
q_0 = \frac{\lambda p_0 a (1 - a^2)^{1/2}}{\kappa p_0^2 + K_3 a^2 (1 - a^2) + K_2 a^4},
\]

(4.4)

and minimization with respect to \( a \) gives

\[
a^2 = \frac{\kappa p_0^2}{K_2} + \sqrt{\frac{\kappa p_0^2}{K_2} \left( 1 + \frac{\kappa p_0^2}{K_2} \right)}.
\]

(4.5)

Equation (4.5) can be compared with the experiment of Ref. [6], which shows the cone angle \( \sin^{-1}(a) \leq 10^\circ \) within the temperature range covered by the DLS data. This result implies that \( p_0(\kappa/K_2)^{1/2} \approx 0.03 \). Because \( p_0 \) is a scaled polarization, which grows to order 1 at low temperature, we estimate that \( (\kappa/K_2)^{1/2} \approx 0.03 \), which shows that the polarization elasticity is small compared with the Frank director elasticity.

Substituting Eqs. (4.4) and (4.5) into the free energy density and expanding for
small $p_0$ and $\kappa$ gives

$$F_{NTB} = \frac{1}{2} \left[ \mu_0(T - T_0) - \frac{\lambda^2}{K_3} \right] p_0^2 + \frac{\lambda^2 \kappa^{1/2} K_2^{1/2}}{K_3^2} |p_0|^3 + \frac{1}{4} \nu p_0^4.$$  \hspace{1cm} (4.6)

From this form of the effective free energy density, we can see that there is a second-order transition from the nematic to the $NTB$ phase at the temperature

$$T_{TB} = T_0 + \frac{\lambda^2}{K_3 \mu_0}.$$  \hspace{1cm} (4.7)

This transition is unusual because the relative magnitudes of the cubic and quartic terms in Eq. (4.6) depends on the relative smallness of $p_0$ and $\kappa$. Close to the transition, where $p_0 \ll (\lambda^2 \kappa^{1/2} K_2^{1/2})/(K_3^2 \nu)$, the cubic term dominates over the quartic term. By minimizing the effective free energy, we see that $p_0$ depends on temperature as

$$p_0(T) = \frac{K_3^2 \mu_0(T_{TB} - T)}{3 \lambda^2 \kappa^{1/2} K_2^{1/2}}.$$  \hspace{1cm} (4.8)

This result is consistent with the scaling presented in chapter 2 [1], with a slight correction in the numerical coefficient. By contrast, farther from the transition, where $p_0 \gg (\lambda^2 \kappa^{1/2} K_2^{1/2})/(K_3^2 \nu)$, the quartic term dominates over the cubic term, and the prediction for $p_0$ becomes

$$p_0(T) = \sqrt{\frac{\mu_0(T_{TB} - T)}{\nu}}.$$  \hspace{1cm} (4.9)
The crossover between these two regimes occurs at

\[ (T_{TB} - T) = \frac{9\lambda^4 K_2}{K_3^4 \mu_0 \nu}. \]  \hspace{1cm} (4.10)

We will see below that this crossover point is extremely close to the transition, so that all of the experimental data are taken in the regime governed by Eq. (4.9) rather than Eq. (4.8).

Now that we have determined the ground state, we will consider fluctuations about the ground state in the nematic and N\(_{TB}\) phases.

### 4.2 Nematic phase

In the nematic phase of TB-forming materials, we must consider fluctuations in the director field about the ground state \( n = z \), and fluctuations in the polarization about the ground state \( p_0 = 0 \). At lowest order, these fluctuations can be described by \( \delta n(r) = (n_x, n_y, 0) \) and \( \delta p(r) = (p_x, p_y, p_z) \). We insert these expressions into the free energy of eqn (2.28), and expand to quadratic order in the fluctuating components. We then Fourier transform from position \( r \) to wavevector \( q \), and express the free energy as a quadratic form in \( n_x(q), n_y(q), p_x(q), p_y(q), \) and \( p_z(q) \).

\[
F = \frac{1}{2} \sum_q \begin{pmatrix} n_{xq} \\ p_{xq} \\ n_{yq} \\ p_{yq} \\ p_{zq} \end{pmatrix}^\dagger M_{\text{nem}}(q) \begin{pmatrix} n_{xq} \\ p_{xq} \\ n_{yq} \\ p_{yq} \\ p_{zq} \end{pmatrix}. \hspace{1cm} (4.11)
\]

The matrix \( M_{\text{nem}} \) is given by the following expression.
\[ M_{\text{nem}} = \begin{pmatrix} m_{11} & m_{12} & 0 & 0 & 0 \\ m_{21} & m_{22} & 0 & 0 & 0 \\ 0 & 0 & m_{33} & m_{34} & 0 \\ 0 & 0 & m_{43} & m_{44} & 0 \\ 0 & 0 & 0 & 0 & m_{55} \end{pmatrix} \] (4.12)

where

\[ m_{11} = K_1 q_x^2 + K_2 q_y^2 + K_3 q_z^2 \]
\[ m_{21} = -m_{12} = i \lambda q_z \]
\[ m_{22} = \mu + \kappa |\mathbf{q}|^2 \]
\[ m_{33} = K_2 q_x^2 + K_1 q_y^2 + K_3 q_z^2 \]
\[ m_{43} = -m_{34} = i \lambda q_z \]
\[ m_{44} = \mu + \kappa |\mathbf{q}|^2 \]
\[ m_{55} = 2 \eta + \mu + \kappa |\mathbf{q}|^2 \] (4.13)

By diagonalizing this quadratic form, we obtain five normal modes:

(1) One hydrodynamic mode is primarily splay-bend director fluctuations, combined with some polarization fluctuations. Its relaxation rate is the ratio of the free energy eigenvalue to the relevant viscosity coefficient \( \gamma_n \), which gives

\[ \Gamma_1^n = \frac{K_1 q_x^2 + K_3^{\text{eff}} q_z^2}{\gamma_n} \] (4.14)
in the limit of long wavelength (small $q$). Here,

$$K_3^{\text{eff}} = K_3 - \frac{\lambda^2}{\mu} = K_3 - \frac{\lambda^2}{\mu'(T - T_0)}$$  \hspace{1cm} (4.15)

is the renormalized bend elastic constant [1], which shows the effect of coupling the director to the polarization. This effect accounts for the softening of bend fluctuations observed in earlier DLS studies of the director modes when $T \to T_{TB}$ from the nematic side [7]. $K_3^{\text{eff}} = 0$ at $T = T_{TB}$.

(2) Another hydrodynamic mode is primarily twist-bend director fluctuations, combined with some polarization fluctuations. Its relaxation rate is

$$\Gamma_2^p = \frac{K_2 q_1^2 + K_3^{\text{eff}} q_2^2}{\gamma_n}$$  \hspace{1cm} (4.16)

(3, 4) Two nonhydrodynamic modes are mostly polarization fluctuations $p_x$ and $p_y$, combined with some director fluctuations. In the limit of $q \to 0$, these modes have relaxation rate

$$\Gamma_2^p = \frac{\mu}{\gamma_p} = \frac{\mu_0(T - T_0)}{\gamma_p}$$  \hspace{1cm} (4.17)

(5) Another nonhydrodynamic mode is polarization $p_z$ by itself. In the limit of $q \to 0$, it has relaxation rate

$$\Gamma_2^{p'} = \frac{2\eta + \mu}{\gamma_{p'}} = \frac{2\eta + \mu_0(T - T_0)}{\gamma_{p'}}$$  \hspace{1cm} (4.18)

Here, $\gamma_p$ and $\gamma_{p'}$ are the mode viscosities.

Overall, we should emphasize the contrast between the nematic phase of the $N_{TB}$-forming material studied here and a typical nematic phase. In the $N_{TB}$-forming
material, we observe a nonhydrodynamic mode with a relaxation rate that decreases with temperature, as the system approaches the transition to the $N_{\text{TB}}$ phase. The theory attributes this mode to polarization fluctuations, which become less energetically costly as the system develops incipient polar order. By contrast, in a typical nematic phase, no such mode can be observed in DLS experiments; presumably polarization fluctuations decay too rapidly to be detected.

4.3 Twist-bend phase

In the $N_{\text{TB}}$ phase, the analysis of normal modes is complicated because of the nonuniform, modulated director structure. However, as mentioned in the Introduction, we can simplify this calculation through a coarse-graining approximation, which averages over the director modulation to find the larger-scale properties of the phase. Such coarse graining has previously been done for the cholesteric phase [10], and it shows that the cholesteric has the same macroscopic elastic properties as a smectic phase. In this section, we generalize the coarse-graining procedure to the more complex case of the $N_{\text{TB}}$ phase. Indeed, it should be an even better approximation for the $N_{\text{TB}}$ than for the cholesteric phase, because the pitch of the $N_{\text{TB}}$ is so short.

We suppose that the director field has a rapid heliconical modulation with respect to a local orthonormal reference frame $(\hat{e}_1(\mathbf{r}), \hat{e}_2(\mathbf{r}), \hat{t}(\mathbf{r}))$, and this orthonormal frame varies slowly in space. Furthermore, the heliconical modulation might be displaced upward or downward by a phase $\phi(\mathbf{r})$, which also varies slowly in space. Hence, the director field can be written as

$$\mathbf{n}(\mathbf{r}) = \hat{t}(\mathbf{r})(1 - a^2)^{1/2} + \hat{e}_1(\mathbf{r})a \cos(q_0z + \phi(\mathbf{r})) + \hat{e}_2(\mathbf{r})a \sin(q_0z + \phi(\mathbf{r})).$$

(4.19)
In this expression, \( \hat{t}(\mathbf{r}) \) is the coarse-grained director, which would be measured in any experiment that averages over the nanoscale heliconical modulation. By analogy with the director field, the polarization field has a rapid helical modulation with respect to the same local orthonormal reference frame, which can be written as

\[
\mathbf{P}(\mathbf{r}) = \hat{e}_1(\mathbf{r}) p_0 \sin(q_0 z + \phi(\mathbf{r}))
- \hat{e}_2(\mathbf{r}) p_0 \cos(q_0 z + \phi(\mathbf{r})) + \delta \mathbf{p}(\mathbf{r}).
\]  

(4.20)

Here, \( \delta \mathbf{p}(\mathbf{r}) = \delta p_x \hat{x} + \delta p_y \hat{y} + \delta p_z \hat{z} \) is a fluctuating additional contribution to the polarization, which varies slowly in space. It is allowed because \( \mathbf{P} \) is not restricted to be a unit vector. The contribution \( \delta \mathbf{p}(\mathbf{r}) \) is the coarse-grained polarization, which would be measured in any experiment that averages over the nanoscale helical modulation.

