Analysis of the dipolar lattice gas as a model for self-assembly in 1- and 2-dimensional systems

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Analysis of the Dipolar Lattice Gas as a Model for Self-Assembly in 1- and 2-Dimensional Systems

DISSERTATION

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* * * * *

The Ohio State University

1992

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To my escapes: Alex, Marie, Ruff, my parents, Bob & Jerry, and the Adirondacks.
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CHAPTER I

Introduction

1.1 Introduction to the Problem

Self-organization is known to occur in a variety of biological and chemical systems. Many aspects of daily life, from detergents to liquid crystal displays, are influenced by self-assembly of particles. Accordingly, a detailed knowledge of the forces behind such processes is of great interest both experimentally and theoretically, and is believed to have application to such diverse systems as ferromagnetic thin films, Langmuir monolayers, micelles, and membranes.

It is postulated that the interplay of long and short-range forces, of repulsions and attractions, plays a key role in the formation of "domains" which are aggregates of many particles. Examples of such domains include micelles or patches of spins oriented in similar directions in a magnet. A short-range attraction will induce formation of domains, while saturation of a long-range repulsion will limit the domain size. Furthermore, this picture seems to give a reasonable approxima-
tion to physical reality, whether one is dealing with exchange and magnetostatic interactions in a ferromagnetic thin film, or with van der Waal’s and dipolar forces in a Langmuir monolayer, systems which at first glance appear disparate.

Domain formation in ferromagnetic thin films has long been a topic of interest. Kooy and Enz experimentally studied domain formation in BaFe$_{12}$O$_{19}$ layers as early as 1960. They noted the conditions necessary to produce stable stripe and bubble phases, as well as an accompanying theoretical analysis of the effect of external field strength on domain widths for simple ordered stripe and bubbles domains. This topic became of special interest in 1967 when Bobeck introduced the notion of bubble domain devices for information storage and other applications. A large amount of time was invested experimentally in studies of domain size, shape, and mobility under various conditions for these systems. Theoreticians presented explicit expressions for the static properties of these domains with some degree of success, although for the most part attention was restricted to simple stripe and bubble phases. There was a renewal of interest in magnetic thin films in the 1980’s. Digital imaging techniques allowed more detailed study of a wider range of systems. Although hysteresis in experimental studies had been noted early on by Kooy and Enz, this was studied more deeply in this later period. More attention was paid to more complex structures, including the formation of non-equilibrium labyrinth phases and mixed (bubble and stripe) states. The concomitant theory was also expanded. Garel and Doniach devised a phase diagram for the dipolar
Ising ferromagnet using a Ginzburg-Landau approach in 1982, analyzing stripe, bubble, and uniform phases. Barker and Gehring\textsuperscript{9} also used a Ginzburg-Landau approach in 1983, adding the modification of finite wall width in the domain for the dipolar ferromagnet. Garel and Doniach also pointed out the analogy between domain formation as seen in magnetic thin films, and the structure and behavior of smectic liquid crystals. This analogy was further extended and solidified in the estimable work of Sornette.\textsuperscript{10} The liquid crystal analogy naturally drew attention to melting transitions in these systems, in particular with respect to the work of Brazovskii,\textsuperscript{11} and of Toner and Nelson\textsuperscript{12} on melting in 2-D layered systems. More discussion will be devoted to these issues in later chapters.

Langmuir monolayers have also been the topic of scientific investigation for many decades. However, in-depth knowledge of the phases found and the transitions between them was limited by the experimental techniques available. Reviewing the state of experiments before 1980, Knobler\textsuperscript{13} states, "These techniques are primarily thermodynamic in nature and therefore provide no direct information about the microscopic nature of the monolayer. Moreover, since the monolayer cannot be seen, the character of surface phases and the transitions between them can only be inferred." This picture changed in the early 1980's with the advent of fluorescence microscopy, as demonstrated by McConnell\textsuperscript{14,15} and Möhwald.\textsuperscript{16-27} In this technique, a fluorescent probe molecule is used to dope the amphiphile in the monolayer. Density differences and/or solubility differences between phases
are reflected by differences in the degree of fluorescence. As shown in Figure 1, this technique opened up the study of monolayers by showing the myriad phases available, and by providing more detail on the transitions between them. As in the case of magnetic thin films, theory swiftly kept pace with the rapid experimental advances. Once again it was postulated that long-range (i.e. dipolar) repulsions and short-range attractions play a key role in the formation of domains. Andelman, Brochard, and Joanny\textsuperscript{28} used mean-field theory to produce an often-cited phase diagram for a system of dipoles (Figure 2). McConnell\textsuperscript{29-41} was able to expand the theory somewhat by reducing the electrostatic energy term in the free energy expression to a line-integral. This allowed him to treat rather more complicated domain shapes than just the stripe and bubble phases most of the previous work was restricted to.

Not all of the work on amphiphile systems done previously has used long-range repulsions. If one ignores the spacial range of interactions and focuses only on attractions and repulsions of short range, what is the result? Early on, this was often the perspective chosen by those studying aggregation of amphiphiles. The typical structure of an amphiphile is a polar (hydrophilic) head group and a long hydrocarbon (hydrophobic) tail. Due to this, the classical picture of micellization has been seen "as a compromise between the tendency of alkyl chains to avoid contact with water and the strong affinity of the polar group to water."\textsuperscript{42}
Figure 1. Domains seen via epifluorescence microscopy. (Reference 18)
Figure 2. Mean-field phase diagram of Andelman, Brochard, and Joanny, where H, S, and H' denote the hexagonal, stripe, and inverted hexagonal phases, respectively. (Reference 28)
In the last 10 years, the literature has reported a marked increase in the number of attempts to simulate micellar behavior in both 2 and 3 dimensions. Results of these early simulations have at best been mixed. Jönsson et al.\textsuperscript{43} performed a series of molecular dynamics simulations on a single sodium octanoate micelle in aqueous solution. This work focused on aging an existing micelle, and therefore provided no information on the micellization process itself. More molecular dynamics work on single micelles was performed by Gruen,\textsuperscript{44,45} by Klein,\textsuperscript{46,47} and by O'Connell.\textsuperscript{48} Despite the fact that these simulations provided valuable insight on such topics as shape fluctuation and charge screening of a micelle of specified size, the constraints of the models used were such that again no useful information was obtained about the actual stability of the aggregate seen in these simulations. The number of monomers comprising the micelle is just guessed in this series of work, not deduced from the interaction model.

A second approach has been adapted which makes no \textit{a priori} assumptions about the microstructures allowed, unlike the aforementioned work. While studies in which micelle size and shape are completely unconstrained are much more difficult and, as a consequence, confined to simplistic models leaving out much of the molecular detail, they are providing much information on self-organization. Pratt's work\textsuperscript{49,50} is a very good example of this, a series of 3-D (three-dimensional) Monte Carlo simulations in which a group of amphiphiles (a head unit attached to a chain of tail units) is moving on a lattice. Interactions, which occur strictly
between nearest neighbors, are limited to tail-tail attractions, head-head repulsions, and a mild head-tail repulsion. It was quickly noted that this model is insufficient to reproduce typical micellization thermodynamics, due to the lack of a repulsive interaction acting on a large enough scale to limit aggregate size. While Care\textsuperscript{51,52} maintains that he is able to produce micellar behavior in a two-dimensional system by introducing only nearest-neighbor head-solvent attractions and tail-solvent repulsions, it may easily be shown that his Hamiltonian reduces to that of Pratt, making his result suspect. Larson\textsuperscript{53-55} has performed a very interesting set of simulations of a system containing oil, water, and amphiphile ($H_iT_j$ where work has been done using various numbers of head and tail units) at various concentrations. However, the results obtained in 2 dimensions are sensitive to lattice size and longer averaging, and conventional micelle formation still was not seen. Smit\textsuperscript{56-58} maintains that he has produced micellization in a series of molecular dynamics simulations on a system containing "oil-like" o-particles, "water-like" w-particles, and surfactant formed by stringing chains of o- and w-particles. All particles interact via Lennard-Jones interactions which have been truncated to be attractive ($2.5\sigma$ for o-o and w-w) or repulsive ($2.4\sigma$ for o-w). Micelles were apparently formed in systems containing longer chain amphiphiles ($W_2O_5$), yet not in systems containing shorter chains ($W_1O_1$). It should be pointed out also that the micelles formed in any of the successful simulations were more aspherical and less compact than the conventional picture.
Having seen that previous results have been only marginally successful, we wish to continue the study of self-organization through simulation and analytic work. The question asked throughout the course of this work is simple. What is the lowest common denominator, the set of interactions which will reasonably reproduce self-assembly behavior as seen in a variety of experimental systems? And once the Hamiltonian is chosen, how far will it take us?

1.2 Introduction to the System

Keeping in mind the results of previous studies, we choose to study the dipolar lattice gas.

\[
\frac{\mathcal{H}}{kT} = -J \sum_{(\mathbf{R}, \mathbf{R}')} n_{\mathbf{R}} n_{\mathbf{R}'} + \frac{A}{2} \sum_{\mathbf{R}, \mathbf{R}'} \frac{n_{\mathbf{R}} n_{\mathbf{R}'}}{|\mathbf{R} - \mathbf{R}'|^3} - \mu \sum_{\mathbf{R}} n_{\mathbf{R}} \quad (1.1)
\]

The $R^{-3}$ dipolar repulsion is chosen to mimic the long range interactions in thin ferromagnetic films and Langmuir monolayers. Variations of this Hamiltonian for 1-D (one-dimensional) systems are examined in Chapter 2. The nearest neighbor attraction mimics a van der Waals's interaction, and the third term is a chemical potential used to scale the density of the system. The occupation variables $n_{\mathbf{R}}$ of lattice site $\mathbf{R}$ take the values 0 or 1 for the lattice gas (or $\pm 1$ for the isomorphic spin lattice model). The above expression is written in terms of the dimensionless variables $A = \frac{A'}{kT}$, $J = \frac{J'}{kT}$, and $\mu = \frac{\mu'}{kT}$ to specify the strengths of the repulsive,
attractive, and chemical potential contributions to the energy, respectively. In this manner, temperature effects are included by scaling all three parameters.

Note that by setting $A = 0$, this model reduces back to an Ising model in the particle representation, a well-studied system which furnishes a convenient reference throughout the course of our study. The phase diagram for the Ising model is given in Figure 3. As stated, a long-range repulsion facilitates breakup of macroscopic phases into finite-size domains at temperatures $T < T_c$.

As stated in the previous section, there has been a considerable amount of work done on continuum versions of the dipolar lattice gas. While previous results are indeed of definite interest, work has for a large part been restricted to the basic domain shapes seen, and work on more complicated shapes has been tentative. The exception to this is the work of Desai et al., who have found complex domain morphologies in Langevin dynamics simulations on the continuum dipolar system. The mean field phase diagram for this system produced by Andelman, Brochard, and Joanny\textsuperscript{28} (Figure 2) has also been unquestioned for the most part.

In what follows, we give the results of study on the dipolar lattice gas both through analytic techniques and Monte Carlo simulation in both 1 and 2 dimensions. By this, we hope to show the applicability of the dipolar lattice gas to study self-assembly in real systems, and determine the phase diagram of the model.
Figure 3. Phase Diagram for the 2-D Ising Model in the temperature-magnetization (T-M) plane.
1.3 Introduction to Monte Carlo

The Monte Carlo method has been known for over one hundred years, and has been used to study everything from the random movement of neutrons in fissionable material to calculating the value of \( \pi \). As is common for powerful techniques, the concept is quite simple. Say we choose to work in the canonical ensemble (i.e. particle number, volume, and temperature are conserved). In general, some thermodynamic quantity of interest \( X \) may be evaluated from an ensemble average

\[
<X> = \frac{\int X(r^N) \exp[-\beta V(r^N)] dr^N}{\int \exp[-\beta V(r^N)] dr^N}
\]  

(1.2)

where \( X \) is a function of \( N \)-particle coordinates. In using the Monte Carlo method, a large number of configurations (say \( N \)) of the \( N \) particles is randomly generated. \( X \) is evaluated by replacing the integrals in the above equation by summations over the \( N \) configurations

\[
<X> \approx \frac{\sum_{n=1}^{N} X(n) \exp[-\beta V(n)]}{\sum_{n=1}^{N} \exp[-\beta V(n)]}
\]

(1.3)

where the label \( n \) denotes the \( n \)th configuration generated from the simulation, and \( V(n) \) is the total potential energy of configuration \( n \). This generic form of the Monte Carlo algorithm is highly inefficient due to the fact that a randomly constructed configuration will tend to have a small Boltzmann weight. In order to improve efficiency, some method of importance sampling must be introduced.

Importance sampling techniques ensure that regions of configuration space which contribute the most to the thermodynamic integral are visited most fre-
quentiy in our simulation. The quantity of interest is then calculated as

\[ < X > \simeq \frac{\sum_{n=1}^{N} X(n) \exp[-\beta V(n)]/W(n)}{\sum_{n=1}^{N} \exp[-\beta V(n)]/W(n)} \]  

(1.4)

where \( W(n) \) is the probability of generating configuration \( n \). If one samples properly on the Boltzmann distribution, then

\[ W(n) = \exp[-\beta V(n)] \]  

(1.5)

and our average finally becomes

\[ < X > \simeq \frac{1}{N} \sum_{n=1}^{N} X(n) \]  

(1.6)

This leaves one with the knotty problem of how to sample configuration space according to the Boltzmann distribution. One method, the Metropolis Monte Carlo algorithm, was proposed in 1953 and is a staple of simulationists everywhere. Simply put, a proposed move from configuration \( l \) to configuration \( k \) is accepted according to the probability distribution

\[ \text{min}[1, \exp[-\beta(V(k) - V(l))]]. \]  

(1.7)

In short, moves which decrease the energy of the system are always accepted, while those which increase the energy of the system are accepted with probability \( \exp[-\beta(V(k) - V(l))] \). There are other sampling schemes which fulfill the above criterion, but the Metropolis algorithm has been historically dominant, ostensibly due to the fact that the sampling is more efficient. A useful introduction to
Monte Carlo techniques and computer simulations in general is given by Allen and Tildesley.59

One difficulty in the interpretation of numerical simulation results lies in finite size effects. It is no secret that a reasonable simulation cell population ($O(100 - 10000)$ particles) is many orders of magnitude smaller than a real system, since a calculation on $10^{23}$ particles is well beyond the reach of all computers. It is common to run a series of simulations at several system sizes. From the trend in the results it is possible to get a determination of the magnitude of error introduced by the finite size of the system. For our two-dimensional system, we determined that results seen in a system of size $29 \times 34$ were likely to display marked finite size effects. These size effects appeared to be less prominent in the results of a $58 \times 68$ system, and increasing the system size yet again to $116 \times 134$ had only a minimal effect. Determining the appropriate system size, as well as the appropriate length of the run, can only be determined from experience. The ultimate goal of course is to ensure that the errors introduced from the finite size effect are no larger than the statistical uncertainties inherent in the method.

Related to this is the boundary conditions of the system studied. It is apparent that particles on the edge of an isolated simulation cell will experience different forces than those in the interior of the cell. If one is interested in studying properties of bulk matter then a simulation on a small number of particles in a cell with a hard boundary will over-emphasize surface effects and will not yield the true bulk result.
Surface effects can be mitigated by the use of periodic boundary conditions. As can be seen in Figure 4, in two dimensions, periodic boundary conditions effectively consist of replicating the simulation cell around itself an infinite number of times. Movement of a particle through one face of the cell is offset by movement of an image of that particle through the opposite face. We choose to make the simulation cell roughly square throughout the course of this study.

While remedying some errors, periodic boundary conditions (PBCs) may entail others. Order within the system may be artificially enhanced by PBCs. When working with a long-range potential, the interaction of a particle in the initial system with its own images in the surrounding boxes is far from negligible, and will tend to impose anisotropy on a system which should be isotropic. The periodicity of the supersystem will suppress spatial fluctuations with a wavelength larger than \(L\), the length of the cell. This is especially a problem when studying the properties of systems near a critical point where fluctuations will diverge.
Figure 4. Periodic boundary conditions. (Reference 59)
One dimensional systems occupy a place of special interest in statistical mechanics. Undeniably, their applicability to the real world is limited compared to 2- and 3-dimensional models, and their behavior is often markedly different. (A striking example is the 1-D Ising model, which does not undergo a phase transition at non-zero temperature.) However, 1-D systems are intrinsically interesting due to the fact that they are often exactly soluble, and techniques used to treat them often may be expanded to treat other systems.

To begin examination of the dipolar lattice gas, we analyze its behavior in 1-D. Even though the 1-D Ising model does not undergo a phase transition at finite temperatures, we will see that a 1-D spin model with competing repulsive and attractive interactions behaves much more like its 2- and 3-dimensional counterparts. This is because domain formation involves correlations over a limited length, while true phase transitions require ordering over the entire system.
Before considering the 1-D spin systems, we examine the droplet model, a common approximation scheme for statistical systems which exhibit aggregation of particles. Most treatments of micelle thermodynamics in the literature are variants of the droplet model. In 1-D, the predictions of the droplet model can be compared with the exact behavior of a statistical model.

2.1 Droplet Model

The droplet model was proposed almost simultaneously in 1939 by J. Frenkel and W. Band. Since then, it has been expanded and re-analyzed by Stillinger, Fisher, and Binder among others. The droplet model was initially proposed as a means of studying condensation phenomena. In the model, the gaseous phase is pictured as consisting primarily of single constituent particles (atoms or molecules), and smaller concentrations of “bound” particles, or clusters (dimers, trimers, ...). Condensation to the liquid phase is signalled by the sudden appearance of macroscopic clusters. The following assumptions are central to the model:

1. Only pairwise interactions between particles are taken into account (no 3-body or higher interactions).

2. The system is assumed to be of volume $V$, and boundary effects and excluded volume effects are neglected.

3. For now, the pair potential is cut off at some distance $b$. 
4. Interactions between particles in different clusters are neglected.

5. Effects of positionally-dependent external fields are neglected.

6. Fluctuations in shape and volume of the droplet are neglected. Only the contribution from the minimum energy shape (i.e. spherical droplet) is taken.

In the grand canonical ensemble, the partition function may be written as a summation over particle number \( N \)

\[
\Xi = 1 + \sum_{N=1}^{\infty} \frac{z^N}{N!} \int \cdots \int \exp[-\beta \sum_{i<j}^{N} v_{ij}] dr_1 \cdots dr_N
\]  

(2.1)

where \( z \) is the activity (\( \propto \exp(\mu/kT) \)) and \( v_{ij} \) is the pair potential, which depends on the distance between two particles, but not on their overall location within the system.

We would like to use the droplet model to simplify this expression, and from it obtain expressions for relevant thermodynamic properties such as pressure (\( pV = kT \ln \Xi \)). Since we considered the pair potential to have a cutoff \( b \), we may picture each particle as being surrounded by a sphere of radius \( b/2 \) (Figure 5). Two particles may be considered to belong to the same cluster if

1. their potential spheres overlap directly, or

2. they are connected by an unbroken sequence of overlapping potential spheres.

