NONSEPARABLE INTERACTIONS AND ORIENTATIONAL PHENOMENA IN LIQUID CRYSTALS

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY in
THE FACULTY OF GRADUATE STUDIES
PHYSICS

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
May 1990
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July 9, 1990
Abstract

Intermolecular interactions are anisotropic since they depend on the orientations of the interacting molecules. They are responsible for the orientational phase transitions observed in molecular systems. The effects of nonseparable interactions, which depend on both the molecular and intermolecular vector orientations, are investigated using Monte-Carlo simulations. It is found that for systems with quenched positional disorder, the nonseparability of the pair potential leads to orientational frustration. Expanding the pair potential in terms of its rotational invariants allows one to isolate random field terms whose presence are shown to be at the origin of the non-frustrated patches observed in such disordered systems.

For liquid crystals, where translational and rotational degrees of freedom are in thermal equilibrium, Monte-Carlo results show that an ordering of the molecular orientations induces an ordering of the nearest-neighbor bond orientations only when the pair potential is nonseparable. These results suggest that it is necessary to reinterpret the mean-field theory of nematic liquid crystals as an approximation which neglects the presence of bond ordering in these systems. As well, they unravel the microscopic origin of the phenomenological coupling between bond and molecular orientations invoked in Ginzburg-Landau theories of liquid crystals.

The nonseparability of the intermolecular pair potential leads to a coupling between the nearest-neighbor bond orientational field and the molecular orientational field. It is shown that such coupling introduces new and interesting effects in liquid crystalline systems where interactions between the molecular and nearest-neighbor bond orientations are usually ignored.
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Acknowledgements

I first want to thank Dr. Birger Bergersen, my thesis advisor, for his ready availability and for the large degree of freedom that he entrusted to me. In particular, I acknowledge a conversation in which he suggested I study van der Waals interactions in a random parking system. This study led, as a by-product, to other investigations, the results of which constitute a large fraction of the work presented in this thesis.

I would like to thank my friends and collaborators, Peter Holdsworth and Zoltan Ràcz for all the interesting discussions about physics and life I had with them in the past five years. Their unfailing interest in physics has provided me with a continuous motivation in my work.

I acknowledge Ian Affleck, Simon Fortin and Raymond Laflamme for helpful discussions.

I am obliged to the Natural Sciences and Engineering Research Council, the Fond pour les Chercheurs et l'Aide à la Recherche, and the Physics Department at UBC for their pecuniary support.

Finally, I would like thank my wife Joanna for carefully editing the manuscript for both grammar and content. More importantly, I am grateful for her moral support in periods of frustration and disillusion.
"The only people for me are the mad ones, 
the ones who are mad to live, mad to talk, 
mad to be saved, desirous of everything at 
the same time, the ones who never yawn or say 
a common-place thing, but burn, burn, burn 
like fabulous yellow roman candles..."

Jack Kerouac

To Jo,
Chapter 1

Introduction to Liquid Crystals

This chapter is a short introduction to liquid crystals and is intended for the reader who is not familiar with the field. It is hoped that it will make this work as self-contained as possible and help the reader to better assimilate the material presented in the following chapters. Sections 1.1 and 1.2 introduce the topic of liquid crystals and the notion of nonseparable interactions we refer to in the title of the thesis. The Sections 1.3 and 1.4 contain a description of the nematics and smectics, the two main classes of liquid crystals that are discussed in this work. An outline of the thesis is presented in Section 1.5.

1.1 Liquid Crystals

The everyday world we live in consists of three phases of matter: gas, liquid and solid. This picture is, however, not quite complete: some organic materials do not show a single phase transition from a liquid to a solid phase upon cooling, but rather one or several extra transitions leading to new phases. Both microscopic and macroscopic properties of these phases are intermediate between those of a liquid and a crystalline solid. For this reason, they are called mesomorphic phases (meso: middle and morph: form). The name liquid crystals was coined by researchers who found it more descriptive, and the
two words are used synonymously.

In order to understand the origin of the various liquid crystal phases, it is useful to recall the distinction between an ordinary (isotropic) liquid and a crystalline solid. In a crystal, the centers of mass of the molecules are regularly positioned on a threedimensional lattice while no such long-range positional order exists in a liquid. The mechanical properties of these two phases are most different: unlike a solid, a liquid does not support a shear force and flows easily.

At the microscopic level, a crystal is recognized by its X-ray diffraction pattern which reveals sharp Bragg reflections characteristic of the regular lattice. The X-ray pattern of an ordinary isotropic liquid, on the other hand, shows only a faint circular ring in reciprocal space with a radius of the order of the inverse of the average intermolecular spacing. As well, the orientational degrees of freedom are completely disordered in an isotropic molecular fluid, as can be deduced from nuclear magnetic resonance (NMR) studies. Hence, mesophases can be obtained in two distinct ways:

1. By imposing positional ordering in one or two rather than three dimensions. Although such proposition may sound surprising, this phenomenon happens frequently in liquid crystalline materials. In most cases, one has positional order in only one direction: such systems, called smectics can be viewed as a set of two-dimensional (2D) liquid layers stacked on top of each other with a well-defined spacing.

---

1 See references [1, 2, 3, 4] for a review of the physics of liquid crystals.

2 The notion of orientational order or disorder is meaningless for atomic fluid (e.g. He, Ar, Kr, Xe) since these can be viewed as 'spherical objects'.

2. By allowing, in the case of nonspherical molecules, the orientational degrees of freedom to order at a temperature other than the melting temperature. Orientational transitions can occur in a crystal, in a liquid or even in a smectic phase. There are three different scenarios which can lead to orientational phase transitions:

- Several crystals exhibit a transition from a low-temperature strongly orientationally ordered phase to higher temperature phase where the molecules commute freely between equivalent orientations. This high-temperature phase is positionally ordered (crystalline solid), but orientationally disordered. One often refers to these systems as plastic crystals. Solid hydrogen ($H_2$) is an example in which such an orientational transition occurs.

- Some mixed crystalline materials like $AB_x - AM_{1-x}$, where $A$ and $B$ are atomic species, $M$ a molecular species and $x$ the concentration of the $B$ atoms, exhibit some kind of orientational phase transition. Unlike in plastic crystals, the molecular species $M$ is orientationally disordered in both the high and low-temperature phases. One observes, however, a dramatic change in the molecular reorientation response times as the system is cooled to low temperature. It appears as if the individual molecular orientational degrees of freedom are frozen out as the system is cooled below the so-called 'freezing temperature'. These systems are called molecular orientational glasses. $KBr_x - K(CN)_{1-x}$ and $N_2_x - Ar_{1-x}$ are examples of systems where such glassy transitions have been extensively studied in the past years.

- A very large number of organic substances show a mesophase where the molecules are oriented on average along a common direction, but without having the long-range positional order characteristic of crystals. These anisotropic liquids are called nematics. Above some critical temperature, the nematic
phase undergoes a first order transition to an isotropic liquid phase.

The term liquid crystals applies to both nematics and smectics. It is now generally accepted that liquid crystalline phases are observed when the constitutive structures consist of elongated (strongly anisotropically steric) objects. The most common of these structures are:

- Small Organic Molecules: A classical example is illustrated in Figure 1.1. The simplest way to induce a transition in these systems is by varying the temperature (although the effect of pressure is also studied). Hence, these systems are often referred to as thermotropic.

- Long Helical Rods: The deoxyribonucleic acid (DNA) and the tobacco mosaic virus (TMV) belong to this category. For these systems, called lyotropic, the phase transition is most easily induced by changing the concentration of rods rather than the temperature.

- Associated Structures: Typical examples in this category are found in the soap-water systems. A system of aliphatic chains with a polar head immersed in water cluster together in a way to minimize (maximize) the contact between the chain (polar head) and the water. The resulting objects give rise to associations and to the mesomorphic behavior observed in the present category.

- Polymer Liquid Crystals: Long polymer molecules can also give rise to liquid crystalline behavior. The molecules themselves can exhibit nematic ordering or their alkyl side-chains can lead to smectic-like ordering.

The situation is completely different for plastic crystals and molecular orientational glasses where the particle undergoing the orientational phase transition is usually nearly
Chapter 1. Introduction to Liquid Crystals

steric Model of PAA

\[ \text{CH}_3-\text{O}-\text{N}=\text{N}-\text{O-CH}_3 \]

\[ \approx 20\text{Å} \]

\[ \approx 5\text{Å} \]

Figure 1.1: Nematic p-azoxyanisole (PAA) and its steric model.

spherical in shape. For this reason, the fields of liquid crystals, plastic crystals and orientational glasses are usually regarded as being distinct and only vaguely related; in this thesis, we concentrate mainly on liquid crystals. We shall, however, illustrate that the thermodynamic behavior of orientational glasses may have the same microscopic origin, at the level of the intermolecular pair-potential, as some interesting orientational phenomena observed in exotic smectic liquid crystals.

1.2 Separable and Nonseparable Interactions

In the last section, we described orientational phase transitions in various systems. It is clear that the interactions between the particles must depend on their relative orientations in order to lead to such transitions. It turns out that a great deal of the physics involved in liquid crystal systems can be learned by considering pair potentials that depend only on the relative orientations between the molecules and not on the orientation of the
intermolecular vector $\vec{r}_{ij}$. A 'model' potential of this form is said to be separable. An example of a separable interaction is the well known isotropic Heisenberg model of a ferromagnet:

$$H_{\text{Heisenberg}} = -\sum_{i,j} J(|\vec{r}_i - \vec{r}_j|) \vec{S}(\vec{r}_i) \cdot \vec{S}(\vec{r}_j) ,$$  \hspace{1cm} (1.1)

where the sum is taken over the sites $i$ and $j$ of some lattice. The strength of the interaction between the spins $\vec{S}(\vec{r}_i)$ and $\vec{S}(\vec{r}_j)$, $J(|\vec{r}_i - \vec{r}_j|)$, depends only on the distance, $|\vec{r}_i - \vec{r}_j|$, separating them, but not on the direction of $\vec{r}_{ij}$.

The most general case, where the interaction depends on the orientation of $\vec{r}_{ij}$, is said to be nonseparable. A picture is worth 1,000 words (Figure 1.2).

The dipole-dipole potential is a common example of a nonseparable interaction:

$$H_{\text{dipolar}} = \frac{1}{r_{ij}^3}(\vec{P}_i \cdot \vec{P}_j - 3\vec{P}_i \cdot \hat{r}_{ij} \hat{r}_{ij} \cdot \vec{P}_j)$$  \hspace{1cm} (1.2)

where $p_i$ and $p_j$ are the strengths of the dipoles and $\hat{r}_{ij}$ is a unit vector parallel to $\vec{r}_{ij}$. For example, two dipoles parallel to each other and to the vector, $\vec{r}_{ij}$, connecting their center of mass have an energy of $-2p_ip_jr_{ij}^{-3}$ while their energy is $p_ip_jr_{ij}^{-3}$ when they are mutually parallel but perpendicular to $\vec{r}_{ij}$.

A system of particles interacting via a separable potential has a complete rotational symmetry of both the molecular variables and the intermolecular vector. A separable system is said to have an $\text{SO}(3) \times \text{SO}(3)$ symmetry. For a nonseparable potential, terms of the form $\hat{r}_{ij} \cdot \vec{P}_i$ lower or break the 'original' $\text{SO}(3) \times \text{SO}(3)$ symmetry of the system. For example, the dipolar Hamiltonian above has only an $\text{SO}(3)$ symmetry. Later in the thesis, will discuss at length a nonseparable potential, $V^{NS}$, which is given by:

$$V^{NS} \propto H_{\text{dipolar}}^2 .$$  \hspace{1cm} (1.3)

$V^{NS}$ is invariant under an inversion of the molecules:

$$V^{NS}(\vec{P}_i, \vec{P}_j) = V^{NS}(-\vec{P}_i, \vec{P}_j) = V^{NS}(\vec{P}_i, -\vec{P}_j) .$$  \hspace{1cm} (1.4)
a) Separable Interaction

\[ H^{(S)}: \begin{pmatrix} \uparrow & \uparrow \end{pmatrix} = H^{(S)}: \begin{pmatrix} \rightarrow & \rightarrow \end{pmatrix} \]

b) Nonseparable Interaction

\[ H^{(NS)}: \begin{pmatrix} \uparrow & \uparrow \end{pmatrix} \neq H^{(NS)}: \begin{pmatrix} \rightarrow & \rightarrow \end{pmatrix} \]

c) Nonseparable Interaction

\[ H^{(NS)}: \begin{pmatrix} \uparrow & \uparrow \end{pmatrix} = H^{(NS)}: \begin{pmatrix} \leftrightarrow \end{pmatrix} \]

Figure 1.2: Separable vs nonseparable interactions. In a Heisenberg ferromagnet, the interaction energy is invariant under any arbitrary rotation of the spin for fixed \( r_{ij} \), as shown in a). In the case of a nonseparable interaction, the interaction energy is not invariant under any rotation of the particles as in b). It remains, however, invariant under a rotation of both the intermolecular vector and molecular orientation as shown in c).
This nonseparable system has an extra discrete (Ising-like) symmetry which is not present in the original $H_{\text{dipolar}}$; it has an $\text{SO}(3) \times \text{Z}(2)$ symmetry.

Liquid crystal molecules are complex objects (see Figure 1.1) which interact via anisotropic repulsive forces (steric effects), dipolar, quadrupolar and van der Waals forces; all these interactions are nonseparable. Hence, one expects the full microscopic pair potential to be nonseparable. In this work, we investigate what effects are introduced by this nonseparability of the pair potential. We examine whether the presence of the nonseparability of the pair potential introduces new physical effects which are absent in separable models. In Chapter 2, we show that this question arises naturally when considering the mean-field theory of the isotropic-nematic phase transition for systems with nonseparable interactions.

In the following two sections we review the basic and most important properties of nematic and smectic liquid crystals.

1.3 Nematic Phase

The name nematic comes from the Greek $\nu\eta\mu\alpha$ which means thread and refers to thread-like defects commonly observed in these systems. A schematic representation of the orientational order present in a nematic phase is shown in Figure 1.3.

The nematic phase is a fluid in which the molecules have long-range orientational order but only short-range positional order, as revealed by the absence of Bragg peaks in their X-ray diffraction pattern. In fact, nematics flow like ordinary fluid with a viscosity of approximately 0.1 Poise (by comparison, water has a viscosity of about 0.01 Poise at room temperature).

The microscopic origin of this phase is most easily understood by simply considering
Figure 1.3: Schematic representation of the orientational order in a nematic phase. Although the molecules carry a dipolar moment, assumed parallel to the molecular axis as illustrated by the arrows, the system organizes itself in such a way that as many dipoles are ‘up’ as are ‘down’. The molecules point, on average, along the director $\hat{N}$.

the steric constraints that occur when filling space with asymmetric objects (see Figure 1.1). These constraints are introduced as the density of the system is increased, either by lowering the temperature or increasing the pressure. A system of asymmetric objects is able to fill the space more efficiently by allowing the build-up of some short-range orientational order where the rod-like objects are, on average, parallel to each other over some microscopic length scale. Theoretical arguments as well as computer simulations show that, for objects with large enough eccentricity, the system undergoes an orientational phase transition to a fluid phase with long-range orientational order as the density is increased above some critical density. This is the isotropic to nematic phase transition.

In the nematic phase, the molecules point on average along a common direction which is called the director and identified by the unit vector $\hat{N}$. Furthermore, although individual the molecules are biaxial (‘brick-like’ and not truly cylindrically symmetric), there are very few cases of thermotropic nematics where there is not complete rotational
symmetry around the axis $\hat{N}$: nematics are uniaxial and not biaxial anisotropic fluids. This anisotropy reflects itself in several bulk tensorial properties such as magnetic and electric susceptibility, optical birefringence, and anisotropic viscosity coefficients. The direction of $\hat{N}$ is arbitrary in the lab frame but, in practice, small forces, such as scratches on the cell holding the fluid, imposes its orientation. This is analogous to the Heisenberg ferromagnet in which all the spins tend to be parallel to the total magnetic moment, but where the energy of the system is independent of the average orientation of the moment.

One of the most important feature of nematics is that the states $\hat{N}$ and $-\hat{N}$ are indistinguishable. Although a single molecule can carry a sizeable electric dipolar moment ($O(10^1)$ Debye), the system organizes itself in such a way that as many dipoles are 'up' as are 'down' and is therefore not ferroelectric (see Figure 1.3).

To summarize, the main features of the nematic phase are:

1. Short-range positional order.
2. Flows like an ordinary fluid.
3. Long-range orientational order along the direction $\hat{N}$.
4. The direction of $\hat{N}$ is arbitrary in the lab frame.
5. Full rotational symmetry around $\hat{N}$ (uniaxial phase).
6. The states $\hat{N}$ and $-\hat{N}$ are indistinguishable.
7. Displays bulk anisotropic properties.

To characterize the amount of orientational order in a nematic sample, one introduces an order parameter $Q$ which is 0 in the isotropic phase and 1 in a perfectly oriented system. Assuming, temporarily, that the orientation of $\hat{N}$ is known, a convenient order
parameter can be defined as:

\[ Q = \frac{1}{N_m} \sum_{i=1}^{i=N_m} \langle P_2(\hat{n}_i \cdot \hat{N}) \rangle, \]

where \( \langle \rangle \) means that a thermal average is taken. \( \hat{n}_i \) is a unit vector along the molecular axis of molecule \( i \). \( N_m \) is the number of molecules in the sample, and \( P_2(x) = \frac{1}{2}(3x^2 - 1) \), is the second Legendre polynomial. One cannot use the simple average \( \langle (\hat{n}_i \cdot \hat{N}) \rangle \) in a nematic phase since it is always 0 due to property 6 above. We shall study the nature and theoretical description of the orientational order in nematics in further detail in the following chapter.

There exists a helical version of the nematics called the cholesteric phase which is similar to the ordinary nematic phase and lacks long-range positional order. However, \( \hat{N} \) is not constant in space and the preferred direction is helical with \( \hat{N}(\tau) = (N_x, N_y, N_z) = (\cos(k_0 z), \sin(k_0 z), 0) \). The phase is periodic along \( z \), and since the states \( \hat{N} \) and \( -\hat{N} \) are again indistinguishable, the spatial period is equal to half the pitch of the helix. The pitch is typically of the order of \( 3000 \AA \) and measurable by optical methods. In this work we are concerned only with the ordinary nematics.

### 1.4 Smectic Fluid Phases

The name smectic (from the Greek \( \sigma\mu\eta\gamma\mu\alpha = \text{soap} \)) was given to the materials belonging to this family because their mechanical properties are reminiscent of soaps. There exist various phases in the smectic family: smectic-A, smectic-B, smectic-C, ..., smectic-K, smectic-L. The reason for these rather mundane names is that the phases were labeled in their order of discovery without attempt to classify them as new phases were found. Some of these phases, initially identified as smectics, were later shown to be three-dimensional crystals. We will often refer to a specific smectic-X phase by its abbreviation sm-X.
In this section we restrict ourselves to the true smectic liquid crystalline phases; these are the smectics A, B_H, C, I, F and L. Such phases can, from a naive structural point of view, be described as a one-dimensional stacking of 2D sheets of liquid along the \( \hat{z} \) direction. The interlayer spacing is well defined and can be measured by X-ray diffraction experiments. Liquid crystalline smectics are thus more ordered than nematics. In fact, for a given material, the smectic phases almost always occur at temperatures below the nematic phase, although there exist some materials which exhibit one or several re-entrant or less ordered phases as the temperature is reduced. For example the following progression of phases may be observed as the temperature is decreased: isotropic\( \rightarrow \)nematic\( \rightarrow \)sm-A\( \rightarrow \)nematic\( \rightarrow \)sm-A\( \ldots \rightarrow \)crystal. In this example, the second nematic phase is said to be re-entrant since it has less macroscopic order than the preceding sm-A phase.

1.4.1 Smectic A

A schematic representation of the order present in a smectic-A phase is shown in Figure 1.4. The main features of this phase are:

1. Well defined interlayer spacing \( d \) close to the full molecular length \( l \).\(^3\)

2. Short-range positional order within a layer (quasi-2D isotropic fluid).

3. The states \(+\hat{z}\) and \(-\hat{z}\) are equivalent.

4. The system is uniaxial and there is full rotational symmetry of the director \( \hat{N} \) around \( \hat{z} \).

Let us comment on feature 2 above. In a well ordered sm-A phase the average molecular orientation, \( \hat{N} \), is strongly pinned in the direction of the layer normal, \( \hat{z} \), and

\(^3\)In some sm-A materials, individual layers are actually bilayers where the molecules are interlaced and the distance between layers is somewhat larger than a single molecule.
Figure 1.4: Schematic arrangement of the molecules in a smectic-A phase. The molecules are, on average, parallel to the layer normal, $\hat{z}$. The distance, $d$, between two consecutive layers is of the order of the full length of a single molecule $l$. The positional correlations within a layer are liquid-like.
individual rotation around the long molecular axis occurs on a short time scale compared to the in-plane motion time scale. Hence, one recognizes that a smectic-A phase consists of a stack of quasi-2D isotropic liquid layers. To illustrate further, consider molecules that look like elongated bricks and exhibit a sm-A phase where the long side of the brick is parallel to $\hat{z}$. Their rapid rotation about $\hat{z}$ averages out the true three-dimensional pair potential and 'transforms' the brick-like molecule into a cylinder-like molecule (see Figure 1.5). The effective, or averaged, intralayer pair-potential is therefore isotropic within the layer (hard disk in the present example) and independent of the orientation, $\phi$, of the molecule around $\hat{z}$. This observation will be very useful when the time comes to classify the various smectic phases.

\textsuperscript{4}In the present example, the pair-potential is purely repulsive and corresponds to the shape of the hard object.
The presence of the layers in the sm-A phase imply a modulation of the mass density \( \rho(z) \). One can expand \( \rho(z) \) in a Fourier series:

\[
\rho(z) = \rho_0 + \frac{1}{\sqrt{2}} (\rho_q \exp(iqz) + \text{c.c.}) + \cdots ,
\]

where \( \rho_0 \) is average mass density and \( q = \frac{2\pi}{d} \). \( \rho_q \) is the order parameter of the sm-A phase; its amplitude and phase describe, respectively, the degree of layering and the displacement of the layers.

1.4.2 Smectic C

A schematic representation of the order present in a smectic-C phase is shown in Figure 1.6. The main features of this phase are:

1. Well defined interlayer spacing with thickness given by the \( \hat{z} \) projection of the molecular length: \( d \approx l \cos(\omega) \), where \( \omega \) is the tilt angle measured from the layer normal \( \hat{z} \). See Figure 1.6.

2. Short-range positional order within a layer. A sm-C phase can be seen as a quasi-2D anisotropic fluid or a quasi-2D liquid crystal system.

3. The in-plane projection of the tilt makes an angle \( \phi \) with respect to an arbitrary in-plane direction \( \hat{x} \) perpendicular to \( \hat{z} \). \( \hat{n} \) is a unit vector parallel to the in-plane projection of the director \( \hat{N} \); we refer to it as the 2D director. See Figure 1.7.

4. The system is biaxial.

The second feature of the sm-C phase deserves some attention. In a well ordered sm-C phase, where the tilt angle \( \omega \) fluctuates very little, it is possible to 'integrate' out the true

\footnote{Due to the coupling between layers displacement and director fluctuations, the sm-A phase exhibits only quasi-long-range positional order along \( \hat{z} \), and the order parameter, \( \rho_q \), vanishes in the thermodynamic limit [4].}
Figure 1.6: Schematic arrangement of the molecules in a smectic-C phase. The average tilt angle with respect to the normal layer \( \hat{z} \) is \( \omega \). The distance between consecutive layers is \( d \approx \ell \cos(\omega) \).
Figure 1.7: Detailed geometry of a smectic-C phase. The director $\hat{N}$ makes an angle $\omega$ with respect to the layer normal and its in-plane projection (unit vector $\hat{n}$) has orientation $\phi$ with respect to the $x$ axis.
pair potential along the $z$ direction and obtain an effective $2D$ pair-potential, $V_{ij}$, between particles $i$ and $j$. In the most general case, this effective potential is nonseparable and depends on $\vec{r}_{ij}$, $\phi_i$ and $\phi_j$, the intermolecular vector between molecule $i$ and $j$ and the in-plane orientation of these molecules respectively (see Figure 1.8):

$$V_{ij} = V_{ij}(\vec{r}_{ij}; \hat{n}_i, \hat{n}_j) .$$ (1.7)

For example, consider a single sm-C liquid crystal layer where the individual molecule is, as a rough approximation, modeled by a cylinder. In a well ordered sm-C phase, where all the molecules have the same $\omega$ and $\phi$, the equivalent $2D$ object of a tilted cylinder is an ellipse. In such a case, one can then consider a simpler $2D$ fluid of perfectly oriented ellipses of eccentricity $1/\cos(\omega)$ and disregard the original three-dimensional problem. A smectic-C phase is thus a realization of a quasi-$2D$ liquid crystal system which, in the
case where only one layer can be stabilized in an experiment, becomes a true 2D liquid crystal.

Since $\langle \omega \rangle \neq 0$ and $\langle e^{i\phi} \rangle \neq 0$ in a sm-C phase, one introduces the following complex order parameter for the sm-C phase:

$$\Phi = \omega e^{i\phi},$$

(1.8)

where $\omega$ and $\phi$ are defined in Figure 1.7. A sm-C phase exhibits long-range order in the azimuthal angle $\phi$. All the molecules have, on average, the same $\omega$ and $\phi$ in a single infinitely large sm-C domain.

We have given a brief description of the sm-A and sm-C phases. However, we mentioned earlier that there exist other smectic fluid phases: sm-B, sm-D, sm-F and sm-L. The liquid-like nature of these phases was demonstrated via X-ray diffraction experiments at the end of the 1970s. It was, at that time, difficult to understand what differentiated these phases from the 'simpler' sm-A and sm-C phases: one needed to introduce new order parameters different than $\rho_q$ and $\Phi$. Defining a 'good' order parameter in a given phase transition problem however requires a great deal of insight into the physics involved. The reward is often great since one can build phenomenological theories once the relevant order parameters have been identified. As discussed in the next section, it is the development of the theory of dislocation-mediated melting of 2D solids which, by introducing the idea of bond-orientational order, has led to a natural classification of the smectic fluid phases.

1.4.3 Two-Dimensional Melting and Classification of Smectic Phases

This section is rather long, but contains a material to which we shall continually refer in the next chapters. We have tried to put the emphasis on the physical picture by keeping

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6The smectics B, D, E, G, H and J are believed to be true three-dimensional solids.
the mathematical burden to a minimum.

Almost all the microscopic devices that result from the microtechnological revolution are made of thin layers of materials. Such devices are nearly two-dimensional and they may have provided the impetus that led researchers to investigate the behavior of various physical processes in 2D systems in the early 1970s. The melting of a 2D isotropic (triangular) solid is an example of such a process (see the review by Strandburg [5]). Before explaining 2D melting itself, we present a simple example which reveals most of the physics involved in 2D systems.

**Kosterlitz-Thouless Transition**

Two-dimensional systems, with short-range interactions and which have an ordered phase with broken continuous symmetry, lack true long-range order at any non-zero temperature. The continuous symmetry implies that at least one branch of elementary excitations has the property that its energy approaches zero continuously at very long wavelength. Consider, for example, a simple ferromagnet with classical spins \( \vec{S} \) (\(|\vec{S}| = 1\)) lying in the xy plane of a square lattice (xy model) and interacting via the following nearest-neighbor Hamiltonian:

\[
H_{xy} = -J \sum_{i,j} \vec{S}_i \cdot \vec{S}_j = -J \sum_{i,j} \cos(\phi_i - \phi_j)
\]  

(1.9)

where \( J \) is a positive constant with units of energy and sets the strength of the interaction, and \( \phi_i \) is the in-plane orientation of the spin \( \vec{S}_i \). The sum is restricted to the nearest-neighbors \( i \) and \( j \). At low temperature, we expect a slowly spatially varying orientation of the spins (spin waves) and \( (\phi_i - \phi_j) \ll 1 \). In this regime, one has \( \cos(\phi_i - \phi_j) \approx 1 - \frac{1}{2}(\phi_i - \phi_j)^2 \). One finds that this quadratic or elastic Hamiltonian leads to a power-law decay of the spin-spin correlation function:

\[
g(r) = \langle \vec{S}(\vec{r}) \cdot \vec{S}(0) \rangle = \langle \cos(\vec{\phi}(\vec{r}) - \vec{\phi}(0)) \rangle \propto r^{-\eta(T)}
\]  

(1.10)
where $\eta(T) \approx k_B T/J$; $T$ is the temperature, $k_B$ is the Boltzmann constant, and $a$ is the lattice constant. Hence, the thermally excited spin waves destroy the ordering in the $xy$ system. If there was true long-range order in this system, $g(r)$ would decay towards a positive constant equal to the square of the magnetization at large distance. However, we know that at high enough temperature, $g(r)$ must decay exponentially to zero. The question of interest is then: what is the mechanism which converts the power law to exponential decay of $g(r)$ as the temperature is raised? As shown above, spin waves have little to do with any phase transition in this system. Another mechanism must be responsible for driving the system to short-range order (exponential decay to zero of $g(r)$).

Kosterlitz and Thouless suggested taking into account the effects of vortices in the system (see Figure 1.9). The energy increase due to the spins a distance $r$ from the core of the vortex is, in the large core approximation,

$$J/2 \left( \frac{2\pi}{2\pi r} \right)^2 2\pi r .$$

Integrating over the area of the system, one finds that the total energy of a vortex, $E_v$, 

![Figure 1.9: Spin vortex.](image)
in a system of size \( L \) and lattice spacing \( a \), is:

\[
E_v = \frac{J}{2} \int_a^L \left( \frac{2\pi}{r} \right) dr = \pi J \ln(\frac{L}{a}) .
\]  

(1.11)

The entropy of such a vortex is simply the logarithm of the number of states (sites) in which the vortex can be: \( k_B \ln(L/a)^2 \). At a temperature \( T \), the total free energy for this free vortex is:

\[
F = E_v - TS_v = \pi J \ln(\frac{L}{a}) - k_B T \ln(L/a)^2 .
\]  

(1.12)

Below \( T_c \) \( (k_B T_c = \pi J/2k_B) \) vortices are rare while they abound above it.

This simple description neglects interactions between vortices of opposite vorticity. Both mean-field [6] and renormalization-group [7, 8] treatments of such vortex-vortex interactions lead to a precise and elegant interpretation of the Kosterlitz-Thouless (KT) transition. These show that, at low temperature, vortices of opposite vorticity attract each other and form tightly bound neutral pairs which screen the effective interaction between other pairs of bound vortices of opposite vorticity. As the temperature is raised, more pairs are excited and the mean radius of a pair (distance between vortices within a pair) increases; the bound pairs are less efficient in screening the pair-pair interaction.

Above some critical temperature, \( T_c \), the screening becomes too small and a rapid increase in the number of pairs, which then dissociate into free vortices, occurs. The transition is thus analogous to a 2D dielectric breakdown where the vortices play the role of lines of charge perpendicular to the plane of the lattice. In fact, the analogy is not coincidental since the vortex-vortex Hamiltonian is just that of a 2D two-component neutral Coulomb gas. In the Coulomb gas problem, the signature of the transition is the divergence of the ‘dielectric constant’ of the system. In the xy problem, as the temperature approaches the critical temperature from below, the effective (renormalized) elastic constant, decreases and eventually vanishes at \( T_c \), where the system becomes unable to react to long wavelength elastic distortions. The unbinding transition of vortices drives the
spin-spin correlation function, \( g(r) \), to be short-ranged above \( T_c \). KT transitions occur in systems where the low temperature phase would be expected to have long-range order, which breaks a continuous Abelian group, if it was not of the underlying fluctuations which destroy the long-range order.

Although now fifteen years old, the detailed predictions of the KT theory are still intensively investigated. The debate is fueled by contradictory results coming from various Monte Carlo simulations.

### 2D Melting and Bond Order Parameter

In a 2D solid, the elastic vibrations (phonons) are the fluctuations (excitations) which destroy the ordering; they are analogous to the spin waves in the xy model. In an X-ray diffraction experiment, one does not observe true Bragg peaks (\( \delta \)-functions centered on the reciprocal lattice vectors of the 2D crystal) but rather peaks whose intensity falls off as a power-law in the vicinity of a reciprocal lattice vector \( \vec{G} \). The amount of positional order is measured by \( g(\vec{R}) \), the density-density correlation function:

\[
g(\vec{R}) = \langle \exp \{i\vec{G} \cdot [\vec{u}(\vec{R}) - \vec{u}(0)]\} \rangle ,
\]

where the positions of the atoms are given by \( \vec{r} = \vec{R} + \vec{u}(\vec{R}) \). \( \vec{u}(\vec{R}) \) is the atomic displacement field (fluctuation around the equilibrium position \( \vec{R} \)). Using the classical elastic Hamiltonian, one finds that \( g(\vec{R}) \) behaves as:

\[
g(\vec{R}) = R^{-\eta(T,|\vec{G}|)} .
\]

In a liquid phase, \( g(\vec{R}) = e^{-R/\xi(T)}/R \), where \( \xi \) is the temperature dependent positional correlation length. Hence, the thermal fluctuations destroy the long-range positional order of the solid phase, but are not sufficiently ‘violent’ to make the correlation functions decay exponentially with distance as in the case of a liquid. By analogy to the
Chapter 1. Introduction to Liquid Crystals

xy model, the question which arises here is: how does a 2D solid melt or, what is the mechanism which converts quasi-long-range order (power-law decay of $g_\sigma$) to short-range order (exponential decay of $g_\sigma$)?

Kosterlitz and Thouless [6] extended their predictions for the xy model to the 2D melting problem. The defect in this case is not a vortex as in the xy model but a dislocation, which can be viewed as an extra row of atoms stuck partway into the crystal. In the KT theory, it is the unbinding of these dislocation pairs which drive the melting of the 2D solid. In this case, as in the xy model, the elastic response of the system vanishes at the transition. The system thus becomes unable to react to a shear stress and becomes a liquid. The unbinding of dislocations in the KT theory of 2D melting drives the system from a solid phase with quasi-long-range order in the density-density correlation $g_\sigma(\vec{r})$ to a liquid phase with short-range order in $g_\sigma(\vec{R})$.

We have argued that phonons destroy the long-range positional order of the solid phase and transform it to quasi-long-range (Equation 1.14). This description is incomplete as pointed out by Mermin [9]. A 2D solid phase has quasi-long-range positional order, but exhibits true long-range bond orientational order. The sixfold symmetry of the triangular solid is not lost at low temperature. In other words, the nearest-neighbor bond correlation function decays to a non-zero constant at large distance in the solid phase.

Consider Figure 1.10. Assuming that the orientation of the bonds between two nearest-neighbors of a central particle at $\vec{r}$ is known to be $\theta(\vec{r})$, one can define a sixfold bond correlation function, $c_6(r)$, as:

$$c_6(r) = \langle \cos\{6\theta(\vec{r}) - 6\theta(0)\} \rangle .$$  \hspace{1cm} (1.15)
The presence of long-range bond orientational order in the 2D solid phase can be mathematically stated as follows:

$$\lim_{r \to \infty} c_6^{\text{solid}}(r) = \text{const}.$$ (1.16)

In a liquid phase, $c_6(r)$ is short-ranged and decays exponentially with distance:

$$c_6^{\text{liquid}}(r) \approx e^{-r/\xi_6},$$ (1.17)

where $\xi_6$ is the bond correlation length.

Halperin and Nelson [10, 11, 12] recognized that the melting process proposed by Kosterlitz and Thouless did not reveal anything about the behavior of the $c_6(r)$ at the melting transition. Halperin and Nelson came up with the interesting suggestion that the melting of a 2D triangular lattice could proceed in two steps (two-step melting) and lead to a novel phase of matter observable between the solid and liquid phase. The intermediate phase was predicted to exhibit exponential decay of the density-density correlation function, $g_\alpha(r)$, as in an ordinary liquid, but power-law decay of the bond correlation, $c_6(r)$, as for quasi-long-range bond orientational order. This intermediate
Figure 1.11: Long-range bond order and short-range positional order. The dots represent periodic triangular lattice points.

Phase was called hexatic due to its sixfold nature. The hexatic phase is analogous to the xy system described above, where the vector connecting nearest-neighbors plays the role of the spin vector $\vec{S}$.

Figure 1.11 illustrates how the positions of the particles can be disordered but still maintain sixfold bond orientational correlation. Although the molecules (open discs) at $\vec{r}_1$ and $\vec{r}_2$ form perfectly symmetric sixfold structures, the centers of mass of the two patches are positionally uncorrelated, as illustrated by the offset of the discs at $\vec{r}_2$ with respect to the dots at $\vec{r}_2$. According to Halperin and Nelson, the above two transitions are both KT transitions. We shall not present the details of these two KT transitions or describe the defects associated with each of them here. The interested reader is invited to refer to the review by Strandburg [5].

The modern theory of defect-mediated melting of a 2D solid is referred to as the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory. Table 1.1 contains a

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7 Young [13] performed a detailed study of the problem and showed that some of the numerical values presented by Halperin and Nelson in their original paper were incorrect.
### Table 1.1: Summary of the KTHNY theory.

Upon heating, the solid shows a melting transition to a hexatic phase which further converts, at still higher temperature, to an ordinary liquid.

A summary of the KTHNY theory. It is worth mentioning that a large amount of experimental work as well as computer simulations have been devoted to investigating the predictions of the KTHNY theory, principally to identify the existence of a hexatic phase. It is, we believe, fair to say that the detailed predictions of the theory have not been entirely confirmed.

Let us summarize the main points we have raised thus far:

- Two-dimensional systems with continuous symmetry lack true long-range order and exhibit quasi-long-range order; the xy model and a two-dimensional solid are examples of such systems.