From Eqs. (4.19–4.20), we can see that the pseudo-layers are surfaces of constant \( q_0 z + \phi(\mathbf{r}) = q_0 (z - u(\mathbf{r})) \), where \( u(\mathbf{r}) = -\phi(\mathbf{r})/q_0 \) is the local pseudo-layer displacement. The local helical axis (or pseudo-layer normal) is given by the gradient

\[
\hat{N}(\mathbf{r}) = \frac{\nabla(q_0 z + \phi(\mathbf{r}))}{|\nabla(q_0 z + \phi(\mathbf{r}))|} = \frac{\hat{z} - \nabla u}{|\hat{z} - \nabla u|}.
\]  

(4.21)

For a well-aligned sample, the coarse-grained director \( \hat{t}(\mathbf{r}) \) has small fluctuations
about \( \hat{z} \), while the phase \( \phi(\mathbf{r}) \) and coarse-grained polarization \( \delta \mathbf{p}(\mathbf{r}) \) have small fluctuations around 0. The full orthonormal reference frame can be written as

\[
\hat{e}_1(\mathbf{r}) = \left( 1 - \frac{1}{2} t_x^2 \right) \hat{x} - \frac{1}{2} t_x t_y \hat{y} - t_y \hat{z},
\]

\[
\hat{e}_2(\mathbf{r}) = -\frac{1}{2} t_x t_y \hat{x} + \left( 1 - \frac{1}{2} t_y^2 \right) \hat{y} - t_y \hat{z},
\]

\[
\hat{t}(\mathbf{r}) = t_x \hat{x} + t_y \hat{y} + \left( 1 - \frac{1}{2} t_x^2 - \frac{1}{2} t_y^2 \right) \hat{z},
\]

(4.22)


to quadratic order in \( t_x(\mathbf{r}) \) and \( t_y(\mathbf{r}) \). One might think that another variable would be needed to specify the vectors \( \hat{e}_1 \) and \( \hat{e}_2 \) in the plane perpendicular to \( \hat{t} \). However, rotations in this plane can be included in the choice of the phase \( \phi \). As discussed in Ref. [10] for the cholesteric case, such rotations are analogous to gauge transformations. Hence, we make the specific choice of gauge in Eq. (4.22). With this choice, our orthonormal basis has small fluctuations away from \((\hat{x}, \hat{y}, \hat{z})\).

We insert Eqs. (4.19–4.20) for the director and polarization fields, together with Eq. (4.22) for the orthonormal basis, into Eq. (4.1) for the free energy of the \( N_{TB} \) phase. We then make the coarse-graining approximation: We integrate over the rapid variations of \( \cos q_0 z \) and \( \sin q_0 z \), assuming that the slowly varying fields are constant over the length scale of the pitch. We thus obtain an effective free energy in terms of the six coarse-grained variables \( \phi(\mathbf{r}), t_x(\mathbf{r}), t_y(\mathbf{r}), \delta p_x(\mathbf{r}), \delta p_y(\mathbf{r}), \) and \( \delta p_z(\mathbf{r}) \). We expand the free energy to quadratic order in these fields, and Fourier transform it.
from position \( \mathbf{r} \) to wavevector \( \mathbf{q} \), to obtain

\[
F = \frac{1}{2} \sum_{\mathbf{q}} \left( \begin{array}{c}
\phi_{\mathbf{q}} \\
t_{x\mathbf{q}} \\
\delta p_{y\mathbf{q}} \\
\delta p_{x\mathbf{q}} \\
\delta p_{z\mathbf{q}} \\
\end{array} \right)^\dagger \mathbf{M}_{\text{TB}}(\mathbf{q}) \left( \begin{array}{c}
\phi_{\mathbf{q}} \\
t_{x\mathbf{q}} \\
\delta p_{y\mathbf{q}} \\
\delta p_{x\mathbf{q}} \\
\delta p_{z\mathbf{q}} \\
\end{array} \right).
\]  

(4.23)

Here, \( \mathbf{M}_{\text{TB}}(\mathbf{q}) \) is a matrix of wavevector-dependent coefficients, which must be diagonalized to find the normal modes.

It is most convenient to understand the mode structure in the limit of \( \mathbf{q} \to 0 \). In this limit, the matrix simplifies to the block-diagonal form

\[
\mathbf{M}(0) = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & m_{22} & m_{23} & 0 & 0 & 0 \\
0 & m_{32} & m_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & m_{44} & m_{45} & 0 \\
0 & 0 & 0 & m_{54} & m_{55} & 0 \\
0 & 0 & 0 & 0 & 0 & m_{66}
\end{pmatrix},
\]

(4.24)
where

\[ m_{22} = m_{44} = p_0q_0\lambda a + \frac{1}{2}(K_1 + K_2 - 2K_3)q_0^2a^2, \]
\[ m_{33} = m_{55} = \mu + 2
\nu p_0^2 + \eta a^2, \]
\[ m_{23} = m_{32} = -m_{45} = -m_{54} = -\frac{1}{2}q_0\lambda a^2, \]
\[ m_{66} = (2\eta + \mu) + \nu p_0^2 - 2\eta a^2. \tag{4.25} \]

Note that, in the nematic side of the transition \((a = 0, p_0 = 0, q_0 = 0)\), the eigenmodes reduce to \(M_{\text{nem}}\) of eq. (4.13) when wave vector equal to zero.

From this block-diagonal form, we can extract the following six normal modes:

1. The phase \(\phi = -u/q_0\) is itself a normal mode. This mode is hydrodynamic, with zero energy (and zero relaxation rate) in the limit of \(q \to 0\). It is analogous to the layer displacement of a smectic-A phase, which costs zero energy for uniform displacement. It is also analogous to the hydrodynamic director mode in a cholesteric phase (which is called the pure twist mode in the theory of cholesteric light scattering [8]). It is visualized in terms of pseudo-layers in Fig. (4.2).

2. The coarse-grained director tilt \(t_x\) and polarization \(\delta p_y\) are coupled by the helicity of the N\(_{\text{TB}}\) phase. Together, they form a pair of normal modes, both of which are non-hydrodynamic, with non-zero energy (and non-zero relaxation rate) in the limit of \(q \to 0\). In the limit of weak coupling, which is given by the criterion \(m_{22}m_{33} \gg m_{23}^2\),

\[ \Gamma^t = m_{22}/\gamma_t, \]
\[ \Gamma^p = m_{33}/\gamma_p. \tag{4.26a} \]
\[ \Gamma^p = m_{33}/\gamma_p. \tag{4.26b} \]
Figure 4.2: Visualization of soft mode in the $N_{TB}$ phase when $q = 0$. Small cylinders represent the heliconical director field $\hat{n}(r)$, and surfaces represent the pseudo-layers. This hydrodynamic mode has uniform rotation of $\hat{n}(r)$ and hence uniform displacement of pseudo-layers; this mode has no energy cost with respect to the ground state. It is merely a rotation of directors about the helical axis keeping the cone angle constant.
Here, $\gamma_t$ and $\gamma_p$ are phenomenological viscosities associated with the normal modes. The two modes are analogous to tilt and polarization fluctuations in a chiral smectic-A phase. The tilt mode is also analogous to the non-hydrodynamic director mode in a cholesteric phase (which is called the umbrella mode in the theory of cholesteric light scattering [8]). The tilt mode is visualized in Fig. (4.3); the polarization mode is not visualized.

A coupling between tilt and polarization (even if weak – i.e., small $m_{23}$) has an important physical significance. If an electric field is applied in the $y$-direction, it induces a polarization $\delta p_y$. Because of the coupling, it must also induce a tilt $t_x$. Hence, the $N_{TB}$ phase has an electroclinic effect, analogous to a chiral smectic-A phase. The sign of the electroclinic effect depends on the sign of $m_{23}$, which is controlled by the sign of the helicity $q_0$. For that reason, domains of right and left-handed helicity must have opposite electroclinic effects. In earlier work, a weak electroclinic effect was observed experimentally and modeled by a different theoretical method [9]. Here, we see that it is a consequence of the coarse-grained free energy. I will also show some preliminary simulation results regarding this electroclinic effect in the conclusion chapter of this dissertation.

(4, 5) The coarse-grained director tilt $t_y$ and polarization $\delta p_x$ form another pair of nonhydrodynamic normal modes, which is degenerate with the previous pair.

(6) The polarization component $\delta p_z$ is itself a nonhydrodynamic normal mode. Its relaxation rate is

$$\Gamma' = m_{66}/\gamma_p,$$

(4.27)

where $\gamma_p'$ is the viscosity of this mode.