This means that we may describe any one configuration contributing to \( \Xi \) as a particular set of clusters \( \{n_s\} \), where \( n_s \) is the number of clusters of size \( s \). Equa-
Figure 5. Cluster connectivity in the droplet model.
tion 2.1 may therefore be written as a summation over sets of clusters.

\[ \Xi = 1 + \sum_{\{n_s\}} \int' \cdots \int' \prod_{s=1}^{\infty} \frac{1}{n_s!} \prod_{\alpha=1}^{n_s} \left( \frac{s^z}{s!} \right) \exp[-\beta \sum \nu(r_{ij}(\alpha))] \prod_{k=1}^{s} dr_k(\alpha). \]  

(2.2)

where we have introduced a product over cluster size \( s \) and a product over each cluster \( \alpha \) of size \( s \). The integrals over position \( \int' \cdots \int' \prod_{k=1}^{s} dr_k(\alpha) \) are constrained to meet the connectivity requirements congruent with the cluster distribution \( \{ n_s \} \).

This may not appear to be a great simplification, since the expression still contains an infinite sum and restricted integrals. However, using the stipulation of no interaction between clusters, and neglecting excluded volume effects, the partition function can be further simplified to

\[ \Xi = 1 + \sum_{\{n_s\}} \prod_{s=1}^{\infty} \frac{1}{n_s!} \prod_{\alpha=1}^{n_s} Q_s^0 z^s = \exp[\beta PV] \]  

(2.3)

where

\[ Q_s^0 = \frac{1}{s!} \int' \cdots \int' \exp[-\beta \nu_{ij}] dr_1 \cdots dr_s \]  

(2.4)

is the individual cluster partition function subject to the connectivity constraints of the cluster. The superscript \( ^0 \) signifies the assumption of non-interaction between clusters. Rewriting the equation 2.3 in terms of summations over cluster size, one obtains

\[ \Xi = 1 + (\sum_s Q_s^0 z^s) + \frac{1}{2} (\sum_\gamma Q_\gamma^0 z^\gamma)(\sum_\delta Q_\delta^0 z^\delta) + \cdots \]  

(2.5)

\[ = \exp(\sum_s Q_s^0 z^s) \]  

(2.6)

\[ = \exp(\beta PV) \]  

(2.7)
where the second term in the above expansion gives the contribution of systems containing a single cluster (of various sizes), the third term represents systems containing two clusters, etc. This leaves us with an expression for pressure as a summation over cluster size $s$

$$\beta PV = \sum_s Q_s^0 z^s. \tag{2.8}$$

In two dimensions, one final simplification is commonly made. The cluster partition function $Q_s^0$ includes an integration over all possible cluster shapes. If surface energy is included either explicitly or implicitly (such as the Ising model where the nearest-neighbor attraction facilitates formation of compact droplets, "spherical" droplets in 3-D) then the dominant contribution to $Q_s^0$ comes from the spherical droplet and we can approximate

$$Q_s^0 \approx Q_s^{0,\text{spherical}} = V \exp(-\beta v(r_{ij})_{\text{spherical}}) \tag{2.9}$$

and we are left with an expression which may be approximately calculated.

In a 1-dimensional lattice model, such as we study here, we will define all particles which are nearest neighbors or connected by chains of nearest neighbors as being in the same cluster. In that case, no approximation for $Q_s^0$ is necessary since only one shape is possible for any droplet. Also, since the interaction potential $v_{ij}$ depends only on distance and not on overall position on the lattice, the cluster partition function reduces to

$$Q_s^0 = V \exp[-\beta \sum_{i<j} v(r_{ij})] = V \exp(-\beta E_s) \tag{2.10}$$
where $E_s$ is the energy of a droplet of size $s$. In one dimension, the pressure then becomes

$$\beta P = \sum_{s=1}^{\infty} \exp(-\beta E_s) z^s = \sum_s \rho_s$$  \hspace{1cm} (2.11)$$

which is an easily computed quantity given the form of the interaction potential. Since $E_s$ grows with $s$, the expansion may be truncated. Particle density, another relevant thermodynamic property

$$\rho = \frac{\partial \beta P}{\partial \ln z} = z \frac{\partial \beta P}{\partial z} = \sum_{s=1}^{\infty} z \exp(-\beta E_s) z^s = \sum_s s \rho_s$$  \hspace{1cm} (2.12)$$

also becomes calculable. In the above expressions, we have defined a number density for clusters of size $s$.

$$\rho_s \equiv \exp(-\beta E_s) z^s$$  \hspace{1cm} (2.13)$$

These expressions will be shown to be extremely useful in putting the 1-dimensional lattice gas into perspective.

### 2.2 Analytic Studies of Micelle Model in 1-D

We choose to write the Hamiltonian for our system in one dimension in terms of four parameters

$$\mathcal{H} = -J \sum_{<i,j>} n_i n_j + A \sum_{i \neq j} \frac{n_i n_j}{|r_i - r_j|^\eta} - \mu \sum_i n_i$$  \hspace{1cm} (2.14)$$

where $A, J$ and $\mu$ all have their previous meanings. We include the parameter $\eta (\geq 1)$ in order to vary the spacial extent of the repulsions as well as the strength.
The micellization behavior of the system may be illustrated graphically by looking at the cluster distribution profiles ($\rho_s$ vs. $s$) and energy profiles ($\Delta F_s$ vs. $s$) shown in Figure 6. If one is in a region of parameter space where micellization is predominant, then the cluster distribution should show a maximum and the energy profile a minimum at some moderate cluster size $s_{max}$. If these extrema tend toward infinite $s$, this is taken as an indication of bulk phase separation in the droplet model, although some of the basic assumptions of the model are being violated at this point.

If one combines the above Hamiltonian with the droplet model profiled in the previous section, then explicit expressions for $\rho_s$ and $\Delta F_s$ may be obtained as functions of $A, J, \mu$, and $\eta$. In this way, we may determine how changing the various parameters affects $s_{max}$, the width of the cluster distribution, and other quantities typifying self-assembly. This also gives a ballpark estimate at which parametric values to perform simulations.

The most probable cluster size $s_{max}$ occurs where

$$\frac{\partial \rho_s}{\partial s} \big|_{s=s_{max}} = 0$$

or equivalently, where

$$-\frac{\partial \ln \rho_s}{\partial s} \big|_{s=s_{max}} = 0.$$  

(2.16)

From equation 2.13, it is trivial to see that $s_{max}$ occurs where

$$-\frac{\partial \ln \rho_s}{\partial s} \big|_{s=s_{max}} = \frac{\partial \beta E_s}{\partial s} - \ln z$$

(2.17)
Figure 6. Schematic cluster distribution profiles and energy profiles for a system displaying micellization. $\rho_s$ represents the number density of clusters of size $s$ and $\Delta F_s$ the energy change on increasing droplet size by 1. $s_{\text{max}}$ is the cluster size at which these quantities display a maximum and a minimum, respectively.
We have partitioned $E_s$ into attractive ($E_s^{att}$) and repulsive ($E_s^{rep}$) terms as given by the Hamiltonian (equation 2.14). The chemical potential term has been absorbed into $z$. This corresponds to the change in energy produced by adding a single particle to a droplet. The first term, $\frac{\partial \beta E^{att}_s}{\partial s}$, is a trivial quantity to calculate in 1-D. Since there are $(s - 1)$ nearest neighbor interactions for any droplet of size $s$, then

$$\frac{\partial \beta E^{att}_s}{\partial s} \rightarrow \Delta \beta E^{att} = \beta E^{att}_s - \beta E^{att}_{s-1} = -J$$

(2.20)

When interactions between droplets are neglected, the change in the repulsive term corresponds merely to the interaction of the new particle with every other site in the droplet.

$$\frac{\partial \beta E^{rep}_s}{\partial s} \rightarrow \Delta \beta E^{rep} = \beta E^{rep}_s - \beta E^{rep}_{s-1} = \sum_{i=1}^{s-1} \frac{A}{|r_i - r_s|^\eta}$$

(2.21)

For a simple lattice gas, this summation may be re-expressed in terms of the lattice spacing $a$

$$\Delta \beta E^{rep}_s = \sum_{i=1}^{s-1} \frac{A}{(na)^\eta}$$

(2.22)

$$= \sum_{n=1}^{\infty} \frac{A}{(an)^\eta} - \sum_{n=s}^{\infty} \frac{A}{(an)^\eta}$$

(2.23)

$$= \frac{A}{a^\eta} \left( \zeta(\eta) - \sum_{n=s}^{\infty} \frac{1}{n^\eta} \right)$$

(2.24)
where \( \zeta(\eta) \) is the Riemann zeta function. Using the Euler-Maclaurin expansion, the second summation may be approximated as

\[
\sum_{n=2}^{\infty} \frac{1}{n^\eta} \approx \frac{1}{(\eta - 1)(s - 1)^{\eta-1}} - \frac{1}{2(s - 1)^\eta} + \frac{\eta}{12(s - 1)^{(\eta+1)}} + \cdots
\] (2.25)

As \( s \) increases, this term becomes negligible and \( \frac{\partial \mathcal{E}^{\text{rep}}}{\partial s} \to A_\gamma \zeta(\eta) \). Equation 2.16 may be rewritten

\[
-\frac{\partial \ln p_a}{\partial s} \bigg|_{s=s_{\text{max}}} \approx -J + \frac{A}{a^\eta} \left[ \zeta(\eta) - \frac{1}{(\eta - 1)(s - 1)^{(\eta-1)}} \right] - \ln z = 0
\] (2.26)

and from this, one may obtain

\[
s_{\text{max}} \approx 1 + \left\{ \frac{A}{a^\eta} \left[ \frac{A}{a^\eta} \zeta(\eta) - J - \ln z \right] \right\} \left( \frac{1}{s_{\text{max}}} \right)
\] (2.27)

where we have truncated the Euler-Maclaurin expansion.

The cluster distributions \((\rho_a vs s)\) typically are rough gaussians, and the width of the peak may be estimated by the quantity

\[
\text{width} \leftrightarrow -\left( \frac{\partial^2 \ln \rho}{\partial s^2} \right)^{-1}
\] (2.28)

Physical systems undergoing micellization often display what is known as a critical micelle concentration (CMC). Below the CMC, no appreciable aggregation is seen. Above the CMC, the amphiphile begins to coalesce into micelles. This is a clearly definable point in many systems, and may be seen on a plot of \( \beta P vs. \rho \), as shown in Figure 7. At low densities, below the CMC, \( \beta P vs. \rho \) is nearly linear, as befits a nearly ideal system of individual particles where interactions are
Figure 7. Schematic $\beta P$ vs. $\rho$ for a system showing a critical micelle concentration.
minimized. The CMC shows as a break from ideality as aggregation begins to occur.

However, if one analyzes the resulting plot of $\beta P$ vs $\rho$ from the droplet model (Figure 8), the curve is quite rounded. There is no specific break point, and location of a definitive CMC is difficult. Furthermore, the linear "ideal" region appears almost non-existent. This roundedness does not seem to be affected by the parameters used, but seems intrinsic. This was explored by examining a series of models with different interactions.

If one considers a "free" droplet in which $E_s = 0$ for all $s$ (i.e. $A = 0, J = 0$), then

$$\beta P = \sum_{s=1}^{\infty} z^s \approx \frac{z}{1 - z} \quad (2.29)$$

and

$$\rho = z \frac{\partial \beta P}{\partial z} \approx \frac{z}{(1 - z)^2}. \quad (2.30)$$

As can be seen in Figure 9, the plot is rounded and the ideal region small. If a hard limit is placed on the cluster size allowed, that is

$$E_s = 0 \text{ for } s \leq L \quad (2.31)$$

$$= \infty \text{ for } s > L \quad (2.32)$$

the equations are modified somewhat, but the behavior is the same (Figure 9).

$$\beta P = \sum_{s=1}^{L} z^s \approx \frac{z(1 - z^L)}{1 - z} \quad (2.33)$$
Figure 8. $\beta P$ vs. $\rho$ for the droplet model. ($J = 8.5, A = 0.75, \eta = 1.0$)
Figure 9. $\beta P$ vs. $\rho$ for the "free" droplet (lower curve) and the "cluster in a box" model for $L=5, 10, 15$ (upper curve).
These two approximation schemes differ only at higher densities where larger clusters are important, and it is seen that the "cluster in a box" model (equations 2.31 and 2.32) crosses over to the "free" droplet model as $L$ increases. Attractions may
be included in the "cluster in a box" model very easily

$$\rho = \frac{\partial \beta P}{\partial z} \approx \frac{z [(1 - z^L) + Lz^L(z - 1)]}{(1 - z)^2}$$

(2.34)

where we have defined the variable $z = ze^{(-J)}$. In comparing these results to equations 2.33 and 2.34, it is obvious that adding attractions to the model scales in a factor of $e^{(-J)}$, while leaving the basic form unchanged.

By adding the repulsive interaction, we are back to the droplet model. We wish to see if the droplet model produces a "free droplet" region at very low densities. If this were the case, then for fixed $J$ and $\eta$, pressure-density plots in the very low density region should be identical for $A = 0$ and $A \neq 0$. It is obvious from Figure 10 that this is not so. From this we see that the form of the interactions used in the droplet model do have an effect, even at very low densities, yet they are not responsible for the "blurring" of the CMC. This seems to be inherent in the form of the expansions for pressure and density in 1-D.
Figure 10. $\beta P$ vs. $\rho$ from droplet model for $A = 0$ (lower curve) and $A \neq 0$ (upper curve), $J = 8.5, \eta = 1$. 
Using the analytic expressions for $s_{\text{max}}$ and peak width (equations 2.27 and 2.28), we tailored a cluster distribution and determined the corresponding values $A = 0.75$, $J = 8.5$, $\eta = 1.0$, and $z = 2.0$. Clustering here seems to occur in the same range of $J$-space as was found for the 2-D system (Chapter 5). If one examines the behavior of the droplet model in a lower $J$ region, a difficulty presents itself.

The CMC is consistently defined as the point where $s_{\text{max}}$ shifts from 1 to 2, or where clusters begin to predominate over monomers. If we use values of $J$ and $\eta$ consistent with physical systems, that is $J = 1$ and $\eta = 2$, we must use an extremely small value of $A$ to facilitate clustering. If equation 2.27 is used to find the value of $z$ consistent with $s_{\text{max}} = 2$, $J = 1$, $\eta = 2$, and $A = 0.0001$, then we find that $z = 0.3679$, and that the particle density (equation 2.12) is much greater than 1 (i.e. we are in an unphysical region.) This is the quandary one faces with the 1-D droplet model: clustering at lower values of $J$ does not appear to occur in a physically relevant region ($\rho < 1$).

2.3 Simulations of Micellization in 1-D

A series of Monte Carlo simulations were performed on a 1-dimensional lattice gas with the hamiltonian given by equation 2.14. As stated in the previous section, the values $J = 8.5$, $A = 0.75$, and $\eta = 1.0$ were chosen from equations 2.27 and 2.28. Particle number was not conserved throughout the course of the run to aid
in equilibration. A system of size $N = 300$ with periodic boundary conditions was used.

The simulation was performed at a range of $z$ values. Cluster distributions were obtained from the simulation and compared to the droplet model. Results agreed well in the very low density region ($\rho < 0.01$). At relatively low densities ($0.01 < \rho < 0.1$), the simulation results conform to the shape of the droplet model cluster distribution, but they differ in the peak height (and therefore in the total density).

From the simulation, an average value of the quantity $\zeta_z$ was obtained for each $z$, as well as an estimate of the standard deviation at each point. A plot of $\langle \zeta_z \rangle$ vs $z$ was obtained and fit with a third-order polynomial. The polynomial fit was then integrated to provide $\beta P$. A pressure-density plot for the droplet model and the fit to the simulation is given in Figure 11. From this, we can make several observations. The droplet model and the simulation results agree well in the very low density region. There is no outstanding CMC in either the simulation results or the droplet model. Neither is there a very large "ideal" region of $\beta P = \rho$.

If one defines the CMC as the point where $s_{\text{max}}$ shifts from 1 to 2, both the droplet model and the simulation place this at $z \approx 0.00044$ ($\rho \approx 0.01$).

We may conclude several things from this study.

1. It appears that in 1-D, the droplet model is a reasonable approximation to use at very low densities.
Figure 11. $\beta P$ vs. $\rho$ for droplet model (lower curve) and simulation (upper curve).
2. The droplet model and the simulations begin to diverge in the CMC region, as soon as clustering becomes important.

3. It is possible to induce self-assembly in 1-D systems, but only by using a large value of $J$.

4. From comparisons of cluster distributions, it seems that self-assembly is more sensitive to changes in $J$ than changes in $A$.

5. Finally, we note that the CMC is a much more elusive entity in 1-D than in 3-D, although there is a recognizable region in which clustering begins to occur.
CHAPTER III

Zero Temperature Results for 2-D System

Domain Energies of the Dipolar Lattice Gas

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We analyze the low-temperature behavior of the dipolar lattice gas in two dimensions. Analytic expressions for the energy of single circular, stripe, rippled stripe, and faceted domains for this system have been obtained in the continuum limit. We have also obtained energy expressions for regular arrays of these structures. These analytic results are compared to the results of direct lattice sums to show the applicability of these expressions in predicting equilibrium domain sizes at low temperatures. The energetics of stripe domain rippling are analyzed. Brief comparisons are also made to Monte Carlo simulation results on this system.

I. Introduction

Self-organization is known to occur in a variety of biological and chemical systems. The balance of forces entailed in self-organization results in a stunning variety of phases from monolayer domains to micelles to liquid crystalline arrays of large amphiphilic molecules. This topic is of great current interest from both an experimental and theoretical viewpoint.

dipoles with short-range attractive forces have long been suggested to support domain structures in ferromagnetic thin films.\textsuperscript{12-18} The short-range exchange interaction between magnetic dipoles induces formation of domains of aligned magnetic spins. The size of the domains is limited by the magnetoelastic repulsions between parallel dipoles. More recently, domain structure in Langmuir monolayers has been attributed to the competition between short-range van der Waals' attraction and dipolar repulsions.\textsuperscript{19} In general, repulsive forces can arise from intrinsic molecular electric moments or from double layer effects in the case of ionic surfactants.\textsuperscript{20}

A simple spin–lattice gas model can be applied to both the ferromagnetic film and Langmuir monolayer systems. In lattice gas language, the model we study consists of lattice gas particles with nearest-neighbor attractions and a long-range $\frac{1}{r^2}$ repulsion characteristic of parallel dipoles. The spin and lattice gas models are isomorphic, and results from one system can be directly applied to the other via a transformation between spin and occupation variables. Although this model has been taken as the starting point for some theoretical treatments of magnetic or monolayer systems, the statistical mechanical behavior of the dipolar lattice gas is largely unknown.

We have recently begun Monte Carlo simulations of the dipolar lattice gas, and we have verified that the model supports domain structures such as the stripe and disk domains shown in Figures 12 and 13.\textsuperscript{20} We have also noted features of the transition from disk to stripe domain structures that have not been appreciated previously.\textsuperscript{20} Monte Carlo simulations of spin systems become increasingly difficult at low temperatures because the number of accepted spin flips rapidly decreases. Moreover, long relaxation times are typically associated with large domain structures. Therefore, as domain structures become well established at low temperatures, longer Monte Carlo runs are needed to equilibrate these systems. In this and a companion article we delineate the low-temperature properties of the dipolar lattice gas, complementing the information available from Monte Carlo simulations at higher temperatures.