- By extending the work of Kosterlitz and Thouless, Halperin and Nelson proposed that a 2D solid need not melt to a liquid phase via a single transition. They postulated the existence of an intermediate hexatic phase between the solid and liquid phase.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$g_6(r)$</th>
<th>$c_6(r)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>solid</td>
<td>quasi-long-range</td>
<td>long-range</td>
</tr>
<tr>
<td>hexatic</td>
<td>short-range</td>
<td>quasi-long-range</td>
</tr>
<tr>
<td>liquid</td>
<td>short-range</td>
<td>short-range</td>
</tr>
</tbody>
</table>
• The hexatic phase has short-range positional order like a liquid but shows quasi-long-range nearest-neighbor bond orientational order.

Classification of Smectic Phases

Recall the problem that we raised at the end of Section 1.4.2 regarding the need to introduce new order parameters in order to classify the sm-B\(_H\), sm-I, sm-F and sm-L phases. Inspired by the new ideas of 2D melting, Birgeneau and Litster [14] suggested in 1978 that some exotic smectic phases might be three-dimensional (3D) realizations of the bond ordered hexatic phase. In their view, each hexatic smectic layer is an almost independent two-dimensional hexatic phase. The role of the weak three dimensional couplings is to transform the quasi-long-range nature of the bond order in the hexatic phase to true long-range order. From this perspective, the sm-B\(_H\) is a 3D hexatic phase, hence the subscript H in sm-B\(_H\). It can also be thought of as a bond orientationally ordered version of the sm-A. The sm-B\(_H\) has short-range positional order, as do ordinary fluid, while the sm-B is a crystalline phase with true long-range positional order and which exhibit Bragg peaks in X-ray diffraction patterns. The sm-I, sm-F and sm-L phases are the hexatic versions of the sm-C, and tilted 'cousins' of the sm-B\(_H\). The in-plane projection of the tilt is along, halfway between, or anywhere between two nearest-neighbor in the sm-I, sm-F and sm-L respectively (see Figure 1.12).

The notion of bond orientational order and the relative orientation of the in-plane projection of the molecular tilt with respect to the nearest-neighbor bond turn out to be the order parameters that are needed to understand what differentiates various smectic phases from each other. The current classification of the smectic liquid crystal phases is presented in Figure 1.13. The isotropic and nematic phases have also been included for completeness.

As described earlier, a sm-A phase can be seen as a quasi-two-dimensional liquid which
Figure 1.12: Schematic representation of the tilt orientation in tilted hexatic smectic phases. The figure illustrates one smectic layer, with the layer normal perpendicular to the page, and with the arrows indicate the in-plane orientation of the tilt. The tilt is along (0°), halfway (30°) and at an arbitrary orientation between the nearest-neighbors in the smectic I, F and L respectively.

exhibits short-range hexatic order. This is because the free energy of a 2D isotropic liquid is minimized by allowing the build-up of some triangular-like patches of molecules. This is easy to visualize in the case of hard discs where the constraints of filling the space at a given density is best realized with a closely-packed configuration (local triangular structure). As a material undergoes a sm-A → sm-B \textsubscript{H} transition, the bond correlation function, $c_6(r)$, acquires quasi-long-range order and the amount of correlation of the triangular patches extends very far in the sample.

In a 2D anisotropic fluid, one notes that the tilted bond-ordered version of the sm-B \textsubscript{H}, the sm-I, sm-F and sm-L phases, will not be perfectly hexatic since the tilt imposes an underlying twofold distortion to the bond order. Again, this is best seen by considering the packing of ellipses of small eccentricity. In this case, the packing is almost perfectly hexagonal, but with a small twofold (orthorhombic) distortion. At the experimental level,
Figure 1.13: Classification of liquid crystal phases according their degree of ordering. For example, the smectic-A phase displays both molecular orientational order and positional order normal to the layer, but not the bond orientational order exhibited by the hexatic phases located just under it in the sequence.
the importance of the distortion must be examined on a case-by-case basis.

Finally, it is important to note that we have described the possible sequence of phases that can occur as the temperature of a liquid crystalline material is lowered. In most cases, a given substance will not exhibit the full sequence of transitions described in Figure 1.13. It might, for example, go directly from an isotropic phase to a sm-A phase, avoiding the nematic phase, and then solidify upon further cooling.

1.5 Outline of the Thesis

The rest of this thesis is organized as follows. In Chapter 2, we present an overview of the mean-field theory of nematic liquid crystals. We show that the mean-field approximation for a true liquid crystal model neglects correlations between the molecular orientation and the orientation of the intermolecular vector. In practice, the mean-field approximation transforms an originally nonseparable intermolecular pair potential into an effective separable pair potential. This implies that, within a mean-field approximation, a nonseparable liquid crystal model behaves very similarly to a separable model. Hence, we are led to ask ourselves if there exist interesting nonseparable effects which are neglected by the mean-field approximation of nematic liquid crystals and which cannot be explained by the mean-field improvements usually considered for lattice models of nematic liquid crystals.

In Chapter 3 we use a nonseparable anisotropic van der Waals potential to investigate, using Monte Carlo simulations, the importance of quenched positional disorder in nonseparable systems. The computer simulation results show that systems with quenched positional disorder cannot be used to model nematic liquid crystal when the pair potential is nonseparable. We present arguments which suggest that such system are much more closely related to molecular orientational glasses than to liquid crystals. This is
not the case for separable models of nematic liquid crystals which can be modelled using perfect Bravais lattices or systems with quenched positional disorder. The conclusion that translational degrees of freedom must be in thermal equilibrium with the rotational degrees of freedom in a nonseparable liquid crystal model leads us to perform a Monte Carlo simulation where the particles are allowed to translate and rotate. We find that the modified van der Waals potential we use in this Monte Carlo simulation exhibits a nematic to isotropic phase transition and a considerable amount of nearest-neighbor bond structure in the nematic phase.

We show in Chapter 4 that the build-up of the nearest-neighbor bond structure in the nematic phase exhibited by the van der Waals system can be explained in terms of the phenomenon of induced bond orientational ordering observed in real smectic-C liquid crystal systems. These results allow us to reinterpret the mean-field theory of nematics as an approximation which neglects the phenomenon of induced bond orientational ordering in a nonseparable system. Furthermore, the same results provide a microscopic origin of the coupling between the nearest-neighbor bond orientational field (BOF) and the molecular orientational field (MOF) invoked in Ginzburg-Landau theories of smectic liquid crystals.

The question which then arises is if the presence of induced bond orientational order in nonseparable liquid crystal models introduces new effects which are commonly neglected in nonseparable systems. We show in Chapter 5 that the finite-size scaling behaviour of two-dimensional nonseparable liquid crystal models can be strongly modified when such BOF ordering exists. In Chapter 6, we investigate how the response of liquid crystal phases to an external magnetic field is modified when there exists an underlying BOF ordering. In particular, we consider the problem of the Fréederickz transition in tilted hexatic smectic films which display such BOF ordering. We find that, due to this BOF-MOF coupling, the Fréederickz transition in these systems can be considerably different
than for ordinary liquid crystals.

In Chapter 7, we take a different approach and investigate a problem where the MOF introduces interesting behavior for hexatic phases with predominant BOF ordering. In particular, the problem of the smectic-I to smectic-F is considered and a preliminary microscopic model is proposed.

In Chapter 8, we investigate whether macroscopic and 'liquid-like' properties of the nonseparability in nematic liquid crystals could introduce interesting and important effects in a problem where the role of anisotropy has proven to be most important. As an example of such a macroscopic manifestation of the nonseparability, we consider the problem of viscous fingering in a system with anisotropic viscosities and investigate whether our previous results obtained for the problem of viscous fingering in isotropic systems are modified.

We conclude with a discussion of possible avenues for extending the work presented in this thesis.
Chapter 2

Mean-Field Theory of the Isotropic-Nematic Phase Transition

The mean-field theory of the isotropic-nematic transition is a simple method for solving the thermodynamic problem of microscopic models of the isotropic-nematic transition. To introduce the subject, we review the mean-field treatment of a lattice model for the nematic phase. We then introduce a proper description of the mean-field approximation for a true liquid crystal model which includes translational degrees of freedom. This latter approach suggests that it is possible to find different potentials which, at the mean-field level of approximation, have the same thermodynamic behavior. In particular, we present a separable and a nonseparable model which are equivalent within a mean-field approximation. This observation leads us to question how the thermodynamic behavior of separable and nonseparable potentials compare when one goes beyond the mean-field approximation. Finally, we present some arguments which motivated us in investigating this problem via computer experiments.

2.1 Mean-Field Description of the Isotropic-Nematic Phase Transition

For a given system, the motion of the particles in phase space is described by a set of variables such as the position, orientation and conjugated momenta of each particle. In any real system, the particles interact with each other, and their interactions are described
by a coupling of their respective dynamical variables. The various couplings that can be constructed and allowed by symmetry are the building blocks of the Hamiltonian which describes the interactions present in the system.

The mean-field approximation is often the starting point for investigating the thermodynamic behavior of a system of interacting particles. Technically, the mean-field approximation consists of transforming the interacting part of the Hamiltonian into an effective Hamiltonian which describes the interaction of a single particle with a fictitious field. This field is a function of the thermodynamical average of the various dynamical variables involved in the interactions. By requiring that the free energy of the system is minimized with respect to all variations of these thermodynamical averages, one obtains a set of transcendental equations which allows the evaluation of the mean-field in a self-consistent manner. This last step leads, most of the time, to a numerical problem which must be solved on a computer. We now illustrate how the mean-field approximation is carried out for a simple lattice model of the isotropic-nematic transition in liquid crystals.

### 2.1.1 Mean-Field Theory of the Lebowohl-Lasher Lattice Model

In its simplest formulation, the Lebowohl-Lasher [15, 16] model consists of an ensemble of classical rotors with orientation \( \hat{n}_i \), sitting on a simple cubic lattice and interacting with the nearest-neighbor Hamiltonian

\[
H_{LL} = -J_2 \sum_{\langle i,j \rangle} P_2(\hat{n}_i \cdot \hat{n}_j) \tag{2.1}
\]

where \( J_2 \) is positive and sets the strength of the interaction, and \( P_2 \) is the second Legendre polynomial, \( P_2(x) = \frac{1}{2}(3x^2 - 1) \). Notice that this Hamiltonian has nematic or inversion symmetry: \( H_{LL}(\hat{n}_i, \hat{n}_j) = H_{LL}(-\hat{n}_i, \hat{n}_j) \). The above interaction favors an average parallel orientation of the rotors which is independent of the orientation of the axis of the lattice; this is the low temperature phase. At sufficiently high temperature, the free energy is
minimized by having a random orientation of the rotors. The low temperature phase is thus a 'nematic-like' phase, and the orientationally disordered high temperature phase is the 'isotropic-like' phase. We will show that, within a mean-field calculation, a first order transition separates these two phases. The Lebowhl-Lasher model is thus believed to grasp the essential physics of the isotropic-nematic transition.

It is generally believed that the coupling between positional and orientational degrees of freedom is weak and does not play an important role in the isotropic-nematic transition. Hence, a lattice model in which the center of mass of the molecules is fixed, would seem to be a reasonable starting point for studying the problem of the isotropic-nematic transition. Indeed, a considerable amount of work has been devoted to this model in the past twenty years or so (1, 15–17, 25–33)

The remainder of this subsection presents a brief derivation of the mean-field theory of the Lebowhl-Lasher model since we will often refer to these results. We start by defining the matrices

$$\sigma_{i\alpha \beta} = \frac{1}{2} (3n_{i\alpha} n_{i\beta} - \delta_{\alpha \beta})$$

(2.2)

where $\alpha, \beta = x, y, z$, and $n_{i\alpha}$ is a Cartesian component of $\hat{n}_i$ while $\delta_{\alpha \beta}$ is the Kronecker delta. Using the $\sigma_{\alpha \beta}$ matrices, the above Hamiltonian can be rewritten as

$$H_{LL} = -\frac{2J_2}{3} \sum_{<i,j>} \sum_{\alpha, \beta = 1}^3 \sigma_{i\alpha \beta} \sigma_{j\beta \alpha}.$$  

(2.3)

The mean-field theory assumes that fluctuations in the elements of $\sigma_{\alpha \beta}$ are small or, technically, by imposing the following approximation:

$$(\sigma_{i\alpha \beta} - \langle \sigma_{i\alpha \beta} \rangle) (\sigma_{j\alpha \beta} - \langle \sigma_{j\alpha \beta} \rangle) \approx 0.$$  

(2.4)

The brackets indicate that a thermal average has been performed.

The thermodynamic properties of the systems are obtained by calculating $Z$, the
partition function:

\[ Z = \int \prod_i d\Omega_i \exp(-H_{LL}/k_B T) \]  \hspace{1cm} (2.5)

\( \Omega_i \) are the polar orientations of \( \hat{n}_i \) with respect to some fixed axis in the lab frame. The free energy, \( F \), of the system is given by

\[ F = -k_B T \ln(Z) \]  \hspace{1cm} (2.6)

The mean-field equations are obtained by requiring that \( F \) is minimized by all variations in the average elements of \( Q_{\alpha\beta} = \langle \sigma_{i\alpha\beta} \rangle \). By analogy to the Weiss molecular field theory of magnetism, there will always be a solution, \( Q_{\alpha\beta} = 0 \), for all \( \alpha \) and \( \beta \). These correspond to the isotropic high temperature phase. At low temperature, nonzero solutions appear, and these correspond to the 'nematic-like' phase. These nonzero solutions will not be unique, due to the overall rotational symmetry of the system. An infinitesimal external field would be required to dictate the orientation of broken symmetry in the nematic phase. However, since \( Q_{\alpha\beta} \) is real and symmetric, there exists a frame in which it is diagonal.

Let be \( \theta \) and \( \phi \) the polar angles of the average orientation of the molecules in the lab frame. Then

\[ n_x = \sin(\theta) \cos(\phi) \], \\
\[ n_y = \sin(\theta) \sin(\phi) \] and \\
\[ n_z = \cos(\theta) \].

We define the following new variables:

\[ p = \frac{3}{2} \sin^2(\theta) \cos(2\phi) \], \\
\[ q = \frac{1}{2} (3 \cos^2(\theta) - 1) \], \\
\[ P = \langle p \rangle \] and \\
\[ Q = \langle q \rangle \].
After some algebra, we rewrite the matrix $Q_{\alpha\beta}$ as

$$Q_{\alpha\beta} = \begin{pmatrix} -(Q - P)/2 & 0 & 0 \\ 0 & -(Q + P)/2 & 0 \\ 0 & 0 & Q \end{pmatrix}$$

If we choose the director to be along the $z$ axis, we have $P = 0$ and, defining $\mu = \cos(\theta)$, we can write $F$ as

$$\frac{F}{N} = -k_B T \ln \left( 4\pi \int_0^1 d\mu \exp \left[ \frac{r J_2}{2 k_B T} ((3\mu^2 - 1)Q - Q^2) \right] \right)$$

where $r$ is the number of nearest-neighbors in the lattice. It is now a simple matter of setting $dF/dQ$ equal to 0 and solving numerically for $Q$.

One finds a first order transition and a jump in the nematic order parameter $Q$ from 0 in the isotropic phase to $Q \approx 0.42$ at the transition. Technically, the transition is first order since there are terms with odd power in $Q$ in the Taylor expansion of $F$. Physically, the definition of the order parameter, $Q = \langle \frac{1}{2} \{3\cos^2(\theta) - 1\} \rangle$, implies that there will be such odd terms in $F$ since the state with $+Q$ does not correspond to the same state or orientation of the molecules as that with $-Q$.

From the mean-field calculation, one finds that the difference between the thermodynamic isotropic-nematic transition temperature, $T_{NI}$, and the limit of stability of a supercooled isotropic phase, $T^*$, is of the order of $0.1 T_{NI}$. Experimentally, this difference is rather of the order of $0.01 T_{NI}$. There has been a long debate over this discrepancy in the liquid crystal literature since it was not clear if the difference between experimental results and the theoretical calculation was due to the mean-field approximation.

\footnote{It can be shown that the phase the lowest free energy phase is uniaxial ($P = 0$) in the present model without an external field.}
or if the Lebowlh-Lasher model could reproduce a difference $T_{NI} - T^*$ of the order of $0.01T_{NI}$. Recent and extensive Monte Carlo simulations [17] indicate that the Lebowlh-Lasher model is indeed able to reproduce a supercooling temperature range of $0.01T_{NI}$. These Monte Carlo results suggest that the supercooling range of $0.1T_{NI}$ found in the mean-field treatment of the Lebowlh-Lasher lattice model is entirely due to the neglect of orientational fluctuations.

Notwithstanding the success of the simple Lebowlh-Lasher model, one would like to go beyond a lattice model and investigate the thermodynamic behavior of true nematic liquid crystal models where translation of the molecules is allowed. The mean-field theory of such models is the subject of the next section.

2.1.2 Mean-Field Theory for a True Liquid Crystal Model – The Maier-Saupe Model

We have shown in the last section how the mean-field calculation for a lattice model of the isotropic-nematic transition is carried out. We now show how such mean-field theory can be constructed for a 'true' nematic liquid crystal model. We shall see that the interpretation of the mean-field approximation in the latter case is not as straightforward as in the Lebowlh-Lasher model. This difficulty in interpreting the mean-field approximation for a true liquid crystal model will lead us to ask a set of questions which differ considerably from the usual questions raised in mean-field calculations of thermodynamical lattice systems.

Consider the $\nu$-particle distribution function for a system of $N$ particles interacting with some pair potential $V_{ij}$:

$$P^{(\nu)}(1, 2, \ldots, \nu) = (8\pi^2)^\nu \frac{N!}{(N - \nu)!} \frac{\int \exp\{-\beta \sum_{i,j} V_{ij}\} d\Omega_{\nu+1} \ldots d\Omega_N dr_{\nu+1} \ldots dr_N}{\int \exp\{-\beta \sum_{i,j} V_{ij}\} d\Omega_1 \ldots d\Omega_N dr_1 \ldots dr_N} .$$

(2.8)
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where $\beta = 1/k_B T$. The position of particle $i$ is $\vec{r}_i$, and $\Omega_i$ is a short notation for the three Euler angles describing its orientation. The $\nu$-particle distribution is the conditional probability density that the particles $(1\ldots\nu)$ have a state with $(\Omega_1\ldots\Omega_\nu; \vec{r}_1\ldots\vec{r}_\nu)$. Of particular interest are the one- and two-particle distribution functions:

$$P^{(1)}(1) = (8\pi^2)N \frac{\int \exp\{-\beta \sum_{i,j} V_{ij}\} \, d\Omega_2 \ldots d\Omega_N \, dr_2 \ldots dr_N}{\int \exp\{-\beta \sum_{i,j} V_{ij}\} \, d\Omega_1 \ldots d\Omega_N \, dr_1 \ldots dr_N} = \rho(\vec{r}_1, \Omega_1)$$ (2.9)

and

$$P^{(2)}(1, 2) = (8\pi^2)^2 N (N - 1) \frac{\int \exp\{-\beta \sum_{i,j} V_{ij}\} \, d\Omega_3 \ldots d\Omega_N \, dr_3 \ldots dr_N}{\int \exp\{-\beta \sum_{i,j} V_{ij}\} \, d\Omega_1 \ldots d\Omega_N \, dr_1 \ldots dr_N}$$

$$= \rho(\vec{r}_1, \Omega_1) \rho(\vec{r}_2, \Omega_2) g(\vec{r}_{12}; \Omega_1, \Omega_2)$$ (2.10)

where we have defined $\vec{r}_{12} = \vec{r}_2 - \vec{r}_1$. The 1-particle density, $\rho(\vec{r}_i, \Omega_i)$, is the probability density that particle $i$ is at a position $\vec{r}_i$ in the sample with orientation $\Omega_i$. The pair distribution function, $g(\vec{r}_1, \Omega_1; \vec{r}_2, \Omega_2)$, is a conditional probability that a particle 1 at $\vec{r}_1$ will have an orientation $\Omega_1$ when there is a particle 2 at $\vec{r}_2$ with orientation $\Omega_2$.

From here on, we restrict ourselves to the case where the particles have complete rotational symmetry ($C_\infty$) around their main molecular axis whose orientation is denoted by the unit vector $\hat{n}_i$. In an isotropic phase, $\rho(\vec{r}_i, \hat{n}_i)$ simply reduces to the number density $\rho$, which is independent of $\vec{r}_i$ and $\hat{n}_i$. In a nematic phase, we have $\rho(\vec{r}_i, \hat{n}_i) = \rho f(\hat{n}_i)$. The probability density is uniform in space, but is a function of the orientation of the molecular axis, $\hat{n}_i$, with respect to the director (see Chapter 1). The problem consists of calculating $f(\hat{n}_i)$.

Taking the derivative of Equation 2.9 with respect to $n_{i,\alpha}$, the $\alpha$ component of the unit vector $\hat{n}_i$, we find:

$$\frac{\partial e(\hat{n}_i)}{\partial n_{i,\alpha}} = \rho \int d^3r_{ij} \int d\Omega_j \frac{\partial V_{ij}(\vec{r}_{ij}; \hat{n}_i, \hat{n}_j)}{\partial n_{i,\alpha}} f(\hat{n}_j) g(\vec{r}_{ij}; \hat{n}_i, \hat{n}_j)$$ (2.12)
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with

\[ f(\hat{n}_i) = \exp\{-\beta \epsilon(\hat{n}_i)\}. \]

We have introduced here the quantity \( \epsilon(\hat{n}_i) \), known as the pseudo-potential.\(^2\)

In Equation 2.13, the number density, \( \rho \), and the pair potential, \( V_{ij} \), are known quantities which are input to the model. The pseudo-potential, \( \epsilon(\hat{n}_i) \), is the quantity to be calculated. Physically, \( \epsilon(\hat{n}_i) \) measures the energy of a particle having some orientation \( \hat{n}_i \) with respect to the average orientation of the rest of the molecules in the sample, hence the name pseudo-potential.

The pair distribution deserves some attention. Clearly, to calculate anything from 2.13, one needs to have some information about how the particles are located with respect to each other. Trying to carry the analysis without assuming that something is known about \( g(\vec{r}_{ij};\hat{n}_i,\hat{n}_j) \) would be the same as trying to find a transition temperature for a ferromagnet problem without knowing on what kind of lattice the spins are sitting on. Well above the isotropic-nematic transition temperature, one assumes that the 'isotropic liquid problem' has been solved and the isotropic part of the pair distribution function, \( g_0^{iso}(r_{ij}) \), has been calculated. As the transition temperature is approached from above, one can write:

\[ g_{ij} \equiv g(\vec{r}_{ij};\hat{n}_i,\hat{n}_j) = g_0^{iso}(r_{ij}) + \Delta g(\vec{r}_{ij};\hat{n}_i,\hat{n}_j) \quad (2.13) \]

where \( \Delta g(\vec{r}_{ij};\hat{n}_i,\hat{n}_j) \) is the change in \( g_{ij} \) occurring due to the build-up of molecular orientational correlations close to the transition. In the spirit of the mean-field approximation, one neglects this increase in the correlations (or orientational fluctuations) and approximates \( g_{ij} \) by the already known \( g_0^{iso}(r_{ij}) \):

\[ g_{ij} \approx g_0^{iso}(r_{ij}) \quad (2.14) \]

\(^2\)Equation 2.13 corresponds to a BBGKY equation [18].
Thus, in the present context, the mean-field approximation amounts to neglecting correlations between the relative orientation of the molecules as well as the correlations between the molecular orientations and the orientation of the intermolecular vector, $\bar{r}_{ij}$. Practically, the second step is equivalent to assuming that the distribution of the centers of mass of the molecules is spherically symmetric with respect to a reference molecule at the origin. This approximation allows us to integrate Equation 2.13 with respect to $\hat{n}_{i,o}$:

$$\epsilon(\hat{n}_{i}) = \text{const} + \rho \int d^{3}r_{ij} \int d\Omega_{j} f(\hat{n}_{j})V_{ij}(\bar{r}_{ij}; \hat{n}_{i}, \hat{n}_{j})g_{0}^{iso}(r_{ij})$$  \hfill (2.15)

where \text{const} is a constant of integration which has to be determined.

One can rewrite Equation 2.15 in the following way:

$$\epsilon(\hat{n}_{i}) = \text{const} + \rho \int r_{ij}^{2} dr_{ij} g_{0}^{iso}(r_{ij}) \int d\Omega_{j} f(\hat{n}_{j}) \int \int V_{ij}(\bar{r}_{ij}; \hat{n}_{i}, \hat{n}_{j}) \sin(\Theta_{ij}) d\Theta_{ij} d\Phi_{ij}$$  \hfill (2.16)

where the intermolecular vector, $\bar{r}_{ij}$, has orientation $\Theta_{ij}$ and $\Phi_{ij}$. In the mean-field approximation, the full anisotropic pair potential is averaged over all the orientations of $\bar{r}_{ij}$, and the resulting spatially averaged pair potential depends only on the relative orientations of the molecules; this is an important point. One finally obtains:

$$\epsilon(\hat{n}_{i}) = \text{const} + \rho \int d\Omega_{j} f(\hat{n}_{j})\bar{V}_{ij}(\hat{n}_{i} \cdot \hat{n}_{j})$$  \hfill (2.17)

where

$$\bar{V}_{ij}(\hat{n}_{i} \cdot \hat{n}_{j}) = \int r_{ij}^{2} dr_{ij} g_{0}^{iso}(r_{ij}) \int \int V_{ij}(\bar{r}_{ij}; \hat{n}_{i}, \hat{n}_{j}) \sin(\Theta_{ij}) d\Theta_{ij} d\Phi_{ij}.$$

If one assumes that $\bar{V}_{ij}(\hat{n}_{i} \cdot \hat{n}_{j})$ is invariant under the change $\hat{n}_{i} \rightarrow -\hat{n}_{i}$, which guarantees that all mesophases predicted within this description have the nematic symmetry (see Section 1.3), then one can expand $\bar{V}_{ij}$ in terms of Legendre polynomials of even order, $P_{2n}$:

$$\epsilon(\hat{n}_{i}) = \text{const} + \rho \int d\Omega_{j} f(\hat{n}_{j}) \sum_{n=0}^{\infty} -J_{2n}P_{2n}(\hat{n}_{i} \cdot \hat{n}_{j})$$  \hfill (2.18)
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The Maier-Saupe [19, 20] approximation consist of keeping only the terms with $n = 0$ and $n = 1$ in Equation 2.18. The anisotropic term, $J_2$, is assumed positive and stabilizes, at sufficiently low temperature, a configuration with the molecules on average parallel to each other. The result, 2.18, could be interpreted as a theoretical justification for studying a lattice model where the particles interact with their nearest neighbors with an anisotropic potential of the form $-J_2 P_2 (\hat{n}_i \cdot \hat{n}_j)$ (Section 2.1.1). From Equation 2.18, the mean-field treatment of the Maier-Saupe model follows the steps outlined above for the Lebowhl-Lasher model and we do not repeat it.

**Energy Scales in the Maier-Saupe Approximation**

Within the Maier-Saupe approximation, there is only one energy scale which is set by the strength of the average anisotropic interaction $J_2$. $J_2$ varies from one potential, $V_{ij}$, to another, but since there is only one energy scale, all thermodynamic properties are functions of the single parameter $\rho J_2 / k_B T$. This feature disappears if higher order terms, such as $P_4 (\hat{n}_i \cdot \hat{n}_j)$, which may be present in the original pair potential, $V_{ij}$, are taken into account in Equation 2.18.

Reconsider the mean-field approximation 2.14 for two different anisotropic potentials $V_{ij}^{(1)}$ and $V_{ij}^{(2)}$. Assume that these two potentials can be chosen such that their average over $\Theta_{ij}$ and $\Phi_{ij}$ gives only an isotropic term and a $P_2$ term without any other higher order terms. In such a case, there is no approximation made by neglecting terms proportional to $P_{2n}$ with $n > 1$ in Equation 2.18 since they are simply absent. The integration over $d^3 r_{ij}$ cannot generate such higher order terms since the mean-field approximation has already been made in 2.14 before carrying the integration over $d \Theta_{ij}$ and $d \Phi_{ij}$. That is, only the isotropic part of $g_{ij}$, $g_{ij}^{iso}(r_{ij})$, which is independent of $\hat{n}_i$ and $\hat{n}_j$, has been retained.
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The only difference between the potentials $V_{ij}^{(1)}$ and $V_{ij}^{(2)}$, is that their $J_2$s are different \(^3\). We thus expect, according to the preceding discussion, that the behavior of these two systems would be identical as a function of their reduced parameter $\rho J_2/k_B T$. This argument holds only within a mean-field treatment. Hence, any major difference occurring in the thermodynamic behavior of the original potentials $V_{ij}^{(1)}$ and $V_{ij}^{(2)}$ can be immediately traced-back to the mean-field approximation, where the replacement $g_{ij} \approx g_{ij}^{iso}(r_{ij})$ is made.

One sees that the mean-field approximation presented here is much more intricate than in the simplest Lebowhl-Lasher model since it is imbedded in approximation 2.14, which is clearly not as transparent as approximation 2.4. As in any other phase transition problem, one would like to understand the importance of the mean-field approximation in the context of the isotropic-nematic transition within a true liquid crystal model and not a lattice model. The approach we have taken to investigate this question is the subject of the next section.

2.2 Mean-Field Theory and Nonseparability

2.2.1 Macroscopic Manifestations of the Nonseparability

For spherically symmetric particles, like argon, the pair potential is isotropic since it depends only on the distance separating the centers of mass of two interacting particles. The Coulomb interaction between point charges and the usual van der Waals interaction, which decay as the inverse sixth power of the distance, are examples of such isotropic interactions.

Practically, only atoms which have an electronic angular momentum of $L = 0$ can

\(^3\)The $J_0$'s are irrelevant in the present discussion since they just shift the average energy scale and do not play any role in an isotropic-nematic transition at constant density. This is true as long as $J_2/J_0$ is large enough to stabilize a nematic liquid phase at a temperature above the solid phase.
be regarded as spherical. For any other particle, a nonspherical distribution of the electronic charge introduces anisotropic corrections to the otherwise isotropic potential. The importance of such corrections vary from one particles to another. Assuming an effective isotropic pair potential for a molecular system in its liquid phase (eg. liquid nitrogen) can be a fairly valid starting point, as long as the liquid phase exhibits isotropic bulk properties.

Clearly, anisotropic liquid phases, such as liquid crystals, must interact via anisotropic forces, which depend on the relative orientation of the particles, in order to lead to the observed mesomorphic behavior. The Lebowhl-Lasher model and the Maier-Saupe model are among the simplest anisotropic models one may investigate to study the isotropic to nematic phase transition. However, both the starting potential in the Lebowhl-Lasher model 2.1 and the effective pair potential $\tilde{V}_{ij}$ in the Maier-Saupe model 2.18, are separable. They depend only on the relative orientation of the particles, and not on the orientation of the intermolecular vector $\vec{r}_{ij}$. A natural question one may ask at this point is: Do nonseparable interactions have to be considered at all in microscopic nematic liquid crystal models, and if so, why?

Elastic Constants of a Nematic Material

As we will now show, the answer to the above question is that all macroscopic properties which depend on the interaction between large domains of highly ordered nematic molecules and on the relative spatial orientation of the ordered domains, would be isotropic if the true intermolecular potential was separable \(^4\).

Consider three domains $D_1$, $D_2$ and $D_3$, their respective directors $\hat{N}_1$, $\hat{N}_2$ and $\hat{N}_3$, and

---

\(^4\)The word domain in a system with continuous symmetry is, formally speaking, incorrect since the boundaries between two regions with different orientation are not sharp, as in the Ising model of ferromagnetism. We loosely use the word domain to refer to a region where the director field is constant within $\pm 45^\circ$ with respect to some location in the sample.
Figure 2.1: Interactions between ordered domains in a nematic phase. The square blocks represent domains of highly oriented nematic molecules. The director $\hat{N}_i$ indicates the average orientation of the molecules within a domain $i$ and varies slowly going from $D_i$ to $D_j$.

their relative spatial orientations $\vec{R}_{13}$ and $\vec{R}_{23}$ (Figure 2.1). Due to thermal fluctuations, long wavelength fluctuations of the director,\(^5\) which are analogous to spin waves in a Heisenberg ferromagnet, will be excited. One would expect, by analogy with the Heisenberg ferromagnet, that this distortion of the director field increases the energy of the system. Experimentally [2, 3], one can measure the energy required to locally distort the director field while keeping the director in a different orientation in a nearby region. One observes that the energy required to distort the orientation of $\hat{N}_2$ with respect to $\hat{N}_1$ is not the same as the energy needed to distort the orientation of $\hat{N}_3$ with respect to $\hat{N}_1$. Hence, unlike for the Heisenberg ferromagnet, nematic liquid crystals are characterized by three elastic constants associated with splay, bend and twist distortions.

\(^5\)By long wavelength we mean long compared to a typical intermolecular separation.
Figure 2.2: Splay, bend and twist deformations in nematics. The thin lines illustrate highly ordered domains. The glass plates can be treated in such a way that they impose a constant orientation of the director on the plates are shown by the thick double arrows.

of the director field. These three types of deformation are illustrated in Figure 2.2. The experimental difference between the elastic constants associated with the above distortions is a macroscopic manifestation of the nonseparability of the pair potential. A system of particles interacting with an isotropic potential would have equal splay, bend and twist elastic constants [21] since the interaction energy of two molecules $i$ and $j$ does not depend on the orientation of the intermolecular vector, $\mathbf{r}_{ij}$, nor does the energy required to rotate one molecule with respect to the other while keeping $\mathbf{r}_{ij}$ fixed.

This example shows that a nonseparable pair potential, although it is formally anisotropic since it depends on $\hat{n}_i$ and $\hat{n}_j$, it is isotropic with respect to the spatial variable $\mathbf{r}_{ij}$. A spatially isotropic anisotropic pair potential is the simplest definition one can give to a separable potential.

Another macroscopic property of a liquid of particles interacting with a separable
potential is that it would have isotropic viscosity coefficients. Again, this does not correspond to the experimental evidence, where different viscosity coefficients are measured depending on the direction of the fluid flow with respect to a director maintained aligned with either surface treatment or with a strong magnetic field [2, 3].

X-Ray Diffraction Pattern of Nematics

For a separable potential, the distance of approach of two particles with a given relative orientation is independent of their angle of approach. From this observation, one immediately concludes that in both the isotropic and nematic phase, the X-ray diffraction pattern should display a perfectly circular ring of uniform intensity.

Consider an attractive anisotropic separable potential. In a mean-field point of view, the anisotropic part of the potential vanishes above the transition since all the \( \langle P_{2n} \rangle \) in Equation 2.18 are zero in the isotropic phase. Further, due to packing constraints, there is a large probability that two molecules are separated by a distance, \( r_{iso} \), in the isotropic phase. Hence, in an X-ray diffraction pattern of an isotropic liquid crystal material, one expects to see a perfectly circular ring of uniform intensity at a momentum transfer \( q_{iso} \approx 1/r_{iso} \) far above the isotropic-nematic transition. The ring is diffuse and has a radial width in reciprocical space of \( 1/\xi \), the positional correlation length (see Figure 2.3a). In the nematic phase, each \( P_{2n} \) component of the pseudo-potential acquires a non-zero value and the mean strength of the attractive potential (isotropic + anisotropic part) increases. Hence, the minimum distance of approach decreases slightly and one should again observe a perfectly circular ring of uniform intensity, but at a momentum transfer \( q_{nematic} \approx 1/r_{nematic} \) with \( q_{nematic} > q_{iso} \). This is not what is observed experimentally [23, 22, 24] as shown in Figure 2.3b.

As discussed in Chapter 1 (see Figure 1.1), the nematics are elongated molecules. The shape of the molecule will prevent nearby molecules from getting as close along the long
Figure 2.3: X-ray diffraction pattern for a nematic liquid crystal both above (a) and below the transition temperature (b). Photographs taken form reference [22].

molecular axis as perpendicular to it. One thus observes two rings modulated in intensity: one along the direction of \( \hat{N} \) at \( q \approx 1/l \), and one in the direction perpendicular to \( \hat{N} \) at \( q \approx 1/r_0 \) where \( l \) and \( r_0 \) are, respectively, a typical molecular length and molecular diameter. Hence, the fact that the X-ray diffraction pattern of nematic liquid crystals do not exhibit a ring of uniform intensity in \( \vec{q} \)-space can be interpreted as another manifestation of the nonseparability of the intermolecular pair potential.

2.2.2 Mean-Field Approximation and Nonseparability

We have argued in the first section of this chapter that the Maier-Saupe mean-field theory neglects orientational fluctuations and, as a by-product, averages out \( V_{ij} \) over \( d\Theta_{ij} \) and \( \Phi_{ij} \) leading to an effective separable potential \( \tilde{V}_{ij}(\hat{n}_i \cdot \hat{n}_j) \). This second step makes the interpretation of the Maier-Saupe mean-field approximation much less transparent than that of the simple Lebowhl-Lasher model. The question we then asked is if the nonseparability of the true pair potential is observable at a macroscopic level. In the
Chapter 2. Mean-Field Theory of the Isotropic-Nematic Phase Transition

previous subsection, we gave examples, taken from experimentally observed facts, which demonstrate that the pair potentials in nematic liquid crystals are nonseparable and manifest themselves at the macroscopic level. It could be argued that such manifestations of the nonseparability are not fundamentally interesting since they do not seem to play an important role in the isotropic-nematic transition. The important questions which arise at this point and that we try to answer in this thesis are:

- Do separable models really grasp the essential physics of the isotropic-nematic transition?

- Do nonseparable effects alter the thermodynamic behavior of the system close to its isotropic-transition, or is the nonseparability of the true pair potential just a cumbersome technical detail?

If the answer to these two questions was yes, it would mean that there are problems with a description of the isotropic-nematic transition in terms of separable models. Further, it would show indirectly that the mean-field approximation 2.14 is missing 'something' which is beyond the improvements that are brought in by the improved mean-field theories devised for the Lebowhl-Lasher model [1, 25, 26, 27, 28, 29, 30, 31, 32, 17, 33].

