The Role of Limited Valency and Bonding Orientation on Phase Behavior

by

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Abstract

Nanoparticles functionalized by single strands of DNA have been shown to be highly customizable building blocks for self-assembled nano-structures, giving rise to complex networks that have very unusual phase diagrams. Specifically, the nanoparticles exhibit a phase diagram which contains three critical points; the presence of two critical points is rare in nature, but has been found in some natural substances like water. In this thesis, we use lattice models to examine which nearest neighbor interactions are important to generate multiple distinct phases. We show that the multiple critical points cannot be reproduced via limiting the number of bonding neighbors alone. Development of more complex lattice models that may include such behavior based on our results is ongoing.
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Chapter 1

Introduction
1.1 Using DNA as a guide for self-assembled Nanostructures

Nanotechnology is a relatively new field of science and has given rise to many areas of research. Nanotechnology is essentially the utilization of techniques to construct atomic or molecular sized structures, on the order of hundreds of nanometers. One of the approaches to nanotechnology is the bottom-up approach where building blocks are created which in turn self-assemble into more complex structures [1, 2, 3, 4].

One of the more recent developments of nanotechnology is the construction of nanoparticle building blocks functionalized with strands of DNA oligonucleotides [4, 5, 6, 7, 8]. These nanoparticles are built by connecting single strands of DNA to a central micro- or nano-sized particle. By choosing an appropriate sequence of DNA bases, these particles form strong directional bonds with each other via DNA hybridization to form double stranded DNA. Controlling the length and sequence of the DNA strand makes it possible to modulate the strength of the interactions. This makes it possible to alter the temperature and concentration at which the self assembly occurs. Using a different number of strands per particle allows for control on the number of bonding neighbors which profoundly influences the structures formed by the particles. Since the number of strands, theoretically, determines the number of bonds that these particles make, the number of strands also controls the bonding valency of the particles. Additionally, these DNA dendrimers demonstrate complex phase behavior that has yet to be seen in other materials in nature.

1.1.1 Phase Behavior of DNA functionalized nanoparticles.

One of the basic characteristics of any material is its phase behavior, or phase diagram. The phase behavior of a substance is the behavior of its observable characteristics, such as free energy and density, with respect to the controllable parameters, e.g. temperature.
and volume. The phase behavior of most substances includes discontinuities in their extensive thermodynamic variable. For example, every non-ideal gas condenses into a liquid at a specific temperature and pressure. This can be seen as a discontinuity in the density of the substance as it is cooled at constant pressure (or compressed at constant temperature). The temperature at which this occurs is known as the critical temperature of the substance. The critical point and coexistence region, the region in phase space where the two densities co-exist, of a system will be defined more precisely in Section 1.2.1.

A recent work [9] studying a simple model for nanoparticles functionalized by four strands of DNA demonstrated complex phase behavior including critical points that not previously been seen in other materials in nature. Whilst a system with four thermodynamically distinct state is previously unknown, studies have shown that two critical points exists in some pure substances such as liquid water and SiO$_2$ [10, 11, 12, 13]. Ignoring crystal states, water and SiO$_2$ have three thermodynamically distinct states: (i) the gas, (ii) a low density liquid, and (iii) a high density liquid. This number of critical points is unusual in natural substances (one expects only a liquid-gas critical point). These critical points can be attributed to the existence of two types of bonding for the substance, each having different characteristics, such as bond length and bond strength. These factors cause the two bonding types to be dominant at different ranges of temperature and density. Using liquid water as an example, water molecules form strong directional hydrogen bonds and weaker intermolecular bonds, which form via the Van der Waal’s forces. These then affect the thermodynamics of the liquid as a whole, giving rise to multiple states.

Specifically, the simulations showed that the DNA dendrimers have a phase diagram that exhibits three critical points, each of which represent the transition to different networked states with different densities, shown in Figure 1.1. One can use the insights from molecular systems to help understand the multitude of phases in the system of four-armed DNA dendrimers. However, DNA dendrimers are much larger than water
Figure 1.1: Phase Diagram of DNA tetramers showing the critical points and coexistence curves. Figure taken from [9]. The density is normalized by the density of an ideal diamond lattice, showing that the coexisting phases occur at integer multiples of $\rho_d$. This is explained by the fact that the high density phases consist of interpenetrating diamond lattices.
and the strands form bonds of much higher energy relative to the Van der Waal’s forces, which are negligibly small in these dendrimer units. As such, the structures and phase behavior are determined only by the bonds formed by DNA strand pairing. The quality of these particles that give rise to the multiple critical points therefore cannot be explained by differing bonding energies that control the structure formed by the system. Instead, the multiple phases appear to result from interpenetrating networks of bonded dendrimers.