Our motivation is to understand a model of self-organization whose behavior is quite rich. While the model may potentially explain domain formation in monolayers, the experimental situation is too uncertain and the model too simple to make quantitative comparisons at this point. By unfolding the complex behavior of the model we hope to furnish reference points for comparison with experiment. Real phospholipid or fatty acid monolayers display at least two first-order phase transitions.\textsuperscript{1} Domain structure is often observed in conjunction with these transitions, and to what extent these are truly equilibrium domains is an open question in many cases.\textsuperscript{1} Möhwald and co-workers have demonstrated that aspects of domain morphology vary in accordance with an electrostatic repulsion model.\textsuperscript{21,22} and that this effect can even be exploited to physically manipulate monolayer domains with electrodes.\textsuperscript{21} In a number of instances, however, they have also shown that the number of domains is kinetically controlled, even if the domain shapes have reached some local equilibrium.\textsuperscript{21,22}

If long-range repulsions are relevant to monolayer domain morphology, then the dipolar lattice gas can be a qualitative model. The strength of the repulsion in the model is related to the difference in repulsion strengths between two phases in real systems. For example, in phospholipid monolayers dipole repulsions may explain observed domain structure near the gas to liquid-expanded transition\textsuperscript{11,12} as well as the liquid-expanded to liquid-condensed transition.\textsuperscript{13,14,19,23} In both cases the dipole density difference of the two coexisting phases would correspond to the repulsion parameter of the model. Of course, the dipolar lattice gas model

\textbf{Figure 12} Typical stripe configuration generated by Monte Carlo simulation of the dipolar lattice gas at $q = \frac{1}{r}, J = 9.5, \mu = 0.50$. The model is defined in section 2. The average density under these conditions is $\rho = 0.50$.

\textbf{Figure 13} Typical disk configuration generated by Monte Carlo simulation of the dipolar lattice gas at $q = \frac{1}{r}, J = 9.5, \mu = 0.65$. The model is defined in section 2. The average density under these conditions is $\rho = 0.22$.\textsuperscript{20}

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\end{thebibliography}
The main results of this paper are expressions for the energy of circular, stripe, and faceted domains as a function of domain size. From these expressions we derive the equilibrium properties of various stripe and disk domain phases at zero temperature. We have made repeated use of a technique introduced by McConnell and co-workers to include faceted polygonal domains. The dipolar lattice gas domains exhibit distinct faceting at low temperatures (Figures 12 and 13) due to line tension anisotropy arising from the underlying spin lattice. Faceting has been observed experimentally by Qui et al. and attributed to regions of distinct amphiphile chain tilt within a domain. We have considered interaction between faceted domains and given stable domain sizes for a periodic array of faceted domains. We have also studied the energetics of stripe rippling. In this paper we focus on energy expressions for various domain shapes, and their equilibrium size at zero temperature. In a companion work we consider phase transitions between the domain phases at zero temperature. We have determined that disk to stripe phase transitions in the dipolar lattice gas occur only for relatively small domains (maximum domain width ~ 20 nearest-neighbor distances). Above this length scale the stripe phase is always most stable. The energy balance between disk and stripe is quite delicate. Although the continuum expressions derived in this paper provide an accurate account of equilibrium domain sizes of a given geometry, they do not provide the accuracy necessary to describe phase transitions among the smaller domains. Therefore, some information from direct lattice sums was incorporated in the companion study of disk to stripe phase transitions at zero temperature.

Section 2 contains a description of the model used and outlines the method used to treat the dipole interaction energy. General forms for interdomain interactions for both stripe and disk phases are calculated in section 3. In section 4, we use the results of section 3 to derive the lattice energy for low-temperature stripe and faceted domains. We then calculate the dipole repulsion energy. These authors calculated the energy and repulsion energies of strength \( A \) which occur between all pairs of dipoles separated by one or more lattice spacings. By setting \( A = 0 \), the system reduces back to a lattice gas, or by the transformation \( n_p = 1/(4\pi \sigma^2 + 1) \), to an Ising model with nearest-neighbor interactions. To differentiate the underlying lattice on which the lattice gas or Ising variables \( n_p \) or \( n_\sigma \) are defined from the lattice of domain structures (Figures 14 and 16), we refer to the former as the "spin lattice." The temperature dependence of \( J, A \), and \( \mu \) is included explicitly as \( J(T) = J(0)/kT, A(T) = A(0)/kT, \mu(T) = \mu(0)/kT \), where \( J, A \), and \( \mu \) are independent of temperature. In this way, temperature effects may be included simply by scaling all three parameters of the system. It is also convenient to define a temperature independent variable which gives relative strengths of the attractions and repulsions \( \eta = A/J(=A'/J') \). This facilitates differentiating those characteristics of the system which depend on the balance of long- and short-range interactions from those which are also functions of temperature. In the grand canonical ensemble, the partition function for our system is given by

\[
Z = \sum \exp[-E(n_\sigma) + \beta \sum n_p]
\]

In what follows, we calculate the total energy of periodic arrays of stripe, circular, and faceted domains. To obtain analytic expressions for the complicated sums necessary to evaluate the Hamiltonian, we approximate these sums in the continuum limit by integrals. For example, the interaction between two domains, \( \mathcal{D} \) and \( \mathcal{D}' \), is written as

\[
A \sum_{\mathcal{D}} \frac{1}{|R - R'|} = \frac{A}{a^2} \int_{\mathcal{D}} \int_{\mathcal{D}'} \frac{1}{|r - r'|} dr dr'
\]

where \( a \) is the area per lattice site. In the continuum limit, the dipole strength per unit area is \( \sqrt{\sigma} \eta \). McConnell and Moy used Green's theorem to transform this double surface integral to a double line integral over the domain perimeters

\[
A \sum_{\mathcal{D}} \int_{\partial \mathcal{D}} \frac{1}{|R - R'|} = \frac{A}{a^2} \int_{\partial \mathcal{D}} \int_{\partial \mathcal{D}'} d\Gamma d\Gamma' - \frac{1}{|R - R'|}
\]

McConnell and Moy initially partitioned each domain into finite elements and applied this formula to each element. Because we use a different justification of the short-range cutoff of the dipole-dipole interaction, we start with a simpler expression. The above formula will also be used for calculating repulsions within a single domain, as will be seen. Numerical comparisons between continuum expressions and direct lattice sums are given throughout this work.

An important scaling property follows from the continuum expression for the dipole interaction energy, either eq 3 or 4. Let us change variables to reduced lengths that are scaled by the surface length \( \rho \) of the domains.

\[
A \sum_{\mathcal{D}} \int_{\partial \mathcal{D}} \frac{1}{|R - R'|} = \frac{A}{a^2} \int_{\partial \mathcal{D}} \int_{\partial \mathcal{D}'} |u - u'| + \rho R d\Gamma d\Gamma' - \frac{1}{|R - R'|}
\]

In the above expression, \( u \) and \( u' \) are reduced distances measured from the center of each domain, \( R \) is the distance between domains, and \( d\Gamma = a^2 d\Gamma \) is a reduced surface element along the domain perimeter. The dependence on domain size emerges as the factor of surface length \( \rho \) before the double line integrals. The rest of the expression depends only on the combination \( R/\rho \), which
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Figure 14 Perfect stripe configuration for a lattice gas, where \( R \) is the domain separation and \( l \) is the stripe width.

Figure 15 Dipole repulsion \( V(R) \) vs domain separation \( R \) for two parallel stripe domains of width \( l = 5 \) on a square lattice. Shown are the results of direct summation on the lattice (**) using techniques discussed in Appendix A, and results from eq 7 (- -).

is purely a function of the density. When all pair interactions are summed over a lattice of domains, the scaling property implies that the total dipole energy arising from interactions between domains is of the form

\[
V = \left( \frac{\text{interdomain}}{\text{repetitions}} \right) \left( \frac{\text{no. of domains}}{\text{length, } R} \right) \left( \frac{\text{function}}{\text{of density}} \right)
\]

(6)

The interdomain dipole interaction enters the theory as a density-dependent line tension. This scaling property has been noted for stripe domains by Keller, McConnell, and Moy.1 It is illustrated in the calculations for the stripe and dipole domains in the following sections.

3. Interaction between Domains

In this section we discuss the form of interdomain interactions. Nearest-neighbor interactions, being short range, do not contribute, so dipole–dipole interactions alone are relevant. We will study two specific cases, the stripe domain phase and the disk phase. Despite the fact that they have previously been given by McConnell and co-workers,14,17 we provide a brief derivation of the continuum formulas for the sake of completeness and to introduce the quantities we need to compare with numerical lattice sums.

Stripe Interactions. Consider the case of two parallel stripe domains of width \( l \) whose leading edges are separated by a distance \( R \). This is shown in Figure 14. If a sufficiently large system or periodic boundary conditions are assumed, each stripe has only two edges to treat explicitly. This means that there are four terms contributing to the line integral:

\[
V(R) = -\frac{4\pi^2}{\sigma^2} \int_0^l \int_0^l dx dy \left[ \frac{1}{(R^2 + x^2)^{1/2}} - \frac{1}{(R^2 + y^2)^{1/2}} - \frac{1}{(R^2 + y^2)^{1/2}} + \frac{1}{(R^2 + y^2)^{1/2}} \right]
\]

(7)

The leading contributions at large separation \( R \) are given as follows

\[
V(R) = \frac{2A}{\sigma^2} l_0 \ln \left[ \frac{R^2}{R^2 - l^2} \right]
\]

(8)

where \( l_0 \) is the length of each stripe in the actual lattice.

The leading term in this expression is the interaction which would arise if the two stripes were collapsed to two lines of dipoles (or "line dipoles" similar to a line of charge) of strength \( 1/\sigma^2 A \) per unit length and a distance \( R \) apart. All terms in this expansion depend upon \( l \) and \( R \), in the combination \( l/R \) and the expansion in \( 1/R \) is multiplied by the total surface length of the domain, \( 2l_0 \), an example of the form predicted in eq 6. In Figure 15 the above result is compared to the direct lattice sum for two stripe domains on a square lattice.

Disk Interactions. Consider two disk domains of radius \( r \) separated by a distance \( R \). If we define an angle \( \phi \) and \( \phi' \) to locate position on the perimeter of each disk, then eq 4 for the interaction between the two disks may be written as

\[
V(R) = -\frac{4\pi^2}{\sigma^2} \int_0^\phi \int_0^\phi' dx dy \sin \phi \sin \phi' \cos \phi \cos \phi' \left[ \frac{R^2}{R^2 - l^2} \right]
\]

(9)

Introducing the variable \( \beta = \phi - \phi' \) this integral reduces to

\[
V(R) = -\frac{4\pi^2}{\sigma^2} \frac{1}{R} \int_0^{2\pi} dx \cos \beta K_{\frac{\beta}{2}} \left( \frac{2}{R} \sin \left( \frac{\beta}{2} \right) \right)
\]

(10)

\[
= \frac{4\pi^2}{\sigma^2} \left[ \epsilon \left( \frac{2}{R} \right) + \frac{1}{4} \epsilon^2 \left( \frac{2}{R} \right) \right] + \ldots + \frac{8\pi^2}{\sigma^2} \left( \frac{2n + 2}{R^2} \right)^{2n+1} \left( \frac{2n + 2}{R^2} \right)^n \epsilon^{2n+1}
\]

(11)

where \( K[-] \) is the complete elliptic integral of the first kind.44

Collapsing the two dipolar disks to two point dipoles of total strength \( \sigma^2 A \) gives the leading term in eq 11. Also note that the energy is given as an expansion in \( 1/R \) times the surface length of the domain.

4. Lattice Energies

It is a relatively simple matter to convert the pair domain interactions found in section 3 into the total interdomain repulsive energy for an ordered system of stripes or disks. These two specific cases will be seen to be specific realizations of the general scaling relation for repulsions in an ordered lattice which was discussed at the end of section 2.

Stripe. In the previous section, we found the repulsive interaction between two infinitely long parallel stripes of width \( l \) separated by a distance \( R \). Consider a lattice system containing \( N_2 \) such stripes. If periodic boundary conditions are assumed,

density disks are separated by a distance \( a D \), then a hexagonal array of disks of radius \( r \). Given that neighboring disks of radius \( r \) are typically introduced in analytical work to force convergence at small \( r \). The path we will follow is to calculate the domain energies of a single disk and a single stripe. Despite the fact that the cutoff used in our work was motivated differently, our resulting expression for the self-energy of a disk will be seen to be equivalent to that derived by McConnell and Moy.13

The dipole interaction for a single domain in our original Hamiltonian is finite because self-interactions are omitted:

\[
V = \frac{A}{2} \sum_{R \in \mathcal{D}_{DA} \cap \mathcal{R}^2} \frac{1}{|R - R'|} \tag{17}
\]

We will reparametrize this sum. If one treats the rest of the system (i.e., everything outside of the domain \( \mathcal{D} \)) as a second domain \( \mathcal{D}' \), then the self-repulsion may be written as:

\[
V = \frac{A}{2} \sum_{R \in \mathcal{D}_{DA} \cap \mathcal{R}^2} \frac{1}{|R - R'|} - \sum_{R \in \mathcal{D}_{DA} \cap \mathcal{R}^2} \frac{1}{|R - R'|} \tag{18}
\]

where \( C_1 \) has been introduced to denote the interaction of a single particle with the rest of the system, and there are \( n_p \) particles in our domain. \( C_1 \) depends on the geometry of the spin-lattice (i.e., square, triangular, etc) and on the nearest-neighbor distance. \( C_1 \) is \( L_0 \) times the cube of the nearest-neighbor distance, where the \( L_0 \) are defined in eq 16 and Table 1.

Now we assume that the domains \( \mathcal{D} \) and \( \mathcal{D}' \) are separated by a distance \( \delta \). If \( \delta \to 0 \), then the integral in the above equation will diverge. Also, the integral approaches zero as \( \delta \) approaches infinity. Some judiciously chosen finite value of \( \delta \) should reproduce the initial lattice sum. Furthermore, this "magic" cutoff distance should lie in the range \( 0 < \delta < \delta (\text{lattice spacing}) \) and be independent of \( \delta \). The dipolar repulsions become increasingly significant. The system responds by creating fewer domains and separating them further to minimize this repulsive interaction. The scaling property states that this effect enters the theory as a density-

![Image](image-url)
A single stripe domain of width $l$ in the continuum limit is separated from the rest of the system by a distance $\delta$. Scaling as the perimeter with the correct sign is easily introduced by making the distance between $D$ and $D'$ smaller than the lattice spacing, which is our procedure. In the following, we treat $\delta$ as a phenomenological parameter. We consistently find that the value of $\delta$ that best reproduces the exact lattice sums is about $1/l$ of the nearest-neighbor distance.

Dipole Energy of Stripes. Consider the case of a single stripe domain of width $l$ separated from the rest of the system by the cutoff distance $\delta$. Instead of evaluating the double surface integral in eq 18, we use eq 4 to write it as a time integral.

$$\phi(l) = \frac{4}{2} \mu C_1 + 2 \sqrt{\gamma} \int_0^l \int_0^\gamma \frac{1}{(l^2 + y^2)^{1/2}} \left(\frac{1}{l} + \frac{1}{y}\right) \, dy$$

where we have assumed that the stripe is of length $L$, and runs parallel to the $y$ axis. The above integral may be evaluated in closed form and the self-energy of a single stripe domain is found to be

$$\phi(l) = \frac{4}{2} \mu C_1 + 2 \sqrt{\gamma} \int_0^l \int_0^\gamma \frac{1}{(l^2 + y^2)^{1/2}} \left(\frac{1}{l} + \frac{1}{y}\right) \, dy$$

As $l \rightarrow \infty$, the second term in eq 22 decreases in importance and $\phi(l)$ approaches the bulk limit $AL_\gamma C_1/2\gamma$. We determined numerical estimates for the value of $\delta$ that correctly describes the approach to the bulk limit from the direct lattice sums on stripe domains. Equation 22 was solved for $\delta$ as a function of $\phi(l)$ and the right-hand side of eq 23 was tabulated as a function of $l/\delta$ using $\phi(l)$ from direct lattice sums. This data was fit to a quadratic polynomial in $l/\delta$ and the limit as $l/\delta \rightarrow 0$ was estimated in this manner. The results of this procedure are given in Table 2 for a square and triangular spin-lattice. Even though the parameter $\delta$ is obtained in the $l \rightarrow \infty$ limit, the data in Figure 10 shows that eq 22 is accurate down to small values of $l$.

Dipole Energy of Disks. The dipole energy of a single disk domain is calculated in an analogous manner to the stripe domain work shown above. Consider a circular domain containing $\pi_0$ lattice sites surrounded by a cutoff distance $\delta$, as shown in Figure 10. Here the line integral reduces to a single term, the interaction between two nested disks of diameter $r$ and $r'$, respectively, where $r' = r + \delta$.

$$\phi(r) = \frac{4}{2} \mu C_1 + 2 \sqrt{\gamma} \int_0^r \int_0^{\gamma(r')} \frac{1}{(r^2 + r'^2)^{1/2}} \, dr'$$

where $\gamma$ is the base of the natural log, and we have made use of the fact that $r' = \gamma(r + \delta)$. The parameter $\delta$ was estimated for approach to the bulk limit from the direct lattice sums on stripe domains. Equation 22 was solved for $\delta$ as a function of $\phi(l)$ and the right-hand side of eq 23 was tabulated as a function of $l/\delta$ using $\phi(l)$ from direct lattice sums. This data was fit to a quadratic polynomial in $l/\delta$ and the limit as $l/\delta \rightarrow 0$ was estimated in this manner. The results of this procedure are given in Table 2 for a square and triangular spin-lattice. Even though the parameter $\delta$ is obtained in the $l \rightarrow \infty$ limit, the data in Figure 10 shows that eq 22 is accurate down to small values of $l$.