Two preliminary questions must be answered before we can tackle the two previous questions:

- At what level or on what footing can we compare the thermodynamic behavior of separable and nonseparable potentials?

- What type(s) of pair potential should be used?
2.2.3 The Anisotropic van der Waals Potential – A Simple Nonseparable Model

We have shown in Equation 2.14 that the Maier-Saupe approximation averages out a nonseparable potential over the orientations of the intermolecular vector $\vec{r}_{ij}$. We shall start from there and make use of the properties of the Maier-Saupe approximation we have described in 2.1.2 to come up with a simple nonseparable model for the pair potential. We need a potential whose spatial average reduces to a separable potential of the form:

$$V_{ij}^{(s)} = V_0(|\vec{r}_{ij}|) + V_2(|\vec{r}_{ij}|) P_2(\hat{n}_i \cdot \hat{n}_j)$$  \hspace{1cm} (2.19)

without higher order $P_{2n}$ terms.

As already illustrated by our description of the X-ray diffraction pattern, the presence of an isotropic-nematic transition in systems of hard objects depends on the degree of anisotropic of their shape, hence their nonseparability. This implies that we will not be able to investigate purely steric models such as hard ellipsoids [34, 35] or hard spherocylinders [36, 37, 38]. In order to study the approximation 2.14, we will have to investigate systems with soft anisotropic potentials.

There is a prejudice against renouncing the investigation of hard steric objects in the problem of the isotropic-nematic transition in liquid crystals. Since the pioneering work of Onsager [39], there has been a strong consensus in the liquid crystal community that anisotropically repulsive forces (steric effects) may be the major forces responsible for stabilizing the nematic phase in liquid crystal materials. Furthermore, it was generally accepted until about two years ago that attractive forces had to be present to stabilize a smectic phase [40, 41, 42]. There is now rapidly increasing evidence from computer simulations that hard objects, such as hard spherocylinders, can exhibit a smectic-A phase without the presence of any attractive forces [36, 37, 38]. Hence, attractive forces have recently attracted little attention regarding the problem of phase transition in liquid
However, we will show in this thesis that attractive forces are important in the physics of liquid crystals. In particular, we will find that several interesting mesomorphic behaviors in some liquid crystals systems are much more easily explained and investigated using soft potentials than with anisotropically steric models.

Some realistic intermolecular pair potentials have been proposed [43, 44] and investigated in computer simulations [45, 46, 47]. These are soft potentials and, in contrast to purely steric contact potentials as in spherocylinders, contain information on both the anisotropic repulsive (steric) and anisotropic attractive part of the potential. Unfortunately, such realistic potentials are complicated and it is useful to investigate whether a simpler model can exhibit the essential features of nematic order. At a more technical level, these potentials [43, 44] do not satisfy our criterion of reducing to the simple form 2.19.

One possibility is to describe the isotropic to nematic transition by purely anisotropic attractive interactions. Assuming that the anisotropy of the pair potential is due to the molecular polarizability, the resulting van der Waals interaction [48] gives rise to an anisotropic part of the pair potential for molecules of cylindrical symmetry of the form:

\[
V_{VDW}(\vec{r}_{ij}; \hat{n}_i, \hat{n}_j) = -\mathcal{J} \left( \frac{r_o}{r_{ij}} \right)^6 (\hat{n}_i \cdot \hat{n}_j - 3\hat{n}_i \cdot \hat{e}_{ij} \hat{e}_{ij} \cdot \hat{n}_j)^2.
\] (2.20)

Here \( \hat{e}_{ij} \) is a unit vector parallel to \( \vec{r}_{ij} \), the intermolecular vector which connects the center of mass of two molecules. The length scale is set by \( r_o \), which is a measure of the effective molecular diameter. \( \hat{n}_i \) and \( \hat{n}_j \) are unit vectors parallel to the symmetry axis of the molecules and \( \mathcal{J} \) is the strength of the interaction which has units of energy.

This potential can be derived from second order perturbation theory [48]. We shall not repeat the derivation here, but rather present a more heuristic approach. Nematics do not necessarily have a permanent electric dipole moment, but at any moment a fluctuation
in the electronic charge distribution can occur which creates a spontaneous dipole. As described in Chapter 1, most of the nematogens have quite a large length to breadth ratio as shown in Figure 1.1. One can thus expect the molecule to have an anisotropic molecular polarizability. The electric field, $\vec{E}(\vec{r}_{ij})$ produced by a spontaneous dipole moment, $p$, of orientation $\hat{n}_i$ at a relative position $\vec{r}_{ij}$ ($\vec{r}_{ij} = \hat{e}_{ij}r_{ij}$) from a molecule $i$ is given by

$$\vec{E}(\vec{r}_{ij}) \propto \frac{p}{r_{ij}^3} (\hat{n}_i - 3\hat{n}_i \cdot \hat{e}_{ij} \hat{e}_{ij}) .$$

(2.21)

If a molecule, $j$, sits at $\vec{r}_{ij}$, it gets polarized by the spontaneous field, $\vec{E}$, created by $i$. The induced moment, $\vec{p}_j$, along $\hat{n}_j$, is

$$\vec{p}_j = \chi \hat{n}_j \hat{n}_j \cdot \vec{E}(\vec{r}_{ij})$$

$$\propto \frac{\chi p}{r_{ij}^3} (\hat{n}_i \cdot \hat{n}_j - 3\hat{n}_i \cdot \hat{e}_{ij} \hat{e}_{ij} \cdot \hat{n}_j) \hat{n}_j$$

(2.22)

where $\chi$ is the molecular polarizability. The potential energy, $V_{VDW}$, of the two dipoles is

$$V_{VDW} = -\vec{p}_j \cdot \vec{E}(\vec{r}_{ij})$$

$$= -\left( \frac{J r_{ij}^6}{r_{ij}^3} \right) (\hat{n}_i \cdot \hat{n}_j - 3\hat{n}_i \cdot \hat{e}_{ij} \hat{e}_{ij} \cdot \hat{n}_j)^2$$

(2.23)

where we have introduced the constant of proportionality $J r_{ij}^6$. This is potential 2.20.

Since the potential 2.20 is so simple, it is useful to investigate its validity as a model for a thermotropic nematic liquid crystal. Indeed, this potential was first introduced in the context of nematics by Maier and Saupe [19, 20] and is the starting point of the improved mean-field theory of Ypma and Vertogen [25]. It is easy to show that 2.20 satisfies the requirement 2.19:

$$\bar{V}_{VDW} = \int \int V_{VDW} \sin(\Theta_{ij}) d\Theta_{ij} d\Phi_{ij}$$

$$= 4\pi J \left( \frac{r_p}{r_{ij}} \right)^6 \left[ \frac{2}{3} \frac{1}{15} P_2(\hat{n} \cdot \hat{n}_j) \right] .$$

(2.24)
Chapter 2. Mean-Field Theory of the Isotropic-Nematic Phase Transition

If the molecules are lying completely into the xy plane, the unit vectors \( \hat{n}_i \) and \( \hat{e}_{ij} \) can be written as \( \hat{n}_i = \{\cos(\phi_i), \sin(\phi_i)\} \) and \( \hat{e}_{ij} = \{\cos(\theta_{ij}), \sin(\theta_{ij})\} \), where \( \phi_i \) and \( \theta_{ij} \) are the orientations of \( \hat{n}_i \) and \( \hat{e}_{ij} \) with respect to a fixed axis \( \hat{x} \) (see Figure 1.8). In two dimensions, the rotational invariant with nematic symmetry\(^6\) equivalent to \( P_2(\hat{n}_i \cdot \hat{n}_j) \) is

\[
2(\hat{n}_i \cdot \hat{n}_j)^2 - 1 = \cos(2\phi_i - 2\phi_j).
\]

Performing the following integration:

\[
\bar{V}_{VDW}^{2D} = \int V_{VDW} \, d\theta_{ij} = 2\pi \mathcal{J} \left( \frac{r_o}{r_{ij}} \right)^6 \left[ \frac{5}{4} + \frac{1}{8} \cos(2\phi_i - 2\phi_j) \right]
\]

we obtain the two-dimensional version of the Maier-Saupe approximation.

It is instructive to look at the dependence of potential 2.20 on the orientation of \( \hat{e}_{ij} \) for various relative orientations of the molecules \( i \) and \( j \) (Figure 2.4). Consider the orientations giving rise to an extremum in energy for a pair of molecules interacting via potential 2.20 for a given separation \( r_{ij} \). The lowest energy configuration has \( \hat{n}_i, \hat{n}_j \) and \( \hat{r}_{ij} \) parallel, with \( V_{VDW} = -4 \) in units of \( \mathcal{J}(r_o/r_{ij})^6 \). The configuration in which \( \hat{n}_i \parallel \hat{n}_j \), but \( \hat{n}_i \) and \( \hat{n}_j \perp \hat{r}_{ij} \), is a saddle point with \( V_{VDW} = -1 \), while the energy has an absolute maximum when all three vectors are mutually perpendicular.

We shall now describe the approach we have taken to investigate potential 2.20 and its mean-field versions (Equations 2.24 and 2.25 respectively).

### 2.3 Towards a Computer Experiment

Several approaches can be taken to investigate systems of particles interacting with anisotropic potentials and exhibiting mesomorphic phases:

1. Lattice models with anisotropic potentials

\(^6\)Again we assume a fluid phase where there is nematic symmetry and where the averages of \( \cos(\theta_{ij}) \) are zero.
Figure 2.4: Dependence of the van der Waals potential, in units of $J$, on the orientation of intermolecular vector $\theta$, for fixed distance $r_{ij}$, and for various relative molecular orientation $|\phi|$. The following planar orientations are assumed: $\hat{n}_i = (0, 1)$, $\hat{n}_j = (\sin(\phi), \cos(\phi))$ and $\hat{e}_{ij} = (\sin(\theta), \cos(\theta))$. The solid curves are for positive $\phi$ while the dashed ones are for $\phi < 0$. For clarity, each curve is shifted by a positive value of +4 from the nearest lower one.
• Theoretical investigations
• Computer simulations

2. True liquid models with anisotropic potentials

• Theoretical investigations
• Computer simulations.

There have been several theoretical and computer simulation investigations of lattice models the isotropic-nematic transition with separable potentials in the past ten years. A brief review of these results was given in Section 2.1.1. We shall illustrate in the next chapter that results for nonseparable lattice models cannot be meaningfully interpreted in the context of an isotropic-nematic transition.

We are interested in the implication of the mean-field approximation within a liquid description (Equation 2.14) of the isotropic-nematic transition. Hence, we are interested in the second class of approaches above.

In recent years, the technique of density functional calculations coupled to numerical evaluations of the Ornstein-Zernike and approximate closure relations [49, 50, 51] have proved to be very good at reproducing the computer simulation results of various model systems [34, 35, 36, 37, 38, 52]. Unfortunately, with a few exceptions [53], this approach does not allow investigation of the nematic phase. Finding a way to describe the nematic phase using such techniques is a very difficult problem, and is the subject of current and intense study.

For all the above reasons, and since we felt there was a need to increase our understanding of the effects induced by nonseparable anisotropic potentials in liquid crystals, we decided to investigate, using computer simulations, the thermodynamic behavior of systems of particles interacting with the van der Waals potential 2.20. The results of
these computer experiments are presented in the next two chapters.
In this chapter, we first present the motives for using computer simulations, and a short overview of common computer simulation methods used to study statistical thermodynamic problems. We then use one of these methods, the Monte Carlo technique, to investigate the behavior of the van der Waals potential (Equation 2.20) for lattice systems and systems with quenched positional disorder. The results obtained for these systems show that the translational degrees of freedom must be annealed (in thermal equilibrium) with the orientational degrees of freedom in order to lead to nematic-like orientational ordering. These observations led us to perform preliminary Monte Carlo simulations of systems where both translation and rotation of the particles are allowed.

3.1 Computer Simulations, Monte Carlo and Metropolis Algorithm

3.1.1 An Impetus for Computer Simulations

Observations are often made in the laboratory which are not immediately explained by existing theories or are perhaps not expected (Figure 3.1, step 1). In response to this, the theoretician may propose a model to explain what is observed. The model is put into
mathematical terms to facilitate comparison with the physical system (step 2). Effects such as nonlinearities, lack of symmetry or a large number of degrees of freedom prevalent in any realistic model are very difficult, if not impossible, to deal with analytically. In the past, arbitrary simplifications had to be made before the model could be compared with the physical system (step 3 and 4). If the experimental results and theoretical predictions were in agreement with each other, the initial model was thought to be appropriate to describe most of the physics going on in the experiments (step 5). However, this is not what happens most of the time; theoretical predictions and experimental results are often in qualitative agreement at the most. In such circumstances one is left to decide if the disagreement comes from the introduction of an oversimplified model at step 2 or from the approximations used at step 3. This is clearly not a simple task.

With the advent of powerful computers, it is now often possible to solve the model 'exactly' (step 6). This gives to the theoretician a way to study the limit of validity of the approximations he relied on in order to obtain some analytical results (step 7). Once a
given model, as well as its set of approximations, are fully understood, it becomes easier to decide how well this model can describe the physical system under study. Computer simulation is adding a new dimension to scientific investigation and establishing a role of equal importance with the traditional approaches of experiment and theory.

3.1.2 What is a Computer Simulation?

Computer simulations have been used for the last three decades as an extension of laboratory and theoretical work, and are becoming especially useful now with the advent of powerful computers. In the field of phase transitions in statistical mechanics problems, simulations are used to calculate statistical properties of the system such as energy, order parameters and correlation functions. They are particularly applicable to the field of liquid crystals because phase transitions predicted by various model systems are easily simulated by computer.

There exist two popular computer simulation techniques used to investigate the thermodynamic behavior of a given model. These are the Monte Carlo method and the molecular dynamics technique. In the context of the present work, a computer simulation consists of $N$ particles interacting through some known potential and each particle is allocated a set of arbitrary initial co-ordinates (position and orientation). The Monte-Carlo method generates a random displacement for each particle, and the move is accepted or rejected depending on its new energy and a certain probability function. No time scale is involved, and the sequence of configurations is entirely probabilistic. The molecular dynamics method uses the known potential to calculate forces and torques, and each particle is moved by integrating its equation of motion over some small time increment. Unlike the Monte Carlo method, the molecular dynamics allows the study real time-dependent phenomena in various systems.
3.1.3 Molecular Dynamics

The molecular dynamics method is based on the microcanonical ensemble rather than on the canonical ensemble: the total energy of the system is conserved during the length of the simulation and the temperature is a fluctuating quantity. The ergodicity assumption is crucial for the applicability of this method. The ergodicity assumption states that during any significant time interval the phase point, \( X_N = (\vec{r}_1 \ldots \vec{r}_N; \Omega_1 \ldots \Omega_N) \), spends equal time in all regions of the constant energy surface. If the ergodicity assumption is applicable to the system under study, one can use a time averaging procedure rather than an averaging over the states of the system.

The molecular dynamics equations are the Newton’s equation for each individual particle in the system. The positions and orientations of the particles are obtained by integrating Newton’s equation forward in time using some finite difference algorithm. The criterion that the total energy of the system must be conserved in this method can be used to check the accuracy of the algorithm used to integrate the equations of motion. The translational temperature of the system, \( T_{tr} \), is not a fixed quantity and must be obtained from the average squared velocities:

\[
k_B T_{tr} = \frac{1}{3N} \sum_{\mu=1}^{\mu=N} m_\mu \langle v_\mu^2 \rangle \quad (3.1)
\]

\[
\langle v_\mu^2 \rangle = \frac{1}{M} \sum_{j=1}^{j=M} v_\mu^2(j) \quad (3.2)
\]

\( M \) is the duration of the molecular dynamics run after disregarding some initial transient. \( v_\mu(j) \) is the center of mass velocity of particle \( \mu \), of mass \( m_\mu \), at step \( j \). A similar equation can be used to calculate the rotational temperature by using a time averaging of the individual angular velocities.

In this work we are primarily interested in the problem of phase transitions in liquid crystal models, transitions which are induced by a change of the temperature and we
are not concerned with time-dependent phenomena. For these two reasons, we have preferred to use a Monte Carlo approach using the standard Metropolis algorithm, rather than a molecular dynamics simulation.

3.1.4 Monte Carlo Simulation and Metropolis Algorithm

We are interested in the thermal average of various functions \( f(X_N) \):

\[
\langle f(X_N) \rangle = \frac{\int \exp\{-\beta V_N(X_N)\} f(X_N) dX_N}{\int \exp\{-\beta V_N(X_N)\} dX_N}
\]  

(3.3)

Ideally, one would replace the integral above by a sum over the \( M \) configurations generated in the Monte Carlo procedure:

\[
\langle f(X_N) \rangle = \frac{\sum_{j=1}^{M_{tot}} \exp\{-\beta V_N(j)\} f(j)}{\sum_{j=1}^{M_{tot}} \exp\{-\beta V_N(j)\}}
\]  

(3.4)

where \( V_N(j) \) is the total potential energy of the configuration, \( j \), and \( M_{tot} \) is the total number of configurations allowed by the system.

Because \( M_{tot} \) is large, even in a very small system, any attempt to calculate \( \langle f \rangle \) from the above prescription is a hopeless task. One may hope that a much smaller number of states, \( M \ll M_{tot} \), could be used to give an adequate estimate of \( \langle f \rangle \):

\[
\langle f(X_N) \rangle \approx \frac{\sum_{j=1}^{M} \exp\{-\beta V_N(j)\} f(j)}{\sum_{j=1}^{M} \exp\{-\beta V_N(j)\}} .
\]  

(3.5)

The problem with the last approach is that randomly selected states are very improbable and contribute very little to the sums. It is essential to introduce some form of importance sampling which removes this bias and where configurations are selected according to a prescribed probability distribution \( \mathcal{P}(j) \). Then, when averaging over the \( M \) configurations, a weight must be assigned to each state which eliminates the bias in the selection

\footnote{As we shall see, this is not to say that one does not have to often wait a very long time to get the system under study in thermal equilibrium!}
Monte Carlo simulation is almost synonymous with the sampling scheme proposed by Metropolis et al. [54] with the choice:

\[
\mathcal{P}(j) = \frac{\exp\{-\beta V_N(j)\}}{\sum_{j=1}^{M} \exp\{-\beta V_N(j)\}}.
\]  

(3.7)

The average \(\langle f \rangle\) is then obtained from:

\[
\langle f \rangle \approx \frac{1}{M} \sum_{j=1}^{M} f(j)
\]

(3.8)

The Markov process allows us to generate the states, \(j\), of the system with the correct probability. Consider a single-step transition probability, \(p_{j,i}\), that the system is in state \(i\) at time \(t\) and in state \(j\) at time \(t + 1\). The transition probability matrix, \(p_{j,i}\), is time independent and its elements satisfy the conditions

\[
\sum_{j=1}^{M} p_{j,i} = 1
\]

(3.9)

\[
p_{j,i} \geq 0.
\]

(3.10)

The system is started in a state \(i_0\) at time \(t = 0\). The probability that the system is in state \(j\) at time \(t\), after \(M\) Markov steps, is:

\[
p_{j,i_0}^{(M)} = \sum_{i_1, i_2, \ldots, i_{M-1}} p_{j,i_{M-1}} p_{i_{M-1}, i_{M-2}} \cdots p_{i_2, i_1} p_{i_1, i_0}.
\]

(3.11)

Furthermore, the limit

\[
\lim_{M \to \infty} p_{j,i_0}^{(M)} = \Pi_j
\]

(3.12)

exists for all \(j\) and \(i\) and is independent of the initial starting state \(i_0\). In a statistical problem, the \(\Pi_j\)'s are known:

\[
\Pi_j = \mathcal{P}(j).
\]

(3.13)
Notice that the transition steps obey the following equality
\[ p_{j,i}^{(M+1)} = \sum_k p_{j,k} p_{k,i}^{(M-1)} \]  
(3.14)

We find that after taking the limit \( M \to \infty \),
\[ \Pi_j = \sum_k p_{j,k} \Pi_k \]  
(3.15)

One is free to choose any form of transition probability \( p_{j,i} \) as long as they lead to the correct limiting distribution 3.13. Most often, the unnecessarily strong condition of detailed balance is imposed:
\[ p_{i,j} \Pi_j = p_{j,i} \Pi_i \]  
(3.16)

In this case, a simple choice for the \( P_{j,i} \) is
\[ p_{j,i} = \frac{1}{N_{acc}^{(i)}} \text{ if } \Pi_j > \Pi_i \ (V_N(j) < V_N(i)) \]  
(3.17)
\[ p_{j,i} = \frac{\Pi_j}{N_{acc}^{(i)} \Pi_i} \text{ if } \Pi_i < \Pi_j \ (V_N(j) > V_N(i)) \]  
(3.18)

where \( N_{acc}^{(i)} \) is the number of states accessible from state \( i \), which does not have to be known.

In practice, the system is in a given configuration, say \( i \). A new configuration (positions and orientations) of the particles is generated. The new configuration is accepted if \( V_N(j) \leq V_N(i) \). If \( V_N(j) > V_N(i) \), the state is accepted with probability \( p_{j,i} = \exp\{-\beta [V_N(j) - V_N(i)]\} \). This last step is done by comparing \( p_{j,i} \) with a random number, \( R \), uniformly generated in the interval \([0,1] \). If \( R < p_{j,i} \), the state is accepted. If \( R > p_{j,i} \), the new state \( j \) is rejected and the old state \( i \) must be taken into account again in the averaging procedure. This process is repeated until averages are acceptable, or until either computing time or funds, are exhausted.
Periodic Boundary Conditions

Both the molecular dynamics and Monte Carlo methods are subject to the limitation of very small sample sizes: in most published works, $N$ is of the order of a hundred to a few thousand particles, which is extremely small by macroscopic standards. Periodic boundary conditions are almost invariably imposed in order to minimize surface effects and to simulate more closely the properties of an infinite system. If a particle leaves the cell, it is brought back in via the opposite boundary. This is most easily visualized with the aid of Figure 3.2 in which nine identical cells are shown, but only the central one is the system of interest. As a particle moves out of the central cell it also moves out of one of the eight surrounding cells and back into the central cell. One runs into problems with either free or periodic boundary conditions when the correlation length of the system reaches a value of the order of one half the size of the system. We have used periodic boundary conditions in all the simulations we have performed.

3.2 Lattice Systems

Before investigating positionally disordered systems, we shall first see what the ground states exhibited by potential 2.20 on some simple Bravais lattices are. These results will prove to be useful in interpreting the results of simulations in systems with either quenched or annealed positional disorder. More precisely, they will give a strong indication that local structure is vitally important if nematic orientational ordering is to exist in a system of particles interacting with a nonseparable potential such as the van der Waals potential.

It is clear from our description of the extremum in energy for the van der Waals potential (Section 2.2.3) that if the ground state of the system has nematic order (i.e. $\hat{n}_i \cdot \hat{n}_j = \pm 1$ for all $i, j$ at $T = 0$), some of the bonds will not be in their lowest energy
configuration. There is thus a possibility that nematic order will not be favored due to this frustration. In the present section we illustrate this observation by a number of examples.

3.2.1 Two-Dimensional Lattices

We first consider the case where the long axis is constrained to lie in the xy plane since it is the easiest to visualize. The ground state for a system of particles interacting via 2.25 has nematic order irrespective of the lattice, but what about potentials such as 2.20 which depend on the angle between \( \vec{r}_{ij} \) and \( \hat{n}_i \) or \( \hat{n}_j \)? In Figure 3.3 we show the lowest energy configurations for a few two-dimensional lattices where we employed the potential 2.20 with the particles constrained to lie in the lattice plane. The ground states were found by zero temperature Monte Carlo simulations on systems of the order of 150 particles, and with periodic boundary conditions. Typically, we used 500 Monte Carlo steps per
Figure 3.3: Lowest energy configurations for two-dimensional lattices. a) Square lattice, b) Triangular lattice and c) Honeycomb lattice.
particle \( (MCS) \) with either random or ordered starting configurations. For the lattices shown in Figure 3.3 no ambiguities arose, and we are confident that we have found the ground state configurations.

The square lattice has a ground state with parallel alignment of the \( \hat{n}_i \)s when only nearest neighbor interactions are included, but there is no continuous orientational symmetry; the director is pinned along one of the square axes (\( <10> \) direction). If more neighbors are included, the ground state changes and is shown in Figure 3.3a. If the lattice is sufficiently stretched into a rectangular lattice, the parallel orientation reappears with the alignment parallel to the short axis.

The potential 2.20 with the molecules constrained to lie in the plane is similar, but not identical, to the quadrupolar interaction between dumbell molecules. A lattice gas model employing quadrupolar interaction has been applied to the adsorption of diatomic molecules such as \( \text{H}_2, \text{N}_2, \text{O}_2 \) on graphite [55]. In the case of the triangular lattice with nearest neighbor interactions, the "railroad track" ground state of Figure 3.3b has two sublattices with different energy per particle for the "rails" and the "tressels". This is in complete analogy with the "herringbones" of Harris et al. [55]. The "pinwheel" ground state of the honeycomb lattice of Figure 3.3c is a linear superposition of three equivalent railroad tracks just as in the case considered by Harris et al. ².

### 3.2.2 Three-Dimensional Lattices

We have examined the lowest energy configurations of a number of three-dimensional lattices in which the particles interact via 2.20, and have found some interesting and highly frustrated configurations. In analogy with the square lattice, the ground state of a simple cubic lattice with nearest neighbor interactions has all the \( \hat{n}_i \) pinned in a

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²The fact that the ground state in Figure 3.3c and its energy was predicted before we found it with a zero temperature Monte Carlo simulation gave us good confidence that our program was working correctly.
<100> direction. Humphries et al. [56] found a transition to an ordered phase of this type in a Monte Carlo simulation where the potential 2.20 was considered as a model of a liquid crystal, but they did not try other lattice structures and therefore did not notice that their result was atypical.

For lattice structures other than the simple cubic, it was necessary to cool the system slowly to \( T = 0 \) rather than quenching it from infinite temperature. If quenched, the system would invariably be trapped in a metastable state. The symmetry of the lattice produces local minima in phase space, from which there is no escape without thermal fluctuations. We will refer to the lowest energy state found as the 'ground state', but we cannot say for certain that this is the true ground state. The ground states that we have found are, for all but the simple cubic lattice, lower in energy than any "nematic" configuration with the \( \hat{a}_i \) aligned parallel to each other.

In Figure 3.4 we show our ground state configuration for a face centered cubic lattice (f.c.c.) lattice. The figure shows a \( <111> \) plane. The structure in the plane above is the same, but translated by a basis vector. The arrow on each rotor is pointing up from the plane, while the length is proportional to the projection in the plane. We observe a configuration which is similar to the pinwheel structure of Figure 3.3b. The rotors at the centre of the wheel have a declination of 15° with respect to the normal to the plane. We measure angles for the projection onto the plane relative to the in-plane basis vector by which successive planes are translated. The in-plane angle of the centre is then 150°. The rotors on the wheel have declinations that alternate between approximately 65° and 55°, and the in-plane angles are 150° ± 120° and 100° ± 120° respectively. The energy per site for the hexagonal closed packed lattice was found to be the same as for the f.c.c., and its structure is very similar.

The simulation for the f.c.c lattice was carried out for 4 of the 6 x 6 layers shown in Figure 3.4, with periodic boundary conditions. The calculation was repeated for a
Figure 3.4: Lowest energy configuration of the face centered cubic lattice. This figure shows a <111> plane. The length of each rotor is proportional to its projection in the plane. The direction out of the plane is indicated by an arrow.

$4 \times 4 \times 4$ structure with an identical outcome (this is, of course, no guarantee that we have found the exact ground state). It was usually sufficient to have 1000-2000 MCS per temperature. The particles were selected at random from the full $4\pi$ solid angle at high temperatures. At lower temperatures only small changes in orientation were attempted. In this way we were able to keep the acceptance ratio in the 30%-40% range until the onset of a high symmetry, low energy configuration.

3.2.3 Discussion of the Results for Lattice Systems

We have shown that lattice systems may display complicated structures when the pair-potential is nonseparable. Furthermore, it is clear that lattice models with particles interacting via nonseparable potentials are not suitable for studying the isotropic-nematic transition. The reasons are twofold:
• In a nonseparable system, the presence of an underlying lattice breaks the continuous symmetry. The discrete symmetry introduced by the lattice is non-existent in a real liquid. Hence, lattice models with nonseparable potentials are inappropriate for the isotropic to nematic transition.

• One way to get around the above argument about lattice models with nonseparable potentials would be to argue that nematics are dense fluids with a rather considerable short-range positional correlation and the underlying lattice could mimic this short-range structure. If this sort of argument should be taken with a grain of salt for 3D systems, it is, in most cases, totally invalid for two-dimensional (2D) lattices. Due to their continuous symmetry, 2D liquid crystals are expected to exhibit quasi-long-range molecular orientational order (see Section 1.4). The presence of an underlying lattice in a nonseparable system will, in most cases [8], destroy this behavior and impose true long-range orientational order.

These two problems do not arise in lattice models with separable potentials since the underlying lattice does not break the continuous symmetry.

Clearly, positional disorder is essential in order to investigate nonseparable models of nematics. Recall the mean-field approximation (Equation 2.14) which led to the spatial averaging of $V_{ij}$ in Equation 2.16. It is very tempting to reinterpret the approximation 2.14 as an averaging of all the possible short-range discrete symmetries allowed by the short-range positional order present in the liquid phase. As described earlier, the approximation 2.14 requires an input which is assumed to be known a priori: the radial distribution function $g_0$. These observations led us to ask the following questions:

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3As we shall discuss in Chapter 7, such lattice models might not be so bad for modelling transitions between tilted hexatic smectic phases.
• Assume, for the moment, that the particles are allowed to rotate, but not to translate, and are randomly distributed such that their center of mass pair distribution function, \( g_0 \), is liquid-like (decays rapidly to a value of 1). How would the orientational degrees of freedom in such a system behave as a function of temperature?

• Is it possible that quenched positional disorder is enough to get rid of the problems encountered with lattice models of nonseparable potentials, restore the spatial averaging invoked in Equation 2.15 and allow the system to exhibit a static nematic-like phase?

These are the questions we shall investigate in the following section.

3.3 Quenched Positional Disorder

By quenched positional disorder we mean that the translation of the molecules occurs on a time scale which is much longer than their rotational time scale, and the centers of mass of the particles do not have long-range positional order. The two degrees of freedom are not in thermal equilibrium in such a case. Systems where the translational degrees of freedom are said to be quenched are experimentally realized with molecules adsorbed on a substrate where the substrate potential is much larger than the interaction between the adsorbed molecules. In our studies of quenched systems, we take the relaxation time for translational motion to be infinitely long and consider only the rotation of the particles.

3.3.1 Random Parking Systems

As mentioned previously, we would like to have a quenched positionally disordered systems with a liquid-like radial density distribution function \( g_0 \). Hence, as a first step in understanding how the system behaves when one introduces the positional disorder
characteristic of a liquid, we carry out Monte Carlo simulations on rotors interacting via the anisotropic potential 2.20. The rotors are placed at the center of sequentially parked circles of diameter $d$ in two dimensions, and spheres in three dimensions.

It is interesting to test the hypothesis that coupling between spatial and orientational correlations in the liquid does not play an essential role in nematic ordering [42]. We therefore wish to represent the liquid by a model containing as few positional correlations as possible and the sequential absorption (random parking) model would seem to satisfy this criterion (see Hinrichsen [57] and references therein).

As the name indicates, random parking consists of sequential placement of objects (circles, squares, spheres, etc.) randomly and without overlap. Once an object is parked, its position remains fixed. As the volume is filled, it becomes more and more difficult to park a new object. Eventually, the time required to park a new object diverges and the system is said to have reached the jamming limit. At this limit, the total volume occupied by the parked objects, divided by the initially accessible volume is called the jamming density. The jamming density is 54.7% for circles adsorbed onto a plane [58] and approximately 34% for spheres randomly parked in a cube [59]. This is significantly smaller than the closely packed density of 90.7% in two dimensions and 74% in three dimensions. Our simulations were performed at a covering density of 1% to 2% below the jamming density.

### 3.3.2 Ground States of Random Parked Systems

#### Two Dimensions

Figure 3.5 shows a typical sequential adsorption pattern in two dimensions. Figure 3.6 shows the radial pair distribution function, $g_0$, of the 2D random parking problem at the jamming limit with the $g_0$ of a hard disc system at the same density. Notice the small
Figure 3.5: Typical sequential adsorption pattern of discs in a plane. A typical infinite temperature configuration ($\beta = 0$) with a rotor at center of each circle is shown.
amount of short-range positional order in this system as illustrated by the small peak at $r \approx 2d$. This is to be compared with a hard disk fluid at the same density where the height of the peak at $r \approx 2d$ is about 20% of the peak at $r = d$. Hence, there is much less positional correlation in a randomly parked configuration than in a 2D hard disc fluid.

We parked 512 circles of diameter $d$ onto a plane of size $28.5d \times 28.5d$. This corresponds to a coverage of 49.5%. The potential was cut off at a distance of either $3.5d$ or $2.15d$ (when the potential strength is 1% of the value at contact). No noticable difference between the results in the two cases was found. Both annealed and quenched simulations were performed. In the first case we initially decreased the temperature from $\beta J = 0$ in 14 intervals of $\beta J = 0.3$. The system was then quenched to $\beta J = \infty$. In the second case we quenched from $\beta J = 0$ to $\beta J = \infty$ directly. In both simulations we picked molecules at random for each Monte-Carlo step per particle ($MCS$), with an average of 2500
MCS at each temperature. The initial and final configurations are shown in Figures 3.5 and 3.7. For the final configurations the results of three runs are superimposed. The quenched and annealed systems look qualitatively the same and lack long-range nematic-like orientational order. However, the zero temperature configurations present some short-range order and look quite different from a totally disordered configuration (see Figure 3.5). An interesting feature of the simulation is the occurrence of regions where is always the same. We shall comment further on this point in Section 3.3.3

Three Dimensions

In the three dimensional case, we randomly parked 512 spheres in a cube of size $10d \times 10d \times 10d$, giving an occupied volume of 26.8%. The potential was cut off at the distance $3.5d$. We performed the same kind of simulations as in two dimensions. The initial and final configurations of some typical slices cut into the cube are shown in Figure 3.8. Once again, no transition from a disordered to a nematic phase was observed.

3.3.3 Microscopic Origin of the Frustrated Islands

It is clear that local structure is important in determining the orientational behavior of a nonseparable system. If the molecules are fixed on a lattice, the nonseparability leads to a crystal field that breaks the continuous orientational symmetry [60, 61]. In an amorphous solid, where the translational degrees of freedom are frozen in a random configuration, the system cannot relax and the orientational degrees of freedom suffer random frustration.

The lack of long-range nematic-like orientational order is due to the frustration caused by the quenched positional degrees of freedom. Figure 3.7 is made up qualitatively of two types of regions: the first, which we call field dominated, is a region where, although disordered, the particles always choose the same orientations, indicating the presence of
Figure 3.7: Superposition of three ground states ($\beta = \infty$) ground state configurations for the two-dimensional random system of Figure 3.5 with the rotors interacting via 2.20.
Figure 3.8: Slices of thickness $d$ of the ground state for a 3$D$ random parking configuration. Only molecules whose centers lie within the slice are shown. Arrows indicate direction out of the plane. The two figures represent two different slices with two superimposed final configurations for each slice.
Figure 3.9: Superposition of 20 orientational groundstate configurations for different values of the random field for a single random park of positions. The figure shows the ground states for the rotors interacting via the van der Waals potential with $f = 0.0, 1.5, 3.0$ and $6.0$ respectively in Equation 3.19.
a field that dictates a unique ground state. The second is what we shall term a spin glass region, where there appear to be many ground state configurations of approximately the same energy, and the subsystem reaches a different one on each simulation.

This interpretation becomes much clearer if we rewrite the potential 2.20 in terms of the angles $\theta_{ij}, \phi_i$:

$$ V_{VDW} = -\frac{J}{8} \left( \frac{r_o}{r_{ij}} \right)^6 (10 + \eta N_{ij} + f\{F_i + F_j\} + g G_{ij}) $$

$$ N_{ij}(\phi_i, \phi_j) = \cos(2\phi_i - 2\phi_j) , $$
$$ F_i(\phi_i, \theta_{ij}) = \cos(2\phi_i - \theta_{ij}) , $$
$$ F_j(\phi_j, \theta_{ij}) = \cos(2\phi_j - \theta_{ij}) \text{ and } $$
$$ G_{ij}(\phi_i, \phi_j; \theta_{ij}) = \cos(2\phi_i + 2\phi_j - 4\theta_{ij}) . \quad (3.19) $$

$\eta = 1$, $f = 6$ and $g = 9$ respectively. Written in this form we can clearly isolate which terms are responsible for the field dominated and the spin glass regions. The function $N_{ij}$ favors parallel orientation of interacting neighbors, independent of the orientation of the intermolecular vector. The function $F_i$ depends on the orientation of a single rotor, $\phi_i$, and the random bond angle, $\theta_{ij}$. Hence, it describes the effect of a random field on particle $i$. The function $G_{ij}$ depends on the orientation of both rotors $\phi_i$ and $\phi_j$ and the random phase $\theta_{ij}$. The random particle configuration leads to random bond frustration and we interpret $G_{ij}$ as a spin glass term.

Changing the relative size of the field and spin glass terms in the potential 3.19 alters the extent of the two regions in a superposition of ground states. Figure 3.9 shows the change in the structure of the ground state as a function of the strength, $f$, of the random field terms. Figure 3.9 shows the result of 20 zero temperature Monte Carlo simulations for this reduced potential. We observe that if the field terms are completely removed,
the areas where a unique ground state exists disappear completely and the figure is now completely frustrated.