In this thesis, our goal is to understand the characteristics necessary to generate phase behavior that features multiple critical points when there is only a single length scale for bonding, as in the DNA dendrimers. To do so, we study on-lattice models to examine how characteristics such as limited valency and bonding orientation affect the critical behavior of simple models. Our results will allow us to gauge which qualities of the DNA dendrimers are essential in generating substances with multiple phases and how well lattice models can describe and replicate the behavior shown in DNA dendrimers.
1.2 The study of Lattice models

Lattice models have been studied for many years and have been instrumental for developing the understanding of phase transition and critical phenomena. However, very few analytical solutions exist for lattice models. The most well known solution is probably the exact solution to the two-dimensional Ising lattice by Onsager[14]. No exact solution is known for the three-dimensional Ising model. In the absence of an analytical solution, a mean field approximation of the model usually gives a qualitatively correct description of the phase transition, though the quantitative details are usually highly inaccurate.

Lattice models serve as a simplistic method to model complex behavior found in physical systems and have been successful in explaining the critical behavior in real systems. The relative simplicity of lattice based models makes it possible to explore exact numerical solutions relatively quickly. The drawback of having the on-lattice models is that they will generally not be quantitatively predictive for most properties of these systems. With the ever increasing speed of computers, numerical simulations are an excellent way to exactly study the phase behavior of system.
1.2.1 The Ising Model

The Ising lattice is a classical example of lattice models. In one dimension, it is defined as an ordered set of spins 1...N each of which are either spin up or spin down. Each spin $i$ has two nearest neighbors, spin $i-1$ and spin $i+1$. When two neighboring spins have the same orientation, they contribute an energy of $-J$ to the model, otherwise they contribute an energy of $J$ thus favoring alignment of spins. This model is easily extended into multiple dimensions. Mathematically, the Hamiltonian for the Ising model is

$$H = -J \sum_{<i,j>} s_is_j - B \sum_{i} s_i$$ (1.1)

where $<i,j>$ signifies that the sum goes over nearest neighbors only. The spin variables $s_i, s_j$ can take the values -1, spin down or 1, spin up. The second term in equation 1.1 represents the energy due to an external magnetic field $B$, which will favor one of the two spin directions.

Figure 1.2 shows a representative phase diagram. The critical point occurs at $B = 0$, expected since that is where the Hamiltonian is symmetric for the two spin states. Below the critical temperature $T_c$, there is a phase transition between magnetized states as a function of field.

Since every lattice site is filled, the model is usually studied in the canonical ensemble. The canonical ensemble consists of a collection of identically prepared systems at fixed temperature $T$, volume $V$, and number of particles $N$ that are in equilibrium with an external reservoir that allows for the exchange of energy. This exchange of energy occurs by the flipping of spins.

The original motivation for this model was to study magnetism and understand how local interactions can propagate over long distances, giving rise to spontaneous magnetization. Moreover, near the critical point, the behavior of many real systems can be mapped onto the Ising model. The set of systems that have the same critical properties...
The lattice gas is a model defined, in one dimension, by $N$ lattice sites that each take values 1 or 0, representing occupied and empty states, respectively. The Hamiltonian of this model

$$\mathcal{H} = -\epsilon \sum_{<i,j>} n_i n_j$$

is nearly identical to the Hamiltonian of the Ising model (equation 1.1) with the exception of the values which the occupancy variables take, 1 or 0. The sum containing
Figure 1.3: Diagram of a sample state in the lattice gas simulation. The dotted lines demarcate the allowed lattice sites. Each square allows for exactly one particle in its center. The energy of this particular state is $-8\epsilon$ (equal to number of bonds).

$B$ is absent. However, since the occupancy can vary, the system is best studied in a grand canonical ensemble, where the occupancy is controlled by $T$ and the chemical potential $\mu$. For the grand canonical solution, $\mu$ biases the system to occupied versus empty states, analogous to the field $B$ in the Ising model. This will be apparent when we discuss Monte Carlo simulations in 2.

This model is particularly useful for examining phase separation behavior where a gas discontinuously “condenses” into a full lattice, analogous to the liquid-gas phase transition.

This model can be mapped onto the Ising model by setting $\epsilon = 4J$ and $\mu = 2\beta(J\gamma - B)$ with $\gamma$ equal to the number of nearest neighbors of any given site and $\beta = \frac{1}{k_bT}$, $k_b$ is the Boltzmann constant[15]. By doing these transformations, the critical phase behavior of the lattice gas maps directly onto the Ising model. Since this model is isomorphic with the Ising model, it is part of the Ising universality class.
1.2.3 The Potts Model

The Potts model [16] is a generalization of the Ising model. Instead of having only two allowed orientations for a spin, each spin can take an orientation $q$ possible orientations, i.e. $s_i = 0, 1, 2...q - 1$. In the absence of an external field, this gives a modified Hamiltonian of

$$\mathcal{H} = -\epsilon \sum_{<i,j>} \delta_{s_i,s_j}$$  \hspace{1cm} (1.3)

The energy contribution from the magnetic field however is usually not included since, for the purpose of critical parameter studies, we know that the symmetry of the orientations occurs at zero field. $\delta_{x,y}$ is the Kronecker delta function, which takes two arguments $x, y$ and is equal to 1 if $x = y$, and equal to 0 otherwise.

This model has been shown to be much richer and more complex in its critical behavior and has been the subject of much research. A relatively brief review can be found at [17].