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$$\phi(r) = \frac{4}{2} \mu C_1 + 2 \sqrt{\gamma} \int_0^r \int_0^{\gamma(r')} \frac{1}{(r^2 + r'^2)^{1/2}} \, dr'$$

where $\gamma$ is the base of the natural log, and we have made use of the fact that $r' = \gamma(r + \delta)$. The parameter $\delta$ was estimated for
A disk domain of radius $r$ has a surface length of $2\pi r$ and contains $\pi r^2/e$ lattice sites. The energy associated with a single disk domain is given by

$$E_{\text{disk}} = \frac{\pi r^2}{2e} (AC_1 - qJ) + 2\pi r \gamma J - \frac{2\pi r^2}{e} \ln \left( \frac{8r}{4e^2} \right)$$

(28)

6. Equilibrium Domain Structures at Zero Temperature

In the limit as $T \to 0$, the disordered stripe and disk domains order into perfect arrays of stripes and disks. One may calculate the domain size and separation which will minimize the energy of the system as the temperature approaches zero. Phase transitions among these phases are treated in a companion work.24

Stripes. We consider a system of $N_s$ stripes of width $l$ separated by a center-to-center distance $\sigma_0$. The energy of the system is given by the sum of the internal energies of each stripe, as derived in section 5, plus the lattice energy or interaction energy between stripes, as given in section 4:

$$E_S = N_S E_{\text{stripe}} + E_{\text{interaction}}$$

(29)

We define a scaled energy per lattice site

$$\epsilon_S = \frac{E_S}{lN_{\text{lat}}}$$

where $N_{\text{lat}}$ is the total number of sites in the spin-lattice. Here we utilize the scaled interaction variable $q = \lambda/l$ which was introduced in section 2. By minimizing $\epsilon_S$ with respect to $l$ at constant density, we pick out the dominant stripe configuration in the canonical ensemble. The width $l_{\text{min}}$ of the minimum energy stripe domain satisfies the equation

$$ln \left( \frac{l_{\text{min}} + \delta}{l_{\text{min}}} \right) = \frac{\gamma J}{\lambda} - \frac{\gamma J^2}{\lambda^2} - L_2(q) = 0$$

(31)

which for $l_{\text{min}} \gg \delta$ has the approximate solution

$$l_{\text{min}} = \frac{\gamma J}{\lambda} \exp \left( \frac{\gamma J^2}{\lambda^2} + L_2(q) + 1 \right) - 2$$

(32)

Note that the line tension $\gamma$ always appears in combination with $L_2(q)$, illustrating how the contribution of interdomain dipole repulsions appears as a density-dependent line tension $L_2(q)$. Substituting the exact eq 31 for $l_{\text{min}}$ back into the energy expression (30), the minimum stripe energy is found to be

$$\epsilon_S = \frac{1}{l} \left( \frac{AC_1}{2} - qJ \frac{\lambda}{\gamma J} - \frac{2\pi r^2}{e} \ln \left( \frac{8r}{4e^2} \right) - L_2(q) \right)$$

(33)

The zero-temperature stripe width as a function of density and repulsion strength $\lambda$ is shown in Figure 20. The general trend to large domain size with increasing density is the result of the density-dependent line tension $L_2(q)$. This result has a physical interpretation. As the density increases, interdomain repulsions become increasingly significant. The system responds by creating fewer domains and separating them further to minimize this repulsive interaction.

Disks. The above process can be repeated for a system of $N_D$ disk domains of radius $r$. The total energy of the system is now

$$E_D = N_D E_{\text{disk}} + E_{\text{interaction}}$$

(34)

and the scaled energy per lattice site becomes

$$\epsilon_D = \frac{1}{l} \left( \frac{AC_1}{2} - qJ \frac{\lambda}{\gamma J} - \frac{2\pi r^2}{e} \ln \left( \frac{8r}{4e^2} \right) - L_2(q) \right)$$

(35)
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Figure 20 Equilibrium stripe width $l_{\min}$ vs density $\rho$ as obtained from eq 32. Results are shown for several values of repulsion strength $\eta$ for both the square lattice in panel a (top) and the triangular lattice in panel b (bottom). Increasing repulsion between particles causes smaller domains to form. Interdomain interactions induce larger domain size with increasing density.

For this case, one finds that the minimum disk radius $r_{\min}$ at constant density and the corresponding energy are

$$r_{\min} = \frac{\beta \sigma^2}{8} \exp \left[ \frac{\gamma \sigma^2}{\eta} + \mathcal{E}(\rho) \right]$$

$$\mathcal{E}(\rho) = \rho \left\{ \frac{1}{2} (\eta C_1 - q) - \frac{2 q}{\sigma r_{\min}} \right\}$$

The effect of interdomain repulsion on disk domain size is shown in Figure 21.

Comparing eqs 33 and 36, we see that domain stability is inversely related to the minimum energy domain length scale $l_{\min}$ or $r_{\min}$ at constant density.

7. Faceted Domains

Faceted domains occur in the dipolar lattice gas because domain edges aligned with the spin-lattice have lower surface energy. On the square lattice, edges in the $x$ and $y$ directions are most stable. There are three minimum energy orientations for a surface on the triangular spin lattice, each $120^\circ$ from each other, as is evident for the domains in Figure 19. In continuous, that is, "off-lattice" models, faceting would occur only if the domains were crystalline.

Figure 21 Equilibrium disk radius $r_{\min}$ vs density $\rho$ as obtained from eq 36. Results are shown for several values of repulsion strength $\eta$ for both the square lattice in panel a (top) and the triangular lattice in panel b (bottom). See the caption to Figure 20 for a discussion of the results.

We are not aware of experimental observations of faceted domains in either thin ferromagnetic films or Langmuir monolayers. Therefore, the analysis of circular domains given in the preceding sections is most appropriate to these physical systems. The clear faceting of lattice gas domains (Figure 19) provides the motivation for the analysis of faceted domains given in this section.

Dipole Energy of Faceted Domains. We consider regular polygonal domains with $m$ edges and $m$ corners. Much of our analysis can be performed for arbitrary $m$, although the important cases are expected to be square domains ($m = 4$) on the square spin-lattice and hexagonal domains ($m = 6$) on the triangular spin-lattice. Our starting point is eq 18 for the dipole repulsion energy within a single domain. This expression applies equally well to faceted and smooth-edged domains. As in section 5, we assume that the inner and outer domains, $\mathcal{S}$ and $\mathcal{S}'$, are separated by a distance $\delta$ chosen to correct for the divergence of the continuum expressions. Equation 4 is employed to convert eq 18 to a double line integral.

$$V \approx \frac{\Delta}{2} \mathcal{E}(\mathcal{S}) + \mathcal{D} \mathcal{S}' \mathcal{D}' \mathcal{S}' \mathcal{D} \sum_{l=1}^{m} \int_{\delta}^{\infty} d\alpha' d\alpha \rho' - \rho$$

(37)

The line integrations for a hexagonal domain are shown in Figure 22. Equation 37 contains sums of double line integrals over straight line segments $\delta$, which are the $m$ edges of the domains.
as examined, the dimensionless quantity expected from the arguments in section S. For the cases we have with numerical data, there is no real gain from evaluating possible to determine analytically for complicated domain shapes. In a few cases it is in favor of the number of particles in the domain

\[ d = \left[ \frac{4n \tan (\pi/m)}{m} \right]^{1/2} \]  

(40)
to obtain the final result.

\[ V(u) = \frac{n C_A}{2} \left[ \frac{4nm \tan (\pi/m)}{\sigma^3} \right]^{1/2} \ln \left( \frac{2 \pi}{\delta} \left[ \frac{4n \tan (\pi/m)}{m} \right]^{1/2} \right) \]  

(41)

Our previous result for circular domains, eq 26, is recovered by taking \( m \to \infty \). The prefactor of the logarithm in eq 26 is reproduced when \( \tan (\pi/m) \) is replaced by \( \pi/m \) in the large \( m \) limit. Evidently \( B \) approaches \( \pi^2/2m \) as \( m \to \infty \).

Dipole Interactions between Faceted Domains. The exact expressions for dipole repulsion between faceted domains depend on both the distance between domains and on their mutual orientation. Since the behavior of faceted domains must approach the less complicated circular domain limit as \( m \to \infty \), results that quantify the departures of faceted domains from circular domains are desirable. We therefore focus on the limiting behavior of the dipole interaction when the faceted domains are separated by distances greater than their own dimensions.

An asymptotic expansion for the domain–domain interaction in inverse powers of the separation between domain centers is obtained by Taylor expansion of the denominator of the right-hand side of eq 3. We denote the vector from the center of mass of \( D \) to \( D' \) as \( \mathbf{R} \). The vectors \( \mathbf{w} \) and \( \mathbf{w}' \) point from the center of mass of domains \( D \) and \( D' \), respectively, to \( \mathbf{r} \) and \( \mathbf{r}' \). Developing \( \mathbf{r}' - \mathbf{R}^{-1} = |\mathbf{R} + \mathbf{w}' - \mathbf{w}|^{-1} \) in powers of \( \mathbf{w}' - \mathbf{w} \), we obtain

\[ V(R) = \frac{\alpha}{\sigma^3} \int d\mathbf{w} \int d\mathbf{w}' \left( R + \mathbf{w}' - \mathbf{w} \right)^{-1} \]  

(42)

Terms linear in \( \mathbf{w} \) or \( \mathbf{w}' \) vanish when integrated over domains \( D \) or \( D' \), respectively. Also, odd powers of \( \mathbf{w} \) and \( \mathbf{w}' \) do not contribute when the number of facets of the polygonal domain has a center of symmetry (\( m \) even). Equation 42 can be further simplified by eliminating all terms linear in the \( x \) and \( y \) components of \( \mathbf{w} \) and \( \mathbf{w}' \), which also vanish when distances are referred to the center of masses, and also by replacing simple integrals over the domain by \( n \), the number of particles in the domain. Equation 42 then reduces to

\[ V(R) = \alpha^2 \int \frac{1}{|\mathbf{R}|} + \frac{3}{|\mathbf{R}|^3} + 5(R_1 - \mathbf{R}_j) \Delta \mathbf{w} + \ldots \]  

(43)

where

\[ \mathbf{R} = \mathbf{R}/|\mathbf{R}| \]  

(44)

and

\[ \Delta \mathbf{w} = \frac{1}{2\alpha} \int d\mathbf{w} \mathbf{w}' \]  

(45)
The parameter \( \Delta \mathbf{w} \) can be evaluated for a polygon of arbitrary number of sides

\[ \mathbf{w}' = \frac{n \pi}{4m \tan (\pi/m)} \left[ 1 + \frac{1}{2} \tan^2 \left( \frac{\pi}{m} \right) \right] \]  

(46)
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Equation 43 provides the leading terms of the domain-domain repulsion, is valid for both faceted and unfaceted domains, and allows us to contrast the behavior of faceted domains to circular domains. Because we have conducted numerical and analytical studies on the triangular spin-lattice where hexagonal domains are favored, we quote some special results for $m = 6$. We can compare the behavior of hexagonal domains to circular domains. The parameter $\Delta_d$ is zero for hexagonal domains, and of course $\Delta_d$ vanishes for the circular domain. From eqs 43 and 46 the leading terms of the domain–domain interaction are found to be

\[
V(R) = \frac{A_n}{|R|^3} \left( 1 + \frac{5}{4\sqrt{3}} \frac{n_e}{|R|^2} + \cdots \right)
\]

(47)

for hexagonal domains. The corresponding results for circular domains are

\[
V(R) = \frac{A_n}{|R|^3} \left( 1 + \frac{9}{4\pi} \frac{n_e}{|R|^2} + \cdots \right)
\]

(48)

Interactions between hexagonal and circular domains of equal particle number are identical at leading order $|R|^3$, both are isotropic through order $|R|^4$, and also the numerical coefficients are quite close at this level.

The dipole energy of a hexagonal array of hexagonal domains (analogous to eq 14 for circular domains) is

\[
E_{\text{hex}} = N \frac{A_n}{\sigma^3} (6d E_f(p))
\]

(49)

where $6d$ is the perimeter of the hexagonal domain

\[
E_f = \frac{\sqrt{3}}{2} \left( \frac{\rho}{2} \cos \frac{\theta}{2} + \frac{1}{2} \frac{\rho}{2} \sin \frac{\theta}{2} + \cdots \right)
\]

(50)

and the lattice sums $E_f$ defined in eq 16 are given for a triangular lattice in Table 1.

Equilibrium Faceted Domain Structures at Zero Temperature.

Equilibrium faceted domain shapes are obtained by adding bulk and surface terms

\[
\frac{q}{2} + m \Delta_f
\]

(51)

which account for the nearest-neighbor attractions to the intra- and interdomain dipole repulsions energies derived above. The values of $q$ appropriate for edges oriented in the minimum energy directions of a square and triangular lattices are $\frac{1}{2}$ and $\frac{1}{3}$, respectively, the same as for stripe domains oriented along low-energy directions.

The total energy of an array of faceted domains is

\[
E = N \left( \frac{n C^2}{2} - m \Delta_f \frac{\rho}{\sigma^2} \ln \left( \frac{2d}{\rho} \right) \frac{q}{2} + m \Delta_f + \frac{A_n}{\rho^3} m d E_f(p) \right)
\]

(52)

where $N_f$ is the total number of faceted disks in the lattice. The above expression is manipulated into a form that is most convenient for minimization at constant density by using a reduced energy,

\[
\epsilon = E/N, \quad \text{where } N \text{ is the total number of spin-lattice sites. It is also convenient to use the variable }
\]

\[
h = \frac{d}{2 \tan \left( \frac{\pi}{m} \right)}
\]

(53)

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Figure 23. Equilibrium faceted radius $h_{\text{eq}}$ vs density $\rho$ as obtained from eq 36 for a hexagonal domain on a triangular lattice. Results are given for several values of repulsion strength $q$. The contribution of interdomain interactions $E_f(p)$ is taken to be that of circular domains which contain the same number of particles as the faceted hexagonal domains. The accuracy of this approximation is discussed in section 7.

the perpendicular distance from an edge to the center of an $m$-sided polygon. In the limit of large $m$, $h$ becomes the radius of a circular domain. Using the relations,

\[
\eta = \frac{\rho}{N} \quad \text{and} \quad \rho = \frac{n N}{\eta}
\]

(54)

eq 52 is transformed to

\[
\epsilon = \frac{1}{2} \left( \frac{2n}{2} - \frac{\rho}{\rho} - \frac{2}{Q} \ln \left( \frac{2d}{\rho} \right) - \frac{q}{Q} - \frac{E_f(p)}{\rho} \right)
\]

(55)

Minimizing with respect to $h$ holding the density fixed we find

\[
h_{\text{eq}} = \frac{B \rho h}{4 \tan \left( \frac{\pi}{m} \left( \frac{2n}{2} - \frac{\rho}{\rho} - \frac{2}{Q} \ln \left( \frac{2d}{\rho} \right) - \frac{q}{Q} - \frac{E_f(p)}{\rho} \right) \right)}
\]

(56)

and by substitution of the result back into eq 55 for $\epsilon$

\[
\epsilon_{\text{eq}} = \frac{1}{2} \left( \frac{2n}{2} - \frac{\rho}{\rho} - \frac{2}{Q} \ln \left( \frac{2d}{\rho} \right) - \frac{q}{Q} - \frac{E_f(p)}{\rho} \right)
\]

(57)

Results that show how the dimensions of faceted hexagonal domains are affected by repulsion strength $q$ and the density $\rho$ are shown in Figure 23.

8. Rippling of Stripe Domains

In our simulations we observe that stripe domains occasionally exhibit a rippled texture at finite temperatures. Here we show that stripe rippling is a thermal excitation of the system; rippling always costs energy. We also show that there is no preferred wavelength for ripple excitations. The energy of ripple excitations decreases monotonically with increasing ripple wavelength.

Since the ripples observed in the simulations are faceted we consider the zig-zag ripples with sharp corners shown in Figure 24. (Smooth sinusoidal ripple contours could also be treated by the methods used below.) Our convention is that the axis of the rippled stripe lies in the $y$-direction. The rectangular unit cell has dimensions $l_x \times l_y$, where $l_x$ is the ripple wavelength. The ripple amplitude is $a$. When $a = 0$, the stripe width $l$ (Figure 14) is equal to $l_x$.

The double line integrals for the intra- and interstripe dipolar interactions (eqs 4 and 10) for an infinite periodic array of rippled stripes appear too complicated to obtain a closed form expression.
as is possible for less complicated domains. We therefore turn
to the method used by Kooy and Enz\textsuperscript{21} to calculate domain
energies. While their method is numerically convenient, it unfor­
tunately does not give closed form analytical results like the
techniques developed by McConnell and co-workers.

Consider particles of periodic dipole density \( \psi(r) \)
interacting via a pair potential \( v(r) \). The sum in eq 58 is over all
reciprocal lattice vectors. Then the energy per unit volume of the
system is given as

\[
E/V = \frac{1}{2} \sum k|\psi(k)|^2 v(k) \tag{59}
\]

provided that the potential has a Fourier transform

\[
v(r) = \int \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k}\cdot\mathbf{r}} v(k) \tag{60}
\]

The \( r^3 \) dipolar interaction cannot be transformed, so we must cut off the interaction at short distances in some manner. We took \( v(r) \) to be the interaction between two finite dipoles in which the charges are separated by a distance \( h \) because its Fourier transform has a simple analytical form.

\[
v(r) = 2 \left[ \frac{1}{r} - \frac{1}{\sqrt{r^2 + h^2}} \right] \tag{61}
\]

\[
v(k) = \frac{4\pi}{k} (1 - e^{-kh}) \tag{62}
\]

The parameter \( h \) is the cutoff parameter. To make the mag­
nitude of the dipole energy agree with previous sections of this work, \( \psi(r) \) is normalized so that

\[
\psi(k=0) = \rho \left( \frac{AC_2}{4\pi \varepsilon h} \right)^{1/2} \tag{63}
\]

\[
\rho_0 = \rho \phi_0 \tag{64}
\]

\( \psi(k) \) for the faceted stripe is given in Appendix B. Fourier series results (eq 59) for zero ripple amplitude are compared with the line integral continuum theory and direct lattice sums in Figure 28. It can be seen that the Fourier series expression does not describe the lattice sum results quite as well as the continuum theory of sections 2–7. For example, if we constrain the cutoff \( h \) to reproduce the leading contribution to the dipole energy for large stripe widths, proportional to \( \ln(l_t)/l_\alpha \), we find that the behavior for small widths is not reproduced as well as by the line integral expression. A value of \( h \) can be found which gives small
errors for all stripe widths, but for which the asymptotic behavior

is not exactly reproduced. Presumably, better agreement with lattice sum results could be obtained with Fourier series expressions with a different cutoff than the one prescribed in eq 61. We have not searched for an improved cutoff.

Stripe domains would spontaneously ripple at zero temperature if the minimum of the total system energy occurred with \( \alpha \neq 0 \).

The energy arising from short-range attractions in the lattice gas depends on the density \( \rho \) and the interface length per area

\[
\frac{1}{l_\alpha} \left[ 1 + \left( \frac{\rho}{\rho_c} \right)^{1/3} \right]^{1/4} = \frac{1}{\alpha_0} \tag{65}
\]

where \( \alpha_0 \) is an effective lattice constant that reduces to \( a_0 \) (section 4) for unrippled stripes. By holding \( \rho \) and \( \alpha_0 \) constant, the contribution from short-range interactions is fixed. Minimization with respect to \( \alpha \) and \( l_\alpha \), with \( l_\alpha \) given by eq 65 at constant \( \alpha_0 \), only depends on the behavior of the dipolar energy. If the dipolar energy has a minimum at \( \alpha = 0 \) under these conditions of constant particle number and interface length, then we can be sure that rippled stripes are never favored and incorporation of short range
attractions will not modify this conclusion.

This is the case for faceted ripples, as shown in Figure 28 for \( \alpha_0 = 10, \rho = 1/2 \). The dipolar energy is shown to be an increasing function of ripple amplitude \( \alpha \) for several ripple wavelengths. Similar results are obtained at other values of \( \alpha_0 \). Since \( l_\alpha \) and \( l_t \) are related to each other by eq 65, increasing \( \alpha \) at fixed \( l_\alpha \) means that \( l_t \) also increases. The increase in interface length caused by the growth of \( \alpha \) is compensated by an increase in unit cell area (wider stripes) to keep the total interface length constant. It is not surprising that this leads to an increase in total dipole energy.