If the wavevector $q$ is small but nonzero, the five nonhydrodynamic modes are
Figure 4.3: Visualization of umbrella mode when $q = 0$. It is also called nonhydrodynamic tilt mode, with the coarse-grained director $\hat{t}$ (average of $\hat{n}(r)$) tilted with respect to pseudo-layer normal. It has the director variations away from optimal cone angles.
only slightly changed. To model their relaxation rates, we can still use Eqs. (4.26) and (4.27) derived above. However, the hydrodynamic mode is more significantly changed. We can consider the cases of \( q \) parallel and perpendicular to the \( z \)-direction separately: When wave vector \( q \) is along \( z \) direction, the matrix \( M(q = q_z z) \) simplifies to the following expression.

\[
M(q_z) = \begin{pmatrix}
    m_{11}(q_z) & 0 & 0 & 0 & 0 & 0 \\
    0 & m_{22}(q_z) & m_{23}(q_z) & m_{24}(q_z) & m_{25}(q_z) & 0 \\
    0 & m_{32}(q_z) & m_{33}(q_z) & m_{34}(q_z) & 0 & 0 \\
    0 & m_{42}(q_z) & m_{43}(q_z) & m_{44}(q_z) & m_{45}(q_z) & 0 \\
    0 & m_{52}(q_z) & 0 & m_{54}(q_z) & m_{55}(q_z) & 0 \\
    0 & 0 & 0 & 0 & 0 & m_{66}(q_z)
\end{pmatrix}
\]  

(4.28)

For \( q \) in the \( z \)-direction, the hydrodynamic mode still involves the phase \( \phi \) by itself, not coupled with any other coarse-grained degrees of freedom. It is zero when \( q_z \) is zero. This mode will give the elastic constant \( B_{\text{eff}} \) associated with compression (dilation) of the pseudo-layers. This mode is visualized in Fig. (4.4). It is a \( z \)-dependent rotation of the heliconical director field \( \hat{n}(r) \), which does not change the coarse-grained director \( \hat{t} \). Equivalently, this mode can be regarded as a \( z \)-dependent displacement \( u = -\phi/q_0 \) of the pseudo-layers, leading to alternating compression and dilation of the pseudo-layer structure. In the limit of long wavelength (small \( q \)), the free energy cost of this fluctuation is \( \frac{1}{2}B_{\text{eff}}q_z^2|u_q|^2 \), where

\[
B_{\text{eff}} = (K_2a^4 + K_3a^2(1 - a^2) + \kappa p^2) q^2.
\]  

(4.29)
Figure 4.4: Visualization of soft mode when $q$ is along $z$ direction. It is a hydrodynamic mode with $q = q \hat{z}$, with $z$-dependent rotation of $\hat{n}(r)$ and $z$-dependent displacement of pseudo-layers (leading to compression and dilation).
Hence, the relaxation rate is \( \Gamma^u(q_z) = \frac{1}{2} \gamma_u^{-1} B_{\text{eff}} q_z^2 \), where \( \gamma_u \) is the relevant viscosity.

When wave vector \( \bm{q} \) is along \( \mathbf{x} \) direction, the matrix \( \bm{M}(\bm{q} = q_x \mathbf{x}) \) simplifies to the following expression.

\[
\bm{M}(\bm{q}_x) = \begin{pmatrix}
  m_{11}(q_x) & m_{12}(q_x) & m_{13}(q_x) & 0 & 0 & 0 \\
  m_{21}(q_x) & m_{22}(q_x) & m_{23}(q_x) & 0 & 0 & m_{26}(q_x) \\
  m_{31}(q_x) & m_{32}(q_x) & m_{33}(q_x) & 0 & 0 & 0 \\
  0 & 0 & 0 & m_{44}(q_x) & m_{45}(q_x) & 0 \\
  0 & 0 & 0 & m_{54}(q_x) & m_{55}(q_x) & 0 \\
  0 & m_{62}(q_x) & 0 & 0 & 0 & m_{66}(q_x)
\end{pmatrix}
\]

(4.30)

In this case the soft mode (pure \( \phi \)) does not decouple from other modes, and depends on wave vector \( q_z \), zero when \( q_x \) is zero as well. This mode will give the effective splay elastic constant \( K_{\text{eff}} \). In order to find the eigenvalues we need to diagonalize the matrix in this case. So, for \( \bm{q} \) in the \( x \)-direction, this hydrodynamic normal mode is a linear combination of \( \phi, t_x, \) and \( \delta p_y \), as visualized in Fig.(4.5). This mode is an \( x \)-dependent rotation of the \( \hat{\mathbf{n}}(\mathbf{r}) \), or equivalently an \( x \)-dependent displacement of the pseudo-layers, leading to curvature of the pseudo-layer structure. This displacement is accompanied by a tilt of the coarse-grained director in the \( x \)-direction, so that the local \( \hat{\mathbf{t}} \) remains normal to the local pseudo-layers. If \( \bm{q} \) is in any other direction in the \( (x, y) \) plane, the same description applies with the corresponding rotation. The free energy cost of this fluctuation is \( \frac{1}{2} K_{\text{eff}} q_\perp^4 |u_q|^2 \), where

\[
K_{\text{eff}} = K_1 (1 - a^2) + \frac{1}{2} \left( \kappa p^2 + K_3 a^2 \right),
\]

(4.31)
Figure 4.5: Visualization of soft mode when \( q \) is along \( x \) direction. It is a hydrodynamic mode with \( \mathbf{q} = q\hat{x} \), with \( x \)-dependent rotation of \( \mathbf{n}(r) \) and \( x \)-dependent displacement of pseudo-layers (leading to curvature), accompanied by tilt so that \( \hat{t} \) remains normal to pseudo-layers. Because of splay director deformations layers get curved.
to lowest order in small $a$. Hence, the relaxation rate is $\Gamma^u(q_\perp) = \frac{1}{2} \gamma_u^{-1} K_{\text{eff}} q_\perp^4$.

In both cases, the effective elasticity of the $N_{TB}$ phase is equivalent to a smectic-A phase, with $B_{\text{eff}}$ and $K_{\text{eff}}$ playing the roles of the elastic moduli for compression and bending of the smectic layers, respectively. In that way, our coarse-graining of the $N_{TB}$ phase is analogous to earlier work on coarse-graining of the cholesteric phase, which also has effective smectic elasticity [10].

To fit the experimental data for relaxation rates as functions of temperature, we combine Eq. (4.17) in the nematic phase and Eqs. (4.25–4.26) in the $N_{TB}$ phase. For the equilibrium cone angle $\sin^{-1}(a)$ and pitch wavenumber $q_0$, we use the leading terms in Eqs. (4.4–4.5) near the second-order transition, which give $a^2 \approx p_0(\kappa/K_2)^{1/2}$ and $q_0 \approx (\lambda/K_3)p_0^{1/2}(K_2/\kappa)^{1/4}$. For the equilibrium polarization $p_0$, we use the approximation of Eq. (4.9), derived with the assumption of small polarization elasticity $\kappa$. The predicted relaxation rates then become

$$
\Gamma^p(T > T_{TB}) = \frac{\mu_0}{\gamma_p} \left[ \frac{\lambda^2}{K_3\mu_0} + (T - T_{TB}) \right], \quad (4.32a)
$$

$$
\Gamma^t(T < T_{TB}) = \frac{\lambda^2(K_1 + K_2)\mu_0(T_{TB} - T)}{2\gamma_1 K_3^2 \nu}, \quad (4.32b)
$$

$$
\Gamma^p(T < T_{TB}) = \frac{\mu_0}{\gamma_p} \left[ \frac{\lambda^2}{K_3\mu_0} + \eta \sqrt{\frac{\kappa(T_{TB} - T)}{K_2 \mu_0 \nu}} 
+ (T_{TB} - T) \right]. \quad (4.32c)
$$

We can compare Eqs. (4.32) directly with the light scattering experimental results. In this comparison, we assume that the orientational viscosities $\gamma_t$ and $\gamma_p$ do not vary strongly with temperature. Both theoretical and experimental results of the Normal Mode energies are plotted in both side of nematic to TB nematic transition in figure
4.6, which is in good agreement. First, fitting Eq. (4.32a) to the data for $\Gamma^p$ in the
Figure 4.6: Temperature dependence of relaxation rates associated with director and
polarization fluctuations in both side of the transition: Experiment and Theory
nematic phase, we find $\mu_0/\gamma_p = 3600 \text{ s}^{-1} \text{ K}^{-1}$ and $\lambda^2/K_3\mu_0 = 31 \text{ K}$. The fit is shown as a solid line in Fig.(4.6) ($T > T_{TB}$).

Second, the data for $\Gamma^d$ in the $N_{TB}$ phase are consistent with the linear dependence
in Eq. (4.32b). This consistency confirms that the experiment is in the regime where
$\rho_0$ follows the approximation of Eq. (4.9) rather than Eq. (4.8). The experimental slope corresponds to the combination of parameters $\lambda^2(K_1 + K_2)\mu_0/(2\gamma_\perp K_3^2\nu) = 84000 \text{ s}^{-1} \text{ K}^{-1}$. This fit is shown as a solid line in Fig.(4.6) (lower plot, $T < T_{TB}$).

Third, the data for $\Gamma^p$ in the $N_{TB}$ phase can be fit to the expression in Eq. (4.32c),
as shown by the solid line in Fig.(4.6) (upper plot, $T < T_{TB}$). In this fit, we use the
parameters $\mu_0/\gamma_p = 3600 \, s^{-1} \, K^{-1}$ and $\lambda^2/K_3\mu_0 = 31 \, K$ obtained from the analysis of $\Gamma^p$ in the nematic phase. The fit yields $\eta K^{1/2}(K_2\mu_0\nu)^{-1/2} = 1200 \, K^{1/2}$.
BIBLIOGRAPHY


CHAPTER 5

Conclusion

5.1 Introduction

This dissertation presents a microscopic theory of polar order and director deformations in nematic liquid crystals, and a macroscopic Landau theory-based analytical calculation. The flexoelectric coupling between polarization and director distortions is attributed to the appearance of spontaneous polarization due to the symmetry breaking transition from nematic to modulated phases [1, 2]. We presented simulations of these modulated phases using the Monte Carlo technique with the simulated annealing randomized optimization method. The simulations and analytical results are in a good qualitative agreement with experiment for the recently discovered twist-bend nematic phase, where the modulation is along one of the space dimensions. If this flexoelectric coupling is strong enough, in addition to 1D modulated phases (twist-bend and splay-bend), here we also predict the formation of a polar analog of chiral blue phases (in both 2D and 3D) made of achiral polar liquid crystal materials by using both Landau theory-based numerical calculations and computer simulations, where a new optimization technique is developed to unfold this physical phenomenon.