1.2.4 Lattice models applied to Water

Since water is expected to exhibit multiple critical points, it is valuable to consider lattice models formulated to study water [18, 19, 20, 21]. These models generally have Hamiltonians that are composed of two separate summations. For example, in reference [18], the Hamiltonian of the model is

$$\mathcal{H} = -\epsilon \sum_{i} \sum_{j} n_i n_j - \frac{J}{4} \sum_{i} \sum_{k} n_i n_k \delta_{i1} \delta_{k1} \sum_{j(ik)} (1 - cn_j).$$  \hspace{1cm} (1.4)

The occupancy variables are identical to the lattice gas, and the $\delta$ functions are as defined for the potts model in Section 1.2.3. The first part of the Hamiltonian, with
energy parameter $\epsilon$, goes over all nearest neighbors and corresponds to the standard lattice gas critical point. The second part, with energy parameter $J$, corresponds to the energy generated by forming Hydrogen bonds and give rise to a second critical point. As mentioned in the beginning of this chapter, DNA dendrimers only form one type of bond and thus these multi-part Hamiltonians are not ideal for modelling DNA. Hence one of our challenges will be to design a Hamiltonian with only a single term that results in multiple transitions.
Chapter 2

The Monte Carlo Method and Lattice Models

This chapter covers the lattice models used to develop our understanding of bonding restrictions so that we may better understand the phase behavior of DNA dendrimers. A variety of models were implemented to examine how a changing valency and cooperativity of bonding arms changes the behavior of the basic model.
2.1 Monte Carlo Simulations

2.1.1 Overview of Monte Carlo Simulations

Monte Carlo simulations, in the context of physics, are simulations involving the use of random numbers to generate data which have statistical relevance to the behavior of the model being simulated. In the context of molecular systems with clearly defined interaction potentials, this is an alternative to molecular dynamics simulations, where the system is simulated deterministically using Newton’s equations of motion.

Lattice simulations necessarily use a Monte Carlo approach since particles are identified by their positions in space and have no associated momentum. Monte Carlo lattice simulations are very useful to examine the qualitative behavior of complex systems since they simplify the internal complexity of molecules, allowing simulations to run much faster. Due to fixed lattice positions, distances in lattice space are exact and complex numerical algorithms to reduce error in the calculation of forces or force integrals are not required.

A Monte Carlo Lattice simulation consists of a set of lattice updates that is repeated $N$ times or timesteps. Each lattice update consists of a lattice modification (e.g. moving a particle from one lattice site to another, removing particles from the lattice, picking an entirely new randomly generated configuration on the lattice, etc...) depending on the ensemble being simulated. For example, simulating the Ising lattice under the Canonical Ensemble, described in 1.2.1, each lattice update consists of attempting to flip the spin of a lattice site.

There are many acceptance probabilities that can be used in a Monte Carlo simulation and two main conditions that they must obey are ergodicity and detailed balance. Ergodicity is the condition that it should be possible for the simulation to reach any state of the system from any other state via a chain of lattice updates. Detailed balance states that the rate at which a system makes transitions into and out of any state must
be equal. In addition, we must insure that the probability of a sampled state conforms to the desired statistical ensemble.

The Metropolis MC algorithm provides acceptance probabilities that satisfy these constraints. We use this algorithm because it is relatively simple to understand, implement and has a high acceptance rate for moves, allowing for efficient sampling of the lattice. First, the detailed balance condition can be expressed as

\[ \sum_a p_a P(a \rightarrow b) = \sum_b p_b P(b \rightarrow a) \] (2.1)

which states that the sum of transition probabilities out of a state multiplied by the probability of being in the state is equal to the sum of transition probabilities into a state, from all other states, multiplied by the respective probabilities of being in those other states. This can be satisfied by choosing a much simpler restriction,

\[ p_a P(a \rightarrow b) = p_b P(b \rightarrow a) \] (2.2)

or rearranged as,

\[ \frac{p(a)}{p(b)} = \frac{P(b \rightarrow a)}{P(a \rightarrow b)} \] (2.3)

where \( p(x) \) is the probability for a given configuration \( x \) and \( P(x \rightarrow y) \) is the transition probability of going from configuration \( x \) to configuration \( y \). This condition states that the ratio of the probability of the system being in state \( a \) to being in state \( b \) is equal to the ratio of the probability of the system going from state \( b \) to state \( a \), to going from state \( a \) to state \( b \).

This defines the ratio \( \frac{P(b \rightarrow a)}{P(a \rightarrow b)} \), but we must select consistent values for \( P(b \rightarrow a) \) and \( P(a \rightarrow b) \). For the canonical ensemble,

\[ p(x) = \frac{e^{-\beta E_x}}{Q} \] (2.4)
where $Q$ is the canonical partition function, which is the sum of the Boltzmann factors over all states, i.e. $Q = \sum_{\text{states}} e^{-\beta E_{\text{state}}}$ [22]. The Metropolis algorithm chooses

$$P(a \to b) = \max(1, e^{-\frac{\Delta E}{k_BT}}),$$

where $\Delta E$ is the energy difference between lattice configurations $a$ and $b$, each found by evaluating the Hamiltonian of the system. The energy difference can be easily evaluated for most lattice models, since the change depends only on the nearest neighbor lattice sites.