Next we specifically consider the type of faceted ripples that arise on a triangular spin-lattice. Interfacial lines of low surface energy can be tilted from each other by either 60° or 120° on the triangular lattice. Hence faceted rippled stripes in which the segments are tilted by either 30° or 60° from the axis of the stripe could be observed. So far we have only found faceted ripples in

\[\text{Figure 28. Faceted ripple domain propagating in } y\text{-direction, as examined in section 8. Labeled are the amplitude } \alpha, \text{ the ripple wavelength } l_\alpha, \text{ and the length of the unit cell in the } x\text{-direction, } l_\alpha. \text{ The ripple angle } \theta_\alpha \text{ can either be } 30^\circ \text{ or } 60^\circ \text{ for faceted rippled stripes on a triangular spin-lattice.}\]

\[\text{Figure 29. Comparison of Fourier series and continuum theory estimates of the dipolar repulsion energy per lattice site vs } \ln(l_t)/l_\alpha \text{ for unrippled stripes. Fourier series results are given by the solid lines for } \alpha = 1.314 \text{ and } \lambda = 1.6. \text{ The dotted line is the continuum result, eq 22. The thin lines indicate the limiting slope of the continuum theory for large domain sizes, or small } \ln(l_t)/l_\alpha. \text{ Exact lattice sums (6) are evaluated using techniques discussed in Appendix A. The Fourier series expression with } \lambda = 1.314 \text{ matches the asymptotic slope of the continuum theory, while a slightly larger value of the cutoff, } \lambda = 1.6, \text{ comes closer to the exact lattice sums.}\]
Density. At higher density the stripe width increases as shown at zero temperature, are predicted by eq 32 and the data in Table 2 to have perpendicular stripes with about 2.9 rows at low density, 4.8 rows at half coverage. (Of course, we obtain a fractional number of rows because the continuum theory does not recognize that the lattice gas domains are composed of discrete particles). We conclude that the width of the stripe domains has not changed significantly upon heating to the conditions of Figure 12 although capillary excitations and topological defects are visible. Also, we note that the angle of the stripes with respect to the underlying spin-lattice is a feature that is very slow to equilibrate in our simulations. Annealing the simulated system until the stripes are aligned with one of the three low-energy directions of the triangular lattice may affect the results. Other features, such as the overall morphology (i.e., stripe vs disk or some intermediate structure), are quite reproducible. The disk domain phase shown in Figure 37 equilibrates rather easily in simulations.

The simulations show that the disk phase is stable at low density and the stripe phase is found at 50% coverage is approached. Phase transitions between disk and stripe phases are treated in a companion work.43 Those results will allow us to decide whether the system undergoes phase transitions upon heating from zero temperature to the conditions of Figure 12 and 13. Analysis of the simulations also confirm that the disk domain lattice disorders at higher temperature and that the system of Figure 37 lies in the disordered region. These issues and the interesting behavior exhibited in simulations between the conditions of Figures 12 and 13 are reported in a separate publication.46

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**Appendix A: Lattice Sums**

In various situations we require the energy of infinite periodic two-dimensional arrays of particles interacting via the $\alpha$ parallel dipole potential. These situations include calculation of the first line of Table 1, and the exact periodic stripe domain energies shown in Figure 37. In this section we give the formula we used to obtain these sums. Energies for single-stripe domains or for the interaction of just two stripes were found by simplification of the techniques presented here.

The sum of the interaction energy of one tagged dipole with all other parallel dipoles in a periodic array converges quite slowly, roughly as

$$2\pi \int \frac{d \theta}{\rho} \sim R_{\text{max}}^{-1}$$

### Domain Energies of the Dipolar Lattice Gas

**Figure 20.** Dipolar repulsion energy per lattice site vs ripple amplitude $\alpha$ as obtained from Fourier series at $\alpha_{\text{max}} = 10$, $\alpha = 1/2$, for a variety of ripple wavelengths $\lambda$.

which the segments are tilted by $30^\circ$. We call the tilting angle $\theta_{\text{ne}}$ (Figure 24). Specifying constant $\theta_{\text{ne}}$ means that

$$l_{\text{dipole}} = l_{\text{perp}} \cos \theta_{\text{ne}}$$

The constraint of constant surface length implies that

$$\alpha_{\text{eff}} = l_{\text{perp}} \cos \theta_{\text{ne}}$$

The family of rippled stripes with constant $\alpha_{\text{eff}}$ and $\theta_{\text{ne}}$ is characterized by just one parameter which we take to be $\alpha$.

A sequence of stripes with constant $\alpha_{\text{eff}}$ and $\theta_{\text{ne}}$ is shown in Figure 27. Infinite $\alpha$ corresponds to the unrippled limit. In this limit the bends are diluted by long lengths of straight stripe domains with periodicity $l_{\text{dipole}} = \alpha_{\text{eff}}$. As the bends become more frequent (as $\alpha$ and $l_{\text{dipole}}$ decrease together according to eq 66), the dipole energy increases, as shown in Figure 27. Finally, in the limit of vanishing $\alpha$ the system behaves as an unrippled stripe once again, but this time as stripes with the larger periodicity $\alpha_{\text{eff}}/\cos \theta_{\text{ne}}$.

We have already established that rippling is not energetically favored in dipolar stripe domains. The fact that the energy cost increases monotonically with the frequency of the ripples in Figure 27 indicates that a favored ripple wavelength does not exist for the ripple excitations. The ripple excitation energy is particularly low for the 30° ripples.

**9. Conclusion**

Let us analyze the simulations shown in Figures 12 and 13 with the results of this paper. They were performed with $\eta = \frac{1}{2}$ and finite temperature ($J = 9.5$). The underlying spin-lattice is triangular. The zero-temperature hexagonal disk phase is predicted by eq 56 and the data in Table 2 to have perpendicular center to edge distance $h = 2.90$ at low density (in units of length where the nearest-neighbor distance on the spin lattice is 1). At higher density, $h$ will increase slightly as shown in Figure 28. The continuum theory predicts the number of particles in each domain should be near 33.5 at low density. Since this is close to the actual domain size in Figure 13 we conclude that the domain size has not changed significantly upon heating from zero temperature. The effect of finite temperature is to disorder the domain lattice and make the domain shapes irregular, but still faceted.

The stripe domains of Figure 12 when aligned with the lattice at zero temperature, are predicted by eq 32 and the data in Table 2 to have a width $l = 2.30$ nearest-neighbor distances at low density. At higher density the stripe width increases as shown in Figure 20. At half coverage ($\eta = \frac{1}{2}$), the stripe width according to eq 32 is 4.14. Each row of particles on the triangular lattice is separated by $\sqrt{3}/2$, so this corresponds to zero temperature stripes with about 2.9 rows at low density, 4.8 rows at half coverage. A t higher density the stripe width increases as shown at zero temperature, are predicted by eq 32 and the data in Table 2 to have perpendicular stripes with about 2.9 rows at low density, 4.8 rows at half coverage. A t higher density the stripe width increases as shown at zero temperature, are predicted by eq 32 and the data in Table 2 to have perpendicular stripes with about 2.9 rows at low density, 4.8 rows at half coverage. A t higher density the stripe width increases as shown at zero temperature, are predicted by eq 32 and the data in Table 2 to have perpendicular stripes with about 2.9 rows at low density, 4.8 rows at half coverage.

**Figure 26.** Dipolar repulsion energy per lattice site vs ripple amplitude $\alpha$ as obtained from Fourier series at $\alpha_{\text{max}} = 10$, $\alpha = 1/2$, for a variety of ripple wavelengths $\lambda$.
where $R_{\infty}$ is the distance from the tagged dipole where the sum is truncated. Therefore, it is important to restart the sum in a form in which convergence is enhanced. To avoid multiple derivations, we present a general way to calculate the energy of a periodically replicated two-dimensional array of parallel dipoles. The unit cell is assumed to be rectangular, but may be nonprimitve so sums for the triangular lattice are easily evaluated using the results given here. It is left to the reader to simplify these expressions in situations where this is appropriate.

The unit cell has dimensions $l_x \times l_y$. If the system contains $N_{\infty}$ unit cells, then the dipole energy per unit cell is

$$E = \frac{1}{2N_{\infty}} \sum_{x_{\infty},y_{\infty}} \sum_{i,j} \left( (x_i + m_i l_x - x_j - n_j l_y)^2 + \right.$$ 

$$+ (y_i + m_i l_y - y_j - n_j l_x)^2 \right)^{3/2}$$

(A2)

where $n_{\infty}$, $m_{\infty}$, and $m_j$ index the unit cells, and the indices $i$ and $j$ run from 1 to $N$ over particles within a unit cell. The prime on the inner sum is a reminder not to count terms with $i = j$ within the same unit cell. In the limit that the number of unit cells becomes infinite, the energy per cell becomes

$$E = \frac{1}{2} \sum_{i,j} \delta(r_{ij})$$

(A3)

and we are left with the problem of evaluating $\delta(r_{ij})$

$$\delta(r_{ij}) = \delta_{ij} \left( (x_i - n_i l_x)^2 + (y_i - m_i l_y)^2 \right)^{-3/2}$$

(A4)

The prime indicates that the $n_i = m_i = 0$ term should be omitted when $n_{\infty} = m_{\infty} = 0$.

We first consider the case of $r_{ij} = 0$. The $n_i = 0$ terms are separated from the rest in the sum: 

$$\delta(0) = 2 \sum_{j} \left( n_j^2 l_x^2 + 2 \sum_{j} \left( n_j^2 l_x^2 + m_j^2 l_y^2 \right) \right)$$

(A5)

$$= 2l_x \left\{ \sum n_j^2 l_x^2 + \sum m_j^2 l_y^2 \right\}$$

(A6)

The last expression contains the Riemann zeta function, $\zeta(3) = 1.20203690316$.

The sum over $n_{\infty}$ is recast using the following relation which is an example of the Poisson sum formula:

$$\sum_{n_{\infty}} \left( t^2 + n^2 \right)^{-3/2} = \frac{2}{\pi} f_a(t)$$

where

$$f_a(t) = \frac{4\pi m}{t} K_0(2\pi mt) \quad m \neq 0$$

(A8)

and $K_0$ denotes the modified Bessel function of order 1.

Rearranging terms and the identity

$$\sum n_{\infty}^2 = s^2/6$$

(A9)

leads to the final result for $r_{ij} = 0$

$$\delta(0) = 2l_x^2 \zeta(3) + \frac{2s^2}{3 l_x^2} + \frac{4}{l_y^2} \sum_{j} \sum_{j} \left( n_j^2 l_x^2 + m_j^2 l_y^2 \right)$$

(A10)

where the function $f_a(t)$ is defined in eq A7. The sums now converge exponentially. Although we have treated the $x$ and $y$ coordinates differently, the result is identical if we switch $x$ and $y$ everywhere. The convergence properties may be somewhat different if the unit cell is very narrow in one direction.

When $r_{ij} \neq 0$ there is no restriction on the sum over $n_i$ and $n_j$ in eq A4. With no lack of generality, we assume that $n_{\infty} = 0$. If $x_{\infty} = 0$ and $y_{\infty} = 0$, then $x$ and $y$ are switched in the following expressions. The sum over $n_i$ is replaced using the Poisson sum formula in eq A4.

$$\delta(r_{ij}) = \frac{1}{l_x^2 l_y^2} \sum_{n_{\infty} m_{\infty}} \left( \frac{1}{n_{\infty}^2 - x_{\infty}^2} \right)^{3/2} +$$

$$+ \frac{1}{l_y^2} \sum_{n_{\infty} m_{\infty}} \cos \left( 2\pi m_{\infty} t_y \right) f_a \left( \frac{x_{\infty} - m_{\infty} t_x}{l_x} \right)$$

(A11)

The second term in the above equation is rapidly convergent. The first term, which corresponds to $m = 0$ in the Poisson sum, is Taylor expanded in the variable $t = x_{\infty}/l_x$.

$$\sum_{n_{\infty}} \left( n_{\infty} t - x_{\infty} \right)^2 = t^2 \sum_{n_{\infty}} \left( (n_{\infty} t - x_{\infty})^2 + (n_{\infty} t + x_{\infty})^2 \right) = t^2 +$$

$$+ \frac{2}{l_x^2} \sum_{n_{\infty}} \sum_{m_{\infty}} \cos \left( 2\pi m_{\infty} t_y \right) f_a \left( \frac{x_{\infty} - m_{\infty} t_x}{l_x} \right)$$

(A12)

In the last step, the leading two nonvanishing terms were summed in closed form and the remainder, which decays as $n_{\infty}^{-4}$, is left as a sum over $n_{\infty}$. Since we have assumed that $x_{\infty} = y_{\infty} = 0$ and $t < 1$, there is no problem with vanishing denominators in eq A12. Our final expression for $\delta(r_{ij})$, for $x_{\infty} = y_{\infty} = 0$ is

$$\delta(r_{ij}) =$$

$$= \frac{2}{l_x^2 l_y^2} t^2 \left[ \frac{1}{l_x^2} \sum_{n_{\infty}} \sum_{m_{\infty}} \cos \left( 2\pi m_{\infty} t_y \right) f_a \left( \frac{x_{\infty} - m_{\infty} t_x}{l_x} \right) \right]$$

(A13)

If $x_{\infty} = 0$ and $y_{\infty} = 0$ then $x$ and $y$ are switched in the above equation. If both $x_{\infty} = 0$ and $y_{\infty} = 0$ then $\delta(0)$ is given in eq A10.

Appendix B: Fourier Coefficients of Rippled Density

The parameters for rippled stripe domains are defined in section 8 and Figure 34. The reciprocal lattice vectors for the rectangular unit cell in Figure 34 are $k_x = 2\pi n_{\infty} / l_x$ and $k_y = 2\pi n_{\infty} / l_y$. The squared modulus of Fourier components of the density enters the energy expression, eq 59. For the faceted ripple discussed in section 8, these are given as

$$|k| = (k_x, k_y) = 0 \quad \rho |k| |f_{\rho}(k_x, k_y)|$$

$$= \rho \phi_0^2 \sin^2 (\pi n_{\infty} / l_x)$$

(B1)

$$|k| = (k_x, k_y) = 0 \quad \rho |k| |f_{\rho}(k_x, k_y)|$$

$$= \phi_0^2 \frac{8\pi^2 \sin^2 \left( \pi n_{\infty} / l_x \right)}{s^2 \left( n_{\infty}^2 - 4 \pi^2 \right)}$$

(B2)

$$|k| = (k_x, k_y) = 0 \quad \rho |k| |f_{\rho}(k_x, k_y)|$$

$$= \phi_0^2 \frac{8\pi^2 \sin^2 \left( \pi n_{\infty} / l_x \right)}{s^2 \left( n_{\infty}^2 - 4 \pi^2 \right)}$$

(B3)

where $\phi_0$ is defined in eq 64.
Phase Transitions at Zero Temperature in the Dipolar Lattice Gas

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The ground state of the dipolar lattice gas is studied as a function of density and the strength of the repulsive interaction between parallel dipoles. This system exhibits a variety of domain structures. We present results for the low-density region where the spacing between domains can be approximated by a continuous parameter. Below a critical repulsion strength, only stripe domains are found. Faceted disk domains are stable above the critical repulsion strength. The size of the disk domain shrinking with increasing repulsion. Disk to stripe transitions are induced by increased density. Domains in the dipolar lattice gas do not spontaneously elongate at zero temperature for systems in equilibrium with respect to exchange of particles between domains. Differences between our findings and previous work are discussed.

1. Introduction

Complex domain morphologies arise in thin ferromagnetic films5 and Langmuir monolayers. Among the observed patterns are stripe and disk domain phases, each with varying concentration of defects and long-range order among the domains (e.g., a solid or fluid array of disk domains). The same physical mechanism for self-organization into domains, competition between short-range attractions and long-range repulsions, in particular, the repulsion between aligned magnetic or electric dipoles, is thought to be at work in both the ferromagnetic and surfactant monolayers.

We are studying the statistical mechanics of perhaps the simplest microscopic model to mimic domain formation governed by dipolar forces, a lattice gas with nearest-neighbor attractions and long-range dipolar repulsions. The purpose of this work is to determine the phase boundaries in the two-dimensional dipolar lattice gas at zero temperature. The dipolar lattice gas is specified by the Hamiltonian

$$H = -J \sum_{\langle i, j \rangle} n_i n_j - \frac{\gamma}{2} \sum_{\langle i, j \rangle} \left( \frac{n_i n_j}{R_i R_j} \right) - \mu n_i$$

where $J$ is an inverse temperature. The occupation variable at the spin–lattice site $R_i$, $n_i$, can take the values 0 or 1. The parameter $\gamma$ controls the strength of dipolar repulsions, and $\mu$ is a chemical potential which sets the particle density. The ground state of the dipolar lattice gas is a complex function of the two parameters, the repulsion strength $\gamma$ and the density $\rho$ or chemical potential $\mu$.

In the preceding work, we gave domain energies in the dipolar lattice gas in the limit of large domain size, building on the continuum expressions of McConnell and co-workers,14,15,16,17 which did not specify a particular microscopic model. The continuum expressions were quite close to direct lattice sums down to domain sizes of only a few nearest-neighbor spacings. By minimizing the domain energy with respect to domain length scale at constant density, the continuum expressions provide useful predictions of domain size at zero temperature as a function of density and repulsion strength. In principle, the continuum theory should also predict phase transitions between stripe and disk phases. In practice, we find that the energy differences between disk and stripe phases are extremely small. Moreover, most of the interesting behavior occurs for fairly small domains. Even though the continuum theory is quite accurate, it is not sufficiently accurate to predict disk to stripe transitions for the dipolar lattice gas. Therefore, in this work we fall back on numerical lattice sum data. Of course, one could introduce more flexibility into the continuum expressions that would bring them into closer agreement with lattice sums. Since the lattice sums were so simple to evaluate directly, we did not explore this option. The interaction energy between various domains was given in the preceding work, including continuum expressions which are asymptotically valid.

In the concluding section we discuss differences between our phase diagram and the continuum theory as we have implemented it. However, the continuum theory provides an excellent guide to domain shapes, including elongated domains. Because we do not know the relative stability of facets and unfacetted domains, showing that faceting is always preferred at zero temperature. In the preceding work the energy of isolated domains was calculated in the continuum limit. We now show that the continuum expressions appropriate for the dipolar lattice gas fail to describe the delicate balance between stripe and disk phase stability. Let us examine the chemical potential of the faceted hexagonal disk phase to fall below that of the stripe phase is equivalent to the condition

\[ \mu_\infty < \mu_{\text{stripe}} \]

and scaled pressure

\[ Q_\infty = \mu_\infty - \mu_\infty \]

In the limit of vanishing density, \( \mu_\infty \) is just \( \rho \) times the energy per particle in isolated domains. Then

\[ \mu_\infty = \mu_\infty / \rho \]

and, of course, \( Q_\infty = 0 = \rho - 0 \) in this limit as well. Equation 5 may be verified explicitly by setting the interdomain interaction term, \( \xi \), equal to zero in the expressions for the stripe or disk phase energy \( \mu_\infty \), \( \mu_\infty \), or \( \mu_\infty \) in paper 1. Coexistence is determined by matching the energy per particle, eq 5, in the vanishing density limit.