The important distinctions between the polarity and chirality driven modulated structures are the scale of the modulation and director orientations. In the polarity driven nematic twist-bend modulated structures, the modulation is found to be of nano-meter scale and the director precesses in a cone about the helical axis with a
fixed cone angle whereas in the chirality driven case it is of micro-meter scale and the
director remains perpendicular to the helix axis.

This dissertation models both first order and second order transition behavior from
regular nematic to twist-bend nematic. Further, the macroscopic elastic properties of
the twist-bend nematic phase have been modeled using a coarse-grained description
of the theory. This theory predicts normal modes of fluctuation on both sides of the
transition, which can then be compared with light scattering experiments [4].

Heliconical modulated structures in nematic liquid crystals are still new and they
are evolving and branching out. There are multiple challenges that need to be over-
come in the next few years. One example is to study the explicit symmetry breaking
due to the interaction of modulated structures with an applied electric field. This
can be modeled by including the field term in the free energy density. Also the
consequence of adding a chiral component to the nematic twist-bend materials can
be studied on top of the method developed in this dissertation. Similarly, the ana-
lytical calculations and simulation studies of flexoelectric and converse flexoelectric
coefficients can be carried out in the model developed.

5.2 Future Work

5.2.1 Electroclinic Effect (ECE)

It can be seen from the coarse-grained theory of nematic twist-bend structures
from chapter 4 eqn 4.24 that, at wave vector \( k = 0 \) the quadratic matrix \( M \) takes
the block diagonal form, where \( t_x \) is coupled to \( p_y \), and \( t_y \) is coupled to \( p_x \). This
coupling will give rise to an electroclinic effect as in chiral smectic-A liquid crystals.
If we apply an electric field along the \( y \) direction, a polarization \( p_y \) will be induced
Figure 5.1: Simulation result of ECE: red rods represent directors and green arrows represent polar order. When an applied field is non-zero, the rotational symmetry in polarization $p$ is broken.

in that direction. As a result of that coupling there will be induced tilt along $t_x$ perpendicular to the applied field. A preliminary simulation result also captures this electroclinic effect as shown in fig. 5.1 and 5.2. This result describes a linear electro-optic effect in the $N_{TB}$ phase, with the field-induced rotation of the optic axis in a plane perpendicular to $E$. These features suggest that it is a close analog to well-known effects in other chiral mesophases.

However, these ideas need further investigation; for example calculation of the average tilt as a function of applied field using a simulation method, and comparison of the results with the theory and experiment of C. Meyer, G.R. Luckhurst, and I Dozov [3], where they studied the electro-optics of this novel twist-bend phase. Their ECE measurements confirmed the ultrafast, submicrosecond response times with this
Figure 5.2: Simulation result of ECE: $p$ vector mostly in $y$ direction, $n_z$ is negative where $p_y$ is positive, which tells that an average director tilts towards negative $z$ directions.

nano-meter scale modulated structure.

5.2.2 Chiral dopants with twist-bend nematic materials

A recent study on a bimesogen mixture of twist bend nematic and a small percentages of a chiral material by Goodby’s group from the UK [5] indicates a potential scope to extend our model. Their phase diagram shows a wide temperature range blue phase at low dopant concentrations, whereas at higher concentrations an additional ‘nematic-like’ mesophase was discovered. They speculated this unknown phase could be one of the higher dimensional structures predicted in chapter 3. An interesting research project would be to add a chiral term in the free energy density developed in eqn. 3.8 of chapter 3, and work out the numerical phase diagram. It is expected that the extra term would secure places for cholesteric and blue phases in the phase
diagram. Transitions among various phases could be particularly interesting due to the presence of chirality and polarity at the same time in a liquid crystal material.

Despite these successes, modulated phases have many challenges to overcome; whether they will be able to make their way towards more potential applications in LCD industries with their ultrafast switching capabilities or they remain only as an interesting liquid crystal physics entity remains to be seen. The potential of these studies are now at a high standard with significant but surmountable challenges. Given the rapid growth of the field in the last few years, advancement in the structural understanding, synthesis of different dimer molecules, discovery of various computational and analytical methods, I am optimistic that heliconical modulated phase studies will make remarkable advancements towards these goals.
BIBLIOGRAPHY


APPENDIX A

Appendix

A.1 Simulation code for twist-bend and splay-bend phases described in chapter 2

/*
This program will calculate Q tensor and b vectors
for twist–bend phase, and write to files
*/

#include <iostream>
#include <fstream>
#include <iomanip>
#include <cmath>
#include <math.h>
#include <cstdlib>
#include <complex>
#include <stdlib.h>

#define nsteps 140000
#define eqsteps 100000
#define PI acos(0.0)*2.0
#define Lx 20
#define Ly 20
#define A 2
#define B1 0.5
```cpp
#define B2 0.4
#define C -2.0
#define Tcut 0.5

using namespace std;

double th, thm;
double ph, phm, mag;

/*function for periodic boundary conditions*/
int period(int ii, int NN)
{
    if (ii==NN){ii=0;}
    if (ii==-1){ii=NN-1;}
    return ii;
}

/*function for random initialization of n and p vectors */
void initialize(double nx[][Ly], double ny[][Ly], double nz[][Ly], double bx[][Ly],
                double by[][Ly], double bz[][Ly])
{
    for (int i=0; i<Lx; i++) {
        for (int j=0; j<Ly; j++) {
            ph=drand48()*PI*2;
            th=acos(2*drand48()-1);
            phm=drand48()*PI*2;
            thm=acos(2*drand48()-1);
            nx[i][j]=sin(th)*cos(ph);
            ny[i][j]=sin(th)*sin(ph);
            nz[i][j]=cos(th);
            mag=sqrt(pow((cos(thm)*sin(ph)*sin(th)-cos(th)*sin(phm)*sin(thm)),2))
        }
    }
}
\[ + \text{pow}( - \cos(\phi) \times \cos(\theta_m) \times \sin(\theta) + \cos(\phi_m) \times \cos(\theta) \times \sin(\theta_m) , 2) \]
\[ + \text{pow}( - \sin(\phi - \phi_m) \times \sin(\theta) \times \sin(\theta_m) , 2)) ; \]
\[ b_{x[i][j]} = (\cos(\theta_m) \times \sin(\phi) \times \sin(\theta) - \cos(\phi) \times \cos(\theta) \times \sin(\phi_m) \times \sin(\theta_m)) / \text{mag} ; \]
\[ b_{y[i][j]} = (\cos(\phi) \times \cos(\theta_m) \times \sin(\theta) + \cos(\phi_m) \times \cos(\theta) \times \sin(\theta_m)) / \text{mag} ; \]
\[ b_{z[i][j]} = (\sin(\phi - \phi_m) \times \sin(\theta) \times \sin(\theta_m)) / \text{mag} ; \]

```c
int main(void)
{

double gamma=PI/36;
double gammalimit=PI/18;
double prob=0.0;
double L=Lx*Ly;

// possible directions in 2D for Monte Carlo walk
int dx[4]={1, -1, 0, 0};
int dy[4]={0, 0, 1, -1};
double nx[Lx][Ly];
double ny[Lx][Ly];
double nz[Lx][Ly];
double bx[Lx][Ly];
double by[Lx][Ly];
double bz[Lx][Ly];
double nxnew, nynew, nznew, bxnew, bynew, bznew;
double cosalp, sinalp, delt, nidotnj, bidotbj, bidotbjnew;