This acceptance probability means that if $\Delta E \leq 0$ we fix the probability at 1, definite acceptance of the configuration change, since the probability of an event cannot be greater than 1. Thus we always accept moves that reduce the energy of the lattice, which makes the Metropolis Algorithm as efficient as it is. More detailed information on detailed balance, and a derivation of the Metropolis Algorithm can be found in [22].

### 2.1.2 Grand Canonical Monte Carlo

A grand canonical Monte Carlo simulation is a modification of the previous scheme to study the grand canonical ensemble. The grand canonical ensemble is defined as a large collection of system configurations that are in equilibrium with an external reservoir that allows for the exchange of both particles and energy, which requires that chemical potential $\mu$, volume $V$ and temperature $T$ be held fixed. For a lattice system, the volume is fixed by fixing the number of lattice sites.

Due to the exchange of particles, the probability of being in a state requires an additional term, the fugacity $z$.

$$p(N, E) = z^N e^{-\beta E}$$
where \( z = e^\mu \). This parameter controls the tendency of the system to prefer differing densities.

At each timestep, we visit each lattice site and it has a 50% probability of insertion or deletion to maintain detailed balance. Since insertion cannot occur when a particle is already in a lattice site, or deletion from an empty lattice site, these moves are ignored. If an insertion or deletion can occur, the free energy contribution/requirement of the move is

\[
\Delta E = \epsilon (\text{bonds broken} - \text{bonds made}) - \mu \Delta N.
\]  

(2.7)

Using this in equation 2.3 gives us the acceptance probabilities to use in the grand canonical simulation.

This process is repeated for a number of timesteps, depending on the model being used and the phase behavior that is being studied, e.g. more timesteps are required to obtain valid data as one gets closer to the critical point or at low \( T \).

Whilst the grand canonical ensemble consists of a large collection of system configurations and the distribution of the values of an observable in the collection is considered the statistical distribution of the observable of the model, we assume the ergodic hypothesis to simplify analysis. The ergodic hypothesis allows us to study a single system and analyze its behavior over a long period of time, after an equilibration time, and take it as the statistical distribution for the observable.

### 2.1.3 Periodic Boundaries

Simulations of lattices typically use on the order of hundreds to thousands of particles at once. However, this is still a small number when compared to actual observable systems where the number of particles are many orders of magnitude larger. To reduce the finite
size and surface effects and more closely approximate the thermodynamic limit, periodic boundary conditions are used.

Conceptually, the three dimensional lattice being simulated is identified as a representative subspace of an infinitely large three dimensional lattice. Therefore, the particles at the “surface” of the lattice have neighbors that are on the “surface” of a neighboring lattice.

For lattice simulations with only nearest neighbor interactions, this is simplified to keep track of a single layer of particles placed at the faces of the lattice. The layer used is the layer of particles from the the face on the side of the lattice facing the opposite direction. This allows us to extrapolate our findings to a system of arbitrary size without having to simulate at the order of Avogadro’s number of particles.

While periodic boundaries reduce finite size effects, such effects are unavoidable, though usually minor if correlation lengths exceed the lattice size.

2.1.4 Histogram Reweighting

Histogram reweighting is a technique used to study histograms that increases the amount of information that we can extract from them [23]. This technique is helpful to locate the critical point, since the critical point properties are only apparent in a very small potion of a system’s phase space.

Given a histogram of occupancy $N$ and energy $E$ at a given $\mu$ and $T$, we know that the probability of that state is

$$P_{\mu,T}(N,E) = \frac{e^{-\beta E} e^{\beta N \mu}}{Z(\mu, T)}$$

(2.8)

where the numerator is the Boltzmann factor of this model and $Z$ is the grand canonical partition function. For a new state with parameters $\mu'$ and $T'$,
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\[ P_{\mu', T'}(N, E) = \frac{e^{-\beta' E} e^{\beta' N \mu'}}{Z(\mu, T)}. \]  
(2.9)

This can be expanded to

\[ P_{\mu', T'}(N, E) = \frac{e^{-\beta E} e^{-\beta (E' - E)} e^{\beta N \mu} e^{\beta N (\mu' - \mu)}}{Z(\mu, T)}, \]  
(2.10)

\[ P_{\mu', T'}(N, E) = P_{\mu, T}(N, E) \frac{Z(\mu, T)}{Z(\mu', T')} e^{-\beta (E' - E)} e^{\beta N (\mu' - \mu)}. \]  
(2.11)

Since we know \( \sum_{N,E} P(N, E) = 1 \) (sum of probabilities of all possible outcomes is unity), we can determine the constant ratio \( \frac{Z(\mu, T)}{Z(\mu', T')} \) by normalisation.

\[ P_{\mu', T'}(N, E) = C \ P_{\mu, T}(N, E) e^{-\beta (E' - E)} e^{\beta N (\mu' - \mu)} \]  
(2.12)

states that given the probability distribution \( P_{\mu, T}(N, E) \) we can scale it via the appropriate multipliers, and a normalising constant to give the probability distribution at another \( \mu', T' \) of the system.