We thus propose that our amorphous nonseparable system is similar to a Ising spin glass problem \((g \neq 0)\), in a random magnetic field \((f \neq 0)\), and with a small ferromagnetic coupling \((\eta \neq 0)\). The quenched bond angles, \(\theta_{ij}\), break the continuous symmetry of the rotational degrees of freedom. Present opinion is that the lower critical dimensionality is larger than two for a lattice system with discrete orientations and nearest neighbor interactions [62] and it seems likely that the same will be true for our system. The effects of random fields on nearest neighbor spin glass models is not known in detail and much work must be done to parameterize such systems quantitatively [61, 63]. However in a recent mean field calculation, Holdsworth [64] has shown that the infinite range Ising model with a Gaussian random field has a stable spin glass phase below a finite critical field variance. A field variance line analagous to the de Almeida-Thouless [65] line for a constant field is predicted.

The above system is analagous to a quadrupolar, or orientational glass such as para-ortho hydrogen or a mixed crystal of KBr-KCN [66] for which there has been a long debate concerning the existence of a glass transition. The quadrupole-quadrupole interaction is nonseparable and can be expanded, in the same way, in field and bond terms. Our results for anisotropic amorphous solids show that orientational glass behaviour is the result of nonseparability in the anisotropic pair interaction when the translational degrees of freedom are quenched.

We have recently investigated the spin glass aspect of the van der Waals potential at finite temperature [63]. We do not present the results here, since it would take us too far from the main subject we are interested in, namely orientational phenomena in liquid crystals.

In the context of liquid crystal models, the main conclusion of this section is that the
translational and rotational degrees of freedom should be in thermal equilibrium in order for a nonseparable potential to lead to nematic-like orientational ordering behavior. In a liquid phase, the system is able to relax and find the minimum free energy for both degrees of freedom. Our results on lattice systems and for amorphous solid already suggest that, if a system interacting with the van der Waals potential (2.20) is to lead to liquid crystalline behavior, there has to be a strong and nontrivial coupling between the translational and rotational degrees of freedom. A preliminary investigation of a system of particles interacting with a modified van der Waals potential in a true liquid phase is presented in the next section.

3.4 Annealed Positional Disorder: Preliminary Results on 2D Liquid Crystal Models

3.4.1 Why Study 2D Liquid Crystalline Models?

We give here only the practical motivations for first studying a 2D fluid instead of a 3D one, and reserve the more theoretical ones for the next chapter. Firstly, for 2D fluids, we have only three degrees of freedom to consider, in contrast to five in three dimensions for molecules with cylindrical symmetry; this reduces the computing time considerably. Secondly, it is much easier to visualize the configuration of the particles in 2D than in 3D (compare, for example, Figures 3.7 and 3.8). Finally, there is a hope that some of the physics present in a 3D nonseparable system can be first observed and at least qualitatively understood, for a fraction of the computing cost, in a 2D system. It will, however, soon become apparent that one has to disregard, from theoretical arguments, the direct comparison of the results obtained for 2D nematic liquid crystals with those for 3D systems.
3.4.2 Pair Potentials

We would like to return to our initial investigation of approximation 2.14. To do this, we proceed as explained in the previous chapter and compare a nonseparable potential with a separable one. The nonseparable potential chosen is:

$$ V_{ij}^{NS}(\vec{r}_{ij}; \hat{n}_i, \hat{n}_j) = 4\epsilon \left[ r_{ij}^{-12} - \alpha r_{ij}^{-6} \right] $$

$$ -4\beta \epsilon \left[ 2(\hat{n}_i \cdot \hat{n}_j)^2 - 1 \right] r_{ij}^{-6} $$

$$ -4\gamma \epsilon [\hat{n}_i \cdot \hat{n}_j - 3\hat{n}_i \cdot \hat{e}_{ij} \hat{e}_{ij} \cdot \hat{n}_j] r_{ij}^{-6} $$  \hspace{1cm} (3.20)

where we have defined $r_{ij} = |\vec{r}_{ij}|/r_o$ with $r_o$ being an effective molecular diameter. Here $\hat{n}_i = (\cos(\phi_i), \sin(\phi_i))$ is a unit vector in the direction of the molecular anisotropy, and $\hat{e}_{ij} = (\cos(\theta_{ij}), \sin(\theta_{ij}))$ is a unit vector in the direction of $\vec{r}_{ij}$.

The last term in 3.20 corresponds to the anisotropic Van der Waals interaction we have used in the previous two sections. The other anisotropic term, proportional to $\beta$, and independent of $\hat{e}_{ij}$, is purely phenomenological. We introduce this term in the nonseparable potential to make sure that the ground state has nematic order and is not a modulated phase as observed in the section on the lattice models [60]. Since the particles are now free to move, a repulsive term is needed to stabilize the interaction at short distance. As discussed in Chapter 2, we have chosen to neglect steric anisotropy. Hence, a simple isotropic repulsive term, $4\epsilon r_{ij}^{-12}$, is added to prevent the particles of collapsing towards each other. Finally, an attractive isotropic term, $4\alpha r_{ij}^{-6}$, is added. $\alpha$, $\beta$ and $\gamma$ are positive constants, and $\epsilon$ is a measure of the strength of the interaction and has units of energy. In the spirit of the discussion presented in Sections 2.1.2 and 2.2.3, we choose $\alpha$, $\beta$ and $\gamma$ be 0, 2/5 and 4/5 respectively so that averaging $V_{ij}^{NS}$ over the orientation $\theta_{ij}$ of $\hat{e}_{ij}$ leads to our separable potential:

$$ V_{ij}^S(\vec{r}_{ij}; \hat{n}_i, \hat{n}_j) = 4\epsilon \left[ r_{ij}^{-12} - r_{ij}^{-6} - J\{2(\hat{n}_i \cdot \hat{n}_j)^2 - 1\} r_{ij}^{-6} \right] $$  \hspace{1cm} (3.21)
with $J = 1/2$. This is best seen if the potential 3.20 is expanded in terms of its rotational invariants:

$$V_{ij}^{NS} = \frac{4\epsilon}{r_{ij}^{12}} - \frac{(4\alpha + 5\gamma)\epsilon}{r_{ij}^6} - \frac{(8\beta + \gamma)\epsilon}{2r_{ij}^6} \cos(2\phi_i - 2\phi_j)$$

$$- \frac{3\gamma\epsilon}{r_{ij}^6} [\cos(2\phi_i - 2\theta_{ij}) + \cos(2\phi_j - 2\theta_{ij})]$$

$$- \frac{9\gamma\epsilon}{2r_{ij}^6} [\cos(2\phi_i + 2\phi_j - 4\theta_{ij})].$$

Hence, the quantities $\alpha$, $\beta$, $\gamma$ and $J$ are not independent but are related by

$$\alpha = 1 - \frac{5\gamma}{4},$$

$$\beta = J - \frac{\gamma}{8}. \quad (3.23)$$

Potential 3.21 corresponds to the two-dimensional Maier-Saupe model for nematic liquid crystals [19, 20]. This potential leads to a 2D nematic phase if $J$ is larger than some critical value $4$. At high temperature, in the isotropic phase, where $\langle e^{2i\theta_{ij}} \rangle \approx \langle e^{4i\theta_{ij}} \rangle \approx 0$ and $\langle (\hat{n}_i \cdot \hat{n}_j)^2 \rangle \approx 1/2$, one recovers an effective Lennard-Jones pair potential from both the separable and the nonseparable potential with the above particular choice of $\alpha$, $\beta$ and $\gamma$.

We note here that the potentials we used exhibit the symmetry

$$V_{ij}(\hat{r}_{ij}; \hat{n}_i, \hat{n}_j) = V_{ij}(\hat{r}_{ij}; -\hat{n}_i, \hat{n}_j) = V_{ij}(\hat{r}_{ij}; \hat{n}_i, -\hat{n}_j),$$

which ensures that the two systems can, in principle, exhibit a mesophase with nematic symmetry.

We next consider the effects of translational motion. Monte Carlo simulations have been performed on these 2D systems (potentials 3.20 and 3.21) at various temperatures where the particles could move and rotate.

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4A lattice version of this model has been studied via renormalization group by Albinet and Tremblay [67] and a Monte Carlo simulation with fixed particles on a triangular lattice has been performed by Denman et al. [68].
3.4.3 Results

A system size of 400 particles at a fixed density $\rho = 0.888$, (in units where lengths and temperatures are given in units of $r_o$ and $\epsilon/k_B$ respectively) was investigated for both potentials 3.20 and 3.21. We performed between 2000 and 3000 MCS for both equilibration and production of data at each temperature. We first present the results for the separable potential 3.21.

When the temperature is varied we find three different phases as illustrated in Figure 3.10. At high temperatures, as in Figure 3.10a, the system is isotropic. At $T = 2.4$, we observe the onset of nematic order, as shown in Figure 3.11, where we plot the nematic order parameter $Q$ given by the average positive eigenvalue of the traceless $2 \times 2$ matrix [69]:

$$Q_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^{i=N} [2n_{i\alpha}n_{i\beta} - \delta_{\alpha\beta}] .$$  

(3.25)

$n_{i\alpha}$ is the $\alpha$ cartesian component of $\hat{n}_i$. $Q = 0$ in an isotropic phase and $Q = 1$ in a perfectly ordered (nematic) phase. The eigenvector associated with $Q$ is called the director (see Chapter 1). Technically, one calculates $Q$ from successive realizations of the particle configuration and one keeps a running average of the $Q$s. Another possibility would be to keep a running average of the elements of $Q_{\alpha\beta}$ and calculate $Q$ from the resulting average. For systems with continuous symmetry, the first procedure is superior since the second technique would give a value for $Q$ which tends to zero as the simulation time is increased. A snapshot taken in the middle of the nematic region is given in Figure 3.10b. When the system is cooled further, it crystallizes in a triangular lattice (Figure 3.10c). The empty regions are characteristic of the phase separation seen in a constant volume simulation.

We next consider the case for the nonseparable potential, Equation 3.20. There is now a strong correlation between orientational and translational motion, and the low
Figure 3.10: Snapshots of particles configurations for the separable system at $\rho = 0.888$.  
(a) Isotropic phase at $T = 4.0$.  (b) Nematic phase at $T = 1.2$.  (c) Low temperature, $T = 0.2$, with the system freezing into a triangular lattice.
temperature crystalline phase is rectangular, allowing parallel alignment of the rotors (see Section 3.2). In the liquid phase we see the build-up of strong short-range positional and orientational correlations. It is interesting to find that the only lattice structure that supports nematic order in its ground state is the one which is favored by the system once translational motion is allowed. Snapshots of configurations at different temperatures are shown in Figure 3.12.

3.5 Formation of Chain-Like Structures

One observes in Figure 3.12b, for the nonseparable potential 3.20 a build-up of bond orientational structure and the formation of chains whose axis lies in the direction of the molecular anisotropy $\hat{n}_i$. As the temperature is reduced, the chains increase in length, become noticeably less flexible and register with respect to each other with the perpendicular distance between chains being somewhat longer than a link along a chain.

In contrast, for the separable potential, there is no obvious evidence of build-up of
Figure 3.12: Snapshots of particles configurations for the nonseparable system at $\rho = 0.888$ for three different temperatures: (a) $T = 4.0$. (b) $T = 2.0$. (c) $T = 0.2$. A strong coupling between the translational and orientational degrees of freedom is observed. The system appears to freeze into a rectangular lattice which favors orientational ordering.
bond correlation in the nematic phase. The microscopic origin of this phenomenon can be understood by calculating the dependence of $V_{ij}^{NS}$ on $\theta_{ij}$ for a distance $r_m(\theta_{ij})$ where $V_{ij}^{NS}$ is minimum. Assuming $\hat{n}_i \parallel \hat{n}_j$, we find that $r_m(\theta_{ij})$ is given by

$$r_m(\theta_{ij}) = 2^{1/6} \left[ 1 + J - \frac{11\gamma}{8} + \gamma \{1 - 3 \cos^2(\theta_{ij})\} \right]^{-1/6}$$

(3.26)

where we have used Equations 3.23. The potential depth, $V_m$, at $r_m$, is given by

$$V_m = - \left[ 1 + J - \frac{11\gamma}{8} + \gamma \{1 - 3 \cos^2(\theta_{ij})\} \right]^2.$$ 

(3.27)

$V_m$ has an absolute minimum at $\theta_{ij} = 0$, a local minimum at $\theta_{ij} = 90^\circ$, and an absolute maximum at $\theta_{ij} = \cos^{-1}(\sqrt{3}/3) \approx 55^\circ$. The $\theta_{ij}$ dependence is shown in Figures 3.13 and 3.14 for $r_m$ and $V_m$ respectively, for several values of $\gamma$. First notice that the maximum at $55^\circ$ disrupts the normal tendency of isotropic, and separable anisotropic potentials to form a local sixfold ($60^\circ$) symmetric nearest-neighbor bond shell. By examining Figure 3.14, we see why, in the nematic phase, where $\hat{n}_i \approx \parallel \hat{n}_j$ and for a large value of $\gamma$, the large depth of the potential for $\theta_{ij} = 0$ will strongly favor the formation of weakly coupled chain-like structures.

We have looked in detail at the formation of chains in the nonseparable system, but at a density $\rho = 1.00$ to avoid the phase separation observed in Figure 3.12. Snapshot configurations of the chains are shown in Figure 3.15 for four different temperatures. We define a chain as follows: take two neighboring particles and calculate the lowest two bond energies for each. If they share one of these bonds then this bond is a link in the chain. This is clearly not a unique definition, but it serves our purpose in analyzing the chain structure appearing in the ordered phase. At high temperature, $T = 4.8$, there are only short chains, but as the temperature is reduced to 3.6, we observe a rapid build-up until, at $T = 2.6$, they span the entire system.

The chains are reminiscent of those observed in dipolar magnetic systems in strong magnetic fields [70, 71, 72, 73]. In our case, the isotropic to nematic phase transition
Figure 3.13: $\theta_{ij}$ dependence of $r_m$ for the nonseparable model with $J = 1/2$. 
Figure 3.14: $\theta_{ij}$ dependence of $V_m$ for the nonseparable model with $J = 1/2$. 
Figure 3.15: Snapshots of chains configurations at $T = 4.8, 4.2, 3.6$ and $2.6$. The criterion used for chain construction is explained in the text.
induces a self-consistent orientational field that plays qualitatively the same role as an external field in dipolar magnetic systems. The potential energy, $E_i$, of a particle $i$ in this field would be given in such a mean field argument by

$$E_i \propto -Q \cos(2\phi_i - 2\Phi_o)$$  \hspace{1cm} (3.28)

where $Q$ is the nematic order parameter and $\Phi_o$ is the orientation of the director in the lab frame. There is, however, a major theoretical difficulty in explaining the formation of chains with the above mechanism in a $2D$ system like the present one.

As discussed in Chapter 1, most two-dimensional systems with continuous degrees of freedom lack long-range order at any non-zero temperature. This result follows from an elastic or continuum description of the fluctuations away from a perfectly ordered state. As in other systems, one finds that an elastic description of director or orientational fluctuations in two-dimensional liquid crystals [2] leads to the conclusion that true long-range orientational order is absent [74]. Practically, this means that $Q$ vanishes in the thermodynamic limit and our interpretation in terms of an effective field as in Equation 3.28 would be meaningless for a very large sample.

The observation that true long-range orientational ordering is forbidden in a $2D$ liquid crystalline phase raises new questions. If true long-range order does not exist, this means that our study of the mean-field approximation 2.14 in a $2D$ liquid phase is ill-defined, as is our comparative study of a separable and a nonseparable potential through the spatial averaging of $\hat{e}_{ij}$ \(^5\). This investigation is, nevertheless, interesting from a theoretical point of view since Straley [75] has shown that the presence of long-range order in two-dimensional liquid crystals is rigorously excluded only if the intermolecular pair potential is short-range and separable. Straley’s failure to rule out true long-range order in a general case opens the small possibility that our system could exhibit true

\(^5\)This is why we said earlier (section 3.4.1) that it would be necessary to renounce directly mapping results for $2D$ systems to those for $3D$ systems.
long-range orientational order. If this were the case, we would not have to give up our original interpretation of the chain formation in terms of a true rotational symmetry breaking in the liquid crystal phase.

Evidence from computer simulations on nonseparable potentials is quite controversial and there is no consensus at present as to the nature of the ordering. Viellard-Baron [76] found an isotropic to nematic phase transition in a hard ellipse fluid which he interpreted as first order, but no attempt was made to distinguish between long-range and quasi-long-range order. Soft ellipses have been studied by Tobochnik and Chester [45]. They found strong evidence for long-range order in the molecular orientational field but were unable to study the system-size dependence of the MOF order parameter because of prohibitively long relaxation times. Frenkel and Eppenga [69] recently studied a two-dimensional system of needle-like particles. They observed a transition to a high density phase that clearly exhibits quasi-long-range orientational order, with the orientational correlation function decaying as a power law with density dependent exponent. They also isolated defect pairs [8, 6, 7] and interpreted the transition in terms of an unbinding of these pairs (Kosterlitz-Thouless transition). Finally, they were unable to reproduce the results of Tobochnik and Chester [45] and their preliminary investigation of the hard ellipse fluid did not support a first order isotropic to nematic phase transition [76]. Very recently, Cuesta and Frenkel [77] have reported further results on the 2D hard ellipse fluid which suggest that this system has quasi-long-range order and not true long-range orientational order.

Although the question regarding the nature of the ordering in 2D liquid crystalline systems remains open, a large number of experiments on nonseparable liquid crystals [78, 79, 80] have been very successfully explained by continuum theories that exclude long-range order. Hence, it would be most surprising if any short-range nonseparable potential led to long-range orientational order in a fluid phase.
If we accept that it is highly probable that our nonseparable system with potential 3.20 would show quasi-long-range order in the large system limit, one is still left to explain the origin of the chain-like structures observed in that system. Indeed, it seems reasonable to assume that, even if the nonseparable system was to exhibit only quasi-long-range order, one would still observe the formation of strongly oriented nearest-neighbor bonds on some length scale, even for an infinite system.

3.6 Discussion

It has often been speculated that the van der Waals anisotropic potential we have studied in this chapter may lead to a nematic phase. We have focused our attention on spherical molecules to avoid a coupling between steric effects and the anisotropic attractive forces in which we are interested.

We observed that different lattices have different ground state symmetries. Nematic-like ground states were found only for the sufficiently stretched rectangular lattices.

We studied randomly parked circles and spheres in two and three dimensions. We did not observe a nematic-like ground state for these systems. One might have expected this result knowing that different lattices have different ground state symmetries. In addition, we have observed for quenched positionally disordered systems, the appearance of frustrated islands and traced back their origin to loose regions with small random fields which arise from the nonseparability of the pair potential.

Preliminary Monte Carlo simulations with translational motion suggest that molecules interacting with the potential 3.20 exhibit strong correlations between translational and rotational degrees of freedom which lead to the formation chain-like structures similar to those observed in dipolar systems in strong magnetic fields. The probable existence of quasi-long-range order in such a system makes it difficult to explain the formation of
these chains within the framework of a self-consistent symmetry breaking field (mean-field scenario). Finding a satisfactory microscopic model for the formation of these nearest-neighbor structures in this system is the subject of the next chapter.
In this chapter, we continue our computer simulation investigations of the orientational phenomena exhibited by the modified anisotropic van der Waals potential in a two-dimensional liquid phase.

In Chapter 3 we observed that the nonseparable van der Waals potential leads to a noticeable build-up of local positional structure. Such a phenomenon is not observed for the separable system. We argued that, from a rigorous theoretical point of view, the interpretation of this increase in positional correlation is not satisfactorily explained in terms of chain formation induced by a self-consistent molecular orientational field appearing below the isotropic-nematic transition. Another mechanism must be found in order to explain the build-up of the observed nearest-neighbor structures.

Several authors have discussed the phenomenon of tilt-induced bond orientational ordering in smectic films from a theoretical point of view [81, 82, 83, 84]. This effect has now been observed experimentally in several systems [85, 80, 86, 87]. We will show that it is possible to reinterpret the increase of positional correlation in the nonseparable system as a manifestation of such induced bond orientational ordering.

We investigate, using Monte Carlo simulations, the presence or absence of an induced
bond orientational order in 2D liquid crystal models. We find that the nonseparable anisotropic van der Waals potential exhibits a nematic phase where the ordering in the molecular director induces an ordering of the nearest-neighbor bond orientations with rectangular symmetry. To make a comparison with this behavior, we study a separable system that also exhibits a nematic phase. Unlike the nonseparable case, we find that the separable system exhibits only short-range order in the correlations of the nearest-neighbor bond orientations. The phenomenological coupling between molecular and bond orientations present in Landau theories of liquid crystals [81, 82, 83, 84] plays an important role in explaining the phase transitions observed in smectic liquid crystal films. Our results lead us to conclude that these couplings have their microscopic origin in the nonseparability of the intermolecular pair potential.

4.1 Induced Bond Orientational Ordering in Smectic Liquid Crystal Films

A freely suspended smectic liquid crystal film is realized in the following way: a drop of liquid crystal material is put on a piece of glass and, using another piece of glass, the liquid is spread across a hole in the plate (see figure 4.1). Depending on the speed at which the liquid is spread across the hole, (of diameter $\approx 10$mm) film thicknesses of between 2 and 100 smectic layers can be stabilized and studied for several months [4].

Nelson and Halperin [81] realized that freely suspended smectic liquid crystals could provide particularly well suited systems to test the new ideas of $2D$ melting theories [10, 11, 12]. We present their ideas in this section since we will use them to explain the bond ordering observed for the nonseparable system studied in Chapter 3.

Chapter 1 we described in various smectic phases. Let us consider the bond angle, $\theta(\vec{r})$, which describes the orientation of the sixfold symmetric nearest-neighbor shell (see
Figure 4.1: Schematic representation of a freely suspended liquid crystal film.

Figure 1.10. Long wavelength spatial fluctuations of the nearest-neighbor bond orientation are described by the following Hamiltonian:

\[ \frac{H}{k_B T} = \frac{1}{2} \int d^2 r \ K_B |\nabla \theta(r)|^2 \]  \hspace{1cm} (4.1)

\( K_B \) is the elastic constant for distortion in \( \theta(r) \), the bond orientational field (BOF).

Below some critical temperature, defects in \( \theta(r) \), which are similar to the vortices in the xy model, are rare and the correlation function, \( c_\theta(r) \), has quasi-long-range order:

\[ c_\theta(r) = \langle \cos \{6(\theta(r) - \theta(0))\} \rangle \approx r^{-\eta(T)} \]  \hspace{1cm} (4.2)

As the temperature is increased, defect pairs are created and reduce \( K_B \). Above the critical temperature, the defects unbind and \( c_\theta(r) \) is driven to short-range order with exponential decay. This transition corresponds to the smectic-B \( \rightarrow \) smectic-A transition in a thin, freely suspended smectic film.

If the molecules are tilted with respect to the layer normal, as in the smectic-C phase, one repeats the above argument and introduces a new term in \( H \), which measures the
energy required to impose long wavelength distortion to \( \phi(\vec{r}) \), the in-plane orientation of
the molecular tilt:

\[
\frac{H}{k_B T} = \frac{1}{2} \int d^2 r \left[ K_B |\nabla \theta(\vec{r})|^2 + K_M |\nabla \phi(\vec{r})|^2 \right]
\] (4.3)

where \( \phi(\vec{r}) \) is defined on the interval \([-\pi, \pi]\). \( K_M \) is the Frank constant for fluctuations
in \( \phi(\vec{r}) \), the molecular orientational field (MOF). The unbinding of vortex pairs in \( \phi(\vec{r}) \)
corresponds to the smectic-C \( \rightarrow \) smectic-A or a smectic-C \( \rightarrow \) smectic-B\( _H \) transition in a
2D smectic film depending on whether \( \theta(\vec{r}) \) has short or long-range order. Notice that,
up to this point in the present discussion, there is nothing that prevents a given liquid
crystalline material from exhibiting both a smectic-B\( _H \) \( \rightarrow \) smectic-C transition, followed
by a smectic-C \( \rightarrow \) smectic-A transition as the temperature is raised (see classification
of smectic phases in Figure 1.13); that is two independent transitions, which are both
expected to be of Kosterlitz-Thouless type [6, 7].

The important idea of Nelson and Halperin [81] was to recognize that the last Hamiltonian
was not the most general, and that one should include a coupling between the
fields \( \theta(\vec{r}) \) and \( \phi(\vec{r}) \):

\[
\frac{H}{k_B T} = \frac{1}{2} \int d^2 r \left[ K_B |\nabla \theta(\vec{r})|^2 + K_M |\nabla \phi(\vec{r})|^2 + 2g \nabla \theta(\vec{r}) \cdot \nabla \phi(\vec{r}) \right] \\
- h_6 \int d^2 r \cos \{6[\theta(\vec{r}) - \phi(\vec{r})]\}.
\] (4.4)

The coupling term, \( h_6 \), arises because both \( \theta(\vec{r}) \) and \( \phi(\vec{r}) \) feel a sixfold symmetric potential
when rotated with the other field held fixed. A gradient cross-coupling term, proportional
to \( g \), would be present in the most general situation. Let us explain the implications of
the periodic coupling term.

Assume that \( K_M \) is larger than \( K_B \). Hence, as the temperature is lowered, the field,
\( \phi(\vec{r}) \), acquires quasi-long-range order before \( \theta(\vec{r}) \), and ordering of \( \phi(\vec{r}) \) occurs on a very
long length scale. On this length scale, \( \phi(\vec{r}) \) picks-up a definite orientation. Once \( \phi(\vec{r}) \) is
quasi-long-range ordered, not all the orientations available to $\theta(\vec{r})$ are equivalent anymore within this region since one particular direction has been picked up by $\phi(\vec{r})$. Because of the $h_6$ coupling term, some induced ordering in $\theta(\vec{r})$ sets in. In some sense, the ordering in $\phi(\vec{r})$ plays the same role on $\theta(\vec{r})$, via the $h_6$ term, as does a magnetic field in a ferromagnet above the Curie temperature. The induced ordering in $\theta(\vec{r})$ eliminates a possible smectic-C $\rightarrow$ smectic-B$_H$ transition at a lower temperature, although remnants of the transition may be observed if $h_6$ is small. This is again similar to the ferromagnetic problem where the presence of a magnetic field washes the transition away since the system has a finite magnetization at all temperature.

If $K_B$ is larger than $K_M$, quasi-long-range order sets in for $\theta(\vec{r})$ at a higher temperature than for $\phi(\vec{r})$. However, the ordering in $\theta(\vec{r})$ does not induce an ordering in $\phi(\vec{r})$ for the simple reason that once $\theta(\vec{r})$ acquires quasi-long-range order, there are still six equivalent direction (the directions of the six nearest-neighbors) for $\phi(\vec{r})$ to choose from, so $\phi(\vec{r})$ can remain disordered.

Bruinsma and Nelson [82] have shown that the above prediction of tilt induced BOF ordering in a thick (three-dimensional) system smectic-C film applies as well. These predictions for both thin [85] (2D) and thick [80] (3D) smectic-C films have recently been verified experimentally. Hence, the classification of smectic phases presented in Chapter 1 (Figure 1.13) is not totally correct: because of this mechanism of tilt-induced BOF ordering, a smectic-C phase is actually a hexatic phase since it has bond order orientational within the smectic layer!

In a general case, one expects that more harmonics will be present in the sixfold periodic BOF-MOF coupling in $H$. In a recent work, Selinger and Nelson [83, 84] have

---

1At the level of a Landau theory, the sm-C $\rightarrow$ sm-B$_H$ is allowed, though most systems that undergo a transition from a sm-C to a hexatic phase exhibit a transition to a tilted hexatic phase such as a sm-C $\rightarrow$ sm-I or sm-C $\rightarrow$ sm-F transition.
extended the above Hamiltonian for tilted smectic films:

\[
\frac{H}{k_B T} = \frac{1}{2} \int d^2 r \left[ K_B |\nabla \theta(\vec{r})|^2 + K_M |\nabla \phi(\vec{r})|^2 + 2g \nabla \theta(\vec{r}) \cdot \nabla \phi(\vec{r}) \right] \\
- \sum_{n=1}^{\infty} \hbar \delta_n \int d^2 r \cos \left\{ 6n \left[ \theta(\vec{r}) - \phi(\vec{r}) \right] \right\}.
\] (4.5)

Using this Hamiltonian functional, they were able to explain both the first order smectic-I \( \rightarrow \) smectic-F transition in a thermotropic material [88], and a sequence of two second order transitions smectic-I \( \rightarrow \) smectic-L \( \rightarrow \) smectic-F in a lyotropic liquid crystal [87].

There is a strong resemblance between a single smectic-C layer and our 2D van der Waals nematic liquid crystal model. Indeed, a well ordered smectic-C phase, where the tilt angle shows only small fluctuations, can be regarded as a realization of a 2D nematic fluid, if there are as many molecules 'up' as 'down' \((\hat{n} \cdot \hat{z} = 0)^2\).

The analogy between smectic-C and 2D nematics, as well as the success of the above Landau theory (Equation 4.5) in explaining the phenomenon of induced BOF ordering observed in smectic-C phases [85, 80, 88, 87], motivated us to investigate the presence of an induced BOF ordering in the nonseparable van der Waals system.

We will show that induced bond orientational ordering is the mechanism we are looking for to explain the build-up of chain-like structures observed in the nonseparable system and described in Chapter 3. As a by-product, we shall gain some physical insight into the microscopic origin of the BOF-MOF couplings invoked in the Landau theories of tilted smectic systems.

\[\text{Recall item 3 in page 15 and the following discussion in page 18.}\]
4.2 Computational Technique

For convenience, we rewrite here the modified van der Waals potential 3.20 we investigated in Chapter 3:

\[ V_{ij}^{NS}(\hat{r}_{ij}; \hat{n}_i, \hat{n}_j) = 4\varepsilon \left[ r_{ij}^{-12} - \alpha r_{ij}^{-6} \right] - 4\beta \varepsilon \left[ 2(\hat{n}_i \cdot \hat{n}_j)^2 - 1 \right] r_{ij}^{-6} - 4\gamma \varepsilon [\hat{n}_i \cdot \hat{n}_j - 3\hat{n}_i \cdot \hat{e}_{ij} \hat{e}_{ij} \cdot \hat{n}_j] r_{ij}^{-6} \] (4.6)

We have studied a nonseparable potential with \( \alpha = 0, \beta = 2/5 \) and \( \gamma = 4/5 \). The separable potential was obtained from 4.6 with \( \alpha = 1.0, \beta = 1/2 \) and \( \gamma = 0 \). The reader is invited to refer to Chapter 3 for a definition of the various parameters in Equation 4.6 and a description of how these two potentials are related to each other.

We have investigated the thermodynamic behavior of systems of particles interacting via the above two potentials with a Monte Carlo simulation using the standard Metropolis algorithm at constant area, number density and temperature. A Monte Carlo step consists of an attempt to move and rotate simultaneously one particle in a cell with periodic boundary conditions. To make the program work as efficiently as possible, a local neighborhood of size \( 3.5r_o \) was recorded around each particle. The particles move in their local environment for a small number of Monte Carlo steps per particle (MCS). After typically 5 MCS, the local environments are reconnected. In this way, the time taken for \( m \) MCS is approximatively linear in the number of particles \( N \). By varying the size of the attempted move in \( \vec{r} \) and \( \hat{n} \) space, we were able to keep an acceptance rate between 30 and 50% at all temperatures.

The density \( \rho = 0.888 \) used in our preliminary investigation (previous chapter) proved to be too low, as phase separation occurred at low temperature. For the results presented below we used a density of \( \rho = 1.00 \) and a system of 400 particles. The separable and
nonseparable potentials were cut-off at a distance of $2.50r_0$.

The results of Chapter 3, and an investigation of the ground states exhibited by the nonseparable potential showed that a rectangular lattice with the particles oriented along the shortest lattice vector ("nematic" ground state) is favored for a range of pressure and degree of nonseparability (ratio $\beta/\gamma$). For the values of $\gamma = 4/5$ and $\beta = 2/5$, we anticipate a rectangular solid with lattice vectors $a \approx 0.91$, $b \approx 1.09$ and with the molecules oriented along the $a$ axis. The ground state bond energies are then $-13.00\epsilon$ and $-1.44\epsilon$ along the $a$ and the $b$ axis respectively.

Two simulations were started at $T = 2.40$, one from the ordered rectangular phase described above and one starting from a random configuration in both positions and orientations. After 120,000 $MCS$ for the random start and 20,000 $MCS$ for the ordered one, the energy, pressure and nematic order parameter statistics became indistinguishable for the two runs. From $T = 2.40$, we heated the system to $T = 4.8$ and cooled it to $T = 0.2$. At each temperature the final configuration from the previous temperature was used as the starting configuration. Enough $MCS$ each temperature enough were performed to re-establish the thermodynamic equilibrium state of the system. Typically, equilibration runs of up to 100,000 $MCS$ were performed, while runs for production of data were 40,000 $MCS$ in both the solid and isotropic fluid phase and up to 200,000 $MCS$ in the nematic phase (500,000 $MCS$ at $T = 3.4$).

The nonseparable system proved to be extremely sluggish and huge relaxation times were observed throughout the liquid crystalline phase. Similar observations were made by Tobochnik and Chester [45] for the nonseparable potential they studied. Hence, we found it most efficient to collect our thermodynamic data each time the local particle environments were reconnected, that is every 5 $MCS$. By comparison, for the separable system at the same density and away from the isotropic-nematic transition, we found that 10,000 to 20,000 $MCS$ for both equilibration and production runs were sufficient to
ensure good statistics in all the thermodynamic quantities we measured.

4.3 Thermodynamic Quantities

To characterize the amount of orientational ordering present in our systems, we reintroduce the order parameter $Q$, which is given by the positive eigenvalue of the $2 \times 2$ matrix [69]:

$$Q_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^{N} [2n_{i\alpha}n_{i\beta} - \delta_{\alpha\beta}]$$

As mentioned in Chapter 3, the eigenvector associated with this eigenvalue is the director (see Chapter 1). It is easy to show that the orientation of the director, $\Phi_o$, in the lab-frame, is such that the quantity

$$\Delta = \frac{1}{N} \sum_{i=1}^{N} \cos \{2(\phi_i - \Phi_o)\}$$

is maximized with respect to $\Phi_o$, and that $\Delta = Q$. This gives another interpretation of the director: it is the direction along which the average projection of the anisotropy axis, $\hat{n}_i$, is the largest.

Figure 4.2 shows the temperature dependence of $Q$ for the nonseparable potential. Even if the low temperature phase has only algebraic order, $Q$ is meaningful for a finite size simulation and should decay to zero as the size of the system increases [69]. This point will be discussed in Section 4.8. There is evidence that an orientational phase transition occurs around $T \approx 3.6$.

Figure 4.3 shows the average configurational energy per particle. One observes a rapid change in the energy at $T \approx 3.6$ as well as a discontinuity in the slope of this curve around $T \approx 1.8$. We also measured the pressure using the virial equation of state:

$$PA = Nk_B T - \frac{1}{4} \sum_{i,j; i \neq j} \vec{r}_{ij} \cdot \nabla_i V_{ij}^{NS} (\vec{r}_{ij}; \hat{n}_i, \hat{n}_j)$$

(4.9)
This quantity gives no indication of a transition at $T \approx 3.6$ but exhibits a discontinuity in the slope around $T \approx 1.8$ which we interpret as the melting temperature (Figure 4.4).

The configurational specific heat at constant volume, $C_v$, calculated from the fluctuations is illustrated by the triangular symbols in Figure 4.5. We also calculated $C_v$ from finite difference of the energy curve. The heat capacity, at a temperature $T$, midway between two neighboring temperatures $T_1$ and $T_2$ and separated by $T_1 - T_2 = 0.20$ on the energy curve, is shown in Figure 4.5 by the square symbols. The two methods lead to similar results suggesting that fairly good thermal equilibrium has been reached. The heat capacity shows a sharp peak at $T = 3.6$, which, from our other thermodynamic data and the orientational correlation functions, appears to be at or very close to the phase transition. This is in contrast with the simple 2D $xy$ model where a broad peak in the heat capacity occurs at a temperature about 15% above the transition. Similar behavior was observed for $Q$, $E$ and $P$ for the separable system. As in the nonseparable system, an orientational phase transition is observed, but at a temperature $T = 2.8$.

For both systems, we interpret the high temperature transition as an isotropic-nematic phase transition. In the following sections, we present results that support this assertion. Two phase transitions were also observed for the separable system and the high temperature one was again interpreted as an isotropic-nematic transition. Most of our efforts and computer power were oriented towards the investigation of the isotropic-nematic phase transition for both potentials. It would also be interesting to study the nature of the melting of these two-dimensional anisotropic solids [89].
Figure 4.2: Order parameter $Q$ vs temperature $T$ (in units of $\epsilon/k_B$) for the nonseparable system at $\rho = 1.00$.

Figure 4.3: Average configurational energy per particle (in units of $\epsilon$) vs temperature ($T$) for the nonseparable system at $\rho = 1.00$. 

Figure 4.4: Pressure vs temperature for the nonseparable system at $\rho = 1.00$.

Figure 4.5: Configurational specific heat at constant volume $C_v$ (in units of $k_B$) vs temperature ($T$) for the nonseparable system. The triangles correspond to $C_v$ obtained from the fluctuations in the energy while the squares correspond to $C_v$ obtained from finite difference of the energy curve.
4.4 Local Structure for the Separable and Nonseparable Systems

By comparing the behavior of the thermodynamic quantities, it appears that the only major difference between the separable and the nonseparable systems is that the isotropic-nematic transition occurs at a lower temperature \((T=2.8)\) in the separable case. A snapshot of a particle configuration below the transition reveals, however, an important qualitative difference in the positional configurations of the two systems (Figures 4.6 and 4.7).

In Figure 4.6 we show a snapshot of the nonseparable system just above and below the transition. As described in Chapter 3, we observe a rapid and considerable increase of bond orientational structure and the build-up of chains whose axis lies in the direction of the molecular anisotropy vector, \(\hat{n}_i\). The nearest-neighbor bonds are illustrated in Figure 4.6 for several particles. The lowest energy configuration is with the chains registered parallel to each other so that many particles have well defined third and fourth nearest neighbors in a line perpendicular to the first and second neighbor pair, forming a local rectangular structure.

