Computer simulation studies of nucleation and structure formation in locally favoured structure lattice models.

> A Thesis Submitted to the College of Graduate Studies and Research in Partial Fulfillment of the Requirements for the degree of Master of Science in the Department of Chemistry University of Saskatchewan Saskatoon

> > By

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ABSTRACT

There is growing evidence to suggest that small energetically favourable clusters play an important role in the thermodynamics and dynamics of liquids. However, identifying and quantifying favoured local structures (FLS) in real liquids remains a challenge. Ronceray and Harrowell [EPL, 96 (2011) 36005] developed a simple spin lattice model that explore the effects such structures have on the properties of the liquid and their ability to freeze. By selecting different FLS, they found the model froze to an array of different crystal structures with varying unit cell sizes and complexities through a range of strong and weak first order transitions. This thesis explores how complex structures are formed through nucleation and contrasts the nucleation mechanism of the $\{1,5\}$ FLS model, which exhibits a weak first order transition, with that of the $\{3,3\}$ FLS model, which freezes through a strong first order transition. Monte Carlo simulation and the mean first passage time method were employed to calculate the nucleation rate and identify the nature of the critical nucleus for the FLS model systems. The $\{1, 5\}$ FLS system accumulates a significant amount of solid-like structure in the metastable liquid phase prior to freezing. As a result, the supercooled liquid contains large equilibrium solid-like clusters that fluctuate in size prior to nucleation. After visualization of the spins, the $\{1, 5\}$ FLS system showed that the system forms a structure close to that of the crystal before crystallization. In contrast, the $\{3,3\}$ FLS system forms most of its structure during the transition process. The energy barrier for the $\{3,3\}$ FLS system was found to be higher than that observed for the $\{1,5\}$ FLS system. This work examines the role the symmetry and structural correlation of the FLS might play in the different freezing and nucleation behaviours of the two systems.

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CHAPTER 1 INTRODUCTION

1.1 Overview

Nucleation is the initial process that controls the formation of new materials such as the crystallization of a solid from solution, the condensation of liquid from a vapour or the self-assembly of viral capsids [1]. Structure formation begins with a small number of molecules coming together to form a seed particle in a pattern characteristic of the new phase and once this seed has reached a critical size, the material forms spontaneously. Classical nucleation theories have been successful in describing the formation of simple materials but they fail to describe the nucleation of complex materials that form different local structures, which are then organized over multiple length scales. For example, colloidal photonic crystals developed for light harnessing [2], materials in CdTe solar cells and zeolites used for catalysts in the petroleum industry and purification/separation technologies [3, 4], all exhibit complex, large unit cells in their crystal structures that are formed from a variety of different local molecular arrangements. These are then structured and organized over many nanometers to form pore structures, or ordered layers. It is clear that a deep understanding of how to control structure formation is essential to our ability to produce high quality, complex materials for applications in energy and separation technologies.

This work addresses the differences in the nucleation mechanism for strong and weak first order phase transitions and how differences in the symmetry of local structures that make up a crystal, often referred to as favoured local structures (FLS) because they have low favourable energies, affects nucleation mechanisms. The remainder of the introductory chapter discusses nucleation, which involves forming clusters of a new phase in the presence of a mother phase. Classical nucleation theory, which is the most common model used to understand nucleation models, will be reviewed along with the kinetics and thermodynamics of nucleation. A spin lattice model that was developed by Ronceray and Harrowell [5] is chosen as the system to address the questions above. The chapter also describes these spin models, which contains energetically favourable local structures and their contribution to glass and crystal formation. The work described in this thesis focuses on two of these models denoted the $\{1,5\}$ FLS and the $\{3,3\}$ FLS systems. These were chosen because they show significant differences in their freezing behaviour . They also show significant differences in their symmetry. To examine these systems, the mean first-passage time (MFPT) method, proposed by Wedekind [6], was employed to calculate the rate of nucleation, the size of the critical embryo, the Zeldovich factor and the nucleation barrier. The MFPT method and the importance of the free energy barrier to nucleation are explained in this chapter.

1.2 Stability, Metastability and Phase Transitions

Consider the process of compressing a gas along an isotherm. Above the critical temperature $T > T_c$, the pressure increases continuously as a function of decreasing volume, as shown in Figure 1.1a. Below T_c , the isotherm exhibits a first order transition from the gas to the liquid phase that is characterized by a discontinuous change in the volume at a constant pressure, denoted by the b - b' line in Figure 1.1a. The pressure then increases rapidly once the system is in the condensed phase. At the equilibrium coexistence point, the temperature, pressure and chemical potential of the two phases are equal and in the single phase regions the equilibrium phase has the lowest chemical potential (see Figure 1.1b).