2.1. Continuum Theory and Stripe-Disk Transitions. In the preceding work the energy of isolated domains was calculated in the continuum limit. We now show that the continuum expressions appropriate for the dipolar lattice gas fail to describe the delicate balance between stripe and disk phase stability. Let us examine the chemical potential of the faceted hexagonal disk phase to fall below that of the stripe phase is equivalent to the condition

\[ \mu_\infty < \mu_\infty + \mu_\infty \]

However,

\[ \mu_\infty + \mu_\infty = k_B T \ln \rho + \mu_\infty - \mu_\infty = 0.4994 e^{2m \pi / \lambda} - 0.1877 \]

where \( \rho \) is the area per spin-lattice site and \( \gamma_5 \) is the surface energy of the stripe domains. We have used \( k_B \) for the triangular spin-lattice from Table 2 of paper 1, and the approximate solution of eq 31 of paper 1 to obtain \( \mu_\infty \). (Using the exact solution of eq 31 of paper 1 does not affect the result.) Evaluating eq 36 of paper 1 for hexagonal domains on a triangular spin-lattice we find that

\[ \mu_\infty = (\sqrt{3} / \xi) k_B T \ln \rho + \mu_\infty = 0.5030 e^{2m \pi / \lambda} \]

The surface energy of stripe and faceted hexagonal domains, \( \gamma_5 \) and \( \gamma_5 \), respectively, are equal.

As the continuum theory is implemented in the previous paper, \( \mu_\infty \) is always greater than \( \mu_\infty + \mu_\infty \) and the theory fails to predict a stripe to hexagonal faceted disk transition. The difference \( \mu_\infty - (\mu_\infty + \mu_\infty) \) drops close to \( \mu_\infty \) for \( \rho \) < 0.2 and never changes sign, as it would if increasing repulsion induced a transition from stripes to disks. According to the continuum theory results, \( \mu_\infty \) transitions to circular disks are even less favored than transitions to faceted disks. Indeed this trend is correct since the surface energy cost to form a faceted domain is greater than for a faceted domain.

The continuum theory provides an excellent guide to domain size and energy within a family of stripes or disk phases. This is verified in Figure 20 where the domain size predicted by the continuum theory is compared to the stable phase found by direct lattice sums. The continuum theory as we have implemented it fails to describe stripe-disk transitions for two reasons. Firstly, the energy balance between stripe and disk phases is quite delicate. Secondly, the stripe phase of the dipolar lattice gas becomes metastable when disks reach a diameter of about 20 nearest-neighbor distances. If this transition were to occur at much larger length scales in this model, we might expect better results from the

\[ V \quad \text{and} \quad \text{energy} \]

\[ \text{within a family of stripes or disk phases. This is verified in Figure 20 where the domain size predicted by the continuum theory is compared to the stable phase found by direct lattice sums. The continuum theory as we have implemented it fails to describe stripe-disk transitions for two reasons. Firstly, the energy balance between stripe and disk phases is quite delicate. Secondly, the stripe phase of the dipolar lattice gas becomes metastable when disks reach a diameter of about 20 nearest-neighbor distances. If this transition were to occur at much larger length scales in this model, we might expect better results from the
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Figure 28 Comparison of the hexagonal disk and stripe domain size predicted by the continuum theory as implemented in our previous work\(^{30}\) and the result of exact lattice sums. The solid lines give the domain size index, either 7 for disks or 1 for stripes, for the most stable phase at zero density as a function of the repulsion strength \(a\). The breaks in the curves separate the regions where stripes (to the left) or disks (to the right) are most stable. Only perfect hexagonal disks, not the elongated disks of section 3, are considered here. The dashed lines are the continuum results, eqs 31 and 36 from paper 1 for stripes or faceted disks, respectively. (Note that \(2l/\sqrt{3}\) corresponds to the integer index 7, and \(2l/\sqrt{3} - 1/2\) to 1.) Since the continuum results for stripes match the exact results so closely, the dashed line is barely visible for the stripe domains.

The relative error of the continuum theory, while never more than a few percent in the transition region, is sufficient to lose the transition. Of course, the continuum expressions can be augmented so they interpolate through the direct lattice sum results for small domains, perhaps by making the cutoff \(k\) depend on domain size. Rather than destroy the simplicity of the continuum picture, we use direct lattice sums for the domain energies in the following. The double sum to calculate the total energy of finite domains is trivial to evaluate for domain sizes of relevance. The Poisson sum formula was used to enhance the convergence of the sum of dipole interactions in stripe domains.

Since \(k_x\) and \(k_y\) were determined by fitting to the asymptotic behavior of lattice sums in the large domain limit, it may be possible that different values of these parameters would induce a stripe-disk transition. Also, there is some ambiguity regarding terms proportional to the cutoffs \(k_x\) and \(k_y\) in the continuum expressions. We have shown in paper 1 that, as implemented, the continuum theory matches lattice sums for the dipolar lattice gas quite well.\(^{30}\) Another version of the continuum theory may give a stripe-disk transition, but the conclusion remains that the transition is so subtle in the dipolar lattice gas that the usefulness of continuum expressions is diminished.

2.2 Thermodynamic Functions at Low Density. The energy per particle for the stripe and faceted hexagonal disk phases

\[
\begin{align*}
\varepsilon_S(p) &= \rho \left( -\frac{q^2}{2} + \frac{2q^2}{\eta} \right) + \varepsilon_{Wp}(p) + \varepsilon_{\text{strip}}(p) \quad (9) \\
\varepsilon_F(p) &= \rho \left( -\frac{q^2}{2} + \frac{q^2 + 1}{\eta} \right) + \varepsilon_{Wp}(p) + \varepsilon_{\text{facet}}(p) \quad (10)
\end{align*}
\]

is given in units of \(J\). The symbols \(\eta\) and \(\rho\) are defined in the beginning of this section (see Figure 28). The first term in the curly brackets is the contribution of nearest-neighbor attractive interactions and is correct for arbitrarily small domain size. The exact lattice sum over the domain \(D\) is

\[
\varepsilon_{Wp} = \frac{1}{n_D} \sum_{R \in D} \left| R - R' \right|^{-1}
\]

where \(n_D\) is the number of particles in domain \(D\). As \(n_D \to \infty\),

\[
\varepsilon_{Wp} \to \frac{C_1}{2} = 5.91709
\]

as explained in paper 1.\(^{30}\) The above equations are the analogues of the continuum expressions, eqs 30 and 55, of the previous work.\(^{30}\)

The lattice energies \(\varepsilon_{\text{strip}}(\rho)\) or \(\varepsilon_{\text{facet}}(\rho)\) represent the contribution from interactions among a periodic array of stripe domains or a triangular lattice of faceted disks, respectively. As discussed in the beginning of this section, the lattice energies are, in principle, a function of the integer number of lattice spacings between stripes or disks. To avoid unnecessary complexity, we work in the low-density limit where the spacing between domains is large and can be approximated by a continuous variable. Only then can \(\varepsilon_{\text{strip}}\) or \(\varepsilon_{\text{facet}}\) be written as a function of \(\rho\). In the low-density, large-domain separation limit the lattice energies are approximated by sums of the leading multipole expansion of the dipole interaction between domains. The leading multipole interaction between two stripe domains is that of two lines of dipoles of strength \((1/e)(\cos \theta)^2\). Summing over the stripe lattice we find

\[
\varepsilon_{\text{strip}}(\rho) = \frac{q^2}{2e} \rho^3 + O(\rho^5) \quad (12)
\]

at low-density, large-domain separation. Since the continuum expression, eqs 12 and 13 of paper 1, is also equivalent to interaction between two line dipoles, we can read the above result for \(\varepsilon_{\text{strip}}\) directly from the continuum theory. The lattice energy for the low-density disk phase is that of an array of point dipoles of total strength \(n \lambda_0(\rho)^{1/2}\).

\[
\varepsilon_{\text{facet}}(\rho) = \frac{s_2}{\sqrt{3} \lambda_0} \left( \frac{\sqrt{3}}{2} \right)^{1/2} \rho^{3/2} \quad (13)
\]

Armed with the above energy expressions, the chemical potential and pressure can be calculated for the stripe phase

\[
\begin{align*}
\mu_S &= \frac{q^2}{2} + \frac{2q}{\eta} + \mu_{Wp}(\rho) + \frac{q^2 \rho^3}{\sigma^2}\rho^2 \\
\Omega_S &= \frac{2q^2 \rho^3}{3\eta}\rho^2
\end{align*}
\]

and for the faceted hexagonal disk phase

\[
\begin{align*}
\mu_F &= \frac{q^2}{2} + \frac{6(2 + \lambda_0)^2}{3(1 + \lambda_0)} + \mu_{Wp}(\rho) + \frac{5s_2}{4\sqrt{3} \lambda_0} \left( \frac{\sqrt{3}}{2} \right)^{1/2} \\
\Omega_F &= \frac{2s_2}{4\sqrt{3} \lambda_0} \left( \frac{\sqrt{3}}{2} \right)^{1/2} \rho^{3/2}
\end{align*}
\]

2.3 Coexistence Parameters. Considering only transitions among stripes and faceted hexagonal domains, the zero-temperature phase diagram is shown in Figures 30 and 31 for the \(\eta - p\) plane, and in Figure 32 for the \(\eta - \beta\) plane. Coexistence regions are shaded.

Because the density change in stripe-stripe and disk-disk transitions is so small, the coexistence regions are barely visible in Figures 30 and 31. The disk phase is favored by increased repulsion, that is, large \(\eta\). Above a critical repulsion strength, \(\eta_c \sim 0.204\), the disk phase is most stable at zero density, and there is a transition from disks to stripes as the density is increased. There may also be a transition from one disk phase to another with larger index \(\eta\) with increasing density, and there are numerous triple
Figure 30 Phase diagram in the $\rho-\eta$ plane for faceted hexagonal disks and stripes on the triangular spin lattice at zero temperature. The indices $F$ and $I$ are explained in section 2 and Figure 28. Coexistence regions are shaded. Because the density difference in disk-disk and stripe-stripe transitions is very small, the coexistence regions for $F \rightarrow I$ and $F \rightarrow I$ transitions are barely visible. Only stripe domains are found below the critical repulsion strength $\eta_c \sim 0.204$.

Figure 31 Enlargement of the $\rho-\eta$ phase diagram for faceted hexagonal disks and stripes. See the caption of Figure 30 for an explanation of the phase diagram. Note that the largest observed hexagonal disk size is indexed by $F_{22}$. This phase is stable in an extremely small region of the phase diagram and coexists with stripe phases at higher and lower values of the repulsion strength $\eta$.

Figure 22 Phase diagram in the $\rho-\Omega$ plane for faceted hexagonal disks and stripes on the triangular spin-lattice at zero temperature. The scaled pressure $\Omega$ is the natural log of the grand partition function of the dipolar lattice gas divided by the number of spin-lattice sites.

Exponents in eqs 14-17, thereby favoring transitions to the stripe phase away from zero density. Below $\eta_c \sim 0.204$ no hexagonal disk phase is found to be more stable than the stripe phase. Domain elongation is not considered until section 3, but, even when distortion of disk domains is allowed, only stripes are stable below $\eta_c$.

At nonzero densities there is always a finite density change at each transition. By equating pressures of the $I$ and $I \rightarrow 1$ stripe phases, the coexistence densities $\rho_I$ and $\rho_{I1}$ for the $I \rightarrow 1 \rightarrow 1$ transition are easily seen to be close to each other and related by

$$\frac{\rho_I}{\rho_{I1}} = \left( \frac{\eta}{\eta_0} \right)^{1/3}$$

(18)

The $I \rightarrow 1 \rightarrow 1$ coexistence curve relating $\eta$ and $\rho_I$, the density of the coexisting phase with the larger stripe width, has the functional form,

$$\eta = \eta_0 \left[ 1 - \left( \frac{\rho_I}{\rho_{I1}} \right)^2 \right]^{-1}$$

(19)

Here $\eta_0$ and $\rho_{I1}$ are parameters with the following meanings: $\eta_0$ is the location of the $I \rightarrow I \rightarrow 1$ transition at zero density, and $\rho_{I1}$ is the infinite $\rho$ limiting density of the large width ($I$) stripe phase, hypothetically assuming the low-density coexistence curve was valid for all values of $\eta$. (Of course, $0 \leq \rho \leq 1$ for the lattice gas and our thermodynamic functions are valid for low densities.) The parameters $\eta_0$ and $\rho_{I1}$ must be calculated from eq 14-17 and the conditions for coexistence.

The same considerations for the $F \rightarrow I \rightarrow 1$ transition between two disk phases yields the relation

$$\frac{\rho_F}{\rho_{F1}} = \left( \frac{\eta_0}{\eta_{F1}} \right)^{1/3}$$

(20)

between coexistence densities and the coexistence curve is of the form

$$\eta = \eta_0 \left[ 1 - \left( \frac{\rho_F}{\rho_{F1}} \right)^2 \right]^{-1}$$

(21)
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Figure 33 An example of an elongated hexagonal domain on the triangular spin lattice. The elongated domain is formed from a perfect hexagonal domain (Figure 32) indexed by $f$. The original domain is extended in one direction until the corner in the direction of extension is near-neighbor distances from the center of the original hexagonal domain. In this example, $f_1 = 3$ and $f_2 = 3$. When $f = f_1$, the perfect hexagonal domain of Figure 32 is recovered.

The parameters $\theta^{(p)}$ and $\phi^{(p)}$ are defined analogously to their counterparts for the stripe phase.

3. Elongated Disks

In this section we address the question whether disk domains spontaneously elongate. The answer, with some qualification, is negative. On the hexagonal spin lattice the appearance of elongated domains in the zero-density limit should be characterized as part of a growth sequence as partial layers are added to perfectly hexagonal domains. When the most favored domain size comes close to a perfect hexagon "magic number", $3(P + v^*)^2 + 1$, $P = 0, 1, 2, ...$, the regular polygon is preferred.

Elongated domains appear at finite temperature in Monte Carlo simulations of the dipolar lattice gas. In this work we are unable to determine whether density, in addition to temperature, will drive domain elongation. Our analysis in this section is confined to the low-density limit, unlike the previous section which was applicable to the zero-density limit. When interdomain interactions can be neglected and packing is irrelevant, the pressure of each phase approaches zero as the system becomes ideal, and coexistence is determined by equality of the energy per particle, which is the zero-density limit of the chemical potential (eq 3). The stable phase in the limit of zero temperature and density is the one with the lowest energy per particle.

Spontaneous elongation of dipolar domains have been examined by Kellers, Korb, and McConnell.14 Vanderlscher and Midelfart,15 and McConnell.22 As discussed in the concluding section, these authors discuss a metastable situation, one that may be most relevant to experiments, in which domains do not equilibrate by exchanging particles and hence domain size is not equilibrated.

In principle, the phase diagram for domains of arbitrary shape is built by comparing the stability of all possible finite domains. In practice, the phase diagram for domains of arbitrary shape is built by comparing the stability of all possible finite domains. This is impossible in practice, and we have studied a class of elongated domains that hopefully is sufficiently inclusive to allow us to make qualitative conclusions. First, a class of irregular hexagonal domains was considered, each with six facets, two of which are elongated. These elongated hexagonal domains are indexed by two integers, $f_1$ and $f_2$, where $f_1$ is a regular hexagon. For the zero density and temperature phase diagram presented in Figure 34, we examined all such domains with $f_1 = 3$, $f_2 = 3$, $P = 30, 60, 90, 120$. The stable phase never came close to the boundaries of this range of $f_1$ and $f_2$. Several small clusters, such as the triangular cluster of three particles, are obvious omissions from the class of elongated hexagonal domains. Therefore, we also examined the triangular cluster and the sequence of quadrilateral domains cut from the $f = 2$ stripe containing up to 50 particles.

The most stable phase was determined from among the class of finite size domains defined above plus stripe phases. The results are shown in Figure 34. Large repulsion precludes particle asso-

Figure 34 Zero-density limit of the dipolar lattice gas phase diagram at zero temperature. The horizontal lines indicate phase boundaries, and successive levels of detail with respect to change of the repulsion strength are shown. All perfect and elongated hexagonal disk domains, some special irregular disk domains (as explained in section 3), and stripe domains were considered. The smallest of the disk domains are simply drawn within their region of stability. The hexagonal disk domains are indexed by the pair of integers $(f_1, f_2)$. Note that the perfect hexagonal disks $(f_1 = 3)$ have larger regions of stability than the elongated disks, and that the degree of elongation is always small.
co-workers in the preceding paper, but our phase diagram expanded upon the continuum calculations of McConnell and stripes and disks increases with increased particle density. At fixed $0.20607$. The elongated disk phase reappears in the continuum limit by Andelman, Brochard, and Joanny. Neither this factor nor the differences between our implementation of the continuum theory and that of McConnell would change the qualitative failure of the continuum theory to describe the phase diagram of the dipolar lattice gas. As mentioned earlier, we have not attempted to modify cutoff parameters or add correction terms to bring the continuum theory into agreement with the microscopic model. The error made by the continuum theory in describing domain energetics is remarkably small, but the subtle energy differences that control the phase transition behavior do not tolerate even this level of error.

Other continuum techniques have been used to analyze systems with repulsive dipolar interactions in thin ferromagnetic films. As discussed in the preceding paper, this form of the continuum theory is not as successful in describing the energetics of lattice gas domains as the methods developed by McConnell and coworkers. However, use of the lattice model also implies a type of coarse-graining such as employed by many actual molecules. While it is useful to study the lattice gas because the Hamiltonian is explicit, this does not imply that the lattice gas necessarily contains an inherently more accurate description of real colloids than do continuum theories. Stripe-disk transitions in systems of parallel dipoles have also been examined in a continuum limit by Andelman, Brochard, and Joanny. Their mean field theory is not applicable in the low-temperature regime.

Our conclusion that domain elongation does not occur in the zero-density limit applies to systems in strict equilibrium, including particle exchange within an ensemble of domains. Therefore, there is no disagreement with the predictions of elongation for isolated domains by Vanderlick and Mihwald and McConnell. The calculations of Vanderlick and Mihwald and McConnell refer to the stability of isolated domains that may not exchange particles, and these authors have recognized that elongation takes place under conditions where the domain areas exceed the equilibrium areas. Indeed, the constraint of constant domain size may be more relevant to actual experiments.

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CHAPTER IV

Simulations in 2-D

4.1 Introduction

Given the low temperature equilibrium domain structure shown in Chapter 3 and the mean-field work of Andelman et al.\textsuperscript{28} as a basis for comparison, we investigate the behavior of the dipolar lattice gas at higher temperatures through Monte Carlo simulations.

One obvious non-physical aspect of lattice-gas studies is the limit on the number of nearest neighbors a particle may have. While the qualitative behavior remains unchanged regardless of the lattice chosen, the choice of lattice can have a quantitative effect on the results, as can be seen in Domb’s\textsuperscript{66} review of the critical behavior of the 2-D Ising model. We choose to work on a triangular lattice where the number of nearest neighbors allowed \( (q=6) \) is larger than in the more mundane square lattice \( (q=4) \). This facilitates formation of hexagonal or faceted domains, which bear more resemblance to experimental results than the square domains one would
obtain with $q=4$. A triangular lattice consists of two sublattices, one of which is translated $1/2$ lattice spacing over from the other, as can be seen in Figure 35. Every site has six neighboring sites a distance $a$ away, and the distance between coterminous rows is $\frac{\sqrt{3}s}{2}$. There are three preferred axes of orientation along which interfaces will lie, labelled A, B, and C (Figure 35).