This method is more accurate when the target point \((\mu, T)\) in phase space is close to the reference point since the range of \(N\) and \(E\) sampled for any \((\mu, T)\) will be limited. As such, this method is used in complement with the standard method of generating a scan of the phase space (running multiple simulations at a range of parameters).
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2.2 Lattice Models

2.2.1 Shared characteristics of the Models

All of the models are based on the nearest neighbor lattice gas with a Hamiltonian of the general form

\[ H = -\epsilon \sum_{\langle i, j \rangle} n_i n_j \delta_{\sigma_{ij}, \sigma_{ji}}(1 - \delta_{x_{ij}, 0}) \]  

where \( \langle i, j \rangle \) limits the sum to only nearest neighbor particles of the lattice. The occupancy variables \( n_i, n_j \) can take the values 0 or 1, for occupied or unoccupied respectively, and \( \epsilon \) as the energy scaling parameter. We take \( \epsilon > 0 \) so that bond formation is energetically favored. Each lattice site also has associated with it an orientation variable for a bonding arm to each nearest neighbor lattice site, \( \sigma_{ij} \), each of which may take a value from 1 to \( q \) (\( q \in \mathbb{N} \)). This parameter is an abstraction representing the complexity of the arms of the physical model as the arms can be in a suitable position for bonding but the molecules making up the arm may not be in the correct orientation to bond. A bond forms if \( \sigma_{ij} = \sigma_{ji} \), i.e. if arms of neighboring sites are in the same direction.

We study the models on a face-centered cubic, FCC, lattice, where each lattice site has 12 nearest neighbors. As such, the valency \( \gamma \) of a model is an integer between and including 0 to 12. At \( \gamma = 12 \) and \( q = 1 \), all the models are equivalent to the lattice gas. We have chosen the FCC lattice because we want to mimic the behavior of continuous space systems, and an FCC lattice has roughly the same structure as a compact lattice of spheres.
Figure 2.1: Diagram of a unit of the face centered cubic lattice. The diagram shows a lattice site (white) and its nearest neighbors. The different colors denote only the different relative positions of the neighbors. The six red neighbours and the central site are coplanar. Setting the axes such that the red neighbors are in the $x$-$y$ plane at $z = 0$, the purple spheres are in the plane above and the orange spheres are in the plane below.

2.2.2 Limited Valency Lattice Gas Potts Model

A lattice model used to study how valency affects the phase behavior of a lattice gas is described studied in [24]. It has the Hamiltonian

$$H = -\epsilon \sum_{<i,j>}^* n_i n_j$$

where the $n_i$, $n_j$ are the occupancy variables of the lattice. The $*$ limits the sum to only bond configurations with a maximum of $\gamma$ bonds, without restricting the number of nearest neighbor occupied sites.

The limited Valency Potts model is an extension of the above model and is the simplest of the three simulated models. However, it is actually the last model we considered in our research. The Hamiltonian for this model is given by

$$\mathcal{H} = -\epsilon \sum_{<i,j>}^* n_i n_j \delta_{\sigma_i, \sigma_j}$$

(2.15)
where \( n_i, n_j \) are the aforementioned occupancy variables and \( \sigma_i \) is the orientation of the particle in lattice site \( i \). This means that given occupied neighbors \( i \) and \( j \), there is a contribution of \(-\epsilon\) by their interaction if and only if \( i \) and \( j \) have less than \( \gamma \) other bonds.

The orientation of a lattice site, unlike the orientation described in the earlier section, is uniform over all its bonding arms. As such, an occupied lattice site may only form bonds with other neighboring lattice sites with the same orientation.

This model allows us to examine how the behavior of the model changes as we reduce the valency of a model which has very flexible and mobile arms. This mobility is simulated by every insertion move attempting to make as many bonds as possible \( i.e. \) the particle being inserted orients itself such that as much energy is produced by the insertion.
2.2.3 Random Orientation Bonding Model

The random orientation bonding model is a bottom-up construction based on the concept randomly placing multi-armed particles in a lattice. The Hamiltonian for this model is precisely given by Equation 2.13, with the additional limitation that we impose a maximum valency, as in the previous model.

Whenever a particle insertion is attempted, a randomly generated lattice site configuration is placed into the lattice. A lattice site configuration is comprised of the location of the lattice site and the positions of the $\gamma$ bonding arms. Since there are 12 nearest neighbors to each lattice site in the FCC lattice, there are $\binom{12}{\gamma}$ unique bonding arm configurations, given $q = 1$. A bond is considered to have formed when 2 neighboring lattice sites $i, j$ have a bonding arm facing each other.

This model examines how a changing valency affects a model that has bonding arms that are flexible but not as mobile with respect to energy changes. Conceptually, this model is alike a particle with bonding arms that do not experience a force when the arms are not in the precise positions that allow for bonding. As opposed to the model studied in [24], where all possible bonds form when particles are inserted, in the random orientation bonding model, bonds occur only at random. As mentioned earlier, these models are identical at $\gamma = 12$ and $q = 1$. 