//ofstream write("splaybendbandnlist.xyzvc");
```
ofstream write1("Qtensors.txt");

// xyzvc file for paraview visualization
ofstream write2("blist.xyzvc");

// ofstream write3("energy.txt");
srand48(time(NULL));

// initialize n abd b vectors
initialize(nx,ny,nz,bx,by,bz);

double etot=0.0,xavg=0.0,yavg=0.0,zavg=0.0,sum=0.0,nxavg=0.0,nyavg=0.0;
double nzavg=0.0,nsum=0.0;

// initialize arrays for b vectors
double bsumx[Lx][Ly]={0.0},bsumy[Lx][Ly]={0.0},bsumz[Lx][Ly]={0.0};

// initialize arrays for Q tensor
double Qxx[Lx][Ly]={0.0},Qyy[Lx][Ly]={0.0},Qzz[Lx][Ly]={0.0},Qxy[Lx][Ly]={0.0};
double Qyz[Lx][Ly]={0.0},Qxz[Lx][Ly]={0.0};

for (int istep=0; istep<nsteps; istep++) {

    // simulated annealing set up
    double T=1.0*pow(0.99, istep/500);
    if (T<Tcut) {
        T=Tcut;
    }
}
int i, j, in, jn, naccept = 0;

for (int itries = 0; itries < L; itries++) {
    i = floor(drand48() * Lx);
    j = floor(drand48() * Ly);
    double eold = 0.0, ux, uy, uz;

    for (int idir = 0; idir < 4; idir++) {
        // loop for calculating energy before the Monte Carlo move
        in = period(i + dx[idir], Lx);
        jn = period(j + dy[idir], Ly);

        nidotnj = nx[i][j] * nx[in][jn] + ny[i][j] * ny[in][jn] + nz[i][j] * nz[in][jn];
        bidotbj = bx[i][j] * bx[in][jn] + by[i][j] * by[in][jn] + bz[i][j] * bz[in][jn];

        eold += -A * pow(nidotnj, 2) - B1 * bidotbj - B2 * pow(bidotbj, 2)
            + C * 0.25 * ((bx[in][jn] * nx[i][j] + by[in][jn] * ny[i][j] + bz[in][jn] * nz[i][j])
            + (-dy[idir]) * (nx[i][j] + nidotnj * nx[in][jn]) - (bx[i][j] * nx[in][jn]
            + by[i][j] * ny[in][jn] + bz[i][j] * nz[in][jn]) * ((-dx[idir]) * (nx[in][jn]
            + nidotnj * nx[i][j]) + (-dy[idir]) * (nx[in][jn] + nidotnj * nz[i][j]));
    }

    cosalp = 2 * drand48() - 1;
    sinalp = sqrt(1 - cosalp * cosalp);
    delt = 2 * PI * drand48();

    ux = sinalp * cos(delt);
    uy = sinalp * sin(delt);
    uz = cosalp;
nxnew = \(nx[i][j] \ast ux + ny[i][j] \ast uy + nz[i][j] \ast uz\) - \((nx[i][j] \ast (-1 + ux \ast ux)) + ux \ast (ny[i][j] \ast uy + nz[i][j] \ast uz)) \ast \cos(\text{gamma}) + (nz[i][j] \ast uy - ny[i][j] \ast uz)) \ast \sin(\text{gamma});

nynew = \(uy \ast (nx[i][j] \ast ux + ny[i][j] \ast uy + nz[i][j] \ast uz) - (ny[i][j] \ast (-1 + uy \ast uy)) + uy \ast (nx[i][j] \ast ux + nz[i][j] \ast uz)) \ast \cos(\text{gamma}) + (nx[i][j] \ast uz - nz[i][j] \ast ux)) \ast \sin(\text{gamma});

nznew = \(uz \ast (nx[i][j] \ast ux + ny[i][j] \ast uy + nz[i][j] \ast uz) - (nz[i][j] \ast (-1 + uz \ast uz)) + uz \ast (nx[i][j] \ast ux + ny[i][j] \ast uy)) \ast \cos(\text{gamma}) + (ny[i][j] \ast uz - nx[i][j] \ast uy)) \ast \sin(\text{gamma});

bxnew = \(bx[i][j] \ast ux + by[i][j] \ast uy + bz[i][j] \ast uz\) - \((bx[i][j] \ast (-1 + ux \ast ux)) + ux \ast (by[i][j] \ast uy + bz[i][j] \ast uz)) \ast \cos(\text{gamma}) + (bz[i][j] \ast uy - by[i][j] \ast uz)) \ast \sin(\text{gamma});

bynew = \(uy \ast (bx[i][j] \ast ux + by[i][j] \ast uy + bz[i][j] \ast uz) - (by[i][j] \ast (-1 + uy \ast uy)) + uy \ast (bx[i][j] \ast ux + bz[i][j] \ast uz)) \ast \cos(\text{gamma}) + (bx[i][j] \ast uz - bz[i][j] \ast ux)) \ast \sin(\text{gamma});

bznew = \(bz\ast (bx[i][j] \ast ux + by[i][j] \ast uy + bz[i][j] \ast uz) - (bz[i][j] \ast (-1 + uz \ast uz)) + uz \ast (bx[i][j] \ast ux + by[i][j] \ast uy)) \ast \cos(\text{gamma}) + (by[i][j] \ast uz - bx[i][j] \ast uy)) \ast \sin(\text{gamma});

double enew = 0.0;
for (int idir2 = 0; idir2 < 4; idir2++) {

  // loop for calculating energy after the Monte Carlo move
  in = period(i + dx[idir2], Lx);
  jn = period(j + dy[idir2], Ly);

  nidotnj = nxnew \ast nx[in][jn] + nynew \ast ny[in][jn] + nznew \ast nz[in][jn];
  bidotbj = bxnew \ast bx[in][jn] + bynew \ast by[in][jn] + bznew \ast bz[in][jn];
}

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\begin{verbatim}
enew += -A*pow(nidotnj,2) - B1*(bidotbj) - B2*pow(bidotbj,2)
  + C*0.25*((bx[in][jn]*nxnew+by[in][jn]*nynew+bz[in][jn]*nznew)
  *((-dx[idir2])*(nxnew+nidotnj*nx[in][jn])+(-dy[idir2]))
  *(nznew+nidotnj*nz[in][jn])- (bxnew*nx[in][jn]+bynew*ny[in][jn]
  +bznew*nz[in][jn])*((-dx[idir2])* (nx[in][jn]+nidotnj*nxnew)
  +(-dy[idir2]))*(nz[in][jn]+nidotnj*nznew));

// Boltzmann probability
prob = exp(-(enew-eold)/T);

if (enew<eold){
  // move is accepted if enew < eold
  naccept += 1.0;
  nx[i][j]=nxnew;
  ny[i][j]=nynew;
  nz[i][j]=nznew;
  bx[i][j]=bxnew;
  by[i][j]=bynew;
  bz[i][j]=bznew;
  // etot+=enew-eold;
}

else {
  // move is accepted with a Boltzmann probability distribution if enew > eold
  if (drand48()<prob){
    naccept += 1.0;
  }
}
\end{verbatim}
nx[i][j]=nxnew;
ny[i][j]=nynew;
nz[i][j]=nznew;
bx[i][j]=bxnew;
by[i][j]=bynew;
bz[i][j]=bznew;
//etot+=enew-eold;
}
}
}

double rate=naccept/L;

// we want acceptance rate to be in between 30 and 50 %
if (rate<0.3) {
    gamma=gamma*0.99;
}
if (rate>0.5) {
    gamma=gamma/0.99;
}
if (gamma>gammalimit) {
    gamma=gammalimit;
}

/*
 we only collect data's when step size is greater than
 the equilibrium steps. By equilibrium steps i mean
 steps needed to equilibrate the system.
 We check this by plotting energies as functions of steps
 */

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if (istep>eqsteps) {
    for (int m=0; m<Lx; m++) {
        for (int n=0; n<Ly; n++) {
            /*
               Averaging the components of $Q$ tensor and $b$ vector
               over Monte Carlo steps
            */
            Qxx[m][n] += (1.5*(nx[m][n])*nx[m][n] - 0.5)/(nsteps-eqsteps);
            Qyy[m][n] += (1.5*(ny[m][n])*ny[m][n] - 0.5)/(nsteps-eqsteps);
            Qzz[m][n] += (1.5*(nz[m][n])*nz[m][n] - 0.5)/(nsteps-eqsteps);
            Qxy[m][n] += (1.5*(nx[m][n])*ny[m][n])/(nsteps-eqsteps);
            Qyz[m][n] += (1.5*(ny[m][n])*nz[m][n])/(nsteps-eqsteps);
            Qxz[m][n] += (1.5*(nx[m][n])*nz[m][n])/(nsteps-eqsteps);
            bsumx[m][n] += bx[m][n]/(nsteps-eqsteps);
            bsumy[m][n] += by[m][n]/(nsteps-eqsteps);
            bsumz[m][n] += bz[m][n]/(nsteps-eqsteps);
        }
    }
}

// for xyzvc file first write lattice size
write2<<Lx*Ly<<endl;

for (int m=0; m<Lx; m++) {
    for (int n=0; n<Ly; n++) {
        // write $Q$ tensor to the txt file declared earlier
        write1<<m<<setw(11)<<0.0<<setw(11)<<n<<setw(21)<<Qxx[m][n]<<setw(21)
    }
}
\begin{verbatim}
<<Qxy[m][n]<<setw(21)<<Qxz[m][n]<<setw(21)
<<Qyz[m][n]<<setw(21)<<Qyy[m][n]<<setw(21)
<<Qyz[m][n]<<setw(21)<<Qzz[m][n]<<endl;

// write b vector to xyzvc file
write2<<m<<setw(11)<<n<<setw(21)<<bsumx[m][n]<<setw(21)
<<bsumy[m][n]<<setw(21)<<bsumz[m][n]<<setw(21)<<1.0<<endl;
}
}

return(0);

// Mathematica code for calculating n vectors from Q tensor
QtensorXbyX = ReadList["Qtensors.txt", {Number, Number, Number, Number,
Number, Number, Number, Number, Number}];
Qtensor[i_] := {{QtensorXbyX[[i]][[4]], QtensorXbyX[[i]][[5]],
QtensorXbyX[[i]][[6]]}, {QtensorXbyX[[i]][[7]], QtensorXbyX[[i]][[8]]},
{QtensorXbyX[[i]][[6]], QtensorXbyX[[i]][[8]]},
QtensorXbyX[[i]][[9]]}}

nlist = Table[If[Abs[Eigenvalues[Qtensor[i]][[1]]] >
Abs[Eigenvalues[Qtensor[i]][[2]]] &&
Abs[Eigenvalues[Qtensor[i]][[1]]] >
Abs[Eigenvalues[Qtensor[i]][[3]]],
Eigenvalues[Qtensor[i]][[1]],
If[Abs[Eigenvalues[Qtensor[i]][[2]]] >
Abs[Eigenvalues[Qtensor[i]][[1]]] &&
Abs[Eigenvalues[Qtensor[i]][[2]]] >
Abs[Eigenvalues[Qtensor[i]][[3]]],

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\end{verbatim}
Eigenvectors[Qtensor[i]][[2]],
If[Abs[Eigenvalues[Qtensor[i]][[3]]] >
Abs[Eigenvalues[Qtensor[i]][[1]]] &&
Abs[Eigenvalues[Qtensor[i]][[3]]] >
Abs[Eigenvalues[Qtensor[i]][[2]]],
Eigenvectors[Qtensor[i]][[3]]], {i, 1, Length[QtensorXbyX]}];

(*
 slist=
 Table[If[Abs[Eigenvalues[Qtensor[i]][[1]]]
>Abs[Eigenvalues[Qtensor[i]][[2]]],
Eigenvalues[Qtensor[i][[1]]],
Eigenvalues[Qtensor[i]][[2]]],{i,1,400}];
*)

xcomp = QtensorXbyX[[All, 1]];  
ycomp = QtensorXbyX[[All, 2]];  
zcomp = QtensorXbyX[[All, 3]];  
xyz = Transpose[{xcomp, ycomp, zcomp}];  
nlistwcolor[k_] := Flatten[Append[xyz[[k]], Append[nlist[[k]], 1]]]
nlisttablewcolor = Chop[Table[nlistwcolor[k], {k, 1, Length[xyz]}], 10^-4];  
Export["nlist.xyzvc", nlisttablewcolor, "Table"]

// C++ code for writing vtk file

#include<iostream>
#include<fstream>
#include<iomanip>
#include<cmath>
#include<stdio.h>
#include<math.h>
#include <cstdlib>

struct point_struct {
    float x, y, z, u, v, w, c;
};

int main() {
    int N;
    float x, y, z, u, v, w, c;

    FILE* in;
    in = fopen("blist.xyzvc", "r");

    fscanf(in, "%d\n", &N);

    point_struct *point;
    point = new point_struct[N];

    for (int n = 0; n < N; n++) {
        fscanf(in, "%f%f%f%f%f%f\n", &x, &y, &z, &u, &v, &w, &c);
        point[n].x = x;
        point[n].y = y;
        point[n].z = z;
        point[n].u = u;
        point[n].v = v;
        point[n].w = w;
    }
}
point[n].c=c;
}
fclose(in);

FILE*out;
out = fopen("blist.vtk","w");

fprintf(out,"# vtkDataFile Version 3.1
");
fprintf(out,"Vector Visualization
");
fprintf(out,"ASCII\n");
fprintf(out,"DATASET UNSTRUCTURED_GRID\n");
fprintf(out,"\n");

fprintf(out,"POINTS%d_FLOAT\n",N);

for(int n=0;n<N;n++){
    fprintf(out,"%f%f%f\n",point[n].x,point[n].y,point[n].z);
}
fprintf(out,"\n");

fprintf(out,"CELLS%d%d\n",N,2*N);
for(int n=0;n<N;n++){
    fprintf(out,"1%d\n",n);
}
fprintf(out,"\n");

fprintf(out,"CELL_TYPES%d\n",N);
for(int n=0;n<N;n++){
```c
fprintf(out,"1\n");
}
fprintf(out,"\n");