In contrast, for the separable potential, there is no obvious evidence of a build-up of bond correlation. In Figure 4.7 we show the nearest-neighbor bonds for several particles; the most probable local structure is hexagonal, as in an isotropic fluid. The hexagonal structures illustrate the sixfold bond orientational field, which remains disordered below the isotropic-nematic transition.

Snapshot configurations of the nearest neighbor bond network are shown in Figure 4.8 for four different temperatures. We have defined the network as follows: take two neighboring particles and calculate the lowest two bond energies for each. If they share one of these bonds then this is part of the network and a link is drawn between the two particles (solid line). Each pair of particles are treated in this way. The procedure is then
Figure 4.6: Snapshot of the configuration of the particles interacting via the nonseparable potential both above ($T = 4.0$, a) and below ($T = 3.6$, b) isotropic-nematic transition. The circle represents the particle and has diameter $r_0$; the line indicates the orientation of the unit vector $\hat{n}_i$. The lines joining the centers of three particles illustrate the onset of order in the twofold bond orientational field at the isotropic-nematic phase transition.
Figure 4.7: Snapshot of the configuration of the particles interacting via the separable potential both above \((T = 3.2, \text{a})\) and below \((T = 2.8, \text{b})\) the isotropic-nematic transition. The lines joining the centers of six neighboring particles illustrate the sixfold bond orientational field.
repeated for the third and fourth lowest energy bonds (dashed line). We have purposely kept the first and second lowest energy bonds and the third and fourth lowest energy bonds separate, because we wish to show the development of the two independent twofold symmetries of the rectangular structure. The positions of the particles are indicated by a small circle.

At $T = 4.2$, well above the isotropic-nematic transition temperature, the system is clearly isotropic and only short-range structure is visible. The figure for $T = 3.6$ shows the network very close to the nematic transition, where the lowest energy bonds form long chain structures along the direction of molecular orientation and the chains begin to register, forming rectangular plaquettes. At $T = 2.6$, the development of the two perpendicular twofold symmetries constituting rectangular bond orientational order is clear, and the network has become more ordered and noticeably less flexible. Finally we show a snapshot taken in the solid phase ($T = 0.8$), where the network is very well defined except for frozen in dislocations. One or two further bonds are, surprisingly missing. This is because the fourth lowest energy bond is occasionally that of a second nearest neighbor along the chain, or short axis of the rectangle (see Figure 3.15 for comparison.)

4.5 Correlation Functions

For all correlation functions we calculated, a bin size of $0.05r_o$ was used. Data was collected every 5 MCS over a total run time of 20,000-50,000 MCS. No smoothing of the resulting correlation functions was performed.

We show in Figure 4.9 the radial distribution function, $g_0(r)$. At high temperature ($T = 4.2$, solid curve) the shape of $g_0(r)$ is characteristic of a liquid distribution, while at $T = 2.6$, well below the isotropic-nematic transition, the distribution function is still liquid-like but displays much more short-range structure (dashed-curve). This is unlike
Figure 4.8: Snapshots of lowest energy bonds network for $T=0.8$, $2.6$, $3.6$ and $4.2$. Solid lines are first and second lowest energy bonds, dashed lines are for third and fourth lowest energy bonds. For detailed definition of the network, see text.
Figure 4.9: Radial pair distribution function $g_0(r)$ vs separation $(r)$ (in units of $r_0$) for the nonseparable system. The solid and dashed curves are for $T = 4.2$ and $T = 2.6$ respectively.

The separable system whose $g_0(r)$ is found to be essentially featureless for all temperatures above the melting temperature. The large-distance behavior of $g_0$ for both the separable and nonseparable systems clearly shows that these are liquid phases since $g_0$ decays quickly to its limiting liquid-like value of 1 (Figures 4.10 and 4.11.)

In order to characterize the correlations in the molecular orientational field (MOF), we measured the orientational correlation function, $g_2(r)$, [45, 69] defined as:

$$g_2(r) = \langle \cos \{2\phi(r) - 2\phi(0)\} \rangle$$

where $\phi(r)$ is the angle, relative to a fixed axis, of the vector $\hat{n}_i$ of some particle at a distance $r$ from a reference particle at the origin. In a phase where there is true long-range order, the limit of $g_2(r)$ when $r \to \infty$ is non zero and equal to the square of the order parameter $Q$. Unfortunately, this criterion cannot be used to check for the existence of long-range order since the same result applies to a system with quasi long-range order; that is, the value of $g_2(r)$ at the edge of a cell of size $L$ is equal to the square
Figure 4.10: Large distance behavior of $g_0(r)$ for the nonseparable system at $T = 4.2$ (solid curve) and $T = 3.4$ (dashed curve).

Figure 4.11: Large distance behavior of $g_0(r)$ for the separable system at $T = 2.8$, which corresponds to the isotropic-nematic phase transition temperature.
Figure 4.12: Molecular orientational pair correlation function $g_2(r)$ vs $r$ for the nonseparable system. The long and short-dashed curves are exponential and power law fits respectively.

of the order parameter observed for that system. Figure 4.12 shows the behavior of $g_2(r)$ around the isotropic-nematic transition. An exponential decay of the envelope (long-dashed curve) is observed for $T = 4.0$ and $T = 3.8$. The decay is a lot slower at $T = 3.6$ and consistent with a power law $r^{-\eta}$ with $\eta \approx 0.27 \pm 0.04$ (short-dashed curve). This suggests that the two-dimensional nematic phase exhibits algebraic order as predicted by harmonic theories. It is, however, also consistent with an exponential decay to finite value (0.39) as would be the case for true long-range order. The long-dashed curve for $T = 3.6$ corresponds to such a fit with a correlation length $\xi = 3.11$.

Nelson and Halperin [81] have shown that algebraic order in the MOF of a smectic-C layer induces algebraic order in the sixfold bond orientational field (BOF). There exist some differences between Nelson and Halperin’s model and our simulation. Their theory applies to a onefold symmetric MOF (due to the in-plane projection of the tilted molecules) coupled to a sixfold symmetric BOF (arising from the triangular short-range
positional order), whereas our simulation is concerned with the coupling of a twofold symmetric MOF (due to the \( \hat{n} \leftrightarrow -\hat{n} \) invariance of the pair potential) with a twofold symmetric BOF (arising from the rectangular short-range positional order). These differences are, however, qualitatively irrelevant for the phenomenon we are interested in. That is, there cannot be ordering in the MOF of a nematic fluid phase without having ordering in a BOF with reflection symmetry.

The similarities between our two-dimensional liquid crystal and the predictions of Nelson and Halperin allow us to reinterpret the chain formation we described in Chapter 3 as a manifestation of the rapid build-up of correlations in the twofold BOF. These observations led us to carry out a calculation of a twofold version of the hexatic order parameter introduced by Nelson and Halperin in the context of two-dimensional melting of an isotropic solid [5, 10, 11, 12, 90, 91].

We define the twofold BOF correlation \( c_2(r) \) as [92]:

\[
c_2(r) = \langle \Psi_2(r)\Psi_2^*(0) \rangle
\]

with

\[
\Psi_2(\vec{r}) = \frac{1}{2} \sum_{j=1}^{2} \exp(2i\theta_{ij}(\vec{r}))
\]

where \( \Psi_2(\vec{r}) \) is the local order parameter of the twofold BOF, and the sum in 4.12 is taken over the bond angles \( \theta_{ij} \) of the two nearest-neighbors (see bond construction in Figure 4.6). Below the transition, these two neighbors are the most probable neighbors that form the two lowest energy links in the chain-like structures. Figure 4.13 illustrates this correlation function. The envelope of \( c_2(r) \) decays exponentially at \( T = 4.0 \) and \( T = 3.8 \), but the decay is much slower at \( T = 3.6 \). The short-dashed curve is a power law fit \((r^{-\eta})\) with \( \eta = 0.39 \pm 0.05 \), and the long-dashed curve is a fit to an exponential decay to finite value \((0.15)\) with correlation length \( \xi = 2.63 \) as would be the case if there was true long-range order in the BOF.
Figure 4.13: First nearest-neighbor bond orientational correlation function $c_2(r)$ vs $r$ for the nonseparable system. The long and short-dashed curve are exponential and power law fits respectively.

We have also measured an order parameter, $\Psi_{2\perp}$, and the correlation function, $c_{2\perp}(r) = \langle \Psi_{2\perp}(r)\Psi_{2\perp}^*(0) \rangle$, for the third and fourth nearest neighbors, which are on average perpendicular to the director (Figure 4.14). The same behavior as for $c_2(r)$ was observed, indicating that the transverse BOF is locked perpendicular to the MOF below the transition and that the chains are not free to slide parallel to each other. We found, however, that the transverse correlation function, $c_{2\perp}(r)$, has an amplitude smaller than $c_2(r)$. This is because bonds along the chain are much stronger than those perpendicular to it (see Section 4.2).

An anisotropic liquid crystalline phase where quasi long-range order in the BOF is driven by the quasi-long-range ordering in the MOF is called a locked phase, and the theory of hexatic films predicts that the exponents $\eta_{BOF}$ and $\eta_{MOF}$ should be the same [81]. The discrepancy between the two exponents in our nonseparable system could be due to
finite-size effects and short-range structural details. Since the theory is based on a continuum approximation which neglects these effects, it would be interesting to investigate a much larger system in order to reduce the importance of finite-size effects, and perform a detailed study of the two correlation functions to check the theoretical predictions. The short-range structural details in the correlation functions can be removed by Fourier transforming the data, filtering the high frequency modes and transforming back to real space. See, for example, reference [93] where such technique has been successfully used.

The separable system also exhibits an isotropic-nematic phase transition. In Figure 4.15 we show in the orientational correlation function, $g_2(r)$, both above and below the isotropic-nematic transition. The envelope of $g_2(r)$ decays exponentially for $T = 3.2$, but decays much more slowly for $T = 2.8$ and $T = 3.0$, and is consistent with a power law decay.

Snapshots of the particle configuration (see Figure 4.7) reveal that the separable
system has a BOF with sixfold symmetry as in an isotropic system [5, 10, 11, 12, 90, 91].

To reflect this sixfold symmetry, we replace the 2 in Equations 4.11 and 4.12 by a 6
\((c_6(r))\) and take the summation over the first six nearest-neighbors (see Figure 4.7). This
definition corresponds to the standard definition of the hexatic bond order parameter for
isotropic two-dimensional fluids [90, 91].

Figure 4.16 shows the behavior of \(c_6(r)\). The envelope of \(c_6(r)\) decays exponentially
with distance both above \((T = 3.2)\) and below \((T = 2.8)\) the isotropic to nematic transi-
tion with correlation lengths of 2.20 and 3.30 respectively (long-dashed fits). The sixfold
BOF of the separable system exhibits short-range order in the nematic phase. The in-
crease in the correlation length is due to the build-up of bond correlations as one gets
closer to the melting point and has nothing to do with any symmetry breaking coupling
between the MOF and the BOF [81]. It thus appears that the separable system ex-
hibits an anisotropic fluid phase with ordering in the MOF but exponentially decaying
correlations in the BOF.
Figure 4.16: Bond orientational correlation function $c_6(r)$ vs $r$ for the separable system. The long and short-dashed curves are exponential and power law fits respectively.

At low temperature the separable system freezes into a perfect triangular solid with nematic orientational order and with the director orientation independent of the lattice vectors. We have not studied the details of the melting transition, but it is tempting to invoke the two stage melting theory $[5, 10, 11, 12]$ and then to interpret the isotropic-nematic transition as a third Kosterlitz-Thouless transition $[6, 7]$ involving the unbinding of vortices of charge $1/2$ in the MOF $[94]$. One should be able to tune the transition so that algebraic order in the MOF appears at any point in the phase diagram by varying the size of the anisotropic constant $J$ in Equation 3.21.

The existence of a solid phase introduces a low temperature bound to the presumed quasi-long-range behavior of the nonseparable system. The solid phase displays true long-range order in the BOF $[9, 10, 11, 12, 81, 89]$, and the presence of BOF-MOF symmetry breaking terms in the pair potential therefore implies true long-range order in the MOF at low temperature (see Equation 3.22). This is not the case for the separable system which displays a MOF with algebraic order at any non-zero temperature, even in the
Defect Structures in the Nonseparable System

The theory of Nelson and Halperin [81] relies on the relevance of the defect density fugacity of the BOF, the MOF, and the BOF-MOF coupling. The isotropic to nematic transition would, according to their theory, be driven by the unbinding of MOF defect pairs of charge 1/2. In order to check if the isotropic-nematic transition for the nonseparable system is compatible with such an unbinding mechanism, it is useful to identify MOF defects (vortices in the director field). Clearly, there are several ways in which this can be achieved; we have chosen to proceed in a way similar to Frenkel and Eppenga [69] where the isotropic-nematic transition was interpreted in terms of the unbinding of director defects.

We introduce at every point \( \vec{r} \) a tensorial field, \( S_{\alpha\beta}(\vec{r}) \), defined as:

\[
S_{\alpha\beta}(\vec{r}) = \frac{1}{N} \sum_{i=1}^{N} w(\vec{r} - \vec{r}_i) [2n_{i\alpha}(\vec{r}_i)n_{i\beta}(\vec{r}_i) - \delta_{\alpha\beta}]
\]

(4.13)

where \( w(\vec{r} - \vec{r}_i) \) is a weight function chosen such that the nearby molecules dominate the field at \( \vec{r} \). We choose a Gaussian weight function:

\[
w(\vec{r} - \vec{r}_i) = \exp\left[-|\vec{r} - \vec{r}_i|^2/\sigma^2\right]
\]

(4.14)

with \( \sigma = 1.0 \) in units of \( r_o \). We then determine \( \Phi(\vec{r}) \), the orientation of the local eigenvector of \( S_{\alpha\beta}(\vec{r}) \) (director), at a grid of points that form a square lattice with spacing \( \delta = 1.0 \) in units of \( r_o \). Disclinations are identified by observing the change in \( \Phi(\vec{r}) \) on going clockwise around an elementary plaquette of grid points. A positive (negative) disclination of the nematic director corresponds to a net change in \( \Phi \) of \( +\pi \) (\( -\pi \)).

The method we choose to calculate the director field suffers from some degree of arbitrariness, but it is still interesting to compare snapshots of defect structures for
various temperatures that have been obtained the same way, that is for a particular choice of $w(r - \tau_i)$, $a$ and $\sigma$. Some typical defect structures are illustrated in Figure 4.17. It is difficult to make a direct comparison between these results and the theory; it is, however, interesting to observe that, as predicted by theory, half-integer defects are rare and tightly bound below $T = 3.4$, but proliferate and unbind above that temperature, where all our other thermodynamic quantities and correlation functions indicate that the isotropic to nematic phase transition occurs.

4.7 Liquid-Like Behavior of the Nonseparable System

One could argue that the intermediate phase we observe for the nonseparable potential corresponds to a phase separated region (partially melted solid) since the simulation was performed at constant density and not at constant pressure. A melange of solid rectangular islands with long-range BOF and MOF, and isotropic fluid regions with short-range order in both fields could, presumably, exhibit properties analogous to a truly homogeneous anisotropic mesophase. Similar arguments [5] have cast very serious doubts upon the results obtained from constant-density computer simulations of the Lennard-Jones system which were originally interpreted in terms of the predicted hexatic phase [90, 91]. We argue that our results are not subject to this criticism.

Firstly, notice that the large distance behavior of $g_0(r)$ for the nematic phase of the nonseparable system (Figure 4.10) decays to its limiting value of 1, as expected for a liquid phase, within six molecular diameters.

Monte Carlo trajectories over 10,000 $MCS$ in the intermediate phase did not show isolated solid-like and fluid-like patches with regions of diffusion, as observed just above the melting temperature of the Lennard-Jones system [5, 91]. As well, our intermediate phase occurs over a relative temperature range $((T_{NI} - T_{Melt.})/T_{Melt.})$ that is over an
Figure 4.17: Typical MOF defect structures for the nonseparable system. Positive and negative disclinations of the discretized director field are indicated by + and - respectively.
order of magnitude wider than the relative temperature range over which an intermediate anisotropic (hexatic-like) region is observed in the Lennard-Jones system [5, 90, 91]. Finally, the fact that we were able to reproduce the same statistics in the middle of the intermediate phase starting either from a random or an ordered configuration (Section 4.2) indicates that the nematic phase is not a superheated state. We thus believe that the intermediate phase we observe in the nonseparable system is a true mesophase and not an artifact due to an unusually wide anisotropic solid–isotropic liquid coexistence region.

4.8 System-Size Dependence of Q

One finds, using a simple elastic Hamiltonian describing only fluctuations in the MOF, that the order parameter $Q$ decays as a simple power law with the size of the system, ruling out long-range order [74, 69]. To test this prediction for our nonseparable system, we have investigated the system size dependence of $Q$ and present here our preliminary results.

We point out that extremely long simulation runs are needed to obtain reliable statistics in $Q$ once nematic ordering has set in the system. If we assume, as did Frenkel and Eppenga [69], that the typical relaxation time, $\tau$, scales as $N^2$, we find that, for the 1600-particle system we investigated at $T = 3.4$, $\tau > 2 \cdot 10^6 \text{ MCS}$ or $3.2 \cdot 10^9$ configurations (see Section 4.2). This estimate indicates that reliable results on the size dependence of $Q$ for our nonseparable system are very difficult to obtain with available computers and without using sophisticated cluster simulation algorithms $^3$. We are not aware of the existence of such algorithm for a disordered system and with an $\tau$-dependent Hamiltonian. Hence, if one looks at independent systems of different sizes, one observes very large

$^3$There has been much interest recently in developing fast simulation algorithms for the Potts model [95], for systems with a Hamiltonian having global (either discrete or continuous) symmetry [96] and for the $xy$ model [97].
and uncorrelated fluctuations in \( Q \) which makes it difficult to extract any meaningful information. We have even observed that, for long periods of time \( (t > 50,000 \text{ MCS}) \), a small system could have a \( Q \) smaller than the \( Q \) of a bigger system. By taking a large system and splitting it into smaller subsystems one finds, however, that the fluctuations are correlated on different length scales (Figure 4.18).

The technique described in the previous paragraph has been used in the past with some success [69]. We have used this method and studied subsystem sizes \( (N_s) \) of 1/16, 1/8, 1/4, 1/2 and 1/1 of a 1600-particle system at \( T = 3.4 \) and \( \rho = 1.00 \). The results are shown in Figure 4.19 where the dashed line corresponds to the best power law fit \( Q(N_s) = \alpha N_s^{-\beta} \). Clearly, the huge error bars prevent us from concluding anything definitive at this time. However, we mention that we have done a calculation using a simple model for BOF-MOF coupling \(^4\) which shows that \( Q(N_s) \) does not decay as a

\(^4\)The results of this calculation are presented in the next Chapter.
Figure 4.19: Subsystem size dependence of the MOF order parameter \( Q(N_s) \) as a function of the subsystem area (in units of \( r^2 \)). The dashed line corresponds to the best straight line fit to the data.

simple power law at intermediate length scale, but in a way similar to the one seen in Figure 4.19 if the error bars are disregarded. This model is described in the following chapter. Finally, we note that Frenkel and Eppenga have also observed such positive curvature in \( \ln [Q(N_s)] \) vs \( \ln (N_s) \) for both the hard needle and hard ellipse fluids [69].

4.9 Summary

We have performed Monte Carlo simulations on a separable and a nonseparable pair potential and found that both exhibit an isotropic-nematic phase transition. Their structures are, however, extremely different.

In the nonseparable case we observe a very strong coupling between the rotational and translational degrees of freedom leading to an orientationally ordered liquid crystalline phase, with a twofold bond orientational field (BOF) and an underlying rectangular symmetry. Both the molecular and bond orientational fields are ordered on a scale of
the size of the system. Furthermore, the nematic phase exhibited by our nonseparable system is clearly reminiscent of the locked smectic-C hexatic phase predicted by Nelson and Halperin's model of thin smectic films [81] where the BOF ordering is also driven by the ordering in the molecular orientations. Hence it is very appealing to interpret our mesophase as a rectangular analogue of this locked hexatic phase with quasi-long-range order.

The separable system is much simpler. It behaves qualitatively like a planar spin system [6, 7, 98] displaying quasi-long-range order in the molecular orientations with short-range positional and bond orientational order. At low temperature it freezes into a perfect triangular lattice as for an isotropic system. If the melting of this system proceeds via a two stage melting [5] we expect that, due to the very weak coupling between the molecular anisotropy and the translational degrees of freedom, it would exhibit three Kosterlitz-Thouless transitions [6, 7, 8]; the phase transition in the molecular orientational field (MOF) driven by the unbinding of vortices of strength 1/2 [94] and occurring independently of the melting.

Our results lead us to conclude that the coupling between MOF and BOF invoked in continuum models of liquid crystals [81, 82, 83, 84] has its microscopic origin in the intrinsic nonseparability of realistic intermolecular pair potentials. In the separable case there exists no such bare coupling and this is the reason why the BOF remains short-range below the isotropic-nematic transition. We also suggest that the theory of Nelson and Halperin is a first approximation to a two-dimensional liquid crystal film where any twofold distortion is ignored and the sole effect of the nonseparability is to couple the MOF to an otherwise perfect sixfold symmetric BOF.

One difference between our simulation and the theory is that our BOF has rectangular symmetry whereas it is triangular in the theory. The symmetry of the BOF depends on the values of the parameters $\alpha$, $\beta$ and $\gamma$ in Equation 4.6. In the weakly nonseparable
limit (small $\gamma$) we would expect the BOF to remain locked to the MOF and to have an almost perfect sixfold symmetry with a small underlying twofold distortion.

We note that X-ray scattering experiments performed in three dimensional nematics reveal the existence of an outer diffuse ring \cite{23, 22, 24} modulated in intensity. The modulation is a manifestation of the uniaxial BOF whose long-range order is driven by a coupling to a MOF with long-range order \cite{99} (see Chapter 2 and Figure 2.3). It would thus be very interesting to extend the work presented in this section to three-dimensional and other two-dimensional liquid crystal models where a nonseparable potential would, presumably, also lead to a coupling between the BOF and the MOF.

Finally, we would like to emphasize a very important point. By comparing the behavior of separable and nonseparable system we have been able to draw a clear picture of what is implied by the mean-field approximation 2.14. By neglecting the correlations between molecular orientations and the orientation of the intermolecular vector, the mean-field theory for nematic liquid crystal transforms an initial microscopic nonseparable potential into an effectively separable one. By showing that separable systems do not exhibit induced bond orientational ordering, we have implicitly shown that the mean-field approximation (Equation 2.14) amounts to ignoring the phenomenon of induced bond orientational ordering in nematic liquid crystals.

Having observed the phenomenon of induced bond orientational ordering, it is natural to ask if the BOF is just a boring slave field locked to the MOF, or if its coupling to the MOF introduces new and interesting effects otherwise absent when the presence of a BOF is ignored. This is the question we shall investigate in the following two chapters.

Having argued in this chapter that an induced BOF ordering is a direct consequence of the nonseparability of the pair potential for an ordered nematic liquid crystal, the above question regarding the importance of BOF-MOF coupling in liquid crystals can be regarded as a rephrasing of the two original questions we asked at the end of Section 2.2.2
concerning the importance of nonseparability in the isotropic-nematic phase transition.
Chapter 5

BOF-MOF Coupling and Director Fluctuations in 2D Liquid Crystals

In the previous chapter, we showed how the ordering in the molecular orientational field (MOF) induces an ordering of the bond orientational field (BOF) when the pair potential is nonseparable. It appears that the BOF would be a slave field, locked to the MOF, and not playing much of a role in the thermodynamic behavior of the system. It is the purpose of this chapter, and the following one, to show that the presence of a BOF-MOF coupling can significantly alter the thermodynamic behavior and the static field response of liquid crystalline systems with bond orientational ordering.

In this chapter, we show that induced nearest-neighbor bond orientational ordering present in some two-dimensional (2D) liquid crystal systems modifies the usual logarithmic infrared divergence of director fluctuations. It is found that the presence of such an induced bond ordering introduces a crossover length scale between two different asymptotic regimes with fluctuations increasing logarithmically with the system size in both regimes. This suggests that, for liquid crystals where induced bond ordering exists, the interpretation of finite-size scaling results, in terms of a model that considers only fluctuations in the molecular orientation, is questionable [100].
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5.1 Nature of the Ordering in 2D Liquid Crystals

It was argued in Chapter 1 that most (2D) systems with continuous symmetry lack long-range order at any non-zero temperature. In a seminal paper, Kosterlitz and Thouless [6] suggested that these systems have, however, a transition from a low temperature phase that exhibits quasi-long-range order to a high temperature disordered phase. In the low temperature phase, the relevant correlation functions decay as a power law rather than exponentially to zero with distance.

We already mentioned in Chapter 3 that, as in other 2D systems with continuous symmetry [74], one finds that long-wavelength elastic distortions of the director field \footnote{We loosely refer here to the director as the unit vector in the direction of the average in-plane orientation of the molecules and do not necessarily reserve the denomination to nematic liquid crystals.} destroy the long-range molecular orientational order in 2D liquid crystals [2]. This can be seen by considering the following elastic Hamiltonian which describes the collective fluctuations, $\phi(\vec{r})$, away from the average molecular orientation:

$$
\frac{H}{k_B T} = \frac{1}{2} \int d^2 \vec{r} \, K_M |\nabla \phi(\vec{r})|^2
$$

(5.1)

where $K_M$ is an effective Frank elastic constant for distortion in the MOF. $T$ is the temperature, and $k_B$ the Boltzmann constant.

The most general form for $H$ would involve two bare elastic constants $K^\parallel_M$ and $K^\perp_M$ associated with distortions parallel and perpendicular to the director. Nelson and Pelcovits [101] have shown, however, that these two constants renormalize to the same value, $K_M$, at large length scales. For smaller systems, where the distinction between $K^\parallel_M$ and $K^\perp_M$ is still meaningful, most of the predictions obtained from Equation 5.1 are still valid provided one introduces an effective elastic constant $K_M = (K^\parallel_M K^\perp_M)^{1/2}$. 
From the above elastic Hamiltonian, one finds that the mean-square of the fluctuations, $\langle \phi^2 \rangle$, diverges logarithmically with the size $L$ of the system:

$$\langle \phi^2 \rangle = \frac{1}{2\pi K_M} \ln(L/r_o)$$

where $r_o$ is a typical intermolecular spacing. Other quantities which are also often calculated in computer simulations of 2D liquid crystals are the order parameters $Q_n$.

These measure the amount of orientational ordering present in the system and vanish as a power law with the system size:

$$Q_n = \langle \cos(n\phi) \rangle = (L/r_o)^{-n^2/4\pi K_M}$$

where $n$ is an integer. Although long-range orientational order is absent, the above elastic description of director fluctuations can be shown to lead to power law decay of the orientational correlation functions [74]. Hence, 2D liquid crystals exhibit quasi-long-range orientational order and one expects the predictions of Kosterlitz and Thouless [6] to apply to these systems [94].

As the temperature is increased, topological defects (vortices) appear in tightly bound pairs [7, 8] and renormalize (reduce) $K_M$ (see Chapter 1). The predictions of the defect-free elastic theory remain valid in the low temperature phase and at very large length scales provided one uses the renormalized elastic constant $K_M^{(r)}$.

In contrast to the above predictions, Straley [75] has shown, using a different approach, that true long-range orientational order in 2D liquid crystals is rigorously excluded only if the pair potential, $V_{ij}$, between molecule $i$ and $j$ is independent of the orientation, $\theta_{ij}$, of the intermolecular vector $\mathbf{r}_{ij}$:

$$V(\mathbf{r}_{ij}; \phi_i, \phi_j) = V(|\mathbf{r}_{ij}|; \{\phi_i - \phi_j\})$$

Notice that the variable $Q$ we calculated in Chapters 3 and 4 is the same as $Q_2$ here.
\( \phi_i \) is the orientation of molecule \( i \) with respect to a fixed axis, and \( |\vec{r}_{ij}| \) is the magnitude of \( \vec{r}_{ij} \). This is a separable potential. We have argued, however, that realistic intermolecular potentials are nonseparable. Although the existence of long-range orientational order in 2D liquid crystal systems of particles interacting via a short-range nonseparable potential remains an open theoretical possibility, the results of recent experiments in various nonseparable 2D liquid crystals [78, 79, 80, 88] have been very successfully explained by continuum theories that forbid long-range order. Hence, it would be most surprising if any 2D liquid crystals would exhibit true long-range molecular orientational order.

One might think that computer simulations could help to resolve this issue. To demonstrate the lack of long-range order (or the existence of quasi-long-range order) with a Monte Carlo or molecular dynamics simulation, one must show that for the 2D liquid crystal model under investigation, the system size dependence of \( \langle \phi^2 \rangle \) and \( Q_n \) behaves as predicted by the elastic theory (Equations 5.2 and 5.3). Unfortunately, the evidence from computer simulations on nonseparable liquid crystal models is most controversial and there is no consensus at present as to the nature of the ordering [45, 69, 76, 92, 102] (see Chapter 4 for a description of the various computer simulation results).

In the previous chapter, we studied a system of particles interacting via an anisotropic van der Waals potential [60]. We found that this nonseparable potential exhibits a 2D nematic phase where the ordering in the molecular orientation induces an ordering of the orientation of the nearest-neighbor bonds with rectangular symmetry. Induced bond ordering has also been observed in various experiments on two [80, 86, 88] and three-dimensional [85, 87] tilted hexatic smectic films and explained in terms of the Landau theories [81, 82, 83, 84] which invoke phenomenological BOF-MOF couplings described in Chapter 4. The results from our computer simulation [92, 102] have led us to conclude that these couplings have their microscopic origin in the nonseparability of the intermolecular pair potential, and that induced bond ordering should be observable
in a large number of nonseparable 2D liquid crystal models.

5.2 BOF-MOF Coupling Model

Theoretically, it is now well established that to fully characterize a 2D isotropic fluid, one must introduce a sixfold or hexatic BOF describing the local orientation of the six nearest-neighbor bonds [5]. We have shown in Chapter 1 how successfully this concept was used in classifying the various smectic phases. In 2D liquid crystals, one has to consider all the relevant couplings between the BOF and the MOF that are allowed by the molecular and local bond symmetries.

Following such a prescription, Nelson and Halperin [81], and more recently, Selinger and Nelson [83, 84], have investigated an effective Hamiltonian functional describing the coupling between the in-plane projection of the molecular tilt orientation of smectic-C molecules, \( \phi(\vec{r}) \), with the orientation of a local nearest-neighbor BOF, \( \theta(\vec{r}) \), having sixfold symmetry. For convenience, we rewrite here this Hamiltonian described in Chapter 4:

\[
\frac{H}{k_B T} = -\frac{1}{2} \int d^2 r \left[ K_B |\nabla \theta(\vec{r})|^2 + K_M |\nabla \phi(\vec{r})|^2 + 2g \nabla \theta(\vec{r}) \cdot \nabla \phi(\vec{r}) \right] \\
- \sum_{n=1}^{\infty} h_{6n} \int d^2 r \cos\{6n [\theta(\vec{r}) - \phi(\vec{r})]\}. \tag{5.5}
\]

The sixfold periodic coupling term between bond and molecular orientations arises because either \( \theta(\vec{r}) \) or \( \phi(\vec{r}) \) feels a sixfold symmetric potential when rotated with the other field held fixed. \( K_M \) is the effective Frank elastic constant for fluctuations in the molecular orientation. \( K_B \) is the stiffness constant for fluctuations in the bond orientation. A gradient cross-coupling term proportional to \( g \) is present in the most general situation.

Nelson and Halperin [81] were the first to recognize that the presence of the \( h_{6n} \) BOF-MOF coupling terms induce bond ordering in a smectic-C film or, in other words, that a smectic-C phase is a hexatic phase [80, 82, 85, 88]. We refer the reader to Chapter 4 for
a description of this phenomenon. In such a phase, the correlation function

\[ C_{\phi_-}(\vec{r}) \equiv \langle \exp(6i [\theta_{\bot}(\vec{r}) - \theta_{\bot}(0)]) \rangle, \tag{5.6} \]

where \( \theta_{\bot}(\vec{r}) \equiv \theta(\vec{r}) - \phi(\vec{r}) \), measures the relative orientation between the bonds and the in-plane projection of the molecular tilt, decays exponentially towards a nonzero value at large distance \( r \). Such behavior is characteristic of a locked phase where the order in the nearest-neighbor orientation is induced by the molecular orientational ordering, and where \( C_{\phi_-}(\vec{r}) \) has long-range order.

Most computer simulations on 2D nonseparable liquid crystals have been performed on nematic models [45, 60, 69, 76, 92, 102] where the field, \( \phi(\vec{r}) \), has a periodicity of \( \pi \) instead of \( 2\pi \) as in the case of smectic-C molecules. We remind the reader that thin smectic-C films are analogs of the \( xy \) ferromagnet model described in Chapter 1: the pair potential does not display the \( \hat{n} \leftrightarrow -\hat{n} \) symmetry as in the case of two-dimensional nematic models \(^3\). The model of Nelson and Halperin [81] remains valid for these systems and one concludes from it that a 2D nematic phase with quasi-long-range order in \( \phi(\vec{r}) \) should induce ordering in a nearest-neighbor BOF with reflection symmetry. However, we showed in the previous chapter that this conclusion does not apply to separable liquid crystal models where there exists no bare BOF-MOF coupling [92, 102].

A modified version of Hamiltonian 5.5, which describes a locked phase in a nonseparable 2D liquid crystal is:

\[
\frac{H}{kT} = \frac{1}{2} \int d^2 r \left[ K_B |\nabla \theta(\vec{r})|^2 + K_M |\nabla \phi(\vec{r})|^2 + 2g \nabla \theta(\vec{r}) \cdot \nabla \phi(\vec{r}) \right] + h_i \int d^2 r \{\theta(\vec{r}) - \phi(\vec{r})\}^2 \tag{5.7}
\]

where \( h_i \) is an effective BOF-MOF coupling in the locked liquid crystalline phase. For simplicity, we take the case where the fields are locked parallel to each other. Also, we

\(^3\)As well as a nonseparable nematic model, Tobochnik and Chester [45] have also investigated a separable model of a 2D smectic-C liquid crystal.
only consider a highly ordered phase in which disclinations in $\theta(\vec{r})$ and vortices in $\phi(\vec{r})$ are rare and can be ignored. Equation 5.7 simplifies upon defining the fields $\theta_{\pm}(\vec{r})$ [81, 83, 84]:

$$
\begin{align*}
\theta_{+}(\vec{r}) &= \alpha \theta(\vec{r}) + \beta \phi(\vec{r}) \\
\theta_{-}(\vec{r}) &= \theta(\vec{r}) - \phi(\vec{r})
\end{align*}
$$

(5.8)

where

$$
\alpha = 1 - \beta = \frac{K_B + g}{K_B + K_M + 2g} \quad (5.9)
$$

In terms of $\theta_{\pm}(\vec{r})$, the diagonalized Hamiltonian reads:

$$
\frac{H}{kT} = \int d^2r \left[ K_{+} |\nabla \theta_{+}(\vec{r})|^2 + K_{-} |\nabla \theta_{-}(\vec{r})|^2 + h_{1} \theta_{+}^2(\vec{r}) \right]
$$

(5.10)

where

$$
K_{+} = K_B + K_M + 2g
$$

and

$$
K_{-} = \frac{K_B K_M - g^2}{K_{+}} \quad (5.11)
$$

The transformation 5.8 is interesting since it diagonalizes 5.7 by expressing it as a free Hamiltonian in $\theta_{+}$ and a massive one for $\theta_{-}$. Physically, this allows one to interpret $\theta_{+}(\vec{r})$ and $\theta_{-}(\vec{r})$ as the acoustic and optical modes of the system respectively [83, 84, 88].

The Hamiltonian 5.10 is quadratic, and fluctuations in the BOF and the MOF, as well as their order parameters, can easily be evaluated; the details of the calculations can be found in standard textbooks [74, 103]. The fluctuations $\langle \phi^2 \rangle$ are:

$$
\langle \phi^2 \rangle = \int \frac{d^2q}{(2\pi)^2} |\phi(q)|^2 = \int \frac{d^2q}{(2\pi)^2} \left[ |\langle \theta_{+}(q) \rangle|^2 + \alpha^2 |\langle \theta_{-}(q) \rangle|^2 \right]
$$

(5.12)

with

$$
|\langle \theta_{+}(q) \rangle|^2 = \frac{1}{K_{+} q^2} \quad \text{and} \quad |\langle \theta_{-}(q) \rangle|^2 = \frac{1}{K_{-} q^2 + h_1} .
$$

(5.13)

\footnote{The choice $\theta = 1 - \beta$ is convenient since the Jacobian of the transformation has absolute value 1.}
Integrating 5.12, one obtains:

\[
\langle \phi^2 \rangle = \frac{1}{4\pi K_+} \ln(N) + \frac{\alpha^2}{4\pi K_-} \ln \left[ \frac{1 + h}{N^{-1} + h} \right]
\]  

(5.14)

where we have defined

\[
h = \frac{h_l r_o^2}{\pi^2 K_-}
\]

(5.15)

with \(N = (L/r_o)^2\), the number of particles in the system. The order parameters \(Q_n\) are:

\[
Q_n = \langle \cos(n\phi) \rangle = N^{-n^2/8\pi K_+} \left[ \frac{1 + h}{N^{-1} + h} \right]^{-n^2 \alpha^2/8\pi K_-}.
\]

(5.16)

Notice that if \(h = 0\) and \(g = 0\), one recovers Equations 5.2 and 5.3 from Equations 5.12 and 5.16 respectively. The averages \(\langle \theta^2 \rangle\) and \(\langle \cos(n\theta) \rangle\) are given by Equations 5.14 and 5.16 respectively, provided the change \(\alpha \rightarrow \beta\) is made.