2.2.4 Fixed Orientation Bonding Model

The fixed orientation bonding model is similar to the random orientation bonding model in all respects, including the Hamiltonian, with the exception of the types of particles inserted. Since it is conceivable that there is a rigidity in the relative orientations of bonding arms in particles, we give rigidity in the relative positions of arms when on a lattice system.

Since there exists only 1 configuration of arms for $\gamma = 12$, this model is equivalent to both the random orientation bonding model and the limited valency potts model, $\gamma$ is equal to the number of nearest neighbors. As such, we study $\gamma = 6$ in order to juxtapose the data against the random orientation bonding model.

Since at each $\gamma$, there exists $\binom{12}{\gamma}$ bonding arm configurations, a subset of them, which have the same relative arm positions, \emph{i.e.} rotationally symmetric configurations, have to be chosen as the set of configurations inserted into the simulation. Since particles can rotate in nature, any configurations which are rotationally symmetric to the set chosen should be in the set as well to minimize lattice effects.

Figure 2.2: Sample configuration of fixed orientation model. Full set of configurations are detailed in appendix A.

The configurations chosen are displayed in appendix A. They were chosen in a way that allows any one of the 12 configurations to span, \emph{i.e.} to create bonds with its neighbors, each of which having the same configuration, the lattice without preferentially creating lattice-born artifacts such as sheets or cones.
The motivation behind this model is the occurrence of a rigidity in the relative arm positions of particle bonding arms. For example, covalent bonds, comprised of a pair of electrons between two atoms, repel other covalent bonds via electric repulsion. As such, the energy minima for the bonded particles is as splayed out as possible so that the bonds are farther apart. In physical lattices such as crystalline systems, the particles of the system form a periodically repeating motif. By only allowing a fixed number of lattice site configurations, we increase the likelihood of this behavior being simulated.

In theory, if the simulation were to form such a crystalline structure by filling the lattice up with only 1 of the $q$ possible orientations (i.e. picking a motif), this forms a lattice configuration with an energy minimum. As such, the model may exhibit a second critical point.
Chapter 3

Results and Comparison

This chapter documents the results of Monte Carlo simulations for each of the models presented in Chapter 2. Whilst none of the models exhibit the many phases of the DNA tetramers that motivated the work, they do provide insight into the effects of changing valency and the cooperativity of bonding arms. These results also serve as a guide to develop more complex lattice systems which may share unusual phase behaviour with the DNA functionalized nanoparticles.
3.1 Random Orientation Model

![Graphs showing isotherms near critical point for Random Orientation Bonding Model]

Figure 3.1: Isotherms near critical point for Random Orientation Bonding Model

We have carried out Monte Carlo simulations to identify precisely the location of any critical points as well as the co-existence lines of the stable phases. The critical point of a system, defined more precisely later, is the point in the phase diagram that terminates the region where the system phase separates into 2 differentiable stable states. These stable states, in the models studied, are differentiated by their densities and co-exist at specific $T$ and $\mu$. Densities between the 2 states are unstable for a single phase and will separate into a combination of the coexisting phases such that the mean density is maintained.
Figure 3.1(a) shows the typical behaviour of $\rho$ as a function of $\mu$ along isotherms and provides an example to describe the identification of critical points in this model. At $T = 2.60$, $\rho$ increases smoothly as $\mu$ increases. At $T = 2.45$, $\rho$ undergoes a “jump” as the simulation crosses $\mu = -6$, more clearly seen at $T = 2.25$. This discontinuity in density is the signature of the liquid-gas phase transition of a system. The temperature at which this transition occurs is the critical temperature $T_c$, which for Figure 3.1(a) is approximately $T = 2.45$. As can be seen in Figure 3.2, the time series graph shows that the system fluctuates between 2 distinct phases, approximately $\rho = 0.7$ and 2. The simulation density does sample values between the 2 phases, but only for a relatively small number of steps as the transition occurs.

![Figure 3.2](image_url): Time series of the density for $\gamma = 9$, $T = 1.200$, $\mu = -3.460$, Random orientation bonding model. Coexistence phases are at distinctly opposing density levels.

For the Ising model, the magnetization parameter exhibits a specific distribution when
Figure 3.3: Histogram of the order parameter at the critical points of the random orientation bonding model at different $\gamma$. This curve is produced by normalization of $\nu$. Normalization is done by shifting $\nu$ by the mean in the negative x direction, $P(\nu) = P(\nu + \text{mean}(\nu))$ and scaled so that $\int P(\nu) d\nu = 1$
the system is at the critical point. The magnetization is defined as

\[ M = \sum_i s_i/N \]  

(3.1)

where \( N \) is the number of lattice sites in the lattice and \( s_i \) takes values -1 or 1, representing “spin up” and “spin down”. For the 3D Ising model, \( M \) has the bimodal distribution seen in Figure 3.3. Moreover, many different systems, including fluids have the same behaviour at the critical point. These systems are said to be in the same universality class. For such a system, a critical point can be identified as a point in phase space where the order parameter, which depends on the model, exhibits the distribution in Figure 3.3. The same distribution can be found in the density of the lattice gas model.