fprintf(out,"POINT\_DATA\_%d\n",N);
fprintf(out,"VECTORS\_director\_FLOAT\n");
for(int n=0;n<N;n++){
    fprintf(out,"%f%f%f\n",point[n].u,point[n].v,point[n].w);
}
fprintf(out,"\n");

fprintf(out,"SCALARS\_color\_FLOAT\_1\n");
fprintf(out,"LOOKUP\_TABLE\_default\n");
for(int n=0;n<N;n++){
    fprintf(out,"%f\n",point[n].c);
}

fclose(out);

return 1;
}

A.2 Simulation code for polar phases described in chapter 3

A.2.1 Code for 3D bcc phase: splay flexoelectricity model

/*
This program will directly calculate 3D bcc directors for splay model, and write it in a vtk file
*/
```cpp
#include<iostream>
#include<fstream>
#include<iomanip>
#include<cmath>
#include<math.h>
#include<cstdlib>
#include<cstdio.h>
#include<complex>
#include<cstdlib>

#define nsteps 500000
#define eqsteps 250000
#define PI acos(0.0)*2.0
#define Lx 20
#define Ly 20
#define Lz 2
#define A 1.25
#define B 0.01
#define C 3.0
#define Tcut 0.35

using namespace std;

double th, ph;

/***** periodic boundary conditions**/
int period(int ii, int NN)
{
    if(ii==NN){ii=0;}
```
if (ii == -1) { ii = NN - 1; }
return ii;
}

void initialize(double nx[][Ly][Lz], double ny[][Ly][Lz], double nz[][Ly][Lz]) {
for (int i = 0; i < Lx; i++) {
    for (int j = 0; j < Ly; j++) {
        for (int k = 0; k < Lz; k++) {
            ph = drand48() * PI * 2;
            th = acos(2 * drand48() - 1);
            nx[i][j][k] = sin(th) * cos(ph);
            ny[i][j][k] = sin(th) * sin(ph);
            nz[i][j][k] = cos(th);
        }
    }
}
}

int main(void) {
    double gamma = PI / 36;
    double gammalimit = PI / 18;
    double prob = 0.0;
    double L = Lx * Ly * Lz;
    int dx[6] = {1, -1, 0, 0, 0, 0};
    int dy[6] = {0, 0, 1, -1, 0, 0};
    int dz[6] = {0, 0, 0, 1, -1, 0};
    double nx[Lx][Ly][Lz];
    double ny[Lx][Ly][Lz];
    double nz[Lx][Ly][Lz];
double nxnew, nynew, nznew;

double cosalp, sinalp, delt, nidotnj, bidotbj, bidotbjnew;

ofstream write("nlist.xyzvc");
write << L << endl;
ofstream write("energy.txt");

srand48(time(NULL));
initialize(nx, ny, nz);

double etot=0.0;

double bsumx[Lx][Ly][Lz] = {0.0}, bsumy[Lx][Ly][Lz] = {0.0}, bsumz[Lx][Ly][Lz] = {0.0};

for (int istep=0; istep<nsteps; istep++) {
    double T=1.0*pow(0.99, istep/900);
    if (T<Tcut) {
        T=Tcut;
    }
    int i, j, k, in, jn, kn, naccept=0;
    for (int itries=0; itries<L; itries++) {
        i=floor(drand48()*Lx);
        j=floor(drand48()*Ly);
        k=floor(drand48()*Lz);
        double cold=0.0, ux, uy, uz;
        for (int idir=0; idir<4; idir++){
            in=period(i+dx[idir],Lx);
            jn=period(j+dy[idir],Ly);
            kn=period(k+dz[idir],Lz);
            nidotnj=nx[i][j][k]*nx[in][jn][kn]+ny[i][j][k]*ny[in][jn][kn];
+nz[i][j][k]*nz[in][jn][kn];
eold += -A*pow(nidotnj,2) - B*ndon - C*0.25*pow(1+ndon,2)
* ((-dx[idir])*(-nx[i][j][k]+nx[in][jn][kn])
+(-dy[idir])*(-ny[i][j][k]+ny[in][jn][kn])
+(-dz[idir])*(-nz[i][j][k]+nz[in][jn][kn]));
}
cosalp=2*drand48()-1;
sinalp=sqrt(1-cosalp*cosalp);
delt=2*PI*drand48();
ux=sinalp*cos(delt);
uy=sinalp*sin(delt);
uz=cosalp;

nxnew=ux*(nx[i][j][k]*ux+ny[i][j][k]*uy+nz[i][j][k]*uz)
- (nx[i][j][k]*(-1 + ux*ux)
+ux*(ny[i][j][k]*uy+nz[i][j][k]*uz)) * cos(gamma)
+ (nz[i][j][k]*uy-ny[i][j][k]*uz) * sin(gamma);

nynew=uy*(nx[i][j][k]*ux+ny[i][j][k]*uy+nz[i][j][k]*uz)
- (ny[i][j][k]*(-1 + uy*uy)+uy*(nx[i][j][k]*ux
+nz[i][j][k]*uz)) * cos(gamma) + (nx[i][j][k]*uz
-nz[i][j][k]*ux) * sin(gamma);

nznew=uz*(nx[i][j][k]*ux+ny[i][j][k]*uy+nz[i][j][k]*uz)
- (nz[i][j][k]*(-1 + uz*uz)+uz*(nx[i][j][k]*ux
+ny[i][j][k]*uy)) * cos(gamma)
+ (ny[i][j][k]*ux-nx[i][j][k]*uy) * sin(gamma);

double enew=0.0;
for (int idir2=0; idir2<4; idir2++) {
in=period(i+dx[idir2],Lx);
}
\[ jn = \text{period}(j + dy[idir2], Ly); \]
\[ kn = \text{period}(k + dz[idir2], Lz); \]
\[ \text{nidotnj} = nxnew * nx[in][jn][kn] + nynew * ny[in][jn][kn] \]
\[ + nznew * nz[in][jn][kn]; \]
\[ \text{enew} = A * \text{pow}(\text{nidotnj}, 2) - B * \text{nidotnj} - C * 0.25 * \text{pow}(1 + \text{nidotnj}, 2) \]
\[ - (dx[idir2] * (-nxnew + nx[in][jn][kn])) \]
\[ + (dy[idir2] * (-nynew + ny[in][jn][kn])) \]
\[ + (dz[idir2] * (-nznew + nz[in][jn][kn])); \]

\[ \text{prob} = \exp((-\text{enew} - \text{eold})/T); \]

\textbf{if} (\text{enew} < \text{eold}) \{ \]
\[ \text{naccept} += 1.0; \]
\[ \text{nx}[i][j][k] = \text{nxnew}; \]
\[ \text{ny}[i][j][k] = \text{nynew}; \]
\[ \text{nz}[i][j][k] = \text{nznew}; \]
\[ \text{etot} += \text{enew} - \text{eold}; \]
\}

\textbf{else} \{ \]
\[ \text{if} (\text{drand48()} < \text{prob}) \{ \]
\[ \text{naccept} += 1.0; \]
\[ \text{nx}[i][j][k] = \text{nxnew}; \]
\[ \text{ny}[i][j][k] = \text{nynew}; \]
\[ \text{nz}[i][j][k] = \text{nznew}; \]
\[ \text{etot} += \text{enew} - \text{eold}; \]
\} \}

\textbf{if} (\text{istep} \% 900 == 0.0) \{ \]
\[ \text{write} << \text{istep} << \text{setw}(11) << \text{etot} << \text{endl}; \]
double rate=naccept/L;
if (rate<0.3) {
    gamma=gamma*0.99;
}
if (rate>0.5) {
    gamma=gamma/0.99;
}
if (gamma>gammalimit) {
    gamma=gammalimit;
}

if (istep>eqsteps) {
    for (int m=0; m<Lx; m++) {
        for (int n=0; n<Ly; n++) {
            for (int p=0; p<Lz; p++) {
                bsumx[m][n][p]+= nx[m][n][p];
                bsumy[m][n][p]+= ny[m][n][p];
                bsumz[m][n][p]+= nz[m][n][p];
            }
        }
    }
}

for (int i=0; i<Lx; i++) {
for (int j=0; j<Ly; j++) {
    for (int k=0; k<Lz; k++) {

        nx[i][j][k]=bsumx[i][j][k]/(nsteps-eqsteps);
        ny[i][j][k]=bsumy[i][j][k]/(nsteps-eqsteps);
        nz[i][j][k]=bsumz[i][j][k]/(nsteps-eqsteps);

        write << i << setw(21) << j << setw(21) << k << setw(21)
          <<nx[i][j][k] << setw(21) << ny[i][j][k] << setw(21)
          << nz[i][j][k] << setw(21) << 1.0<<endl;