5.3 Results

In a nematic system exhibiting a hexatic phase, the renormalized elastic constants, \(K_B^{(r)}\) and \(K_M^{(r)}\), are equal to \(72/\pi\) and \(8/\pi\) respectively at the decoupled multicritical fixed point [94, 81, 12]. This point is the location where the hexatic-isotropic (sm-BH - sm-A) and nematic-isotropic phase transition boundary meet in the \(K_B^{(r)} - K_M^{(r)}\) phase diagram. Figure 5.1 shows the system size dependence of the fluctuations \(\langle \phi^2 \rangle\) for various reduced BOF-MOF coupling strengths and where we have set \(K_B\) and \(K_M\) to the above critical values, and \(g = 0\). Figure 5.2 shows the system size dependence of the MOF order parameter \(Q\) (\(Q \equiv Q_2\)) for various reduced BOF-MOF coupling strengths and for the same values of \(K_B\), \(K_M\), and \(g = 0\) as in Figure 5.1.

Clearly, the director fluctuations for a nonseparable system, where induced bond ordering is present, do not increase logarithmically with the system size. This is unlike what is predicted by Equation 5.3. A different choice for \(K_B\), \(K_M\) and \(g\) would not give qualitatively different results.
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Figure 5.1: System size dependence of the reduced molecular orientational fluctuations $4\pi K_+\langle \phi^2 \rangle$ as a function of $N$ for various strengths of the reduced BOF-MOF coupling parameter $h$.

Figure 5.2: System size dependence of the MOF order parameter $Q$ as a function of the size of the system, $N$, for various strengths of the reduced BOF-MOF coupling parameter $h$. 
Two asymptotic regimes, linear in \( \ln(N) \), are observed. For small length scales (small \( N \)), both the acoustic and optical modes are strongly fluctuating and \( \langle \phi^2 \rangle \) increases rapidly with the system size. However, the optical mode must relax towards a constant value since the BOF-MOF locking interaction, \( h_l \), induces long-range order in \( C_{\phi_-} \). Hence, one observes a reduction of \( \langle \phi^2 \rangle \) for a crossover system size \( N_c \) of the order \( \sim (\xi_{op}/r_0)^2 \sim K_-/h_l r_0^2 \sim h^{-1} \), where \( \xi_{op} \) is the correlation length of the optical mode. We find that for a reduced coupling strength \( h \sim 10^{-3} - 10^{-1} \), curvature in \( \langle \phi^2 \rangle \) and in \( \ln(Q_n) \), as a function of \( \ln(N) \), is observable for system sizes that are typically investigated in finite-size scaling studies of nonseparable 2D liquid crystal models \( (N_c \sim 10^1 - 10^3) \) [45, 69, 102].

Let us briefly summarize the major points we have discussed in this chapter:

- We assumed that a harmonic description of BOF and MOF fluctuations in 2D nonseparable liquid crystal models is valid. Hence, we find that such models should exhibit quasi-long-range order.

- We assumed that in the anisotropic phase of a nonseparable system there is an induced ordering of the BOF, and Equations 5.14 and 5.16 are the ones that apply.

- The predictions of Equations 5.2 and 5.3 apply only for separable systems, where induced bond ordering is absent.

These predictions are quite unambiguous and we now test them against the finite-size scaling results that are available in the literature.

As predicted, one finds that a linear dependence of \( \langle \phi^2 \rangle \) vs \( \ln(N) \) is observed in the data for the separable system studied by Tobochnik and Chester [45] (Figure 5.3). The potential they used is very similar to the separable potential we used in Chapter 3 and in Chapter 4:

\[
V(r) = 4\epsilon f(r)[1 - \mu \cos(\phi_i - \phi_j)] \quad \text{with}
\]
Figure 5.3: System size dependence of \( \langle \phi^2 \rangle \) for a separable system. The results are from reference [45]. \( k_B T/\epsilon = 1.6, \rho r_\phi^2 = 0.856 \) (\( \rho \) is the number density) and \( \mu = 0.80 \). System sizes of \( N = 16, 64, 256, 1024 \) and 4096 particles were investigated.

\[
f(r) = \left( \frac{r_\phi}{r} \right)^{12} - \left( \frac{r_\phi}{r} \right)^6
\]

where \( r = |\vec{r}_i - \vec{r}_j| \), \( \epsilon > 0 \) and \( \mu > 0 \).

Frenkel and Eppenga [69] performed some scaling studies of \( Q_2 \) for 2D hard-needle and hard-ellipse fluids. Their results were presented in the form of tables; we reproduce them graphically in Figures 5.4 and 5.5. These two fluids are nonseparable systems and one might suspect that the presence of a BOF may invalidate the interpretation of the results in terms of the simple model (5.2 and 5.3). The behavior observed in Figures 5.4 and 5.5 is to be compared with that shown in Figure 5.2.

Finally, we recall the results that we have obtained for the system size dependence study of \( Q \) (\( Q \equiv Q_2 \)) for the nonseparable system (Figure 4.19). There also, a curvature in the data was observed. The presence of an induced bond ordering and of the resulting BOF-MOF coupling in the above nonseparable systems could be responsible for the
Figure 5.4: System size dependence of $Q$ for a hard-needle fluid. The results are from reference [69]. Calculations were done for systems of number density $\rho = 8.75, 7.50$ and 7.00. Systems with $N = 50, 200, 800$ and 3200 needles were studied.

Figure 5.5: System size dependence of $Q$ for a hard-ellipse fluid. The results are from reference [69]. The aspect ratio of the ellipses is 6.0 and the number density is $\rho = 0.6\rho_0$ ($\rho_0$ is the density of close packing). Systems with $N = 46, 186, 744$ and 2976 ellipses were investigated.
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observed curvature. This interpretation is further substantiated by the fact that the data for a separable system [45] (Figure 5.3) do not show any curvature.

5.4 Discussion

We have shown that induced nearest-neighbor bond ordering in a nonseparable 2D liquid crystal modifies the usual logarithmic infrared divergence of director fluctuations. As a consequence, the power law decay of the order parameters with the system size is also modified. The presence of bond ordering introduces a crossover system size \( N_c \) and two different asymptotic logarithmic regimes. Our results suggest that the interpretation of finite-size scaling studies of 2D liquid crystals is more involved than predicted by a simple model that ignores BOF-MOF coupling and fluctuations in the orientation of the nearest-neighbor bonds.

We propose that to clearly show quasi-long-range order, a computer simulation of a 2D nonseparable liquid crystal system should demonstrate whether induced bond ordering is present or not. When bond ordering exists, finite-size scaling investigations should be performed for system sizes well above the crossover system size \( N_c \). However, in the case of weak BOF-MOF coupling, this crossover system size could be as large as \( N_c \sim 10^3 \) particles, making the finite-size scaling study of director fluctuations very difficult with currently available computers.

A word of caution is needed here. The model we have presented is based on a harmonic approximation, Equation 5.7, and applies only when slowly varying fluctuations of \( \phi(\vec{r}) \) and \( \theta(\vec{r}) \) are present. In other words, it applies in a well-ordered liquid crystalline phase. In a finite system, especially of the size investigated in computer simulations, non-harmonic corrections will become important as the temperature is raised. Such non-harmonic corrections can manifest themselves in two ways: via interactions between
director fluctuations of different wavevectors $^5$, or via the presence of defects, like vortices in the MOF (see Chapter 1). In the Kosterlitz-Thouless theory, the vortices are assumed to have a large core and the elastic deformation of the director field outside the core of the vortex is the only one that is considered. A renormalization calculation [7, 8], which applies to large systems (thermodynamic limit), shows that the main effect of the vortices is to reduce the effective elastic constants $K_M$ and $K_B$. However, in a system size of $O(10^3)$ particles, the presence of even a small number of bound vortex pairs will have a disastrous effects on the behavior of the orientational fields if the core of the vortices, where the harmonic approximation breaks down, is sufficiently large. These remarks apply to both separable and nonseparable systems.

We expect that both BOF-MOF coupling effects and non-harmonic corrections will contribute to reducing the applicability of Equations 5.2 and 5.3 to finite-size studies of 2D liquid crystal models. We believe, however, that it would be a very difficult task to isolate these two effects in a computer experiment.

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$^5$This is analogous to interactions between spin-waves in a Heisenberg ferromagnet.
Chapter 6

BOF-MOF Coupling and Response to an External Field: The Fréedericksz Transition in Tilted Hexatic Liquid Crystals

In the previous chapter we showed that the coupling between the BOF and the MOF modifies the finite-size scaling behavior of nonseparable 2D liquid crystals. It is natural to ask if other properties of liquid crystals are modified when the presence of a BOF coupled to a MOF is considered. In this chapter, we investigate how the response of a tilted hexatic liquid crystal film to an external field is affected when the system exhibits bond orientational ordering as in smectic-C, smectic-I and smectic-F phases. We shall concentrate on effects induced by magnetic fields in order to clearly expose the new effects introduced by the presence of a BOF-MOF coupling and to avoid the mathematical burden and complications arising when electric field induced distortions are considered [104].

6.1 Response of a Liquid Crystal Material to an External Field

Liquid crystals are usually diamagnetic, and the diamagnetization is particularly strong in aromatic molecules. Consider Figure 1.1. When a magnetic field is applied normal to a benzene ring, a current of electrons builds up inside the ring and generates a magnetic moment which reduces the flux going through it; the lines of magnetic field are thus expelled and this raises the energy of the system. When the benzene ring is parallel
to the field, the lines are practically undistorted and the magnetic energy density is not raised. Hence, the molecules tend to orient themselves in a way to minimize the magnetic energy increase, that is, with their benzene ring(s) parallel to the field. For most liquid crystal molecules, this corresponds to a favored orientation of the long molecular axis parallel to the field (see Figure 1.1).

We mentioned in Chapter 2 that samples of liquid crystal material can be oriented by chemically treating the walls of the container. An external field can be applied and tuned such to be perpendicular to the undistorted orientation of the molecules. This introduces a competition between the orientation imposed by the walls and the one favored by the magnetic field. Hence, one sees that there is a possibility that a liquid crystal sample uniformly aligned between parallel plane surfaces can undergo a transition to an elastically deformed state when subject to an external field larger than some critical value. This transition was first observed by Fréedericksz and Zolina [105], and has been the subject of considerable study in the past fifty years.

In this chapter we are interested in the response of tilted hexatic liquid crystals to an external field. Tilted hexatic liquid crystals are characterized by the tilt angle of the molecules with respect to the layer normal, and by an ordered BOF which describes the orientation of their nearest-neighbor bond structure (see Chapter 1). The BOF does not couple directly to the external magnetic field, but interacts with the MOF which is directly coupled to the magnetic field. We will show that the presence of a BOF can drastically influence the field response of the MOF of a tilted smectic film.

Until now, most experimental and theoretical work has concentrated on nematic liquid crystals (see Frisken [104] and references therein). There have been a few theoretical and experimental investigations of the Fréedericksz transition in smectic-C phases [2, 106, 107, 108, 109], but we are not aware of any work that has addressed the question of the
role played by an underlying induced BOF on the Fréedericksz transition in this system.

### 6.2 Model

Consider a tilted hexatic phase where the layers are parallel to the \( x - y \) plane with the layer normal along \( \hat{z} \) (see Figure 1.7). We assume that the magnetic field, \( \vec{H} \), is applied in the \( \hat{y} \) direction and that the boundary, at \( y = 0 \) and \( y = L \) are parallel to the \( x - z \) plane and treated in such a way that the director, \( \vec{N} \), is constrained to be in the orientation

\[
\omega(y = 0) = \omega(y = L) = \omega \\
\phi(y = 0) = \phi(y = L) = 0
\]

(6.1)

where the orientation of \( \vec{N}(y) \) is

\[
\vec{N}(y) = \{\sin(\omega) \cos(\phi), \sin(\omega) \sin(\phi), \cos(\omega)\}.
\]

(6.2)

\( \omega \) is the tilt angle and \( \phi \) is the azimuthal angle which indicates the orientation of the in-plane projection of the tilt.

We shall assume that the system is far from a nematic-smectic-A transition, and that the layers are incompressible, hence the layer spacing and tilt angle are constant. The azimuthal angle is the soft mode of the system and its original direction (\( \phi = 0 \)) can be modified by applying an external magnetic field. The magnetic field, parallel to \( \hat{y} \), induces a mixed bend-splay elastic distortion of the in-plane tilt projection, \( \phi(y) \), whose MOF elastic free energy density \( F^\text{elast.}_M \) is given by [2]:

\[
F^\text{elast.}_M = \frac{A}{2} \int_0^L dy \ K^s_M (\vec{\nabla} \cdot \vec{N})^2 + K^b_M (\vec{N} \times \vec{\nabla} \times \vec{N})^2
\]

(6.3)

\( K^s_M \) and \( K^b_M \) are the splay and bend elastic constant respectively [2] and \( A \) is the area of the cell walls parallel to the \( x - z \) plane. We also assume that a BOF is present in

\(^1\)Recall that the smectic-C phase is a tilted hexatic phase (Chapters 4 and 5).
the $x - y$ plane and write a simple phenomenological, one-elastic constant free energy density for BOF distortions, $F_{B}^{\text{elast.}}$ (see Chapters 4 and 5):

$$F_{B}^{\text{elast.}} = \frac{A}{2} \int_{0}^{L} dy \left( K_{B} \left( \frac{d\theta(y)}{dy} \right)^{2} \right). \quad (6.4)$$

We assume that it is energetically favorable for the system to have a BOF parallel to the cell walls at $y = 0$ and at $y = L$. This can be understood in terms of the packing constraint of the molecular cores which arise at the solid-liquid interface. Henceforth, we set $\theta(0) = \theta(L) = 0$.

We choose a BOF-MOF coupling analogous to Equation 5.5:

$$F_{B-M} = A h_{2n} \int_{0}^{L} dy \cos[2n\{\phi(y) - \theta(y)] \right] \quad (6.5)$$

where we have imposed inversion symmetry for the interaction $F_{B-M}$. $h_{2n} = h_{\delta_{n,3}}$ corresponds to the original coupling proposed by Nelson and Halperin [81]. In a binary liquid crystal mixture of smectic-C materials, the BOF in the present description would play the role of the MOF of the other component, and the term $h_{2n} = h_{2n,1}$ would correspond to the coupling between the two MOFs.

The magnetic free energy density, $F_{\text{mag.}}$, is given by:

$$F_{\text{mag.}} = -\frac{\chi_{\parallel}}{2} (\hat{N} \cdot \vec{H})^2 - \frac{\chi_{\perp}}{2} \left[ H^2 - (\hat{N} \cdot \vec{H})^2 \right]. \quad (6.6)$$

Introducing a new reduced variable, $u = \pi y / L$, we rewrite the total free energy of the system as

$$f_0 = \frac{2F}{L} + \chi_{\perp} H^2 + 2h_{2n} = \frac{2A}{\pi} \int_{0}^{\pi} du \mathcal{F}(u)$$

$$\mathcal{F}(u) = \left\{ \frac{\bar{K}}{2} + \frac{\Delta K}{2} \cos(2\phi) \right\} \left( \frac{d\phi}{dy} \right)^2 + \bar{K}_{B} \left( \frac{d\phi}{dy} \right)^2 + \frac{W}{4}(\cos(2\phi) - 1) - h_{2n}[\cos(2n\phi - 2n\theta) - 1]$$
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where

\[ W = (\chi_\parallel - \chi_\perp)H^2 \sin^2(\omega) \]

\[ \Delta K = \frac{K_1 + K_2}{2} \]

\[ K_1 = (\frac{\pi}{L})^2 K_M^\perp \sin^2(\omega) \]

\[ K_2 = (\frac{\pi}{L})^2 K_M^\parallel \sin^2(\omega) \]

\[ \bar{K}_B = (\frac{\pi}{L})^2 K_b \]

and \( f_0 = 0 \) in the undistorted state.

6.3 Results

The state of the system which is realized is such that \( f_0 \) is minimized with respect to \( \phi(u) \) and \( \theta(u) \). The functions \( \phi(u) \) and \( \theta(u) \) which minimize \( f_0 \) are the solutions of the Euler-Lagrange equations

\[ \frac{d}{du} \frac{\partial F}{\partial q} - \frac{\partial F}{\partial q} = 0 \]  

(6.8)

where \( q = \theta \) or \( \phi \) and \( \dot{q} = d\theta/du \) or \( d\phi/du \). This results in two coupled, nonlinear, second order differential equations. Since the MOF and BOF are anchored at \( y = 0 \) and \( y = L \), one has, by symmetry, the maximum distortion in the two fields at \( y = L/2 \) in the elastically distorted state. Hence, the boundary conditions are

\[ \theta(u = 0) = \frac{d\theta}{du} \bigg|_{u=\pi/2} = 0 . \]

\[ \phi(u = 0) = \frac{d\phi}{du} \bigg|_{u=\pi/2} = 0 . \]

Three cases are easily solved:

1. \( h_{2n} = 0 \). In this case, the Euler-Lagrange equations are decoupled and the solution corresponds to the usual Fréedericksz transition where the presence of a BOF is ignored. One finds that for \( W < W_c \), the state of the system is with no distortion in either the BOF or the MOF. For \( W \geq W_c \), the angle of maximum distortion in
the MOF at $y = L/2$, $\phi_m$, increases continuously from zero while the BOF remains undistorted ($\theta(y) = 0$); this is the usual second order Fréedericksz transition [106, 107, 2, 108, 109]. We shall not discuss this situation any further.

2. $h_{2n} = \infty$. Here the BOF is locked to the MOF since it would take an infinite amount of energy for the system not to have $\theta(y) = \phi(y)$ for all $y$. This problem reduces to the previous one with a second order Fréedericksz transition since the net result of the infinite BOF-MOF locking is just to increase $\bar{K} \rightarrow \bar{K} + \bar{K}_B$.

3. The limit $\bar{K}_B \rightarrow \infty$ is interesting and corresponds, as a first approximation, to a system which is deep in the tilted hexatic phase (e.g., sm-I or sm-F). In this case, one has $\theta(y) = 0$ for all $y$ since it would cost an infinite amount of BOF elastic energy if it were otherwise. A first integral of the resulting differential equation for $\phi(y)$ can be found and the final solution expressed in terms of an elliptical integral. Although exact, this approach is not very instructive at this point of the discussion since we have very little feeling of what the physical phenomena involved in the Fréedericksz transition in tilted smectics are. Hence, we shall, instead, first solve the problem by using the approximate ansatz described below.

The general case is usually referred to as a two point boundary value problem. In the present situation this turns out to be a difficult problem to solve and one must resort to a numerical investigation using an iterative procedure [110]. As in item 3 above, such a solution, even when available, is of little use if one does not have some physical insight into the problem.

A slowly varying approximate (SVA) solution of the form

$$\phi(u) = \phi_m \sin(u)$$
$$\theta(u) = \theta_m \sin(u)$$

(6.9)
leads to a better understanding of the problem than the an ‘exact’ numerical solution. This ansatz fulfills the above boundary conditions. $\phi_m$ and $\theta_m$ are the ‘order parameters’ of the problem. They are both zero in the undistorted state, and acquire a non-zero value in the elastically distorted phase when the effective field $W$ is increased beyond some critical value $W_c$. Using the above ansatz for $\phi(u)$ and $\theta(u)$, Equation 6.7 is integrated over $du$ to give

$$ f = \frac{1}{2} K_B \phi_m^2 + \frac{1}{2} K_B \theta_m^2 + \frac{\Delta K}{2} \phi_m^2 [J_0(2\phi_m) + J_2(2\phi_m)] + \frac{W}{2} [J_0(2\phi_m) - 1] - 2h_{2n} [J_0(2n\phi_m) - \theta_m) - 1] \tag{6.10} $$

where $J_p$ is the ordinary Bessel function of order $p$.

### 6.3.1 Infinite BOF Elastic Constant

Consider case 3 above where $\lim K_B \to \infty$ and $\theta_m = 0$. It is instructive to construct a Landau free energy by expanding $f_0$ in powers of $\phi_m$. Up to fourth order, we find

$$ f_0 = (K_1 - W + 4n^2 h_{2n})\phi_m^2/2 + (W - \Delta K - 4n^4 h_{2n})\phi_m^4/8 \tag{6.11} $$

In the absence of a BOF-MOF coupling ($h_{2n} = 0$), we recover the results of previous calculations [106, 107, 2, 108, 109] where the Fréedericksz transition, in the geometry considered here, was found to be second order when the presence of an intrinsic (sm-I, sm-F) or induced BOF (sm-C) is ignored. We find, however, that the BOF-MOF coupling can drive the Fréedericksz transition first order provided that

$$ 4n^2 h_{2n}(n^2 - 1) \geq K_2 \tag{6.12} $$

There is a tricritical point at $h_{2n}^t = K_2(4n^2(n^2 - 1))^{-1}$. The state of the system, within the SVA approximation, is given by $df_0/d\phi_m = 0$. We have solved this equation with
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\[ \bar{K}_B = \infty. \] Figure 6.1 shows some typical results for \( \phi_m \) as a function of applied field, \( W \), for various hexatic BOF-MOF couplings \( h_6 \) (see Chapters 4 and 5).

It is interesting to note that first order Fréedericksz transitions have been observed in systems where two (static and/or optical) fields are applied, where feedback is present, and in systems where the alignment of the molecules at the boundaries is tilted. In these examples, the appearance of a first order Fréedericksz transition is due to the presence of another aligning field which competes with the external applied field. In the present case, it is the BOF anchored at the boundaries which plays the role of the 'internal' aligning field.

The tricritical point is found by setting an equality sign in Equation 6.12. One cannot have a first order Fréedericksz transition if \( n = 1 \) since \( K_2 \geq 0 \) by definition. As mentioned earlier, this situation corresponds to a simple model of a binary liquid crystal mixture where the component which plays the role of the BOF has zero anisotropic magnetic susceptibility. The location of the line of second order transition, hence the limit of stability of the uniform state, and the location of the tricritical point, are predicted exactly by the above SVA.

At the first order phase transition boundary, the system experiences a jump in \( \phi_m \). The results of the SVA are inaccurate as the jump in \( \phi_m \) becomes large. As mentioned above, this problem could be solved in terms of elliptical integrals and one could compare the exact solution with the above Landau expansion or with the full SVA solution (Equation 6.10). This would give some indication of the range of validity of both the Landau expansion and the full SVA ansatz. This type of approach has been investigated by Frisken [104] for systems in crossed magnetic and electric fields. It was found that, although the Landau expansion and the full SVA solution are inaccurate deep in the first order regime, the full solution does not introduce any new or interesting physics which is not already predicted by the approximate solutions. Since we are not interested
Figure 6.1: Fréedericksz transition in tilted hexatic phase with an infinite BOF elastic constant. The squares, triangles, crosses and stars are for $h_6 = 0, 10^{-3}, 5 \times 10^{-3}$ and $10^{-2}$ respectively. We have set $\Delta K = 0$ and $w$ and $h_6$ are measured in units of $K_1$. First (1st) and second (2nd) order transitions occur at the locations marked by the arrows. The minimum free energy state of the system follows the solid line upon an increase of the magnetic field $w$. 
in investigating the location of the first order phase transition boundary, we shall not pursue the infinite $\tilde{K}_B$ limit any further, but look instead at the more realistic case with $\tilde{K}_B \neq \infty$.

### 6.3.2 Finite BOF Elastic Constant

We showed earlier that the infinite $h_{2n}$ case is trivial since the the BOF and the MOF must remain locked together ($\theta(y) = \phi(y)$). Due to this locking mechanism, the BOF and the MOF become indistinguishable and one recovers the original Fréedericksz transition problem for a single effective MOF in an external magnetic field for which the Fréedericksz transition is second order. We found in the previous section that if the limit $\tilde{K}_B \to \infty$ is taken first, the transition is first order for all $h_{2n}$ larger than $h^4_{2n}$, where $h^4_{2n}$ is the value of $h_{2n}$ at the tricritical point. These observations lead us to suspect that there might be, for finite $\tilde{K}_B$, a reentrant second order transition regime on the phase boundary as $h_{2n}$ is increased beyond a value $h_{2n} = h^6_{2n}$.

To qualitatively illustrate this effect we perform an expansion to first order in $h_{2n}^2/\tilde{K}_B$. The effective MOF free-energy is, to first order in $h_{2n}^2/\tilde{K}_B$, given by

$$ f_0 = \frac{1}{2} \tilde{K} \phi_m^2 + \frac{1}{2} \Delta K \phi_m^2 \left[ J_0(2\phi_m) + J_2(2\phi_m) \right] + \frac{W}{2} \left[ J_0(2\phi_m) - 1 \right] - $$

$$ 2h_{2n} \left\{ J_0(2n\phi_m) - 1 \right\} - \left( \frac{8n^2h_{2n}^2}{\tilde{K}_B} \right) J_1^2(2n\phi_m) . \tag{6.13} $$

Expanding 6.13 up to fourth order in $\phi_m$, we find

$$ f_0 = (K_1 - W + 4n^2h_{2n} - 16n^4h_{2n}^2/\tilde{K}_B)\phi_m^2/2 + $$

$$ (W - \Delta K - 4n^4h_{2n} + 64n^6h_{2n}^2/\tilde{K}_B)\phi_m^4/8 . \tag{6.14} $$

The limit of stability of the undistorted state with $\phi_m = \theta_m = 0$ is, up to order $h_{2n}^2/(\tilde{K}_B)$,
given by
\[ W_c = K_1 + 4n^2h_{2n}\left[1 - \frac{4n^2h_{2n}}{K_B}\right]. \] (6.15)
This is to be compared with the exact solution obtained by locating the change in sign of one of the eigenvalues of the quadratic expansion of \( f_0 \):
\[ W_c = K_1 + \frac{4n^2h_{2n}K_B}{K_B + 4n^2h_{2n}}. \] (6.16)
We find that, up to fourth order in \( \phi_m \), one has a first order transition if the coefficient of the fourth order is negative at \( W_c \) or when
\[ 4n^2h_{2n}(n^2 - 1) + 16\frac{n^4h_{2n}^2}{K_B}(1 - 4n^2) \geq K_2. \] (6.17)

Compare 6.17 with the infinite \( K_B \) result (Equation 6.12). For \( h_{2n} \) smaller than \( h_{2n}^0 \), one has a second order transition; this is the situation described earlier. For a BOF-MOF coupling with \( h_{2n} \) larger than \( h_{2n}^0 \), the MOF and the BOF are locked together and one recovers the second order Freedericksz transition as expected for strongly locked BOF-MOF. For couplings with \( h_{2n}^0 < h_{2n} < h_{2n}^0 \), there exists a first order transition regime provided that
\[ \left(\frac{K_B}{4}\right)\left(n^2 - 1\right)^2 \geq K_2. \] (6.18)

\( h_{2n}^0 \) and \( h_{2n}^0 \) are found by setting an equality sign in Equation 6.17.

Because of the approximation \( h_{2n}^2/\tilde{K}_B \ll 1 \), the location of \( h_{\phi}^0 \) and \( h_{\theta}^0 \) is inaccurately predicted and one must resort to a numerical investigation of Equation 6.10 via the full SVA solution. These results are presented in Figures 6.2, 6.3 and 6.4 which show the behavior of \( \phi_m, \theta_m \) and \( f_0 \) respectively, for various values of \( h_6 \) above \( h_6^0 \) as a function of the applied field \( W \).

The curves with the crosses represent all the solutions that we found by solving the equations
\[ \frac{\partial f_0}{\partial \phi_m} = \frac{\partial f_0}{\partial \theta_m} = 0. \] (6.19)
Figure 6.2: Magnetic field dependence of the MOF distortion, $\phi_m$, for a Fréedericksz transition in tilted hexatics with finite BOF elastic constant. The values of $h_6$ were set to 0.1, 0.2 and 0.5 for the figures from top to bottom respectively. We have chosen $\Delta K = 0$ and $\bar{K}_B = \bar{K}$. $W$ and $h_6$ are measured in units of $K_1$. The crosses show all the states which are free energy extrema. First (1st) and second (2nd) order transitions occur at the locations marked by the arrows. The minimum free energy state of the system follows the solid line upon an increase of the magnetic field $W$. 
Figure 6.3: Magnetic field dependence of the BOF distortion, $\theta_m$, for a Fréedericksz transition in tilted hexatics with finite BOF elastic constant. Refer to Figure 6.2 for details.
Figure 6.4: Magnetic field dependence of the free energy measured in units of $K_1$ for a Fréedericksz transition in tilted hexatics with finite BOF elastic constant. The various branches correspond to local extrema of $f_0$ which are observed in Figures 6.2 and 6.3 for $h_6 = 0.5$.

The solid line shows the field dependence of the state with absolute minimum of the free energy $f_0$. The $W - h_6$ phase diagram obtained by solving Equation 6.19 (3) numerically is shown in Figure 6.5 and where we have set $\kappa = 1$. For small applied field (small $W$), the system is in the undistorted state with $\phi_m = \theta_m = 0$. As anticipated, we find that as $W$ is increased, the system initially undergoes either a second (solid boundary) or a first order Fréedericksz transition (short-dashed boundary between point $\alpha$ and $\beta$) depending on the value of $h_6$. Interestingly, we find that the phase diagram is much richer than expected. One observes that if $h_6 > h_6^\alpha$ or if $h_6^\beta < h_6 < h_6^\alpha$, a subsequent first order transition order occurs if $W$ is increased beyond some $h_6$-dependent threshold (long-dashed boundary). The point $c$ is a critical point as shown in the inset of Fig. 1. Since the two long-dashed curves meet the short-dashed one with a continuous slope at $h_6^\alpha$ and $h_6^\beta$, one can regard these three first order phase transition boundaries as being a single first order boundary which extends from $h_6 = h_6^\beta$ to $h_6 = \infty$. 
The subsequent first order transitions (long-dashed curves) correspond to reorientation transitions of the bond field with respect to the tilt field. As $W$ is increased sufficiently far beyond the second order phase transition boundary (solid curve), the bond and tilt fields undergo a large elastic distortion. Since the bond field does not interact directly with the magnetic field, the system increases its bond elastic free energy by keeping a small angle between the tilt and bond orientational fields. At sufficiently large $W$, the magnetic interaction $F_m$ becomes saturated and, since the bond distortion is considerable, the bond field 'springs back' to a small $\theta_m$, hence reducing its bond elastic free energy. This is possible since the tilt can then reorient itself closer to one of the other sixfold symmetry axis of the bond field and the system does not increase its tilt-bond coupling free energy during the process. This interpretation is substantiated by observing, in Fig. 2, the behavior of $\phi_m$ and $\theta_m$ as a function of $W$ for $h_6 = 0.5$. Similar behavior for $\phi_m$ and $\theta_m$ is observed in the region $h_6^c < h_6 < h_6^\alpha$.

The isolated first order Fréedericksz transition boundary (short-dashed curve) is a remnant of the first order regime predicted above for $h_6 > h_6^t$ in the infinite-$\kappa$ approximation. Indeed, the dependence of $\phi_m$ on $W$ across this first order Fréedericksz transition boundary for $\kappa = 1$ is very similar of the one observed for $h_6 > h_6^t$ when $\kappa = \infty$.

The structure of the phase diagram depends strongly on the value of $\kappa$. As $\kappa$ is increased, the points $h_6^c$ and $h_6^\alpha$ move to smaller and larger values respectively, and the length of the $h_6^c - h_6^\alpha$ branch decreases rapidly until it vanishes for $\kappa \approx 1.25$. In smectic-C films, the hexatic bond ordering is entirely due to the molecular tilt and one has $\kappa \ll 1$. As $\kappa$ is decreased, the points $h_6^c$ and $h_6^\alpha$ move to larger and smaller values respectively, until the first order Fréedericksz transition regimes in-between the two second order branches disappear. This occurs for $\kappa \approx 0.607$. However, the first order tilt-bond reorientation transition above the second order Fréedericksz transition is still present with $c$ moving to smaller values of $h_6^c$ as $\kappa$ is decreased further.
Figure 6.5: Phase diagram for Fréedericksz transition in tilted hexatics with finite BOF elastic constant. Continuous lines correspond to second order phase transitions while the dashed line is a first order phase transition boundary. We have set $\Delta K = 0$ and $\hat{K}_B = \hat{K}$ and $W$ and $h_6$ are measured in units of $K_1$. The values of $h_6$ at alpha, beta and c are $h_6^\alpha$, $h_6^\beta$ and $h_6^c$. The values of $h_6^\alpha$, $h_6^\beta$ and $h_6^c$ are 0.009, 0.153 and 0.007 respectively. (Note the logarithmic scale for $h_6$.)
6.3.3 Numerical Investigation of the Euler-Lagrange Equations

We briefly present some results which compare the SVA solution with a full numerical solution of the Euler-Lagrange Equation 6.8 which, for $\Delta K = 0$ read

$$
\ddot{\phi} + \frac{W}{2} \sin(2\phi) - 2nh_{2n} \sin(2n\phi - 2n\theta) = 0
\quad
\ddot{\theta} + 2nh_{2n} \sin(2n\phi - 2n\theta) = 0 .
$$

We have attempted to solve these coupled equations using the following Fourier series expansion:

$$
\phi(u) = \sum_{q=0}^{\infty} A(q) \sin((2q + 1)u)
\quad
\theta(u) = \sum_{q=0}^{\infty} B(q) \sin((2q + 1)u) .
$$

We calculated the Fourier coefficients using an iterative procedure

$$
\ddot{A}_{l+1}(q) = \frac{W}{2\pi q^2} \int_{0}^{2\pi} du \sin(qu) \sin(2n \sum_{q'=1}^{\infty} A_{l}(k) \sin((2q' - 1)u)) -
\frac{2nh_{2n}}{\pi q^2} \int_{0}^{2\pi} du \sin(qu) \sin(2n \sum_{q'=1}^{\infty} \{A_{l}(k) - B_{l}(k)\} \sin((2q' - 1)u))
$$

$$
\ddot{B}_{l+1}(q) = \frac{2nh_{2n}}{\pi q^2} \int_{0}^{2\pi} du \sin(qu) \sin(2n \sum_{q'=1}^{\infty} \{A_{l}(k) - B_{l}(k)\} \sin((2q' - 1)u))
$$

where the index $l$ in $A_{l}(q)$ and $B_{l}(q)$ means the $l^{th}$ iterate. The Fourier coefficients $A(1)$ and $B(1)$ correspond to $\phi_m$ and $\theta_m$ respectively. It is easy to show that for $A(q) = B(q) = 0$ for all $q \geq 0$, one recovers the algebraic equations obtained from Equations 6.19.

This technique was found to converge rapidly for not-too-large values of $W$ and $h_6$. Figure 6.6 shows a comparison of the full numerical solution (square symbols) using the above iterative procedure with the SVA solution (crosses) for $\Delta K = 0$, $\ddot{K}_B = \ddot{K}$ and
Figure 6.6: Comparison of 'exact' and SVA solution for a Fréedericksz transition in tilted hexatics with finite BOF elastic constant. We have set $\Delta K = 0$, $K_B = \bar{K}$ and $h_6 = 0.02$. $W$ and $h_6$ are measured in units of $K_1$. See text for details.

$h_6 = 0.02$ (in units of $K_1$). A first order transition is observed for $W \approx 1.35$ (dashed line). The amplitudes $A(3)$ and $A(5)$ were found to be smaller than $1^\circ$ for $1.35 \leq W \leq 1.60$ so, clearly, the SVA solution is quite satisfactory.

For large values of $W$ or $h_6$, we found numerical instabilities which invalidate the use of the above iterative procedure. For example, at fixed $h_6$ ($h_6 = 0.02$) and small $W$ ($W < 1.65$), we could find an unambiguous and unique solution to the Euler-Lagrange equations. We observed, upon an increase of $W$, a doubling sequence in the number of solutions (1,2,4,8) up to $W \approx 2.38$ where the iterative procedure was found not to converge. We interpret this behavior as the well-known period doubling route to chaos (see Figure 6.7).

The iterative technique we used is therefore inappropriate and one would have to devise a more subtle numerical technique in order to find a full solution of the Euler-Lagrange equations beyond the SVA approximation. It is often possible to find converging
iterative solutions of a given set of equations by rewriting the iterative map in a different form. We have applied this approach to Equations 6.20. Unfortunately, we could only find one stable fixed point corresponding to the undistorted state with $\phi_m = 0$. Nevertheless, we believe that the main features of the system are explained by only considering the SVA solution and we shall not pursue the present numerical study of Equations 6.20 any further.

6.3.4 Application to a Well Characterized Hexatic Material — 8OSI

We conclude this chapter by investigating whether the behavior predicted for the Fréedericksz transition in tilted hexatics is experimentally accessible. The important parameter to calculate is the BOF-MOF coupling, $h_6$. We are aware of only one material, abbreviated as 8OSI, in which $h_6$ has been determined [111]. 8OSI exhibits a smectic-C to smectic-I
(hexatic) phase transition. Using a phenomenologic parametric equation of state, Garland et al. [111] have estimated the value of $h_6$ to be

$$h_6^{(8 OSI)} \approx 10^{-5} T_c \text{ with } T_c \approx 350K .$$

This gives a value

$$h_6^{(8 OSI)} \approx 5 \times 10^{-26} J/\text{molecule} .$$

Assuming a molecular weight of 300 g and a density of the order of 1 g/cm$^3$, we get a BOF-MOF coupling free energy density of the order of

$$h_6^{(8 OSI)} \approx 5 \times 10^{-26} J/\text{molecule} \left( \frac{6 \times 10^{23}}{300g} \right) 1g/cm^3 \approx 100J/m^3 .$$

Typical values for molecular Frank elastic constants are [2]

$$K_M \approx 10^{-6} - 10^{-7} \text{dyne} \approx 10^{-11} - 10^{-12} N .$$

Finally, we find that the quantity we are interested in, $h_6/K_1$, is

$$\frac{h_6}{K_1} \approx 10 - 100 \left( L/\mu m \right)^2$$

where the length of the cell, $L$, is expressed in $\mu m$.