\[ \text{Figure 3.4: Histogram of } \rho \text{ at the critical point for the random orientation bonding model at } \gamma = 6 \]

Since we know the density should behave as an order parameter, we seek to find the location where the distribution \( P(\rho) \) is bimodal. As shown in Figure 3.4, we can locate
the bimodal behaviour of $\rho$, but the distribution does not match that expected for the Ising universality class. This is due to an energetic effect caused by the average $\rho$ not being at 0.5, causing an asymmetry in the density peaks. Unlike the lattice gas model, where the occupied and unoccupied states are symmetric about $\rho = 0.5$, this model (and the others with a reduced valency) are asymmetric in their liquid and gas phases since lattice sites cannot bond with all of their neighbors. To account for the energetic contribution, the correct order parameter to consider is a mix of the density and energy, namely $\nu = \rho - su$ where $u$ is the energy per occupied site, and $s$ is referred to as the field mixing parameter[15]. By picking a test value for $s$, we can identify the appropriate value for $s$, since only one value of $s$ will produce a $\nu$ that has the bimodal distribution desired.

Figure 3.3 is the histogram of $\nu$ at the critical points of the random orientation model. To expedite locating the critical point (which can be quite time consuming since it is only a single point), we first find a region where the density distribution is bimodal. This is readily recognized by the types of fluctuations seen in Figure 3.2. We use the histogram reweighting method (described in Section 2.1.4) to iteratively search the phase space until further iterations showed no observable changes in the distribution of $\nu$. We expect this model to be in the universality class of the Ising model, and indeed the distributions of $\nu$ are identical when the systems are at their respective critical points.

The model exhibits a first order phase transition at lower $T$, higher $\mu$ and at a lower average $\rho$ as the valency of the molecule drops. This is consistent with a similar model studied in [24]. As $\gamma$ drops, the coexistence curves also broaden to their maximum limit faster, i.e. are ‘flatter’.

For $\gamma < 12$, the phase boundaries differ from those of the Sastry model [24]. The differences are shown in $\gamma = 9, 6$, where the curves are much wider and lower than in the Sastry limited valence model. This can be explained by a small but significant\footnote{Approximate values only.}
Figure 3.5: Table of Critical Parameters for Random Orientation Bonding Model

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>$T_c$</th>
<th>$\mu_c$</th>
<th>$\rho_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>2.453</td>
<td>-6.000</td>
<td>0.500</td>
</tr>
<tr>
<td>9</td>
<td>1.249</td>
<td>-3.466</td>
<td>0.396</td>
</tr>
<tr>
<td>6</td>
<td>0.461</td>
<td>-1.701</td>
<td>0.215</td>
</tr>
<tr>
<td>4$^1$</td>
<td>0.080</td>
<td>-1.000</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Figure 3.6: Critical Parameters for Random Orientation Bonding Model
Figure 3.7: Coexistence curves for Random Orientation Model. △ denote the critical points.

Figure 3.8: Coexistence curves for Sastry model [24] shown as a reference. The density $\rho = \langle n \rangle$.
difference in the models used. Particle insertions in the Sastry model automatically make bonds up to a maximum of $\gamma$. In the Random Orientation Bonding model, particles are inserted with random arm orientation, i.e. can only form bonds if arms are facing each other. Since the probability of forming bonds is lower, the lattice exhibits a phase transition at a lower temperature.

To understand the width of the coexistence region, it is reasonable to expect the dense liquid boundary of the coexistence curve to roughly coincide with the value at which the density is equal to the ratio of $\gamma$ to the number of neighboring lattice sites at low $T$, since this is the density at which the lattice can form all bonds, and thereby minimize the energy. Since all particles can potentially be fully bonded at that density, particle insertions should have minimal energetic contributions and removals should require a maximal energy input. Indeed, this is what is observed in the Sastry limited valence model as shown in Figure 3.8. However, for our model, the liquid coexistence line occurs at a larger $\rho$ which can be explained by the reduced probability of bonding. For particle insertions with randomly oriented bonding arms, the lattice requires many more particles to attain its minimal energy configuration. This translates to a stable liquid phase with much higher density for the same $\gamma$.

Originally, simulations for $\gamma = 4$ runs were planned, but the coexisting phases are not easily identified at the lattice size used. Specifically, the low density peak is located at $\rho = 0$ as shown in Fig. 3.9. This is due to the lattice size being too small to obtain statistically detailed information for the low density phase of the system at $\gamma = 4$. To resolve the low density phase, we would require lattice sizes which are computationally infeasible at this time.
Figure 3.9: Normalized histogram for $\gamma = 4$. $T = 0.088 \mu = -1.006$ and an inset graph of the same histogram on a log scale.