Whenever one is modelling something involving large scale changes in the system (i.e. formation of stripe domains involving several hundred particles) trial moves involving a single grid site will make equilibration a long, arduous process. One wishes to speed up the process by incorporating multi-site moves and preferential site choice, while still ensuring that detailed balance is obeyed.

We have expedited this set of simulations in several ways. Series of attempted triple site flips and seven-site flips (Figure 35) are interspersed throughout the traditional single site attempts. Other innovations employed will be discussed in later sections.

Another difficulty inherent in the simulation work is the treatment of long-range forces. In systems interacting via a short-range potential the treatment is simple. It is a common approximation in an $N$-particle system to allow each particle to interact only with the closest periodic images of the other $N-1$ particles. This is known as the minimum image convention. However, when the effect of the forces is significant at distances longer than half the simulation cell size, this is no longer a viable option. As was shown by Smith and Perram, higher order images can make
Figure 35. Triangular lattice used in Monte Carlo simulations. A, B, and C label preferred axes of orientation. Sites labeled 3 and 7 demonstrate typical 3- and 7-cluster moves, respectively.
a significant contribution to the potential. The preferred solution, which would require no approximation, would be to increase the simulation cell to diminish this effect, but this is computationally impracticable. We choose to handle this problem by the Ewald summation method, in which each particle interacts with all the periodic images of the other particles. A drawback to this is the resulting overemphasis of the periodic nature of the system. Also, under Ewald summation, the interaction between two particles (and all their replicas) is of the form

\[
V_{ij} = \sum_{n_x n_y = -\infty}^{\infty} v \left( |r_i - r_j + n_x L_x + n_y L_y| \right) \quad (4.1)
\]

\[
\sum_{n_x n_y = -\infty}^{\infty} \left( (x_i - x_j + n_x L_x)^2 + (y_i - y_j + n_y L_y)^2 \right)^{3/2} \quad (4.2)
\]

where \(L_x, L_y\) represent the simulation cell length in the \(x\) and \(y\) directions and \(n_x, n_y\) label the replicated cells. This may be a slowly convergent quantity. We enhance convergence by subtracting off the large term

\[
\sum_{n_x n_y = -\infty}^{\infty} \left( n_x^2 L_x^2 + n_y^2 L_y^2 \right)^{3/2} \quad (4.3)
\]

(\(\text{where the summation is constrained so that } n_x = n_y \neq 0\)) and adding it back in after calculating the rest of the summation. This quantity may be expressed in terms of the modified Bessel function \(K_1(x)\) and precisely calculated without explicit sums.

A series of simulations were performed at values of \(J\) and \(A\) chosen so that the ratio \(\eta = \frac{J}{A}\) remains constant. This is done to ensure that the changes in
the domain morphology seen are strictly due to temperature and density changes, and not due to a shift in relative repulsion strength. The periodically replicated simulation cell contains 3944 (58 × 68) particles from the triangular spin lattice in a nearly square arrangement. The computations are demanding for several reasons: the simulation cell is relatively large; a long-range interaction with all other spins, not just nearest neighbors, must be calculated for each attempted spin flip; and long runs are needed to equilibrate the system for certain values of \( J, \eta, \) and \( \mu. \)

The specific value of \( \eta = \frac{3}{7} \) was chosen for practical reasons on the basis of the zero temperature studies. The typical domain size would be comparable to or greater than the simulation cell size if \( \eta \) were reduced much below the chosen value. An increase in \( \eta \) would drive the domain width too close to the nearest neighbor spacing.

In many cases, "snapshots" of the system are sufficient to specify the domain morphology. Two order parameters were chosen to quantify this through the course of the simulations. The \( m \)-fold symmetry of a phase is quantified by:

\[
f_m = \sum_k \exp(\im \phi_k) S(k),
\]

(4.4)

where \( S(k) \) is the structure factor and the sum over \( k \) extends over the set of reciprocal lattice vectors of the system. Particular attention was paid to \( f_2 \) and \( f_6 \) as indicators of the stripe (S) and hexagonal (H, H') phases. The two-fold stripe order can also be quantified by a more conveniently accumulated order parameter.
that signals long-range interfacial orientational correlation.

\[ g_2 = \sum_{(R,R')} \exp[2i\theta_{R,R'}] \{n_R(1 - n_{R'}) + (1 - n_R)n_{R'}\} \]  

(4.5)

The sum extends over all nearest neighbor pairs on the lattice. The combination of occupation variables in the curly brackets identifies those bond pairs at an interface, and \( \theta_{R,R'} \) is the angle between the normal to that interface (along the vector \( R - R' \)) and a reference direction.

Calculations have, for the most part, been performed on a Stellar model GS1000 graphics supercomputer with 4 processors. While optimization is difficult in an inherently sequential algorithm like Monte Carlo, vectorization and parallelization significantly speed up the floating point calculation of interaction energies. Due to the long-range interactions in this system, where every spin is interacting with every other spin in the system, optimization of the code in this case provided a substantial time savings.

4.2 Initial Results and Hexagonal Phase Analysis

It was quickly ascertained from the simulation results that the model does support a range of domain morphologies. The progression shown in Figure 36 is representative of the system behavior as density is increased at constant temperature. Isolated lattice gas monomers coalesce into faceted disk domains at very low density, an effect analogous to micelle formation at the CMC, which is analyzed in
Figure 36. Instantaneous configurations at several values of the chemical potential \( \mu \) for \( J = 9.50 \) and \( \eta = \frac{3}{4} \).
more detail in a later section. As density increases, the disk domains elongate and the snake-like domains also seen experimentally in epifluorescence microscopy appear. Eventually the elongated domains form a stripe phase as quantified by the orientational order parameter $g_2$. This behavior is repeated over the range of temperatures accessible by standard Monte Carlo techniques.

This leads to the question of the location of the hexagonal phase for the dipolar lattice gas. The nature of the isotropic-hexagonal transition in 2-D systems has been under investigation for the last ten years, yet it has remained difficult to establish either theoretically or through simulations whether this is a first order phase transition or two second order phase transitions with an intermediate hexatic phase. Molecular dynamics simulations of dipolar systems have been performed by Kalia and Vashista and by Bedanov, Gadiyak, and Lozovik, and an apparently first order phase transition was detected. The mean-field phase diagram of Andelman et al. also shows a first-order transition. While determination of the order of a transition is extremely difficult, and is outside the range of this study, it is clear that in these studies, the hexagonal phase is found.

Based on previous simulation and mean-field results, one would expect to encounter isotropic-to-hexagonal and hexagonal-to-stripe transitions at constant temperature as the density is increased. From the configurations shown in Figure 36, it is not apparent whether the disk phase in that series of simulations exhibits hexagonal order of a two-dimensional super-crystal of disk domains. We sought a definitive
answer to this question by lowering the temperature at $\rho \approx 0.15$ and monitoring the 6-fold order parameter $f_6$ to determine the location of the isotropic hexagonal boundary. (At densities much higher than $\sim 0.15$ the question of whether the domains form a two-dimensional solid rapidly loses meaning as the domains elongate.)

At this density, no increase in six-fold order was evident through the range of temperatures accessible by normal Monte Carlo methods. As we attempted to lower the temperature below $J = 9.5$, a difficulty inherent in the Monte Carlo algorithm presented itself. Attempted moves are accepted with less and less frequency as the temperature is lowered. Due to this inefficient sampling, ordinary MC is impractical at temperatures much lower than $J = 9.5$.

We made low temperature simulations feasible by freezing certain degrees of freedom that tend to disrupt the solid (e.g. changes in disk shape), thereby establishing an upper limit for the isotropic-hexagonal boundary. We investigated a system of perfect hexagonal domains with $\rho \approx 0.15$. These frozen disk systems can be simulated at low temperatures using trial Metropolis Monte Carlo domain displacements in random directions on the lattice, analogous to off-lattice particle simulations. Freezing domain shape fluctuations only serves to enhance crystalline order and drive the freezing temperature to a higher value than the original lattice model. This helps affirm the assertion that the hexagonal phase is not present at the higher temperature shown in Figure 36. A system of 16 faceted hexagonal
disks, each containing 37 particles, produces an almost perfect triangular domain crystal within our simulation cell. The domain size chosen was consistent with the normal Monte Carlo results, and was corroborated by the analytic results of Chapter 3. Only the repulsion term controlled by the parameter $A = J \eta$ plays a role in the frozen-domain studies. This is due to the fact that the nearest neighbor interaction energy is constant unless two domains come into contact. This was seen from earlier simulation results to be an unlikely event. In fact, moves resulting in overlap or contact between two domains were not allowed in the frozen domain simulations, due to the fact that such a move would violate detailed balance. (Splitting of domains is not allowed, therefore domain mergence is similarly disallowed.)

The hexagonal order parameter $f_6$ for frozen disk domains as a function of $A$, the coefficient of repulsion, is shown in Figure 37. It is apparent both from the order parameter and from "snapshots" of the system that crystalline order arises in the range $30 < A < 40$. This implies that the upper limit to the freezing temperature at $\eta = \frac{3}{\gamma}$ and $\rho \approx 0.15$ occurs in the range $70 < J < 90$.

This is corroborated by the work of Kalia and Vashista, and Bedanov, Gadiyak, and Lozovik. In both of these studies, molecular dynamics simulations were performed on a 2-D system of particles interacting with the pair potential $v(r) = \epsilon \left( \frac{2}{r} \right)^3$, where a "particle" in this system corresponds to an entire domain in our
Figure 37. 6-fold order parameter $|f_6|^2$ as a function of the repulsive Hamiltonian coefficient $A$ from low temperature whole-cluster simulation.
simulation. If we define the dimensionless parameter

\[ \Gamma = \beta \varepsilon \left( \sigma \sqrt{\pi \rho'} \right)^3 \]  

(4.6)

where \( \rho' \) is the number density of particles, then both of the above-mentioned sets of simulations apparently show a first order transition at \( \Gamma \approx 62 \).

We do not have a truly continuous system, and the interaction between whole domains in our study differs slightly from \( \frac{1}{\sigma^2} \) at small \( r \). If we neglect these differences, we can approximately apply results for the \( \frac{1}{\sigma^2} \) particles to the dipolar lattice gas. Equating each lattice gas domain to a single \( \frac{1}{\sigma^2} \) particle, equation 4.6 becomes

\[ \Gamma = An^2(\pi \rho')^{\frac{3}{2}} \]  

(4.7)

where \( n \) is the domain size, \( \rho' \) is again the number density of domains, and \( A \) is as defined in the Hamiltonian. From this form of the equation, we can see that for our system of 16 domains containing 37 particles each, \( \Gamma = 62 \) corresponds to a freezing transition occurring at \( A_f \approx 25.9 \) (or \( J_f \approx 59 \) for \( \eta = \frac{3}{7} \)). Our data shows the system is isotropic at \( A = 20 \), disordered at \( A = 40 \), and exhibits coexistence at \( A = 30 \) and 35. This corresponds to a much lower temperature than would be expected from the mean-field results. The comparison with our frozen lattice domain calculations is reasonable given the inherent differences between continuous and lattice systems. This supports our contention that hexagonal disk domain order is not present in the \( J = 9.5 \) results shown in Figure 36.
We can extend these results by assuming that the transition temperature scales with density as would the continuous system of particles

\[ \frac{1}{J} \propto [n_D(\rho)]^\frac{1}{2} \rho^\frac{1}{3}. \quad (4.8) \]

This extrapolation of the work of Kahlia et al. is the dashed line given in the proposed phase diagram (Figure 49). We have incorporated the fact that the equilibrium domain size \( n_D \) will be a function of density, and we have used the domain size of faceted hexagonal domains at zero temperature (Chapter 3) to estimate this dependence. This estimate of the hexagonal-isotropic boundary is shown as a dashed line on the phase diagram in Figure 49. We note that this line does not reach the stripe melting region \((J \sim 9)\) until almost half-coverage. Therefore, it is unlikely that disk domains will crystallize with increasing density at these higher temperatures before the disk-like morphology is completely lost.

### 4.3 Low Density Studies and Quest for CMC

We now repeat the question previously asked for the 1-D system: will this model display a CMC? We will analyze the behavior of the system at low density in two ways, by simulation and through a virial expansion.

In the low density limit, systems behave ideally, i.e. they follow the famous equation of state

\[ P = \rho kT \quad (4.9) \]
Physically, this is interpreted as meaning that at low densities, particles spend most of their time far apart and therefore any interaction between them is negligible. At higher densities, interparticle interactions have a greater effect and must be taken into account. A large number of equations of state have been proposed to describe the behavior of real systems as they deviate from ideality. One of the most useful of these is the virial equation, which describes corrections to ideality as an infinite power series in $\rho$

$$\frac{P}{kT} = \rho + B_2\rho^2 + B_3\rho^3 + \cdots$$

(4.10)

where the virial coefficients $B_2, B_3, \cdots$ depend on the temperature of the system and the form of the interaction potential. Given our Hamiltonian, we may derive $B_2$ and $B_3$ for the dipolar lattice gas. This is equivalent to the usual expressions for the virial coefficients in terms of Mayer f-functions in 3-dimensions.

We will begin by expressing the grand canonical partition function $\Xi$ as a power series in the activity $z = e^{\beta \mu}$

$$\Xi = \sum_N z^N Q(N, V, T)$$

(4.11)

$$= z^N q_N$$

(4.12)

$$= 1 + q_1 z + q_2 z^2 + \cdots$$

(4.13)

where $q_N$ is the N-body configuration integral.

$$q_N = \int \cdots \int e^{-\beta V_N} dr_1 dr_2 \cdots dr_N$$

(4.14)
The interaction potential \( V_N \) contains only the attractive and repulsive interactions given by the first two terms in the Hamiltonian. The chemical potential term is contained in \( z \). Taking the natural log of both sides of equation 4.13 yields

\[
\ln \Xi = \ln (1 + q_1 z + q_2 z^2 + \cdots) \equiv \ln (1 + x)
\]  

(4.15)

If we use the expansion \( \ln (1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} + \cdots \), make the substitution \( x = q_1 z + q_2 z^2 + \cdots \), and collect like powers in \( z \), then we obtain \( \Xi \) as an expansion in \( z \)

\[
\ln \Xi = q_1 z + \left( q_2 - \frac{1}{2} q_1^2 \right) z^2 + \left( q_3 - q_1 q_2 + \frac{1}{3} q_1^3 \right) z^3 + \cdots
\]  

(4.16)

Since we know that

\[
P = \frac{\ln \Xi}{\beta V}
\]  

(4.17)

and that

\[
\rho = \frac{\partial P}{\partial \mu} = \frac{z}{V} \frac{\partial \ln \Xi}{\partial z}
\]  

(4.18)

it is a trivial matter to obtain \( \beta P \) and \( \rho \) as expansions in \( z \).

\[
\rho = \frac{q_1}{V} z + \frac{2}{V} \left( q_2 - \frac{1}{2} q_1^2 \right) z^2 + \frac{3}{V} \left( q_3 - q_1 q_2 + \frac{1}{3} q_1^3 \right) z^3 + \cdots
\]  

(4.19)

\[
\beta P = \frac{q_1}{V} z + \frac{1}{V} \left( q_2 - \frac{1}{2} q_1^2 \right) z^2 + \frac{1}{V} \left( q_3 - q_1 q_2 + \frac{1}{3} q_1^3 \right) z^3 + \cdots
\]  

(4.20)

To obtain \( \beta P \) as a series in \( \rho \), we need to invert the series given in equation 4.19, obtain \( z \) as a series in \( \rho \), and substitute into equation 4.20. If this is done, we obtain our desired final result

\[
\beta P = \rho - b_2 \rho^2 + \left[ 4 b_2^2 - 2 b_3 \right] \rho^3 + \cdots
\]  

(4.21)
where

\[ b_2 = \frac{1}{V} \left( q_2 - \frac{1}{2} q_1^2 \right) \]  
(4.22)

\[ b_3 = \frac{1}{V} \left( q_3 - q_1 q_2 + \frac{1}{3} q_1^3 \right) \]  
(4.23)

We use a short computer code and the Hamiltonian to evaluate all possible interactions of 1, 2, and 3 particles on a 58 × 68 triangular lattice to obtain

\[ q_1 = 3944 = V \]  
(4.24)

\[ q_2 = 8105350 \]  
(4.25)

\[ q_3 = 1.176051 \times 10^{10} \]  
(4.26)

at \( J = 6.00 \) and \( \eta = \frac{3}{7} \). Using these numerical results, we find

\[ \beta P = \rho - 83.109 \rho^2 - 9.55 \times 10^4 \rho^3 \]  
(4.27)

A plot of this is shown in Figure 38. How does this compare to our simulation results?

As we can see from our simulation results shown in Figure 39, clustering begins at very low densities for the dipolar lattice gas. Even at densities as low as \( 10^{-3} \), 6, 7, and higher body interactions begin to appear, so we do not realistically expect a virial expansion truncated at third order to describe the system for very long. Density was plotted against activity \( z \) for a series of Monte Carlo simulations run at \( J = 6.00 \). It was determined that a 6-term polynomial provides a very nice fit to the data to provide \( \rho \) as an expansion in \( z \). This may be integrated to obtain \( P \) as
Figure 38. $\beta P$ vs $\rho$ from the virial expansion for the dipolar lattice gas.
a function of $z$. We may then plot pressure vs. density as given by the simulation (Figure 39).

From these results, we draw several conclusions

1. The simulation results and a virial expansion for the dipolar lattice gas agree well in the very low density region ($\rho < 0.001$) before the CMC is reached and clustering becomes important.

2. The dipolar lattice gas does display a CMC.

3. The slope following the break in the $P$ vs. $\rho$ curve is roughly $\frac{1}{6}$, or $1/(\text{typical aggregate size})$, exactly as would be expected for an ideal coexistence of clusters and monomers.

If one examines typical snapshots of the system obtained from the simulation, one can see that clusters do begin to proliferate in the CMC region shown on our pressure-density plot (Figure 39).

4.4 Stripe Phase

By the progression shown in Figure 36, it is clear that an isotropic-stripe phase transition occurs with increasing density (Figure 49). A transition between the isotropic and stripe phases can be driven by temperature as well (Figures 40 and 49). Figure 40 clearly shows that 2-fold stripe order is lost while the domain interface is still sharp. Our system size is too small and equilibration times too long to establish
Figure 39. Pressure vs. density obtained from fit to simulation results. Points A, B, C, and D show typical configurations from points along curve.
$J = 9.5, \quad |\langle g_2 \rangle| = 0.348$

$J = 7.0, \quad |\langle g_2 \rangle| = 0.062$

$J = 4.0, \quad |\langle g_2 \rangle| = 0.005$

$J = 3.0, \quad |\langle g_2 \rangle| = 0.009$

$J = 2.0, \quad |\langle g_2 \rangle| = 0.006$

$J = 1.0, \quad |\langle g_2 \rangle| = 0.004$

Figure 40. Instantaneous configurations at several temperatures for $\eta = \frac{3}{4}$ and $\rho \approx \frac{1}{2}$. 
the melting point precisely. It is, however, possible to fix a transition region from 
these results. Stripe character is clearly absent at \( J = 7.5 \), yielding an upper 
limit to the transition. The lower limit seems to be set at \( J = 9.5 \), where stripe 
order appears fixed. Between these temperatures, the simulated system makes 
infrequent transitions between the ordered and disordered states (Figures 42 and 
41), as would be expected for a small system.