In two-dimensional tilted hexatics, the bond and tilt elastic constants are $72k_BT/\pi$ and $2k_BT/\pi$ respectively at the decoupled fixed point [81]. For 3D hexatics, we also expect $\kappa = \bar{K}_B/\bar{K}_T \gg 1$. Hence, for definitiveness, we fix $\kappa = 36$. Assuming a tilt angle $\omega \approx 20^\circ$ and typical magnetic anisotropic susceptibility [2], we find that for a thickness $L \approx 1\mu m$, the system is at or very close to the interesting region near $\beta$ with a magnetic field strength, $H$, of the order of 1 to 10 Tesla.

It was assumed in the above calculations and numerical estimates that a strong anchoring of tilt and bond fields prevailed. Previous experiments have shown that it is possible to realize a strong anchoring of the molecular tilt in smectic-C liquid crystals.
for the planar geometry we consider [109]. However, to impose strong anchoring on the
bond field, interfaces with bond orientational order at $y = 0$ and $y = L$ are required. Monocrystalline boundaries could be used to impose strong anchoring of a well defined bond orientation.

Instead of the planar geometry studied here, one could consider the $N$-geometry, first discussed by Rapini [107] and later by Meirovitz [108], in which the anchoring of the BOF and the BOF is at $z = 0$ and $z = L$. This geometry would allow to take advantage of the fact that free interfaces of suspended smectic liquid crystal films tend to favor more ordered tilted smectic phases [4, 112, 113].

For example, the formation of hexatic smectic-I layers at the free interfaces of smectic-C films has been observed [112]. Further, recent experiments have shown that the rotational viscosity in thin smectic-I films is much larger than in the smectic-C phase [78, 88]. An experiment in which a smectic-C film is slowly cooled (annealed) in a strong magnetic field would lead to free interfacial smectic-I layers with inner smectic-C layers with both well defined tilt and bond orientation. At the same time as the annealing field is turned off, a field applied parallel to the layers could induce a dynamical Fréedericksz transition of the inner layers before the outer smectic-I layers could respond to the field which induces the dynamical Fréedericksz transition.

6.4 Discussion

In this chapter we have investigated the response of tilted hexatic materials to an applied magnetic field, concentrating on the Fréedericksz transition. We have found that the presence of BOF ordering can drastically modify the behavior of the response of the system under an applied field. Rough estimates suggest that some tilted hexatic materials could exhibit the phenomena described in this chapter.
The BOF-MOF coupling strength is material-dependent and the interesting parts of our phase diagram in Figure 6.5 could be investigated in experiments performed with materials with a different $h_6$. For example, previous X-ray diffraction experiments [114] in a material abbreviated as 70.7 showed no induced BOF ordering in a smectic-C phase, hence a smaller $h_6$ coupling than for 8OSI. Experimental results from Fréedericksz transitions in tilted hexatic would be of considerable interest since they would provide a new experimental way to determine important parameters, such as $K_T$, $K_B$ and $h_6$, and help to characterize these systems.
In Chapter 4 we found that a strong nonseparability of the pair potential can induce a considerable amount of bond orientational ordering in a liquid crystal phase with an ordered MOF. We argued that the presence of induced BOF ordering is an intrinsic feature of liquid crystal phases where the particles interact via nonseparable potentials. Although it appeared, at first sight, that the induced BOF in these systems behaves as a locked slave field, we showed in the previous two chapters that the presence of a BOF can significantly modify the finite-size scaling behavior of 2D liquid crystals (Chapter 5) and the magnetic field response of tilted smectic liquid crystals (Chapter 6).

Our approach, in Chapters 5 and 6, was to investigate the effects of a BOF on common properties of liquid crystalline systems where the presence of such bond ordering is usually neglected. In this chapter, we do the reverse: we investigate whether the presence of a MOF coupled to the BOF introduces interesting effects in systems with predominant BOF ordering and in which the MOF would seem to play an unimportant role.

As an example of this type of investigation, we propose a microscopic model for the smectic-I – smectic-F (I-F) transition in a freely suspended hexatic liquid crystal film. We suggest that the transition between these two hexatic phases can be easily explained by assuming that it is driven entirely by an increase in the molecular tilt angle, which
plays the role of the MOF in the present problem.

We present ground state calculations which show that our model exhibits two types of zero temperature close-packed phases, which we call 'I-like' and 'F-like' phases, depending on the favored molecular tilt direction with respect to the nearest-neighbor bond. We refer to them as 'I-like' and 'F-like' phases since they are solid phases, and not true liquid crystalline phases. Assuming that the tilt angle increases upon a decrease of temperature, our results provide an explanation for the experimental observation that the smectic-F phases always occurs at a lower temperature than the smectic-I phase [4]. As well, we argue that the transition exhibited by our model is not confined to a solid phase and that its presence could be investigated for a true liquid crystalline phase with a computer simulation.

7.1 The Smectic-I – Smectic-F Transition

Before deriving our microscopic model for the I-F transition, we present a brief description of this transition.

Some of the hexatic smectics that have recently been studied are tilted phases [85, 80, 88] (see Chapter 1 for description of hexatic smectic phases). These can be characterized by the relative orientation of the in-plane projection of the tilt with respect to the nearest-neighbor bond (see Figure 1.12). The in-plane molecular projection can be along the nearest-neighbor bond as in the smectic-I phase (0°), or halfway between nearest-neighbor bonds as in the smectic-F phase (30°). In all cases where both phases are present, the smectic-F phase is the most ordered one [4] since it occurs at a lower temperature. This is a feature that any microscopic model of the I-F transition should be able to reproduce.

In a recent experiment, Dierker and Pindak [88] observed a first order I-F transition in a thermotropic liquid crystal material they studied. Using a Landau theory, Selinger
and Nelson [83, 84] were able to explain this first order I-F transition. This is the model we described in Equation 4.5 and in Equation 5.5.

For a strongly first order I-F transition, one can neglect the fluctuations in $\phi(\vec{r})$ and $\theta(\vec{r})$ and consider only the periodic coupling. The phase of the system is such that the BOF-MOF coupling energy, $V_{B-M}(\theta - \phi)$, is minimized with respect to the BOF-MOF offset $(\theta - \phi)$. Selinger and Nelson considered only the first two harmonics with $h_6$ and $h_{12}$ in Equation 4.5:

$$V_{B-M}(\theta - \phi) = -h_6 \cos\{6(\theta - \phi)\} - h_{12} \cos\{12(\theta - \phi)\}.$$  \hspace{1cm} (7.1)

Taking $h_{12} > 0$, they find that for $h_6 > 0$, the minimum energy state is with $\theta - \phi = 0$ which is a smectic-I phase. For $h_{12} > 0$ and $h_6 < 0$, the minimum energy state is with $\theta - \phi = 30^\circ$ which is a smectic-F phase. A first order phase transition separates the two states at $h_6 = 0$.

Unfortunately, the microscopic origin of the phenomenological coupling between the MOF, $\phi$, and the BOF, $\theta$, invoked in Equation 7.1 is not known. In particular, one would like to find a microscopic model which exhibits a I-F transition and for which the couplings $h_6$ and $h_{12}$ can be evaluated and check if a I-F transition does indeed occur when $h_6$ changes sign while $h_{12}$ remains positive. This would allow a direct check of Selinger and Nelson's model and largely improve our understanding of the hexatic smectic phases.

### 7.2 Model for the I-F Transition and Intermolecular Pair Potential

#### 7.2.1 Preliminaries

It is difficult to construct microscopic models for systems as complicated as hexatic liquid crystals. The presence of quasi (in $2D$) or true (in $3D$) long-range bond orientational
order is a feature not easily incorporated into a microscopic model. In fact, we are not aware of any successful attempts in that direction. The I-F transition can be considered as a 'sort of' structural transition between two phases that both have the same very long distance behavior of their bond orientational correlation function. Since the main feature of this transition is a reorientation of the tilted MOF (see Figure 1.12), it seems plausible that the microscopic explanation for the transition lies in the competition between different nonseparable interactions present in the system. This is the point of view we shall adopt here.

We indicated in Chapter 3 that one should not use lattice models with nonseparable interactions to model nematic liquid crystals since the underlying lattice breaks the continuous rotational symmetry of the high temperature isotropic-like phase. In a hexatic phase, the system exhibits bond ordering and often has a positional correlation length larger than 20 to 50 molecular diameters [4]. The presence of such 'long' short-range positional order in these systems suggests that a lattice model for these systems might be a valid starting point for modelling the I-F transition. This provides a motivation for considering a model for the I-F transition where the particles are arranged on a perfectly regular lattice. Selinger and Nelson [84] have recently proposed such lattice model as a method to calculate the couplings constants appearing in their Landau theory for the I-F transition.

In Chapter 2 we found that a large amount of physical insight can be gained by first considering the ground state orientational behavior of system of particles interacting via nonseparable potentials. This is also the approach we shall adopt in this chapter where we investigate a simple nonseparable lattice model which exhibits both an 'I-like' and an 'F-like' phase, depending on the value of some parameters to be defined below. We shall then argue that such a microscopic model may, in some circumstances, exhibit the equivalent I-F transition, but in a true liquid phase.
Chapter 7. Microscopic Model for the Sm-I – Sm-F Transition

At a more practical level, this lattice-model type of approach is useful since ground state calculations are orders of magnitude faster and cheaper to perform than Monte Carlo or molecular dynamics simulations, and can quickly reveal a potentially interesting behavior of the system in its liquid crystalline phase.

7.2.2 Interactions between Tilted Molecules

Steric Interactions

The molecules are tilted with respect to the layer normal in both the smectic-I and the smectic-F phases (see Figure 1.7). We assume that we are far from the smectic-A → smectic-C transition [4] and that the fluctuations of the tilt angle, \( \omega \), are negligible. Hence, all the molecules have the same \( \omega \). Since we are trying to understand the I-F transition with the simplest model possible, we take for granted that we have a tilted phase and do not question the microscopic origin of the tilt \(^1\). From now on, the tilt angle, \( \omega \), will be considered an independent variable which, in a true liquid crystal, is a measure of the temperature of the system. The motivation for this assumption is that, in real liquid crystal systems, the tilt increases as the temperature is lowered and going from the smectic-C phase to the smectic-I phase [4, 116].

Furthermore, we shall neglect the coupling between smectic layers and consider a single liquid layer of tilted rods. Assuming a single layer is an uncontrolled approximation and its importance should be carefully investigated in later studies since it has been experimentally demonstrated that, for a given material, the smectic-I phase is not present in thick smectic films [117].

First, we take a simple case where individual molecules can be modeled by hard

\(^1\)Once such 'given-tilt' model for the I-F transition has been devised, one could introduce a more sophisticated model similar to the one introduced by McMillan [115] which proposes a microscopic origin of the tilt in tilted smectics.
spherocylinders [36, 37, 38]. Since the tilt angle does not fluctuate, the effective interaction between the spherocylinders reduces to the interaction between their in-plane cross-section; the spherocylinders have become hard ellipses [76, 77]. The length of the major and minor axis of the ellipses are $2a/cos(\omega)$ and $2a$ respectively, where $a$ is the radius of the spherocylinder. The aspect ratio, $k$, is defined as $k = 1/cos(\omega)$. This effective two-dimensional liquid crystal system is similar to a smectic-C phase, and one expects that it will exhibit induced bond orientational ordering [85, 80, 81, 83, 84, 82].

A perfectly oriented hard ellipse liquid crystalline phase is also realized by uniformly increasing (rescaling), in some direction, the diameter of hard discs in a dense fluid phase. This direction becomes the major axis of the ellipses and corresponds to the orientation of the tilt in the smectic plane. In a dense hard disc fluid phase, each disc has, on average, six nearest-neighbor bonds at about every 60°. We call this anisotropic phase 'I-like' or 'F-like' depending on whether tilt lies along or halfway between the original nearest-neighbor bonds of the original hard discs fluid ².

Recall, however, that for our model of the I-F transition, we assume that the above liquid crystalline phase can be modelled as close-packed lattice model of tilted rods. This anisotopic solid is obtained by distorting a perfect close-packed lattice of hard-discs in the direction of the in-plane projection of the tilt. Having started with a perfect triangular lattice of hard-discs, the resulting distorted lattice is the closest-packed lattice one can build-up with ellipses, whose packing fraction, and free-energy, is independent of the direction of the distortion (orientation of the ellipses). Hence, ground state calculations show that 'I-like' and 'F-like' lattices have the same free energy ³. Other forces must be taken into account in order to lift the degeneracy between all the equivalent hard-ellipse

²The presence of a tilt introduces a small twofold distortion which alters the sixfold symmetric structure of the original triangular lattice [85, 80].

³These results may indicate that induced bond orientational order would be small in a liquid crystal phase of uniformly oriented hard fluid ellipses.
configurations in the solid phase and induce either an ‘I-like’ or ‘F-like’ phase.

**Attractive Interactions - Part I**

The obvious candidates which might removes the degeneracy between all the above close-packed lattice of ellipses are isotropic attractive forces. We have calculated the ground states of a system of hard ellipses interacting with each other via an isotropic attractive van der Waals interaction of the form:

\[ V_{ij} = -r_{ij}^{-6} \]  

(7.2)

The distance, \( r_{ij} \), between the centers of mass of the ellipse \( i \) and ellipse \( j \), is measured in units of the original triangular lattice spacing, \( a \). The ellipses are uniformly aligned on a close packed lattice, and the total energy of the system is calculated as a function of the orientation of the ellipses with respect to the lattice orientation. We find that the interaction 7.2 lifts the degeneracy between all the equivalent close-packed lattices of hard ellipses and, independently of the tilt angle \( (\omega > 0) \), the resulting ground state is ‘F-like’, with the major axis of the ellipse oriented halfway (30°) between two nearest-neighbors.

These results suggest that an orientationally ordered 2D hard ellipse fluid interacting via attractive van der Waals forces would have a nearest-neighbor bond structure strongly reminiscent of a smectic-F phase, and not an ‘F-like’ solid phase, provided parameters such as temperature, pressure and aspect ratio of the ellipse are suitably chosen. It would be interesting to investigate this prediction via computer simulations. As well, these results suggest that competing interactions must be present if a ‘I-like’ phase is to exist.
Attractive Interactions - Part II

In the calculation above, we have assumed that the global effect of the attractive intermolecular van der Waals forces can be taken into account by introducing an effective source of van der Waals interactions at the center of each molecule (ellipse). We now improve this approximation by considering the presence of van der Waals centers of interaction (atoms) away from the geometrical center of the cylindrically symmetric molecule.

This introduces an attractive nonseparable interaction in our model which already contains a stericly repulsive part (the hard ellipse part), and an isotropic attractive one (the \(-r^{-6}\) term in Equation 7.2). These three competing interactions will prove to be sufficient to lead to both ‘I-like’ and ‘F-like’ ground states.

We introduce an atom of type ‘o’, located at the geometric center of the the cylindrical molecule and on the symmetry axis (see Figure 7.1). As well, we introduce four other atoms, two of type ‘a’ and two of type ‘b’. The ‘a-atoms’ are located on the long molecular axis, parallel to \(n\), and their position is \(\pm r^\parallel\) with respect to atom ‘o’. The ‘a-atoms’ are located on the transverse, or short molecular axis, \(n^\perp\), which is perpendicular to \(n\), and their position is \(\pm r^\perp\) with respect to atom ‘o’.

The purpose of the ‘o’, ‘a’ and ‘b’ atoms is to introduce several energy scales in the problem. Assuming that all atoms interact via isotropic van der Waals forces, as in Equation 7.2, we find that the total intermolecular pair potential, \(V_{ij}\), is given by:

\[
V_{ij} = -(\epsilon_{oo} + 2\epsilon_{aa} + 2\epsilon_{bb})
- \epsilon_{aa} \left( |\vec{r}_{ij} + 2r^\parallel \hat{n}^\parallel|^{-6} + |\vec{r}_{ij} - 2r^\parallel \hat{n}^\parallel|^{-6} \right) - \epsilon_{bb} \left( |\vec{r}_{ij} + 2r^\perp \hat{n}^\perp|^{-6} + |\vec{r}_{ij} - 2r^\perp \hat{n}^\perp|^{-6} \right)
- 2\epsilon_{ao} \left( |\vec{r}_{ij} + r^\parallel \hat{n}^\parallel - r^\perp \hat{n}^\perp|^{-6} + |\vec{r}_{ij} - (r^\parallel \hat{n}^\parallel - r^\perp \hat{n}^\perp)|^{-6} \right)
- 2\epsilon_{bo} \left( |\vec{r}_{ij} + (r^\parallel \hat{n}^\parallel + r^\perp \hat{n}^\perp)|^{-6} + |\vec{r}_{ij} - (r^\parallel \hat{n}^\parallel + r^\perp \hat{n}^\perp)|^{-6} \right)
- 2\epsilon_{ab} \left( |\vec{r}_{ij} + (r^\parallel \hat{n}^\parallel - r^\perp \hat{n}^\perp)|^{-6} + |\vec{r}_{ij} - (r^\parallel \hat{n}^\parallel + r^\perp \hat{n}^\perp)|^{-6} \right).
\]
Figure 7.1: Schematic arrangement of atomic species on interacting tilted smectic molecules. Figure a) shows the long molecular axis, $\hat{n}$, which makes an angle $\omega$ with the normal of the smectic layer, $\hat{z}$. $\hat{n}_\perp$ is a unit vector perpendicular to $\hat{n}$, and $\hat{b}$ is the in-plane projection of $\hat{n}$ and is in the direction of the major axis of the ellipse. Figure b) shows the locations of the van der Waals centers. The atomic species 'o' is at the geometrical center of the molecule while the atoms 'α' and 'β' are located at a distance $r_\parallel$ and $r_\perp$ from the o-atom, on the $\hat{n}$ and $\hat{n}_\perp$ axis respectively.
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$\varepsilon_{oo}, \varepsilon_{oa}, \varepsilon_{o\beta}, \varepsilon_{a\alpha}, \varepsilon_{\beta\beta}$ and $\varepsilon_{a\beta}$ are, respectively, the strengths of the $o-o$, $o-\alpha$, $o-\beta$, $\alpha-\alpha$, $\beta-\beta$ and $\alpha-\beta$ van der Waals interactions.

7.3 Results and Discussion

It is instructive to expand 7.3 up to second order in $r_{ij}/r_{ij}$ and $r_{ij}/r_{ij}$. This shows that, at least up to that order, the anisotropic correction has the lowest energy for a configuration with two ellipses parallel to their intermolecular vector. Such anisotropic terms tend to favor an 'I-like' phase:

\[
V_{ij} = -[\varepsilon_{oo} + 4(\varepsilon_{oa} + \varepsilon_{o\beta} + \varepsilon_{a\alpha} + \varepsilon_{\beta\beta})] r_{ij}^{-6} - 3[\varepsilon_{oo} + 2\varepsilon_{oa} + 2\varepsilon_{o\beta}] r_{ij}^{2} (8 \sin^{2}(\omega)(\hat{e}_{ij} \cdot \hat{b})^{2} - 1) r_{ij}^{-8} 
- 3[\varepsilon_{o\beta} + 2\varepsilon_{\beta\beta} + 2\varepsilon_{a\beta}] r_{ij}^{2} (8 \cos^{2}(\omega)(\hat{e}_{ij} \cdot \hat{b})^{2} - 1) r_{ij}^{-8}.
\]  

(7.4)

$\hat{e}_{ij}$ is a unit vector parallel to $\vec{r}_{ij}$, and $\hat{b}$ is a unit vector parallel to the in-plane projection of the molecular tilt and indicates the orientation of the major axis of the ellipse (see Figure 7.1).

At this point we can already make two observations from Equation 7.4:

- The intermolecular potential, $V_{ij}$, is strongly attractive for $\hat{e}_{ij}$ parallel to $\hat{b}$ and and favors an 'I-like' configuration. Hence one should be able to observe a competition between these terms and the isotropic $o-o$ interaction which favors an 'F-like' state.

- The contribution to $V_{ij}$ coming from the term proportional to $r_{ij}^{2}$ (second term) is much less important than the one coming from the term proportional to $r_{ij}^{-2}$ (third term). For small tilt angle, the effect of the nonseparable $\hat{e}_{ij} \cdot \hat{b}$ interaction in the second term is considerably reduced since it is multiplied by $\sin^{2}(\omega)$. For large $r_{ij}$, the 'o' atoms are far from the 'o' and 'b' atoms and the $r^{-6}$ dependence in the full
potential 7.3 kills its contribution. Finally, for large tilt angle, the \( \sin^2(\omega) \) term may play some role. We found, however, that for the case we have concentrated on with all the \( \epsilon_{ab} \) interactions being equal, the eccentricity of the ellipses is such that, when this happens, the system has already been driven to the 'F-like' phase by the \( o-o \) interactions.

The ground states exhibited by potential \( V_{ij} \) in Equation 7.3 were obtained in the following way: an arbitrary frame, \( x' - y' \), with the \( x' \) axis having an orientation \( \phi \) with respect to the \( x \) axis of a perfect triangular lattice (\( x - y \) frame) is chosen. The coordinates, \((i,j)\), of each lattice point in the \( x - y \) frame are calculated, and once their projection along the \( x' \) axis is known, it is increased by a factor \( k > 1 \). This produces a close packed lattice of hard ellipses oriented along \( x' \), at an angle \( \phi \) with the \( x \)-axis and with major (\( x' \)) and minor (\( y' \)) axis of length \( ka \) and \( a \) respectively. The energy of the system (Equation 7.3) is then calculated as a function of \( \phi \in [0, 30^\circ] \), for fixed \( k \), \( r_\parallel \) and \( r_\perp \). Once the lowest energy state is found, the aspect ratio, \( k \), is slightly increased, and the procedure is repeated.

We present the results for a case where all the \( \epsilon_{ab} \) interactions are set equal. Figure 7.2 shows the \( r_\perp - \omega \) phase diagram we have obtained with the full interaction 7.4 and where the lattice sum was carried up to \((i,j) = (\pm8, \pm8)\). A different cut-off range does not alter the results significantly. \( r_\perp \) is measured in units of the molecular radius, which is half the lattice spacing of the original triangular lattice. The distance \( r_\parallel \) was set to 2 in the same units, but as discussed above, the results for \( r_\parallel = 1 \) and 3 were found to be very similar to the case with \( r_\parallel = 2 \).

For small tilt angle (high temperature), the ground state is 'I-like' with the ellipses (molecular tilt) oriented along the nearest-neighbor bond of the original triangular lattice. At larger tilt (low temperature), the system favors an 'F-like' state and a 'first order'
Figure 7.2: Phase diagram of close-packed ellipses interacting with distributed sources of isotropic van der Waals centers. The tilt angle, \( \omega \), is expressed in degrees, and \( r_\perp \) is measured in units of the molecular radius. The dashed-curve corresponds to a 'first order' phase transition boundary between the 'I-like' and the 'F-like' ground states. The orientations of the tilt with respect to the nearest-neighbor bond of the original perfect triangular lattice is illustrated by the orientation of ellipses at the top right of the phase diagram, but where \( k \) has been exaggerated for clarity.
phase transition separates the two states. Two points which deserve particular attention
are discussed in the following two subsections.

'First Order' I-F Phase Transition Boundary

In Figure 7.2, we refer to the boundary separating the 'I-like' phase from the 'F-like' phase
as a first order phase transition boundary. This categorization is not totally adequate as
we now explain.

Since the smectic-I and the smectic-F phase have the same symmetry, one generally
expects to find a first order transition separating these two phases. In most systems
which exhibit a first order phase transition from one state to another, there exists a free
energy barrier separating the two phases. This is not what we found when calculating the
I-F boundary illustrated in Figure 7.2. We first explain what one would normally expect
to occur close to the I-F boundary in a phase diagram such as the one in Figure 7.2.

In the 'I-like' phase, but very close to the I-F boundary, one would expect an absolute
energy minimum for $|\theta - \phi| \equiv \theta_- = 0^\circ$, a local minimum at $\theta_- = 30^\circ$, and an absolute
maximum for some $\theta_- \text{ between } 0^\circ \text{ and } 30^\circ$. As the system crosses the boundary, the state
with $\theta_- = 30^\circ$ would become the absolute minimum, the state with $\theta_- = 0^\circ$ would then
become the absolute maximum, and there would still be an energy barrier separating the
two states. We found, instead, that in the 'I-like' phase, below the dashed-line, the energy
is minimum for $\theta_- = 0^\circ$ and increases monotonically up to $\theta_- = 30^\circ$, with no
energy barrier between the state with $\theta_- = 0^\circ$ from the state with $\theta_- = 30^\circ$. This behavior
persists until the boundary is reached. On the phase boundary, and beyond (larger $\omega$),
we find that the energy is now a maximum for $\theta_- = 0^\circ$, decreases monotonously up to
$\theta_- = 30^\circ$, with still no energy barrier separating the two states.

The origin of this behavior lies in the discontinous 'stretching-unstretching-stretching'

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4By symmetry, the state with $30^\circ - |\delta|$ has the same energy as the state with $30^\circ + |\delta|$.
of the triangular lattice which we use to find the lowest energy state of the system. Due to the impenetrability of the hard-ellipses, we cannot perform a continuous transformation (rotation of the triangular lattice) from the state with \( \theta_\perp = 0^\circ \) to the state with \( \theta_\perp = 30^\circ \). Although the procedure we use to cross the I-F boundary does not correspond to the path a real system follows when undergoing an I-F transition, the location of the I-F boundary we find is still meaningful, since we do find the lowest energy state of the system for a given \( \omega \).

Since the transformation we used to find the energy of the states with \( \theta_\perp \in [0^\circ, 30^\circ] \) is not continuous, we cannot evaluate the \( h_6 \) and \( h_{12} \) coefficients the BOF-MOF interaction 7.1. This brings up the second point.

**Success of the Present Model and Suggested Improvements**

The inability to evaluate \( h_6 \) and \( h_{12} \) is a unfortunate drawback of our hard-ellipse + van der Waals interactions model. However, this model has allowed us to identify mechanisms which can lead to an I-F transition. Furthermore, assuming that the tilt angle increases with a decrease of temperature, our model provides an explanation for why the F phase occurs at a lower temperature than the I phase.

At a more pedagogical level, our model could be considered as one of the few microscopic models for a liquid crystal phase in which competition between steric forces, isotropic attractive forces and anisotropic attractive forces is necessary to explain the transition of interest.

Identifying some mechanisms which drive a I-F transition is a useful first step. The same kind of approach as the one outlined in this chapter could be taken with soft-ellipses\(^5\) where off-center van der Waals sources of interaction would also be introduced.

\(^5\)Soft-ellipse models have been proposed in the context of nematics \([43, 44]\) and investigated in computer simulations \([45, 46, 47]\).
Since they are not impenetrable, soft-ellipses would allow a continuous rotation from the state with $\theta_- = 0^\circ$ to the state with $\theta_- = 30^\circ$. One could then calculate the coefficients of the Fourier series for the BOF-MOF interaction, such as the one described in Equation 7.1. Using such a microscopic model exhibiting an 'I-like' to an 'F-like' transition would provide a first check of the Landau theory of Selinger and Nelson [83, 84]. If the behavior of soft-ellipses with off-center van der Waals sources in the solid phase did exhibit an I-F transition, it would be interesting to investigate that system in a truly liquid phase.
Chapter 8

Nonseparability and Anisotropic Viscosities:
Application to Viscous Fingering

In this thesis we have concentrated on the strong coupling between positional and molecular orientational degrees of freedom which originates from the nonseparability of the pair potential. We did, however, discuss in Chapter 2 that there exist more ‘common’ manifestations of the nonseparability than those we have investigated. For example, the difference in the splay, bend and twist elastic constants or the anisotropy of the viscosity coefficients are such common manifestations.

We would like to conclude our study of nonseparable effects in liquid crystals by looking at more macroscopic ‘liquid-like properties’ of the nonseparability. To do so, we ask ourselves whether the nonseparability-induced anisotropy in bulk properties of liquid crystals introduces interesting effects in some phenomena where the presence of anisotropy plays a crucial role.

8.1 Importance of Anisotropy in Problems of Pattern Formation

Several problems of pattern formation within the Laplacian growth mechanism have been found to exhibit drastically different behavior when anisotropy is present then when it is not. The following examples are illustrative.
• Computer simulation of diffusion-limited aggregation (DLA) of large clusters of particles reveal that the anisotropy imposed by the underlying square lattice, on which the particles random walk, introduces a noticeable fourfold symmetry to the DLA cluster [118]. In this case, one observes structures strongly reminiscent of the dendrites observed in crystal growth [119].

• It has recently been shown that the presence of crystalline anisotropy plays a fundamental role in selecting the growth velocity of a parabolic crystalline dendrite [120, 119].

• Finally, it has recently been observed that the formation of viscous fingers in a Hele-Shaw filled with a liquid crystal material behave quite differently depending on the temperature at which the experiment is performed [121, 122, 123] For some range of temperatures, stable parabolic fingers are formed and do not tip-split as happens in experiments with isotropic fluids [124, 122].

The above examples clearly illustrate that anisotropy may play an important role in the Laplacian growth problem.

We have recently studied the range of applicability of the linear stability analysis in the problem of viscous fingering for isotropic fluids [125]. The results we obtained in [125] led us to propose a morphological phase diagram for the problem of viscous fingering using results from a linear stability analysis [126]. Knowing the importance of the role played by the anisotropy in the problem of pattern formation, we felt it was a worthwhile exercise to extend our previous results [125, 126] to a case where anisotropy in the viscosity is taken into account. A brief report of our results on the importance of

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1In all the system we described, one has to solve a Laplace equation on a moving boundary, the solution of which determines the local normal growth velocity of the interface, hence the name Laplacian growth.
anisotropic viscosities in the problem of viscous fingering for nematic liquid crystals is presented in this chapter.

8.2 Anisotropic Viscosities and Viscous Fingering in a Radial Geometry

This Chapter is a continuation of the work presented in appendices A and B and, as the notations and experiments considered here are the same, it is suggested that the non-experts refer to these appendices prior to reading Chapter 8.

Consider a Hele-Shaw cell of radius \( R_c \), with two parallel plates separated by a distance \( b \). The fluid between the two plates is assumed to be a liquid crystal material in its nematic phase. Air at constant pressure is injected into the cell through a hole at the center of one of the plates which pushes the fluid away, leaving behind a circular air bubble.

The plates are treated in such a way that the orientation of the director is normal to the plates before the injection of air (homeotropic alignment). In most cases the alignment imposed by the surface treatment is weak compared to the viscous torque \(^2\) produced by the fluid flow. The torque reorients the director in a radial direction in front of the moving air-fluid interface. The planar orientation of the director field is the origin of the anisotropy in this system. The viscosity coefficient along the director, in the radial direction, is \( \mu_r \), while it is \( \mu_\theta \) in the azimuthal direction \(^2\). If inertial terms are neglected in the Navier-Stokes equation, one derives a depth-averaged equation of motion for the velocity field \( \vec{v} \) of the fluid:

\[
\frac{\mu_r v_r \hat{e}_r + \mu_\theta v_\theta \hat{e}_\theta}{12} = \frac{b^2}{12} \left[ \hat{e}_r \frac{\partial P}{\partial r} + \hat{e}_\theta \frac{\partial P}{\partial \theta} \right]
\]  

(8.1)

where \( P \) is the pressure field. Assuming that the fluid is incompressible, one finds that

\(^2\)Since we are working in cylindrical coordinates, we should adopt the convention where the azimuthal angle is \( \phi \). We have preferred to use \( \theta \) in order to keep the same notation as in Appendix A, Equation A.6.
Chapter 8. Viscous Fingering

\( P \) obeys the following equation:

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial P}{\partial r} \right) + \frac{\alpha^2}{r^2} \frac{\partial^2 P}{\partial \theta^2} = 0. \quad (8.2)
\]

\( \alpha = \mu_r/\mu_\theta \) and is typically of the order of 1. In the case of an isotropic liquid, \( \mu_r = \mu_\theta \), and \( P \) obeys Laplace's equation. Notice that all the effects of the anisotropy of the liquid crystal material have been lumped into the variable \( \alpha \).

We extend our earlier work [125] and present here a linear stability analysis using the boundary condition with kinetic correction. The motivation for this is to check whether kinetic effects coupled to anisotropy in the viscosity introduces extra effects which are not present otherwise. Hence, we use the boundary equation A.3 rather than A.4. After finding the solution for a uniform bubble, we carry a linear stability analysis following the steps described in Equations A.6 to A.12.

The general solution of Equation 8.2 is

\[
P(r, \theta) = A \ln(r) + B + \sum_{m>1} (C_m r^\alpha + D_m r^{-\alpha}) \exp(im\theta). \quad (8.3)
\]

As in Appendix A, we seek a linear perturbative solution for the perimeter of the bubble in the form

\[
R_b(\theta, t) = R(t) \left[ 1 + \sum_{m=1}^{\infty} \epsilon_m(t) \cos(m\theta + \varphi_m) \right] \quad (8.4)
\]

where \( \epsilon_m \) is the relative amplitude of the pertubations at the air-fluid interface.

One can show that the evolution of the noise amplitude, \( \epsilon_m \), for the azimuthal mode \( m \) is given by the following set of equations:

\[
g_m = \frac{\dot{\epsilon}_m/\epsilon_m}{R_o/R_o} = -2 + \alpha m \left[ 1 + \frac{\nu \ln(1/x)}{1-\nu} - \frac{(m^2-1)(\ln(1/x))}{1-\nu} \right] \left[ \frac{m \sigma \nu}{1-\nu} \right] \ln(1/x) + \left( \frac{1-x^{2\alpha}}{1+x^{2\alpha}} \right) \quad (8.5)
\]

\[
\frac{\nu^{1/\gamma}}{1-\nu} = \frac{(7.6)^{1/\gamma}}{12} \frac{(\xi x - 1)^{1-1/\gamma}}{x^{2-1/\gamma} \ln(1/x)} \left( \frac{b}{R_c} \right)^{2-1/\gamma} \quad (8.6)
\]
$R_0(t)$ is the average increasing circular radius of the bubble. $x = R_0(t)/R_c$, $\xi = 4P_0R_c/(\pi \sigma)$, and $\gamma = 2/3$ in the viscous fingering problem [122, 125].

It is worthwhile noticing that the influence of anisotropy in the present problem manifests itself within a linear stability analysis. This is to be compared to the problem of dendritic growth [120] where the effect of anisotropy is introduced within an anisotropic surface tension correction. Anisotropic corrections in the surface tension enters in the problem only when the growth occurs away from the local interfacial normal which, to first order, is in a constant direction during the growth process. Hence, we have found that surface tension anisotropy does not come into consideration within a linear study.

The first mode to become unstable is $m = 2$, with all the modes $m > 2$ being stable. One notices that a circular interface is stable if

$$\alpha < 1/2; \quad \text{or} \quad \mu_\theta/\mu_r > 2. \quad (8.7)$$

The same anisotropy effect has been invoked to explain the absence of tip splitting in viscous fingering experiments in nematic liquid crystals [122].

In [125] we investigated the behavior of Equation 8.6 with no anisotropy ($\alpha = 1$) and no kinetic term ($v = 0$). Typically, the range of experimental parameters is such that $\xi x \gg 1$ and $m^* \approx O(10^1)$, where $m^*$ is the fastest growing unstable mode. Hence, if $\alpha > 1/2$, and the system is in the unstable regime, one can approximate $m^2 - 1/(\xi x - 1)$ by $m^2/(\xi x)$.

Let us assume that $m$ can be taken as a continuous variable. This is not a bad approximation for $m^* > 10$ [125]. By redefining $\alpha m = \bar{m}$ and $\alpha^2 \xi = \bar{\xi}$, one recovers the growth equation previously obtained by Buka and Palffy-Muhoray [122] for viscous fingering in an isotropic fluid. Hence, for $\alpha > 2$ and in the unstable regime, the present anisotropy does not introduce any new interesting physics in the problem of viscous fingering. As well, the morphological phase diagram obtained in appendix B would also apply in the
present anisotropic case if a new variable, $s$, was defined as $s = s/\alpha^2 = \pi\sigma/(4\alpha^2 P e R_0)$.

8.3 Discussion

The role of anisotropy has proven to be most important in the problem of Laplacian growth. Nematic liquid crystals are anisotropic systems in which the amount of anisotropy can be easily tuned by varying the temperature. At a microscopic level, the anisotropy of the viscosity coefficient in nematics arises from the nonseparability of the intermolecular interactions.

We have extended our previous analysis of the breakdown of a linear stability analysis in the viscous fingering problem by including anisotropy in the viscosity. We find that, unlike a case where anisotropy is included only in the surface tension, $\sigma$ [120], the anisotropy in the viscosity coefficients manifests itself in a linear regime. We find, however, that this correction is unimportant in the unstable regime since the viscosity ratio, $\alpha$, can be scaled out of the problem by redefining the fastest growing mode, $m^*$, and the effective driving force, $\xi$. 
Chapter 9

Conclusion and Avenues for Future Work

9.1 Conclusion

In this thesis, we investigated some effects that nonseparable interactions can have on the orientational behavior exhibited by liquid crystalline systems. In particular:

- We showed that the standard mean-field theory of nematic liquid crystals transforms an initial nonseparable pair potential, via a spatial averaging over the orientations of the intermolecular vector, into an effective separable potential. We then argued that the mean-field theory of nematic liquid crystals differs considerably from the ordinary mean-field approximation for lattice systems. This led us to re-examine, using Monte Carlo simulations, the physical meaning of the mean-field approximation in the context of nematic liquid crystals.

- We showed that the spatial averaging invoked in the mean-field theory of nematics must be dynamical and not static in order to lead to 'nematic-like' orientational ordering in a nonseparable system. We found that a quenched positionally disordered system, with a spherically symmetric center of mass distribution, leads to 'glassy-like' behavior in a system of particles interacting via nonseparable forces.
We found that a system of particles interacting via a nonseparable anisotropic van der Waals potential, where translation and rotation are allowed, displayed a noticeable increase of nearest-neighbor bond orientational correlation below the isotropic-nematic transition. This behavior was not observed for an 'equivalent' separable model. We showed that this phenomenon could be explained by invoking the phenomenon of induced bond orientational ordering observed in smectic-C films.