### 3.2 Fixed Orientation Bonding

The simulations done on this model are more limited due to time constraints and complexity of finding a ‘good’ set of particle bonding arm configurations to simulate. We determine the critical point location and coexistence lines in the same fashion as the previous model. To compare with the previous model, Figure 3.10 shows that the coexistence curves for the random orientation bonding model and fixed orientation bonding model at $\gamma = 6$ are the same. This implies that having a specific structure to the particles does not change $T_c$. Slight differences in the data are minute and are most likely computational artifacts due to finite time sampling of the phase space.

The phase diagram observed in both models is the liquid-gas phase transition. This is a transition that occurs, evidently, independent of the internal structure of the particles. Mathematically, in either model, picking a bonding configuration at random is equivalent
Figure 3.10: Comparison of coexistence curves for $\gamma = 6$. Parameters for critical point are $T_c = 0.4702$, $\mu_c = -1.6748$, $\rho_c = 0.3335$. 

$T$ and $\rho$ are the temperature and density, respectively.
to each lattice arm site having a 50% probability of having a bonding arm. This means that the dynamics of the model with respect to its liquid-gas phase transition is not necessarily affected by having a fixed bonding structure.

If this phase transition also takes the system across the entire density space, a possible second phase transition due to self assembly (i.e. entire lattice is occupied by particles of the same configuration) may be subsumed by the liquid-gas transition.

An alteration of the model that we can make to change this is to use a combination of this model and the limited valency potts model, which is described in section 2.2.2. From these, we create a model which whilst retaining fixed orientation amongst its bonding arms, attempts to find the orientation which makes as many bonds as possible. This will narrow the coexistence region and due to fixed orientation of the bonds, it is also possible to have the lattice undergo the transition described at the end of Section 2.2.4.

This will not work for the random orientation model since in the data simulated of that model (which has $q = 1$), attempting insertions that make as many bonds as possible translates the model directly into the Limited Valency Lattice Gas Potts Model with $q = 1$. $q$ are orientations for both of the models, but are implemented differently in each. In the random orientation model, each bonding arm may have a different orientation, but in the lattice gas potts model, the orientation is associated with the lattice site. The findings of that model are discussed in Section 3.3.
3.3 Limited Valency Lattice Gas Potts Model

We initially did simulations on this model to examine how increasing the potts orientation changes the phase behavior. Contrary to expectations, our results showed that $\rho_c$ and $T_c$ increase as $q$ increases.

Our naïve expectation was that $T_c$ should drop as $q$ increases since this reduces the number of bonds at a given $T$, similar to reducing $\gamma$ in the random orientation bonding model. In the same vein, we expect $\rho_c$ to drop since the likelihood of forming a large network of particles, where the particles have the same orientation, falls as $q$ increases.

![Figure 3.11: Histogram of the Order Parameter at Critical Point of $q = 2$ - Potts Lattice Gas Model. $T_c = 2.490, \mu_c = -3.576$. As a comparison, $T_c = 2.453$ for $q = 1$. Whilst the histogram does not appear to fit perfectly to the reference histogram, the histogram reweighting method was used multiple times without finding a much better $T$ and $\mu$.](image)

Identification of the critical point is also complicated by a second-order phase transition.
that occurs for $q \geq 2$. This second order transition occurs in the “magnetization”, which is defined as the largest fraction of the lattice filled by a particular orientation, at a $T$ that is close to but higher than $T_c$. The effects of the second order transition is a discontinuous change in the rate of change of $\rho$ with respect to $\mu$. This and an apparently increasing $T_c$ obscures the critical point of the model. Work continues for this model, though it is not anticipated to give rise to multiple critical points.
Chapter 4

Conclusion

The current results show that whilst limited valency has a large effect on the phase behaviour of the system there is no indication that it is sufficient to generate multiple critical points in the models. Given the results of the simulations, we are further developing our models to examine which properties are needed to give rise to the multiple critical points in the DNA model.

We plan to extend the research by running further simulations for the random orientation bonding model with higher numbers of $q$. Whilst this has a direct and simple effect on the $\gamma = 12$ model, it may give rise to more complex behaviour when combined with reduced valency. These simulations were not performed since we needed to properly understand the effects of valency before adding more complex parameters to the model. Moreover, the low probability of accepting MC moves caused by the multiplicity of non-bond orientations would increase the runtimes of the simulations.

Additionally, we plan to create a combination of the fixed orientation Bonding model and the limited valency lattice gas model. As shown in [24], this will, reduce the density of the high-density side of the coexistence curves, giving a chance for the model to exhibit a second first-order phase transition at higher density.
Whilst the limited valency lattice gas model with Potts orientations is not yet properly understood, we may eventually combine this model with the fixed orientation model. This may result in more complex behavior than in the previously studied models.
Appendix A

Fixed Orientation Bonding
Configurations
Appendix A. Fixed Orientation Bonding Configurations

Figure A.1: Bonding configurations for the fixed orientation model. Diagram A.1(a) shows the relative positions of the arms of all neighbors. The red, green, blue neighbors and white central particles are coplanar. The purple neighbors are coplanar and above the plane of the RGB neighbors, orange neighbors are below. All the neighbors are oriented identically in the different configurations, but are scaled differently.
Bibliography