A modification was introduced in the code at this point to aid equilibration of 
the system. Previously, a Monte Carlo “pass” on the system consisted of 3944 (i.e. 
58 \times 68) attempted single site flips, 3944 attempted triple site flips as shown in 
Figure 35, 3944 additional attempted single site flips, and 3944 attempted 7-spin 
flips (Figure 35). We added an additional series of 50 \times 3944 attempted single site 
flips, where we restricted ourselves to sites located on the interface. This improved 
equilibration greatly, since flips of sites located on the interface are far more likely 
to be accepted, and domain growth and domain motion occur at the interface. To 
 improve this further, we have also introduced a series of attempted moves in which 
we attempt to flip a line of sites along the interface. These two modifications have 
greatly facilitated the studies of stripe melting discussed in the next section.

By beginning the simulations from a variety of starting conditions (including 
starting from a completely empty lattice) we tested the reproducibility of the 
stripe phase for this system. Regardless of the conditions, we found that the drive 
to spontaneous stripe order (as evinced by the order parameter \( g_2 \)) at moderate 

Figure 41. Evolution of the stripe order parameter $g_2$ as a function of the number of Monte Carlo passes through the system at $J = 9.0$. Solid and dashed lines show $g_2$ for a 3944 particle system initialized in a completely disordered configuration and in a perfect stripe array, respectively. Also shown is $g_2$ for a 15776 particle system initialized in a perfect stripe array. A "pass" consists of (54 x lattice size) attempted moves as outlines in Section 4.4.
Figure 42. Evolution of the stripe order parameter $g_2$ as a function of the number of Monte Carlo passes through the system at $J = 8.50$. 
temperatures \((J \geq 9.5 \text{ at } \eta = \frac{3}{7})\) is highly reproducible at densities \(\rho \sim \frac{1}{2}\). A good example of this is shown in Figure 41.

We also find that the stripe width is highly reproducible. The average equilibrium stripe width \(l_{eq}\) agrees well with the analytic zero-temperature result of Chapter 3. Runs started from nonequilibrium stripe width (both > and < \(l_{eq}\)) quickly return to the expected width. Nucleation of new stripes does not appear to be an insuperable barrier in our system. Thanks to effective MC algorithms, the simulations may actually differ from experimental systems with regard to stripe nucleation. Clark and Meyer\(^73\) suggest that stripe nucleation will occur solely at system boundaries, which do not truly exist for our periodic system.

This opens the question of finite size effects. From the aforementioned results, we conclude that a stripe phase has been stabilized at a temperature apparently well above the melting point for the hexagonal phase, in direct contradiction to the mean-field result (Figure 2). In order to determine if the appearance of the stripe phase at these higher temperatures is due to artificial stability imparted by the periodic boundary conditions, the system size was quadrupled to 15776 particles (a 116 x 136 triangular lattice). A Monte Carlo “pass” was also expanded for this system to mean 54 x 15776 attempted flips on the system in a similar sequence to that outlined above for the smaller system. Due to the computer time necessary to complete a series of runs on this larger system, we have not as yet been able to show spontaneous stripe formation. However, as can be seen in
Figure 41, when initialized from a perfect stripe array and aged at a temperature within the transition region found above \((J = 9.0)\), the underlying stripe order remained intact for more than \(10^4\) attempted moves per spin, or \(1.7 \times 10^8\) total attempted moves on the entire system. At higher temperatures \((J = 8.50\) and \(8.0)\), the stripe order begins to decay in exactly the same manner as was found in the smaller system. While we cannot preclude the possibility that further enlargement of the system will alter these findings, we feel that the results for the larger system support the phase diagram shown in Figure 49.

4.5 Stripe-Isotropic Phase Transition

Much time and effort has been devoted to study of melting in 2-D systems\(^{12,68,69,74-76}\) such as smectic and cholesteric liquid crystals and ferromagnetic thin films. There is an immediate similarity seen between stripe melting in the dipolar lattice gas in the sharp interface region \((a, b, c, \text{ and } d \text{ in Figure } 40)\), and melting in such systems as 2-D smectics.\(^{8,77}\) Layered systems like the afore-mentioned are governed by the same continuum Hamiltonian at low-T, small-k and similar elementary excitations.

The Kosterlitz and Thouless\(^{68}\) (K-T) mechanism, as applied to melting in 2-D layered materials by Toner and Nelson,\(^{12}\) involves the unbinding of dislocations into oppositely charged disclination pairs (Figure 43). Phonon excitations occur (Figure 43) at very low temperatures, well before the melting transition occurs. This mechanism has also been noted in disordering of the lamellar phase in thin
Figure 43. Dislocation (b) unbinding into oppositely charged disclination pairs (c & d) triggers melting in 2-D layered materials in a Kosterlitz-Thouless type phase transition. Phonon excitations (a) occur at very low temperatures. (Reference 12)
garnet films. We believe the Kosterlitz-Thouless mechanism is also occurring in the dipolar lattice gas, as shown in the simulation results in Figure 44. In this figure, we see a time sequence at $J = 8.50$ in which a stripe phase disorders in exactly this manner. Phonon excitations are intrinsic (a). Appearance (b) and unbinding (c) of dislocation pairs produce the disordered phase (d). We also wish to point out the similarity between our resulting labyrinth phase, and the labyrinth phase displayed in ferromagnetic thin films (Figure 45).

As in the hexagonal-isotropic transition discussed earlier in this chapter, determination of the order of the transition is extremely difficult via simulation and will not be broached here. Brazovskii performed a perturbation analysis of melting in 3-D systems, and concluded that fluctuations of a preferred class of non-zero wave vector will produce a first-order transition. Garel and Doniach performed a Ginsburg-Landau analysis which produced a phase diagram similar to Figure 2. They view fluctuations of the Brazovskii class as an alternative mechanism to dislocation unbinding in the Kosterlitz-Thouless theory, rather than believing them to be two different theoretical treatments of the same phenomenon. No final assessment of the order of the transition can be given here.

The phase diagram of the dipolar lattice gas (Figure 49) is qualitatively similar to the Brazovskii phase diagram, and differs from the Landau theory phase diagram obtained by Garel and Doniach, and by Andelman et al. (Figure 2). However, despite the fact that the Brazovskii treatment is generally considered more sophis-
Figure 44. Time series from simulation at $J = 8.5$ show phonon excitations, as well as dislocation formation and unbinding as melting occurs.
Figure 45. Labyrinth phases from experiments on thin garnet films (Reference 79) and from simulation.
ticated, some fluctuations are neglected in it as well. Also, Brazovskiĭ does not
give special consideration to the borderline case of 2-D, and we have reservations
concerning the application of the Brazovskiĭ treatment on this basis.

4.6 Long Wavelength Fluctuations and Spacial Order

While it appears from snapshots of the dipolar lattice gas that stripe melting is
occurring well before the domain interface begins to decompose (Figure 40), we wish
to ascertain that simulation results of \( \langle \rho_k \rangle \) and the structure factor \( S(k) \equiv \langle \rho_k \rho_{-k} \rangle \)
are indeed consistent with a sharp interface limit. We therefore wish to devise a
sharp interface model for comparison to our simulation results.

A Hamiltonian for a 2-D smectic liquid crystal at low \( T \) and small \( k \) has been
derived by de Gennes\(^{80}\) and utilized by Sornette\(^{10}\) and by Toner and Nelson,\(^{12}\)
among others. If one considers the layers of the smectic to be stacked in the \( x \)
direction, then this 2-parameter Hamiltonian may be written as

\[
\mathcal{H} = \int \int dx dy \left[ \frac{B}{2} \left( \frac{\partial u}{\partial x} - \frac{1}{2} \left( \frac{\partial u}{\partial y} \right)^2 \right)^2 + \frac{K}{2} \left( \frac{\partial^2 u}{\partial y^2} \right)^2 \right] \tag{4.28}
\]

where the first term represents the stripe compression, while the second term
represents a splay energy. \( B \) and \( K \) are the elastic moduli for the system. This
Hamiltonian is presumably valid for long wavelength phenomena (like long-range
order) at low temperatures.
It has been well established that $\langle \rho_{k\neq0} \rangle = 0$ in the low temperature limit for systems obeying this Hamiltonian. (This is discussed in more detail in Toner and Nelson\textsuperscript{12} and references therein.) This implies that $\langle \rho_{k\neq0} \rangle = 0$ at all temperatures. While we should find that $\langle \rho_{k\neq0} \rangle$ vanishes in the thermodynamic limit, we find some residual order in our finite-sized system. Weakly non-zero $\langle \rho_{k\neq0} \rangle$ are nothing but an artifact of our periodically replicated system cell. However, we propose this is a useful artifact for the following reason: The Kosterlitz-Thouless melting theory on which the Toner-Nelson paper is based makes definite predictions about elastic moduli governing long-range fluctuations. If we can characterize fluctuations in our periodically replicated system, then we can estimate elastic constants for the dipolar lattice gas and compare our results more precisely to the predictions of Toner and Nelson.

We considered a continuum model which is more appropriate for comparison to our simulations than equation 4.28. The stripes are perfectly sharp (Figure 46). We assume a box of dimension $L_x \times L_y$ containing $N_x$ stripes. We neglect the linear tilt term $\left( \frac{\partial u}{\partial y} \right)^2$, and the Hamiltonian becomes

$$\mathcal{H} = \sum_{j=1}^{N_x} \int_0^{L_y} dy \left[ \frac{B}{2} \left| (u_j(y) - u_{j-1}(y)) \right|^2 + \frac{K}{2} \left( \frac{\partial^2 u_j(y)}{\partial y^2} \right)^2 \right]$$

(4.29)

where we have introduced the stripe index $j$. This expression assumes infinitely sharp walls, and defects other than phonon excitations are completely neglected.
Figure 46. Continuum stripe model with infinitely sharp walls.
The quantity $\rho_k$ is defined as

$$\rho_k = \int_0^{L_x} \int_0^{L_y} dx \, dy \, \exp(-i k \cdot r) \rho(r)$$  \hfill (4.30)

where we integrate over the length of the box in the $x$ and $y$ directions ($L_x$ and $L_y$, respectively). Since the interface is assumed to be infinitely sharp, the integral in $x$ may be broken into a summation over the stripe index $j$, and an integration over the width of each stripe

$$\rho_k = \sum_j \int_{j l_x + u_j(y)}^{j l_x + u_j(y) + l_x} \int_0^{L_y} dx \, dy \, \exp(-i k_x x - i k_y y)$$  \hfill (4.31)

Here $l_x$ represents the stripe repeat unit, or distance between the leading edge of consecutive stripes. $u_j(y)$ represents the displacement of stripe $j$ from its unperturbed state (i.e. straight stripes) at point $y$ in its length. The averaging necessary to produce $\langle \rho_k \rangle$ is done over all possible displacements $\{u_j(y)\}$ of all stripes $j$ at all points $y$.

This average may be reduced to

$$\langle \rho_k \rangle = \frac{2 \sin(\frac{k_x l_x}{2})}{k_x} \sum_j \exp[-i k_x l_x] \int_0^{L_y} dy \, \exp[-i k_y y] (\exp[-i k_x u_j(y)])$$  \hfill (4.32)

where the averaged quantity on the right hand side is ultimately seen to be independent of $j$ and $y$.

To analyze the applicability of the sharp wall limit to our simulation system, we pay specific attention to the cut in $k_y = 0$ to neglect fluctuations in $y$ and focus
on breakdown of the wall as $T$ increases. For this case $\langle \rho_k \rangle$ becomes

$$\langle \rho_{k_x, k_y=0} \rangle = \frac{2N_x L_y \sin\left(\frac{k_x L_y}{2}\right)}{k_x} \exp\left[\frac{-k_x^2}{4N_x L_y} \sum_{b,m_y} \frac{1}{\mathcal{K}(b,m_y)}\right]$$

(4.33)

where

$$\mathcal{K}(b,m_y) = \frac{4B}{l_z^2} \sin^2\left(\frac{\pi b}{N_x}\right) + K \left(\frac{2\pi m_y}{L_y}\right)^4$$

(4.34)

and $N_x$ is the number of stripes in our system.

In a similar manner, we may investigate the quantity

$$\langle S_k \rangle = \langle \rho_k \rho_{-k} \rangle$$

(4.35)

$$= \frac{4 \sin^2\left(\frac{k_x L_y}{2}\right)}{k_x^2} N_x L_y \sum_{j} \int dy e^{i\theta y} e^{ik_y y} \sum_{b,z} \frac{\sin^2(\frac{\theta}{2})}{N_x L_y} [\sum_{b,y} \sum_{y > 0} \frac{\sin^2(\theta)}{N_x L_y}]$$

(4.36)

where we have defined the variables $\theta$ and $\Gamma$ so that

$$\theta = 2\pi \left( \frac{j b_x}{N_x} + y b_y L_y \right)$$

(4.37)

$$\Gamma = \frac{4B}{l_z^2} \sin^2\left(\frac{\pi b_x}{N_x}\right) + K \left(\frac{2\pi b_y}{L_y}\right)^4.$$  

(4.38)

Both equations 4.33 and 4.36 may be calculated using short (< 150 line) codes, using the number of stripes and the cell size of our simulations.

We compared the values of $S(k)$ from equation 4.36 to simulation results obtained at $\rho \approx \frac{1}{2}$ to obtain an estimate for $B$ and $K$. In our simulations $S(k)$ has a large peak at $k = 0$, and one barely visible secondary peak at $k_x^{max} = \frac{2\pi}{L_x}, k_y = 0$. We roughly optimized the fit of the sharp wall model to the simulation results by eye, constraining $B$ and $K$ of the model to give the exact secondary peak height,
and adjusting the peak width to agree as closely as possible with the simulations. Cuts of $S(k_x,k_y)$ in two perpendicular directions through the secondary peak are shown in Figure 47. The large peak at $k = 0$ is not shown for clarity.

Having estimated the elastic moduli by looking at $S(k)$, $\langle \rho_k \rangle$ of the sharp wall model is also compared with the simulation result (Figure 48). Since the averaged $\langle \rho(r) \rangle$ is periodic with period $l_x$ in the $x$ direction, $\langle \rho_k \rangle$ is non-zero only for $k_y = 0$ and $k_x$ equal to integer multiples of $\frac{2\pi}{l_x}$.

Simulation of stripe phases are extremely demanding and the simulation results suffer from incomplete averaging, making it difficult to fix elastic moduli with great precision. Furthermore, the elastic moduli to be compared with K-T predictions are those which govern long wavelength fluctuations. Finite size effects will obscure this comparison.

Despite these caveats, this comparison has furnished some valuable results. No matter what specific values of $B$ and $K$ were chosen, fluctuations cause the first $\langle \rho_k \neq 0 \rangle$ peak to be much smaller than the $k = 0$ peak. Further peaks in both the simulation and the sharp wall model are not visible. All of these non-zero $\langle \rho_k \neq 0 \rangle$ peaks represent finite size effects. We can see that our simulation results are indeed consistent with a sharp wall model, and that stripe melting is occurring in the sharp interface limit.
Figure 47. Cuts in structure factor $S(k)$ from the simulation and the sharp wall model. $\lambda$ gives the ratio of the elastic moduli, $\frac{K}{B}$. 
Figure 48. Cuts in $\langle \rho_k \rangle$ from the simulation and the sharp wall model. $\lambda$ is the ratio of the elastic moduli, $\frac{K}{B}$.
CHAPTER V

Discussion

5.1 Discussion

In this work, we have attempted to demonstrate the applicability of the dipolar lattice gas to a variety of systems displaying self-organization behavior. Undeniably, much physical detail is omitted from this model. For example, conformational effects which are an essential part of a true monolayer system have been completely neglected. While we have attempted to minimize finite size effects and lattice effects, these are, to some extent, unavoidable. Due to this, a complete analysis of such aspects of the system as the order of the hexagonal-isotropic and stripe-isotropic transitions has eluded us. More precise assessment of the elastic moduli for the model, while feasible, will require substantially longer runs and is left to future work.

However, we do assert that the dipolar lattice gas does reproduce the qualitative behavior of many experimental systems, and, due to this, is worthy of
attention. This model does show a CMC in both 1- and 2-D. Many of the complex domain morphologies demonstrated by monolayer systems, 2-D smectics, and ferromagnetic thin films are also seen in the dipolar lattice gas, extending even to the non-equilibrium labyrinth phase. The model also shows a similarity to these latter two systems in the manner in which it undergoes stripe melting, where both phonon excitations and dislocation unbinding are displayed.

Based on these studies, we also propose a revision in the accepted phase diagram for the dipolar lattice gas. While the mean-field phase diagram shows an isotropic-hexagonal and hexagonal-stripe transitions at all relevant temperatures (Figure 2), we have succeeded in locating a temperature regime in which it is possible to stabilize the stripe phase, but not the hexagonal phase. Accordingly, we propose that the phase diagram for the dipolar lattice gas actually is as shown in Figure 49. This phase diagram is appropriate near $\eta = \frac{3}{7}$, the sharp interface limit studied in this work. The hexagonal-stripe (H-S) and inverted hexagonal-stripe (H'-S) boundaries at zero temperature were established in the work of Chapter 3. The height of the stripe phase region and the direct isotropic-stripe (I-S) transition have been determined through the simulation results presented in this chapter. The I-H-S and I-H'-S triple points are conjectured.

There are a number of interesting branches which this study may follow. A new algorithm has been introduced based on the microcanonical Monte Carlo studies of Creutz,81,82 and the work on multispin updates done by Wolff.83 The idea
Figure 49. Proposed phase diagram for the dipolar lattice gas on the basis of this study at $\eta = \frac{3}{4}$ (I=isotropic, H=hexagonal, H'=inverted hexagonal, S=stripe). The dashed line indicates an upper limit to the isotropic-hexagonal (I-H) boundary based on the scaling of particles with $R^{-3}$ interactions (equation 4.8).
behind this is simple. While the interfacial single site moves and the interfacial cluster moves introduced in the previous chapter have proven useful in this study, in this standard algorithm we are still left using a slightly modified version of the Metropolis acceptance rate. This means that our acceptance rate for attempted moves may only be as high as 16%, and lower in many cases. Time spent growing clusters and attempting moves which are rejected is computer time wasted. Accordingly, we propose an algorithm in which the energy change is built into the criterion for accepting a site into the cluster, which we then attempt to flip with a higher acceptance rate than the standard Metropolis algorithm would provide. Using this new algorithm, we hope to speed equilibration and improve our study of stripe melting in the model. Initial studies on the 2-D Ising model have proven successful, and application to the dipolar lattice gas is underway.

A closer look at the labyrinth phase is also in order. Experimental results have shown that there is a reproducible segment length in the labyrinth structure, based on digital line pattern analysis of video polarization microscopy studies in thin garnet films. The question of whether the labyrinth patterns displayed by the dipolar lattice gas also have a reproducible segment length seems worthy of future study.

Many 2-D monolayer studies show formation of chiral domains. A possible avenue for future work is derivation of a model which will reproduce these very complicated and elegant domain structures.
Finally, we also note that expansion of this model to three dimensions will also expand the range of experimental systems to which it applies. This should also be undertaken at some point in the future.
Bibliography