Our Monte Carlo results show that the nonseparability of the pair potential leads to induced bond orientational order in a nematic phase. As a by-product, they show that the coupling between the bond orientational field (BOF) and the molecular orientational field (MOF) invoked in Ginzburg-Landau theory of liquid crystals has its microscopic origin in the nonseparability of the pair potential.

The difference in behavior between the separable and nonseparable potentials we investigated led us to reinterpret the mean-field theory of nematic liquid crystals as an approximation which neglects the phenomenon of induced bond orientational order in these systems.

We showed that the presence of an underlying ordered BOF in nonseparable two-dimensional nematic liquid crystal models invalidates the interpretation of finite-size scaling analysis of these systems in terms of a simple model which neglects the presence of such BOF.

We presented results which show that the elastic response (Fréederickz transition) of tilted smectic materials subject to an external field can be substantially modified when the presence of a coupling between the BOF and the MOF in these systems is considered. In particular, we found that the sixfold symmetric BOF in a tilted hexatic phase can drive the Fréederickz transition first order if the BOF-MOF
coupling and the strength of the applied magnetic field are appropriately chosen.

- The coupling between the BOF and the MOF can induce 'structural' transitions in tilted hexatic liquid crystals. A preliminary microscopic model of such transition, the smectic-I to smectic-F transition, was proposed. This model has allowed us to isolate some microscopic parameters which are responsible for driving a transition from a smectic-I to a smectic-F. More importantly, we were able to argue, assuming that the tilt angle increases upon a decrease in temperature, why the smectic-F always occur at a lower temperature than the smectic-I phase.

- The anisotropy of the viscosity coefficients in nematics is also a manifestation of the nonseparability of the pair potential. We investigated whether anisotropic viscosities could modify our previous results obtained for the problem of viscous fingering in isotropic fluids. We found that, at least in the linear regime, the anisotropy in the viscosity coefficients can be scaled-out and does not introduce new effects in the problem of viscous fingering.

9.2 Avenues for Future Work

This section briefly present some possible extensions to the work presented in this thesis.

- In the context of orientational glasses, it would be instructive to extend our investigations of two-dimensional van der Waals and quadrupolar glasses [63] to three-dimensional systems to see if a true thermodynamical glass transition is observed. As well, the importance of the random symmetry breaking fields in such a three-dimensional system could be studied.

- In Chapter 4, we investigated the modified nonseparable anisotropic van der Waals potential with the particular choice: \( J = 1/2, \alpha = 0, \beta = 2/5 \) and \( \gamma = 4/5 \).
This choice of parameters led to a liquid crystalline phase with induced bond orientational order with rectangular symmetry. We expect this rectangular liquid crystalline phase to convert into a hexatic phase with a slight twofold distortion upon reducing $\gamma$, while keeping the value $J = 1/2$.

We find that the above transformation occurs in the ground state via a first order transition from a distorted triangular lattice (large pressure, small $\gamma$) to a rectangular lattice (low pressure, large $\gamma$). It would be interesting to verify if this first order transition is observable in the liquid crystalline phase. If the transition were observed, the Fourier coefficients of the BOF-MOF coupling could be evaluated and their behavior close to the transition compared with a Landau theory of the type proposed by Selinger and Nelson for the problem of transition among tilted hexatics [83, 84]. This would constitute the first direct microscopic test of this type of phenomenological Landau theory for liquid crystals with bond orientational ordering.

- It would be interesting to extend the calculations of the Fréederickz transition in tilted hexatics. In particular, a direct numerical investigation of the Euler-Lagrange equations and its comparison with the slowly varying approximation (SVA) would be useful.

- Finally, another line of study would be to improve the microscopic model smectic-I to smectic-F presented in this thesis. In particular, it would be interesting to repeat the same calculations, but for soft-ellipses. As explained in Chapter 7, soft-ellipses would allow a continuous transformation from the 'I-like' state to the 'F-like' state. This would provide another check of the theory of Selinger-Nelson for transitions among tilted hexatics.
Appendix A

Noise and the Linear Stability Analysis of Viscous Fingering

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A linear stability analysis of the Saffman-Taylor instability in a radial Hele-Shaw cell is presented. It is shown that the limit of validity of the linear stability analysis can be estimated without having to solve the problem to higher orders. The formation of fingers initiated by the presence of white noise is also examined. We find that, depending on the amplitude of the noise, the number of fingers that is observed as the limit of the linear regime is reached may differ significantly from the number of fingers predicted by the fastest growing mode.

Appendix A. Noise and the Linear Stability Analysis of Viscous Fingering

A.1 Introduction

Pattern formation in systems driven far from equilibrium has attracted much attention recently. One of the most studied processes is the so called diffusion-controlled growth which produces characteristic morphology in dendritic solidification\(^1\), viscous fingering\(^2\) and diffusion-limited aggregation (DLA)\(^3\)\(^1\). The detailed mechanism of pattern formation in the above examples is not quite understood but it is suspected that apart from the instabilities inherent in moving diffusive fronts, noise may play an important role. The following examples are illustrative. DLA is often considered as the noisy limit of diffusion-controlled growth processes\(^4\). Viscous fingering resembles DLA if the fingering occurs in a porous media\(^5\). The sidebranching activity observed in dendritic growth might arise from the presence of noise at the tip of the dendrite\(^6\), although other mechanisms may also be responsible\(^1\),\(^7\). Finally, the wobbles of the Saffman-Taylor fingers and the seemingly random patterns in viscous fingering may also be produced by the presence of noise\(^8\).

Unfortunately, the sources of noise in diffusion-controlled growth problems are usually not known. Noise may be produced by thermal fluctuations or by the presence of impurities in case of dendritic growth\(^1\). In two-dimensional viscous fingering\(^2\), on the other hand, irregularities in either the glass plates or in the aperture where the less viscous fluid enters may be the origin of randomness. Another source of noise, which may play a role in the pattern formation in liquid crystals is the anisotropy of ordered domains\(^9\). The above examples have been selected to illustrate that noise may appear in the mathematical description of the corresponding phenomena through i) initial conditions, ii) boundary conditions and iii) the dynamical equations. A systematic study of the above possibilities should, in principle, contribute to our understanding of unstable growth processes.

\(^1\)The reader should note that the reference numbers in the present appendix are local and the appropriate references appear at the end of the appendix and not in the main bibliography.
Appendix A. Noise and the Linear Stability Analysis of Viscous Fingering

Investigation of the sources of noise is hampered by the fact that diffusion-controlled growth problems are highly nonlinear and nonlocal making the experimental regimes rather inaccessible to calculations. Various schemes can be used to bridge the gap. For example, noise can be applied locally at the tip of the growing dendrite, the relevant randomness may be assumed to be present in the initial conditions or noise may be completely forgotten by using linearization procedures in conjunction with the assumption that the fastest growing mode determines the pattern. These phenomenological approaches are surprisingly successful in explaining experimentally observed facts. We believe, however, that the reason for their success is yet to be understood.

One would expect that investigating the earliest stage of growth of a given diffusion-controlled growth process and comparing the results with the predictions of a linear theory would provide important clues about the origin of the noise. Unfortunately, there are few experiments where such early linear regime has been clearly identified and investigated. Experiments performed in a linear geometry indicate that the local perturbations caused by the sidewalls initiate the pattern formation. The problems introduced by the sidewall interference effects make the interpretation of experimental results obtained in the linear geometry very difficult. These problems are eliminated in the circular geometry and an example where direct comparison between the linear theory and experiment may be possible is the viscous fingering experiment performed by Buka and Palffy-Muhoray. In this experiment, a stable circular interface is prepared as an initial condition in a radial Hele-Shaw cell. Then a stepwise increase in pressure is used to make the system unstable and the growth of perturbations on the interface is monitored. As a quantitative measure of the state of the system, the 'number of fingers' (number of throughs in the perturbation) is counted. Since the amplitudes of the perturbations are small at the initial stages of growth, Buka and Palffy-Muhoray assume that this regime may be described by using the linearized equations of motion. Making
then the additional assumption that the fastest growing mode determines the number of fingers, and using the surface tension as a fitting parameter, they obtain good agreement between the observed and calculated numbers of fingers.

The above experiment is conceptually simple and its analysis contains the ingredients used in the mathematical description of later stages of growth\textsuperscript{12,13}. Thus, we believe it is worth examining the assumptions underlying the analysis. The questions which naturally arise are as follows:

i) What is the extent of the regime where linearized equations can be used?

ii) Does the fastest growing mode determine the number of fingers?

Question ii) actually addresses the problem of the initial amplitude of various unstable modes and thus brings up the last questions:

iii) What is the role of noise in selecting the number of fingers? Can we deduce the noise amplitude from the experiment?

In this paper we address the above questions. In Section II, we present the model and derive the equations which govern the evolution of the unstable modes in the linear regime. A visibility parameter which measures how much structure is present at the interface is also introduced. Then, in Section III, we establish a criterion for the limit of validity of the linear regime using the fact that no inward motion of the interface is observed experimentally. Next (Section IV), the problem of the connection between the fastest growing mode and the number of fingers is examined. We find that the number of fingers is well approximated by the fastest growing mode only if the amplitude of the noise initiating the formation of patterns is sufficiently large. In particular, we deduce that the initial roughness of the bubble perimeter in Buka and Palffy-Muhoray's experiment\textsuperscript{15} should be on a lengthscale of $10^{-3} cm$. 

A.2 The Model

Pattern formation in hydrodynamics is a common phenomenon, and the Saffman- Taylor problem\textsuperscript{17} in which two fluids move in a narrow space between two parallel plates (Hele-Shaw cell) is a frequently studied example. In this paper we restrict ourselves to the radial version of the Saffman-Taylor problem\textsuperscript{12,13,15} and a Hele-Shaw cell of radius $R_c$ is considered. The plate separation is $b$ and the plates are assumed to be horizontal so that the gravity does not enter the problem. Air is injected into the cell at constant pressure through a hole located at the center of one plate. If inertial terms are neglected, the velocity field, $\mathbf{v}$, of the fluid parallel to the plates is given by

$$\mathbf{v} = -\frac{b^2}{12\mu} \nabla P$$

where $\mu$ is the viscosity of the fluid and $P$ is the pressure field. Equation A.1 constitutes Darcy's approximation. It is derived from the Navier-Stokes equation by assuming a parabolic flow profile with vanishing velocity at the plates and by averaging the velocity over the vertical direction. If the fluid is assumed incompressible, the pressure field obeys Laplace's equation

$$\nabla^2 P = 0 ,$$

(A.2)

and the boundary conditions to Equation A.2 are as follows. The applied air pressure in the bubble and the pressure at the outer radius of the cell are constant with $P_0$ being the difference between the two. The pressure jump across the air fluid interface, $\delta P|_a$, is given by a Gibbs-Thompson type relation which can be derived from an asymptotic analysis of the full set of hydrodynamical equations\textsuperscript{18}

$$\delta P|_a = \frac{2\sigma}{b} \left[ 1 + 3.80(Ca)^{2/3} \right] + \frac{\pi}{4} \sigma \kappa .$$

(A.3)

Here $\sigma$ is the surface tension, $\kappa$ is the curvature in the plane of the plates and the capillary number is given by $Ca = \mu v_n/\sigma$, where $v_n$ is the normal velocity of the interface.
Appendix A. Noise and the Linear Stability Analysis of Viscous Fingering

This boundary condition has been much discussed recently. Comparisons of experiments\(^{19}\) with numerical solutions\(^{20}\) the Saffman-Taylor problem seem to indicate that the wetting layer which produces both the kinetic term and the \(\pi/4\) coefficient in the curvature term may be important. Nevertheless, experimental results\(^{12-15,21}\) have been successfully analyzed by changing the exponent of \(Ca\)^\(^{13}\), by ignoring the \(\pi/4\) coefficient\(^{12,13,15}\) or by leaving out the kinetic term altogether\(^{12,15,21}\). Thus we feel that in our initial studies of the effect of noise it is adequate to neglect the kinetic term and use a mathematically simpler boundary condition\(^{22}\)

\[
\delta P|_s = \frac{\pi}{4} \sigma \kappa .
\] (A.4)

Equations A.1, A.2 and A.4 have a solution corresponding to a circular bubble of radius \(R(t)\). The time evolution of \(R(t)\) is given by

\[
\frac{dR}{dt} = \frac{b^2}{12\mu R} \left[ P_0 - \frac{\pi \sigma}{4R} \right] \frac{1}{\ln(R_0/R)} .
\] (A.5)

One can see that the bubble expands if the pressure difference \(P_0\) is larger than the pressure due to the surface tension \(\pi\sigma/(4R)\). The question of linear stability of the expanding bubble has been the subject of several studies\(^{12,13,15}\). In these studies, a perturbed circle of radius \(R_b(\theta, t)\) is assumed

\[
R_b(\theta, t) = R(t) \left[ 1 + \sum_{m=1}^{\infty} \epsilon_m(t) \cos (m\theta + \varphi_m) \right]
\] (A.6)

where \(\theta\) is the azimuthal angle, while \(\epsilon_m\) and \(\varphi_m\) are the relative amplitude and phase of the mode of wavenumber \(m\). Then, using a linearization procedure, one obtains the equations governing the time evolution of the perturbations

\[
\frac{\dot{\epsilon}_m}{\epsilon_m} = -2 + m \left[ 1 + \frac{m^2 - 1}{\xi x - 1} \ln(x) \right] F_m(x)
\]

\[
F_m(x) = \frac{(1 + x^{2m})}{(1 - x^{2m})}
\] (A.7)
where \( x = \frac{R(t)}{R_c} \) and \( \xi = \frac{4P_0 R_c}{(\pi \sigma)} \). Typically, \( P_0 \approx 1kPa, R_c \approx 10cm \) and \( \sigma \approx 10^{-2} Pa \cdot m \) so \( \xi \approx 10^3 - 10^4 \) and \( x \approx 10^{-1} \). It is, therefore, a good approximation to say that \( \xi x \gg 1 \) and \( x^{2m} \ll 1 \) for the modes that play some role in the formation of patterns at the interface. Using these approximations, Equation A.7 is integrated and we obtain

\[
\epsilon_m(t) = \epsilon_m(0) \exp(\Gamma_m).
\]

Here \( \Gamma_m \) is given by

\[
\Gamma_m = (m - 2) \ln \left( \frac{x}{x_0} \right) - \frac{m(m^2 - 1)}{\xi} \left[ \frac{1 + \ln(x)}{x} - \frac{1 + \ln(x_0)}{x_0} \right] \tag{A.9}
\]

and \( x_0 = x(t = 0) \).

Two numbers of importance can be derived from Equations A.7. There exists a fastest growing mode \( (m = m^*) \) that maximizes the growth velocity in Equation A.7. It has often been assumed\textsuperscript{12,13,15} that the number of fingers that are observed at the air-fluid interface is given by \( m^*(x) \). Another quantity which, we feel, may be a better measure of the number of fingers is the azimuthal number, \( m = m_i(x) \), of the largest-amplitude mode. These two numbers which will be discussed in Section IV are obtained from the following equations

\[
m^* = \frac{1}{\sqrt{3}} \left[ \frac{\xi x - 1}{\ln(1/x) + 1} + 1 \right]^{1/2} \tag{A.10}
\]

\[
\frac{\partial}{\partial m} \ln(\epsilon_m(0))|_{m=m_i} = \frac{3m_i^2 - 1}{\xi} \left[ \frac{1 + \ln(x)}{x} - \frac{1 + \ln(x_0)}{x_0} \right] - \ln \left( \frac{x}{x_0} \right) \tag{A.11}
\]

The linear regime is of course valid only for a short initial period \( (t < t_{nl}) \) beyond which nonlinear effects take over. We will discuss in the next Section how the limit of validity of the linear regime can be estimated. Assuming that \( t_{nl} \) is known, there still remains the question whether the pattern formed in the linear regime can be observed in a given
experiment. Thus it is useful to introduce a visibility coefficient, $V$, that gives a measure of the deviation from the circular form:

$$V^2 = \int_0^{2\pi} \frac{d\theta}{2\pi} \left[ \frac{R_b(\theta, t) - R(t)}{R(t)} \right]^2 = \frac{1}{2} \sum_m \epsilon_m^2(0) \exp(2\Gamma_m).$$ \hspace{1cm} (A.13)

One can detect the presence of structures (fingers) only if the resolution of the apparatus that is used to monitor the interface is greater than or equal to $V$. This is in complete analogy with the study of fringes in interferometry.

Finally, to complete the description of the model, we must discuss the origin of noise in the system in order to estimate the amplitude of the initial values of the perturbations ($\epsilon_m(0)$). The sources of randomness may, of course, be rather diverse. They may come, for example, from the irregularities in the interplane spacing ($b$). These irregularities could be mathematically described by introducing a multiplicative noise term in Equation A.1. Also, Equation A.2 would have to be modified and, furthermore, the pressure jump at the interface (Equation A.3) would be influenced. Similarly, modifications would be caused by thermal fluctuations or by fluctuations of the air pressure inside the bubble.

Equation A.7 does not contain any information about the above sources of noise since it was derived by assuming a uniform interplane spacing as well as constant pressure and temperature. Some of the noise effects, however, survive through the initial conditions $\epsilon_m(0)$. In the present work, we omit the dynamical sources of noise and assume that the effect of noise can be described through the initial amplitudes of the perturbations at the circular interface. The motivation for this assumption comes from the fact that the initial disturbances are exponentially amplified and one might expect that the role of later perturbations will be less significant. Some support for this assumption comes from the studies of diffusion controlled growth where DLA type structures were obtained by introducing randomness only in the initial conditions$^{10,11}$.

An estimate of the lower limit for $|\epsilon_m(0)|$ can be obtained in the following way. Assume
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that fluctuations on the initial bubble occur on all length scales and that their amplitude
is of the same order of magnitude as the lengthscale on which irregularities in the plate
spacing occur. The size of irregularities for optical quality glass plates cannot be larger
than \((\lambda/10)\) where \((\lambda)\) is the wavelength of the visible light \((\lambda \approx 500 \text{nm})\). Thus we have
\[\lambda/10 \approx \varepsilon_m(0)R(0)\]
for all \(m\) and consequently
\[\varepsilon_m(0) = \varepsilon \approx \frac{\lambda}{10 \sigma R_c} \approx \frac{5 \cdot 10^{-7} m}{10 \cdot 0.1 \cdot 5 \cdot 10^{-2} m} \approx 10^{-5}\] (A.14)

For the purpose of the discussion in the following sections, we shall call the noise pro-
ducing these equal amplitude perturbations white noise.

Another possible source of perturbation is the thermal noise. The amplitude of the
fluctuations in this case can be estimated by assuming equipartition of energy. The
change in the energy of the system due to fluctuations of the surface, \(S\), resulting from
the mode \(m\), is given by \(\delta E = \sigma \delta S \approx k_B T\) where, up to second order in \(\varepsilon_m\), \(\delta S\) can be
written as \(\delta S \approx \pi b R m^2 \varepsilon_m^2(0)/2\). As a result we find
\[\varepsilon_m(0) = \frac{1}{m} \sqrt{\frac{2 k_B T}{\pi \sigma b R}} \approx 10^{-6}\] (A.15)

where we used \(b \approx 10 \mu m\), \(R \approx 1 \text{cm}\), \(\sigma \approx 10^{-2} \text{Pa} \cdot \text{m}\) and \(T = 300 K\). Since the
thermal noise is at least an order of magnitude smaller than the noise coming from the
irregularities of the plates, we shall ignore its presence. It should be noted, however, that
in case of small \(\sigma\) (almost miscible fluids) the thermal fluctuations may play an important
role. We shall assume in the following that other types of noise would also have a white
noise spectrum and thus would only change the value of \(\varepsilon\) in Equation A.14.

A.3 Limit of validity of the linear regime

The range of validity of a linear stability type calculation can, in principle, be checked
by evaluating second and higher order terms in a perturbative expansion. Unfortunately,
the solution of the equations beyond the first order is very involved for pattern formation in diffusive growth processes. Thus, one would like to find a criterion that establishes the limit of validity of the linear regime without recourse to higher order terms. In order to see how such a criterion may be obtained, we consider the evolution of a bubble using the linearized equations of motion A.8, A.9. We choose typical values for both the initial reduced radius of the bubble \( x_0 = R(0)/R_c = 0.1 \) and the reduced pressure \( \xi = 7000 \). The amplitude of perturbations on the interface are set somewhat arbitrarily to the lower limit \( (\epsilon = 10^{-5}) \) calculated in Equation A.14 and the phases \( \varphi_m \) are chosen randomly from the interval \([0, 2\pi]\). The results shown in Figure A.1 were obtained by drawing the successive surfaces at equidistant values of \( x(t) \) (\( \delta x = 0.015 \)). Comparing Figure A.1 with an adaptation of a multiple exposure photograph taken during the injection of air into a Hele-Shaw cell filled with glycerin (Figure A.2), one can see some resemblance for small radii. It can also be observed, however, that in contrast to the experiments.
Figure A.2: Adaptation of Figure 3 of reference 12. The original figure corresponds to a multiple exposure photograph taken during the injection of air into a Hele-Shaw cell filled with glycerine.

(Figure A.2) the base of the fingers in Figure A.1 starts to move inwards as the radius becomes larger. This behaviour is an artifact of the linear approximation which should not be present in the exact solution of the equations. Thus the time, \( t_- \), when the radial velocity becomes negative for the first time gives an upper limit for the period (\( t_{nl} < t_- \)) in which the linear description is valid.

The quantity of experimental interest is actually not \( t_- \) but the breakdown radius \( x_- = x(t_-) \) at which the linear stability analysis ceases to be applicable. We have numerically studied how \( x_- \) varies as a function of the reduced pressure \( \xi \) at fixed \( \epsilon = 10^{-5} \) and \( x_0 = 0.1 \). Since the initial phases \( \phi_m \) are random, there are some fluctuations in the values of \( x_- \). The results shown by the solid curve in Figure A.3 were obtained by averaging over 500 growth processes. The breakdown radius may also be calculated by assuming that the evolution of the interface is determined by the mode with the largest
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Figure A.3: Reduced breakdown radius $x_0/x_0$ versus reduced pressure $\xi$ for $x_0 = 0.1$ and $\epsilon = 10^{-5}$. The solid curve describes the numerical results averaged over 500 different realizations of the random phases $\varphi_m$. The dashed curve was obtained by considering only the mode with the largest amplitude.

amplitude ($m_l$) (dashed curve in Figure A.3). This approximation leads to a fair agreement with the results obtained from the numerical solution. The partial disagreement can be understood from the Fourier spectra of the interface during the growth (Figure A.4). One finds that the spectrum is not particularly peaked at $m_l$; the modes $m_l \pm 1$ have an amplitude that is not less than 85% of the maximum amplitude. These satellite modes contribute to the r.m.s. inward velocity of the base of the fingers and thus they reduce the breakdown radius compared to what is predicted by considering the largest-amplitude mode alone.

We note here that the large-amplitude modes have relative amplitudes of the order of $10^{-2}$ at $x_-$. It has been observed in Ref.13 that predicting the morphological transition from DLA to dense branching morphology was beyond the scope of the linear theory and would require a full nonlinear study; our results suggest that such nonlinear effects are already important at the early stages of patterning and they should, in principle, be
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Figure A.4: Fourier spectra of the amplitudes of the perturbations $\epsilon_m(t)$. The solid line corresponds to time $t = 0$ and each successive curve, going upward, was plotted at equidistant values of $x(t)$ ($\delta x = 0.015$). The parameters are the same as in Figure A.1.

taken into account in perturbative calculations.

A.4 Number of fingers in the linear regime

A quantity which is observed experimentally is the number of fingers. The number of fingers at the breakdown of the linear regime ($N_f$) can be obtained numerically by counting the number of maxima in $R_b(\theta, t)$. The results from an average over 500 growth simulations are shown by the solid curve (squares) in Figure A.5.

Assuming that the growth is entirely controlled by the mode with the largest amplitude ($m_l$), one obtains the dashed curve (crosses) shown in Figure A.5. It is of interest to compare these results with the azimuthal number of the fastest growing mode at the breakdown radius ($m^*(x_-)$) and also with the initial fastest growing mode ($m^*(x_0)$). The results are shown in Figure A.5 by the chain-dashed (triangles) and dotted (diamonds) curves for $m^*(x_-)$ and $m^*(x_0)$ respectively. The agreement with the numerical results is
Figure A.5: Average number of fingers ($N_f$) observed at the breakdown of the linear regime ($x = x_-$) versus the reduced pressure $\xi$. The parameters are the same as in Figure A.1. The solid curve was obtained by averaging the numerical results over 500 different realizations of the random phases $\varphi_m$. The dashed (crosses) curve corresponds to the azimuthal number of the largest-amplitude mode $m_l$ evaluated at the breakdown radius $x_-$. The chain dashed (triangles) and dotted (diamonds) curves correspond to the azimuthal number of the fastest growing mode $m^*$ evaluated at $x_-$ and $x_0$ respectively.
good only for \( m_t \). The small discrepancy between \( m_t \) and \( N_f \) is again due to the role played by the satellite modes in the growth of the interface.

Figure A.5 was obtained using a noise amplitude \( \epsilon = 10^{-5} \). In this case the breakdown radius \( (x_-) \) is significantly larger than the initial radius \( (x_0) \). This implies that during the growth \( m^* \) and \( m_t \) which are initially equal but change at different rates have time to diverge from each other. For an increased initial noise level the limit of validity of the linear regime is reached earlier. One then expects that the difference between \( m^* \) and \( N_f \) is smaller and, consequently, the hypothesis that the fastest growing mode determines the observed number of fingers works better. Indeed, we find (Figure A.6) that both \( m^*(x_-) - N_f \) and \( N_f - m^*(x_0) \) decreases with increasing \( \epsilon \), and for the range of parameters \( \xi \) which are typical in experiments, the difference \( m^*(x_-) - N_f \) vanishes for \( \epsilon \geq 10^{-3} \).

We shall now try to use the above results to extract the noise amplitude in Buka and Palffy-Muhoray's experiment. In their setup the radius of the initial bubble is 0.5 or 1 cm and they use a relatively large pressure difference so that \( \xi \approx (1 - 4) \cdot 10^4 \). The change in the radius by the time the pattern is observed is of the order of 10%, i.e. \( x/x_0 \approx 1.1 \). The amplitude of the interface modulation is of the order of the change in the radius, thus the visibility coefficient (equation 12) has a value of \( V \approx 0.1 \). Assuming that the observations can be accounted for by the linear theory and that the noise initiating the pattern formation is a white noise \( (\epsilon_m(0) = \epsilon) \), we can use equation (12) to estimate the amplitude of the initial roughness of the interface \( \epsilon R(0) \). The result is \( \epsilon R(0) = (2 \pm 1) \cdot 10^{-3} \text{cm} \) where the uncertainty comes from the fact that neither \( x/x_0 \) nor \( V \) is known precisely and, consequently, we obtain different values for \( \epsilon \) for the various points which can be examined in Figure 2 of reference 15. Provided the initial roughness is caused by the variations in the plate separation \( (b) \), the above result means that the lengthscale on which the fluctuations in \( b \) occur is of the order of \( 2 \cdot 10^{-3} \text{cm} \). Note that the above calculation does not provide an estimate for the amplitude of the variations in
Figure A.6: Difference between the azimuthal number of the fastest growing mode and the average number of fingers ($N_f$) observed at the breakdown of the linear regime ($x = x_-$) versus the noise level $\epsilon$. The initial condition is $x_0 = 0.1$. The squares, triangles and crosses correspond to values of reduced pressure $\xi = 5000, 10000$, and $15000$ respectively. The upper part of the figure corresponds to the difference between the fastest growing mode at the average breakdown radius ($m^*(x_-)$) and $N_f$. The lower part of the figure corresponds to the difference between the initial fastest growing mode ($m^*(x_0)$) and $N_f$. The dashed lines are linear fits and are guides to the eye.
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Having estimated $\epsilon$, one may ask whether this estimate is consistent with the assumption that the pattern is formed in the linear regime. We find that for most of the experimental points one has just reached the limit of validity of the linear theory. The observation that the limit of the linear regime must have been reached is also clear from the fact that the size of the fingers is of the same order of magnitude as the increment in the radius. Another consequence of the $\epsilon R(0) = 2 \cdot 10^{-3} cm$ result is that the number of fingers is well accounted by $m^*$ (see Figure A.6). This provides a justification for Buka and Palffy-Muhoray's assumptions that the linear theory can be used and that their fingering experiment can be analysed in terms of $m^*$.

A.5 Final Remarks

Although noise is believed to play an important role in most systems where pattern formation occurs, a quantitative description is lacking. In this paper, we have shown how the properties of noise in growth processes may be investigated by studying an initial linear regime. It is hoped that the criterion we introduced to describe the range of validity of linear theories will be helpful in designing experiments where the linear regime can be investigated and the noise extracted.

A.6 Acknowledgement

The authors would like to thank B. Bergersen, A. Buka, G.M. Homsy, P. Palffy-Muhoray, and M. Plischke for helpful discussions and D.A. Reinelt for providing us with a preprint of his results prior to publication. One of us (M.G.) would like to acknowledge a scholarship from NSERC and FCAR as well the financial support and the hospitality of the members of the Institute of Theoretical Physics at the Eötvös University. This research
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was supported by the Hungarian Academy of Sciences through Grants No. OTKA 819 and 425.
A.7 References

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   A deterministic mechanism for the sidebranching activity in viscous fingering is discussed in J.S.Langer; Science, 243, 1150 (1989).


22. The term \(2\sigma/b\) can be incorporated in the overall pressure drop \(P_0\).

23. The quantity \(\epsilon_m(0)\) is, within the above description, analogous to the roughness factor introduced in the study of turbulent flow in pipes. See for example B. S. Massey; Mechanics of Fluids, (Van Norstrand Reinhold, U.K., 1983).


Appendix B

Stability Analysis of Laplacian Growth: Breakdown of a Linear Regime

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It is shown that the limit of validity of a linear stability analysis for diffusive-growth type problems such as viscous fingering and crystal growth can be estimated without solving the problem to higher orders. As an application, we derive a rule often used by experimentalists, namely that the linear regime breaks down when the amplitude and the wavelength of the perturbations are approximately equal. Assuming that noisy (DLA-type) growth occurs when no linear regime exists at all, a morphological phase diagram is drawn for viscous fingering.

To appear in the Proceedings of the 2nd Woodward Conference,
San José, November 17-18, 1989.
B.1 Amplitude-wavelength Relationship at the Breakdown of the Linear Regime

Stability analysis is a standard method in the theory of pattern formation. Typically, homogeneous or highly-symmetric solutions of a given problem can be found easily and their stability can be examined by linearizing the equations of motion with respect to small perturbations around the known solutions. This approach has been effectively used in determining both the limit of stability of a given state and the properties of the new state which appears at the onset of instability\(^1\). Unfortunately, a drawback to this approach is that unless the problem is solved to higher order in the perturbations, the range of applicability of the linear analysis is unknown.

This problem becomes crucial when the pattern formation is not a static phenomenon but results from the loss of stability as the system evolves towards an unknown state at a much later time. Examples are the initial roughening in solidification instabilities\(^2,3\) or the first stages of viscous fingering\(^4-8\). The difficulty in comparing the experimentally observed patterns with the results of a linear stability analysis is that a macroscopic pattern grows out of microscopic fluctuations in a finite time \(t_1\) after the system has lost its stability at \(t_0 = 0\). Thus, a direct comparison is possible only if the linear approximation is valid in the time interval \(t_1\). Information about the validity of the linear analysis can be obtained, in principle, by taking into account higher order terms in a perturbative expansion. Such calculations are rather involved, however, and they are rarely carried out\(^9\). Recently, we suggested\(^10\) a way out of this situation for irreversible growth processes and used our estimate of the validity of the linear regime to extract the noise amplitude in a viscous fingering experiment\(^6\). Here we show that our method can be used to derive a 'visual' criterion for the breakdown of the linear regime and,

\(1\)The reader should note that the reference numbers in the present appendix are local and the appropriate references appear at the end of the appendix and not in the main bibliography.
Figure B.1: The velocities of a planar front moving with velocity $v$ and perturbed by a sine wave of amplitude $A_k(t)$ are in the range of $[v + v_k, v - v_k]$ where $v_k = \dot{A}_k$. The linear regime breaks down when $v = v_k$.

Furthermore, assuming that the absence of linear regime is related to the onset of 'noisy growth', we propose a morphological phase diagram for viscous fingering.

The basic ingredient in our estimate of the validity of the linear regime is the observation that the normal velocity of a moving surface never changes sign in a process which is equivalent to an irreversible aggregation of particles. On the other hand, if a perturbation of wavenumber $k$ and amplitude $A_k(t)$ is added to an unstable interface moving with a velocity $v$ then there are places on the perturbed surface which move with velocity $v - v_k = v - \dot{A}_k(t)$ (see Figure B.1). A linear stability analysis yields $\dot{A}_k(t) = \omega_k A_k(t)$ and consequently an exponentially growing amplitude $A_k(t) = A_k(0) \exp(\omega_k t)$. Since generally $v$ and $\omega_k$ are constant or slowly varying functions of time, it is clear that the linear theory predicts an unphysical change of sign in the normal velocity of the surface at a time $t_-$ which can be calculated from the following condition:

$$v = \omega_k \cdot A_k(t_-)$$  \hspace{1cm} (B.1)
where $k^*$ is the wavenumber of the largest amplitude mode at time $t_-$. Within the linear stability analysis, $k^*$ is usually assumed to be of the order of the wavenumber of the fastest growing mode and is thus determined as the value which maximizes $\omega_k$. For diffusive growth problems, $\omega_k$ can be rather generally written as

$$\omega_k = vk[1 - f(k, \{\rho\})] . \quad (B.2)$$

Here the term $vk$ results from the instability inherent in moving diffusive interfaces² while $f(k, \{\rho\})$ describes the stabilizing forces such as the surface tension or kinetic effects and $\{\rho\}$ is a notation for the control parameters. The function $f(k, \{\rho\})$ is smooth in all the examples studied so far (in the simplest case $f(k, \{\rho\}) \approx k^2$), and the maximum of $\omega_k$ is well approximated by

$$\omega_k^* \approx vk^* . \quad (B.3)$$

Using this estimate, we arrive at the first result of our paper by rewriting the condition for the breakdown of the linear regime (1) in the following form:

$$k^*A_k^*(t_-) \approx 1 . \quad (B.4)$$

The above condition means that the amplitude of the dominating perturbation at the breakdown of the linear regime is of the order of the characteristic wavelength of the pattern. It should be noted that experimentalists have been using Equation B.4 as a rule of thumb for estimating the extent of the linear regime⁷.

### B.2 Breakdown of the Linear Regime and Morphological Phase diagram

The central idea here is that the value of $t_-$ which is found from Equation B.1 depends on the initial amplitudes, $A_k(0)$, of the perturbations. For large enough $A_k(0)$, the result is $t_- = 0$, i.e. no linear regime exists at all. Assuming that pattern formation
Appendix B. Breakdown of the Linear Stability Analysis of Laplacian Growth

is qualitatively different for \( t_\rightarrow = 0 \) and for \( t_\rightarrow > 0 \), one may draw a phase boundary separating the two morphological phases. The remaining problems are how to find the \( A_k(0) \)-s needed for the calculation and how to characterize the morphological phases.

The initial amplitudes \( A_k(0) \) are determined by the fluctuations (noise) present in the system. In general, it is not known which are the relevant fluctuations but there are a few cases, such as viscous fingering and crystal growth between closely placed parallel plates, where the noise is believed to come from the irregularities on the plates\(^{11-13} \). In these cases, \( A_k(0) \) is of the order of the characteristic wavelength (\( \epsilon \)) of the irregularities on the plates\(^{10} \). Thus we have \( A_k(0) = \epsilon \) and the phase boundary is obtained from the following equation

\[
v = \omega_k \cdot \epsilon .
\]

As an application of this equation, we studied viscous fingering in a radial Hele-Shaw cell\(^5 \) and used the simplest approximation in which the only stabilizing effect is the surface tension (\( \sigma \)). In this case, the control parameters are the noise amplitude (\( \epsilon \)) and the ratio of the surface tension to the excess pressure (\( p \)) driving the growth of the bubble (\( s = \sigma / p \)). The phase diagram we find is displayed in Figure B.2.

For small driving force (\( s > s_c = 1/6 \)), one finds that a circular bubble is stable against small perturbations. As \( s \) is decreased below \( s_c \), the bubble becomes unstable and this unstable growth can be specified further by examining the existence of a 'linearly' unstable regime. The dividing line between the presence or absence of a linear regime is obtained by solving equation (5) with the result shown by the solid line in Figure B.2. We call the region above the solid line 'noisy growth' regime. The reason for this name is that, due to the large noise amplitude, no linear regime exists in this region. Since it is known from experiments\(^{11,12} \) that large noise results diffusion-limited-aggregation (DLA) type growth in both viscous fingering and crystal growth, we speculate that this region
Figure B.2: Morphological phase diagram for viscous fingering in a radial Hele-Shaw cell. Both the noise amplitude ($\epsilon$) and the ratio of the surface tension to the excess pressure driving the growth of the bubble ($s = \sigma/p$) are measured in units of the radius of the bubble.
should be identified as a DLA regime. Another reason for the use of the expression 'DLA regime' is that viscous fingering in the zero-surface-tension limit \((s = 0)\) yields DLA structures\(^{14}\).

There exists a linear regime below the solid line in Figure B.2. The morphology in this region is not obvious to us but it is a distinct possibility that the structures characterizing this regime belong to the much discussed\(^{15}\) dense branching morphology (DBM). An admittedly not very strong argument for this identification is that a generalized linear stability analysis has been successfully used in explaining the results of experiments in which DBM is observed\(^{15}\). Thus if the DBM exists at all, it must lie below the solid line in Figure B.2.

The morphological phase diagram may actually be more complex than the one predicted. We believe, however, that the 'noisy growth' regime is a distinct part of the real phase diagram. A partial verification of this belief could come from an experimental investigation of the phase diagram for small \(s\) where the boundary separating the noisy regime from the others is given by \(\epsilon \approx \sqrt{3}\).

### B.3 References

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