    }
}

//writing vtk file for paraview visualization

struct point_struct{
    float x,y,z,u,v,w,c;
};

int N;
float x,y,z,u,v,w,c;

FILE*input;
input = fopen("nlist.xyzvc","r");

fscanf(input,"%d\n",&N);
point_struct *point;
point = new point_struct[N];

for (int n=0;n<N;n++){
    fscanf(input ,"%f%f%f%f%f%f\n",&x,&y,&z,&u,&v,&w,&c);
    point[n].x = x;
    point[n].y = y;
    point[n].z = z;
    point[n].u = u;
    point[n].v = v;
    point[n].w = w;
    point[n].c = c;
}
fclose(input);

FILE*out;
out = fopen("nlistout.vtk" ,"w");
fprintf(out,"# vtk DataFile Version 3.1\n");
fprintf(out,"Vector Visualization\n");
fprintf(out,"ASCII\n");
fprintf(out,"DATASET UNSTRUCTURED_GRID\n");
fprintf(out,"\n");

fprintf(out,"POINTS %d FLOAT\n",N);

for (int n=0;n<N;n++){
    fprintf(out,"%f%f%f\n",point[n].x,point[n].y,point[n].z);
}

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fprintf(out,"\n");

fprintf(out,"CELLS_%d_%d\n",N,2*N);
for(int n=0;n<N;n++){
    fprintf(out,"1\n",n);
}
fprintf(out,"\n");

fprintf(out,"CELL_TYPES_%d\n",N);
for(int n=0;n<N;n++){
    fprintf(out,"1\n");
}
fprintf(out,"\n");

fprintf(out,"POINT_DATA_%d\n",N);
fprintf(out,"VECTORS director FLOAT\n");
for(int n=0;n<N;n++){
    fprintf(out," %f %f %f\n",point[n].u,point[n].v,point[n].w);
}
fprintf(out,"\n");

fprintf(out,"SCALARS color FLOAT_1\n");
fprintf(out,"LOOKUP_TABLE default\n");
for(int n=0;n<N;n++){
    fprintf(out,"%f\n",point[n].c);
}

fclose(out);
A.2.2 Code for 2D hexagonal phase: bend flexoelectricity model

This program will calculate Qtensor and b vectors for splay model, and write Qtensor in a txt file and b vectors in a vtk file.

#include <iostream>
#include <fstream>
#include <iomanip>
#include <cmath>
#include <math.h>
#include <cstdlib>
#include <complex>
#include <stdlib.h>

#define nsteps 150000
#define eqsteps 125000
#define PI acos(0.0)*2.0
#define Lx 48
#define Ly 48
#define Lz 3

#define A 2.5
#define B1 0.4
#define B2 0.5
#define C -3.0
#define Tcut 0.45
using namespace std;

double th,thm;

double ph,phm,mag;

/*periodic boundary conditions*/
int period(int ii,int NN)
{
    if(ii==NN){ ii=0; }
    if(ii==1){ ii=NN-1; }
    return ii;
}

/*functions for calculating energy*/
double calcE(i,j,k){
    for (int idir=0; idir<6; idir++){
        in=period(i+dx[idir],Lx);
        jn=period(j+dy[idir],Ly);
        kn=period(k+dz[idir],Lz);

        nidotnj=nx[i][j][k]*nx[in][jn][kn]+ny[i][j][k]*ny[in][jn][kn]
            +nz[i][j][k]*nz[in][jn][kn];
        bidotbj=bx[i][j][k]*bx[in][jn][kn]+by[i][j][k]*by[in][jn][kn]
            +bz[i][j][k]*bz[in][jn][kn];

        eold+=-A*pow(nidotnj,2)-B1*bidotbj-B2*pow(bidotbj,2)
            +C*0.25*((bx[in][jn][kn]*nx[i][j][k]+by[in][jn][kn]*ny[i][j][k]
                +bz[in][jn][kn]*nz[i][j][k])*((-dx[idir])*nx[i][j][k]
                +ny[i][j][k]*(-dy[idir])*ny[i][j][k]
                +nz[i][j][k]*(-dz[idir])*nz[i][j][k])
                +(dx[idir])*nx[in][jn][kn]+(dy[idir])*ny[in][jn][kn]
                +(dz[idir])*nz[in][jn][kn]);
    }
}
+nidotnj*nz[in][jn][kn])−(bx[i][j][k]*nx[in][jn][kn]
+by[i][j][k]*ny[in][jn][kn]+bz[i][j][k]*nz[in][jn][kn])
*((−dx[idir])*(nx[in][jn][kn]+nidotnj*nx[i][j][k])
+(−dy[idir])*(ny[in][jn][kn]+nidotnj*ny[i][j][k])
+(−dz[idir])*(nz[in][jn][kn]+nidotnj*nz[i][j][k]));
    return eold;
};

/*function for initialization of lattices*/
void initialize(double nx[][Ly][Lz], double ny[][Ly][Lz], double nz[][Ly][Lz],
double bx[][Ly][Lz], double by[][Ly][Lz], double bz[][Ly][Lz]){
    for (int i=0; i<Lx; i++)
        for (int j=0; j<Ly; j++)
            for (int k=0; k<Lz; k++)
                ph=drand48 ()*PI*2;
                th=acos(2*drand48())−1);
                phm=drand48 ()*PI*2;
                thm=acos(2*drand48())−1);
                nx[i][j][k]=sin (th)*cos (ph);
                ny[i][j][k]=sin (th)*sin (ph);
                nz[i][j][k]=cos (th);
                mag=sqrt (pow((cos (thm)*sin (ph)*sin (th)*cos (th)*sin (phm)*sin (thm)),2)
                +pow((−cos (ph)*cos (thm)*sin (th)+cos (phm)*cos (th)*sin (thm)),2)
                +pow((−sin (ph−phm)*sin (th)*sin (thm)),2));
                bx[i][j][k]=(cos (thm)*sin (ph)*sin (th)−cos (th)*sin (phm)*sin (thm))/mag;
                by[i][j][k]=−cos (ph)*cos (thm)*sin (th)+cos (phm)*cos (th)*sin (thm))/mag;
                bz[i][j][k]=−sin (ph−phm)*sin (th)*sin (thm))/mag;
*/main function*/

int main(void){

double gamma=PI/36;
double gammalimit=PI/18;
double prob=0.0;
double L=Lx*Ly*Lz;

// In 3D there are six directions for each lattice
int dx[6]={1,-1,0,0,0,0};
int dy[6]={0,0,1,-1,0,0};
int dz[6]={0,0,0,0,1,-1};

double nx[Lx][Ly][Lz];
double ny[Lx][Ly][Lz];
double nz[Lx][Ly][Lz];
double bz[Lx][Ly][Lz];
double by[Lx][Ly][Lz];
double bx[Lx][Ly][Lz];

double nxnew, nynew, nznew, bznew, bynew, bxnew;
double cosalp, sinalp, delt, nidotnj, bidotbj, bidotbjnew;

// files to be written
ofstream write("energy.txt");
ofstream write1("bendflexo3DQtensor.txt");
ofstream write2("bendflexo3Dblist.xyzvc");

srand48(time(NULL));

// initialize lattices
initialize(ux,ny,nz,bx,by,bz);

double etot = 0.0;

double Qxx[Lx][Ly][Lz] = {0.0}, Qyy[Lx][Ly][Lz] = {0.0}, Qzz[Lx][Ly][Lz] = {0.0};

double Qxy[Lx][Ly][Lz] = {0.0}, Qyz[Lx][Ly][Lz] = {0.0}, Qxz[Lx][Ly][Lz] = {0.0};

double bsumx[Lx][Ly][Lz] = {0.0}, bsumy[Lx][Ly][Lz] = {0.0};

double bsumz[Lx][Ly][Lz] = {0.0};

for (int istep=0; istep<nsteps; istep++) {
    // simulation annealing set up
    double T=1.0*pow(0.99,istep/500);
    if (T<Tcut) {
        T=Tcut;
    }

    int i, j, k, in, jn, kn, naccept=0;
    for (int itries=0; itries<L; itries++) {
        i=floor(drand48()*Lx);
        j=floor(drand48()*Ly);
        k=floor(drand48()*Lz);
        double eold =0.0,ux,uy,uz;
        eold = calcE(i, j, k);
        cosalp=2*drand48()-1;
        sinalp=sqrt(1-cosalp*cosalp);
        delt=2*PI*drand48();
        }
ux = sin(\theta) \cdot \cos(\varphi);
uy = sin(\theta) \cdot \sin(\varphi);
uz = \cos(\varphi);

nx_{new} = ux \cdot (nx_{i}[j][k] \cdot ux + ny_{i}[j][k] \cdot uy + nz_{i}[j][k] \cdot uz)
- (nx_{i}[j][k] \cdot (\Delta + ux \cdot ux) + ux \cdot (ny_{i}[j][k] \cdot uy
+ nz_{i}[j][k] \cdot uz)) \cdot \cos(\gamma) + (nz_{i}[j][k] \cdot uy
- ny_{i}[j][k] \cdot uz) \cdot \sin(\gamma);

ny_{new} = uy \cdot (nx_{i}[j][k] \cdot ux + ny_{i}[j][k] \cdot uy + nz_{i}[j][k] \cdot uz)
- (ny_{i}[j][k] \cdot (\Delta + uy \cdot uy) + uy \cdot (nx_{i}[j][k] \cdot ux
+ nz_{i}[j][k] \cdot uz)) \cdot \cos(\gamma) + (nx_{i}[j][k] \cdot uz
- nz_{i}[j][k] \cdot ux) \cdot \sin(\gamma);

nz_{new} = uz \cdot (nx_{i}[j][k] \cdot ux + ny_{i}[j][k] \cdot uy + nz_{i}[j][k] \cdot uz)
- (nz_{i}[j][k] \cdot (\Delta + uz \cdot uz) + uz \cdot (nx_{i}[j][k] \cdot ux
+ ny_{i}[j][k] \cdot uy)) \cdot \cos(\gamma) + (ny_{i}[j][k] \cdot ux
- nx_{i}[j][k] \cdot uy) \cdot \sin(\gamma);

bx_{new} = ux \cdot (bx_{i}[j][k] \cdot ux + by_{i}[j][k] \cdot uy + bz_{i}[j][k] \cdot uz)
- (bx_{i}[j][k] \cdot (\Delta + ux \cdot ux) + ux \cdot (by_{i}[j][k] \cdot uy
+ bz_{i}[j][k] \cdot uz)) \cdot \cos(\gamma) + (bz_{i}[j][k] \cdot uy
- by_{i}[j][k] \cdot uz) \cdot \sin(\gamma);

by_{new} = uy \cdot (bx_{i}[j][k] \cdot ux + by_{i}[j][k] \cdot uy + bz_{i}[j][k] \cdot uz)
- (by_{i}[j][k] \cdot (\Delta + uy \cdot uy) + uy \cdot (bx_{i}[j][k] \cdot ux
+ bz_{i}[j][k] \cdot uz)) \cdot \cos(\gamma) + (bx_{i}[j][k] \cdot uz
- bz_{i}[j][k] \cdot ux) \cdot \sin(\gamma);

bz_{new} = uz \cdot (bx_{i}[j][k] \cdot ux + by_{i}[j][k] \cdot uy + bz_{i}[j][k] \cdot uz)
- (bz_{i}[j][k] \cdot (\Delta + uz \cdot uz) + uz \cdot (bx_{i}[j][k] \cdot ux
+ by_{i}[j][k] \cdot uy)) \cdot \cos(\gamma) + (by_{i}[j][k] \cdot ux
- bx_{i}[j][k] \cdot uy) \cdot \sin(\gamma);
\begin{verbatim}
double enew=0.0;

enew = calcE(i, j, k);

for (int idir2=0; idir2 < 6; idir2++) {
    in=period(i+dx[idir2],Lx);
    jn=period(j+dy[idir2],Ly);
    kn=period(k+dz[idir2],Lz);
    nidotnj=nxnew*nx[in][jn][kn]+nynew*ny[in][jn][kn]
       +nznew*nz[in][jn][kn];
    bidotbj=bxnew*bx[in][jn][kn]+bynew*by[in][jn][kn]
       +bznew*bz[in][jn][kn];
    enew+=A*\text{pow}(nidotnj,2)-B1*(bidotbj)-B2*\text{pow}(bidotbj,2)
       +C*0.25*((bx[in][jn][kn]*nxnew+by[in][jn][kn]*nynew
       +bz[in][jn][kn]*nznew)*((-dx[idir2])*nxnew
       +nidotnj*nx[in][jn][kn])*(-dy[idir2])*nynew
       +nidotnj*ny[in][jn][kn])*(-dz[idir2])*nznew
       +nidotnj*nz[in][jn][kn])-(bxnew*nx[in][jn][kn]
       +bynew*by[in][jn][kn]+bznew*nz[in][jn][kn])
       *((-dx[idir2])*nx[in][jn][kn]+nidotnj*nxnew)
       +(-dy[idir2])*ny[in][jn][kn]+nidotnj*nynew)
       +(-dz[idir2])*nz[in][jn][kn]+nidotnj*nznew));
}

prob = exp(-(enew-eold)/T);

if (enew<eold) {
    naccept+=1.0;
    nx[i][j][k]=nxnew;
    ny[i][j][k]=nynew;
    nz[i][j][k]=nznew;
    bx[i][j][k]=bxnew;
}
\end{verbatim}
by[i][j][k]=bynew;
bz[i][j][k]=bznew;
etot+=enew-eold;
}
else {
    if (drand48()<prob){
        naccept+=1.0;
nx[i][j][k]=nxnew;
ny[i][j][k]=nynew;
nz[i][j][k]=nznew;
bx[i][j][k]=bxnew;
by[i][j][k]=bynew;
bz[i][j][k]=bznew;
etot+=enew-eold;
    }
}

double rate=naccept/L;
if (rate<0.3) {
    gamma=gamma*0.99;
}
if (rate>0.5) {
    gamma=gamma/0.99;
}
if (gamma>gammalimit) {
    gamma=gammalimit;
}
/*collect Q tensor and b vector components after the system equilibrates*/

if (istep>eqsteps) {
    for (int m=0; m<Lx; m++) {
        for (int n=0; n<Ly; n++) {
            for (int p=0; p<Lz; p++) {
                Qxx[m][n][p]+=(1.5*(nx[m][n][p])*nx[m][n][p]*0.5);
                Qyy[m][n][p]+=(1.5*(ny[m][n][p])*ny[m][n][p]*0.5);
                Qzz[m][n][p]+=(1.5*(nz[m][n][p])*nz[m][n][p]*0.5);
                Qxy[m][n][p]+=(1.5*(nx[m][n][p])*ny[m][n][p]);
                Qyz[m][n][p]+=(1.5*(ny[m][n][p])*nz[m][n][p]);
                Qxz[m][n][p]+=(1.5*(nx[m][n][p])*nz[m][n][p]);

                bsumx[m][n][p]+=bx[m][n][p];
                bsumy[m][n][p]+=by[m][n][p];
                bsumz[m][n][p]+=bz[m][n][p];
            }
        }
    }
}

// for xyzvc file we need lattice dimensions
write2<<(Lx*Ly*Lz)<<endl;

/*write energy, Qtensor and b vectors to files*/
for (int m=0; m<Lx; m++) {
    for (int n=0; n<Ly; n++) {
        for (int p=0; p<Lz; p++) {
            write<<(istep)<<setw(21)<<etot<<endl;
            write1<<(m)<<setw(11)<<n<<setw(11)<<p
            write2<<Qxx[m][n][p]<<endl;
            write2<<Qyy[m][n][p]<<endl;
            write2<<Qzz[m][n][p]<<endl;
            write2<<Qxy[m][n][p]<<endl;
            write2<<Qyz[m][n][p]<<endl;
            write2<<Qxz[m][n][p]<<endl;
            write2<<bsumx[m][n][p]<<endl;
            write2<<bsumy[m][n][p]<<endl;
            write2<<bsumz[m][n][p]<<endl;
        }
    }
}
<<setw(21)<<Qxx [m] [n] [p] / ( nsteps - eqsteps )
<<setw(21)<<Qxy [m] [n] [p] / ( nsteps - eqsteps )
<<setw(21)<<Qxz [m] [n] [p] / ( nsteps - eqsteps )
<<setw(21)<<Qyy [m] [n] [p] / ( nsteps - eqsteps )
<<setw(21)<<Qyz [m] [n] [p] / ( nsteps - eqsteps )
<<setw(21)<<Qzz [m] [n] [p] / ( nsteps - eqsteps )
<<endl;
write2<<m<<setw(11)<< n <<setw(11)<< p
<<setw(21)<<bsumx [m] [n] [p] / ( nsteps - eqsteps )
<<setw(21)<<bsumy [m] [n] [p] / ( nsteps - eqsteps )
<<setw(21)<<bsumz [m] [n] [p] / ( nsteps - eqsteps )
<<setw(11)<<1.0<<endl;
}
}
}

// writing vtk file

struct point_struct {
    float x, y, z, u, v, w, c;
};

int N;
float x, y, z, u, v, w, c;

FILE* in;
in = fopen("bendflexo3Dblist.xyzvc", "r");
fscanf(in,"%d\n", &N);
point_struct *point;

point = new point_struct[N];

for(int n=0; n<N; n++){
    fscanf(in, "%f %f %f %f %f %f \n", &x, &y, &z, &u, &v, &w, &c);
    point[n].x = x;
    point[n].y = y;
    point[n].z = z;
    point[n].u = u;
    point[n].v = v;
    point[n].w = w;
    point[n].c = c;
}

fclose(in);

FILE*out;

out = fopen("bendflexo3Dbl list .vtk", "w");
fprintf(out, "# & vtk & DataFile & Version & 3.1 \n");
fprintf(out, "Vector & Visualization \n");
fprintf(out, "ASCII \n");
fprintf(out, "DATASET & UNSTRUCTURED_GRID \n");
fprintf(out, "\n");

fprintf(out, "POINTS & %d & FLOAT \n", N);

for(int n=0; n<N; n++){
    fprintf(out, "%f %f %f \n", point[n].x, point[n].y, point[n].z);
}

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fprintf(out,"n");

fprintf(out,"CELLS%d%d\n",N,2*N);
for(int n=0;n<N;n++){
    fprintf(out,"1%d\n",n);
}
fprintf(out,"n");

fprintf(out,"CELL_TYPES%d\n",N);
for(int n=0;n<N;n++){
    fprintf(out,"1\n");
}
fprintf(out,"n");

fprintf(out,"POINT_DATA%d\n",N);
fprintf(out,"VECTORS\nFLOAT\n");
for(int n=0;n<N;n++){
    fprintf(out,"%f%f%f\n",point[n].u,point[n].v,point[n].w);
}
fprintf(out,"n");

fprintf(out,"SCALARS\nFLOAT\n");
fprintf(out,"LOOKUP_TABLE\ndefault\n");
for(int n=0;n<N;n++){
    fprintf(out,"%f\n",point[n].c);
}
fclose(out);
return(0);