However, experiments show that first order phase transitions do not always occur exactly at the equilibrium point between two phases. For example, gases can be compressed below the gas-liquid equilibrium density without condensing to form a supersaturated vapour. Liquids can also be cooled below their equilibrium melting temperature without freezing to form what is known as a supercooled liquid. In fact, most water in clouds exists in the form of supercooled liquid droplets [7].

Figure 1.1: Phenomenological picture of metastability in vapour liquid equilibrium adapted from P. G. Debenedetti [7]. The blue line is the binodal, while the red line is the spinodal, b and b' are equilibrium states on the binodal, c is the binodal, e and f are the limits of stability. T is the temperature and Tc is the critical temperature.



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(b)

The states beyond the equilibrium points are metastable extensions of a phase beyond the equilibrium phase transition. To understand their properties and their relations to thermodynamic quantities, it is necessary to consider the effect of fluctuations around a local equilibrium point. A macroscopic body that cannot interact with its surroundings is known as an isolated system and cannot exchange mass, heat or do work on its surroundings. The second law of thermodynamics states that the state of entropy of the entire universe, as an isolated system, will always increase over time for a spontaneous process and will reach a maximum at equilibrium. For a system that is in equilibrium, any process that disturbs the equilibrium via a fluctuation must satisfy the equation,

$$[\Delta S]_{U,V,N} \le 0, \tag{1.2.1}$$

where S is the entropy, U is the internal energy, V is the volume and N is the number of moles of the system. ΔS is the change of the entropy caused by the fluctuation. This equation can be rewritten as,

$$[\Delta U]_{S,V,N} \ge 0, \tag{1.2.2}$$

which indicates that the internal energy is a minimum at equilibrium, so fluctuations away from equilibrium cause U to increase. The effect of a fluctuation can be explored by considering an expansion around the equilibrium point. Using a Taylor expansion, the energy variation can be expanded as,

$$\left[\delta U + \frac{1}{2!}\delta^2 U + \frac{1}{3!}\delta^3 U + \dots\right]_{S,V,N} \ge 0.$$
(1.2.3)

At a minimum, a vanishing linear and positive second order term exists for a stable equilibrium when considering all variations at constant S, V, N. This gives

$$\delta U|_{S,V,N} = 0, \text{ and } \delta^2 U|_{S,V,N} > 0.$$
 (1.2.4)

It shows that fluctuations away from equilibrium are restored to their initial equilibrium position. The system is in an unstable equilibrium when both terms equal zero,

$$\delta U|_{S,V,N} = 0$$
, and $\delta^2 U|_{S,V,N} = 0.$ (1.2.5)

This represents the point where the energy surface is flat so there is no restoring force and fluctuations will continue to grow. The internal energy at constant temperature, T, pressure, p, and chemical potential, μ , are given by the fundamental equation

$$dU = TdS - pdV + \mu dN. \tag{1.2.6}$$

This relates to changes in energy, entropy, volume and number of molecules of a single component fluid along a reversible path. For an n-component mixture, the equation becomes

$$dU = TdS - pdV + \sum_{j=1}^{n} \mu_j dN_j.$$
 (1.2.7)

Equations 1.2.6 and 1.2.7 can be written in a general form as,

$$dU = \sum_{j=1}^{n+2} Y_j dX_j,$$
 (1.2.8)

where X represents the natural independent extensive variables for energy (entropy, volume, number of moles), and Y corresponds to the conjugate intensive variables (temperature, minus pressure, chemical potential), thus, $[X, Y] = [S, T; V, -P; \mu_i (i = 1, ...n)]$. By taking partial derivatives, we obtain the conjugate intensive variables,

$$Y_j = \left(\frac{\partial U}{\partial X_j}\right)_{X_1, X_2, \dots, X_{j-1}, X_{j+1}, \dots, X_{n+2}}.$$
(1.2.9)

The right hand side of Equation 1.2.4 can be written as,

$$\left(\frac{\partial Y_{n+1}}{\partial X_{n+1}}\right)_{Y_1,Y_2,\dots,Y_n,X_{n+2}} > 0.$$
(1.2.10)

When a macroscopic system satisfies Equation 1.2.10, the system is said to be in stable or metastable equilibrium. Once the limit of stability is reached,

$$\left(\frac{\partial Y_{n+1}}{\partial X_{n+1}}\right)_{Y_1, Y_2, \dots, Y_n, X_{n+2}} = 0.$$
(1.2.11)

These equations are valid for confirming stability of a homogenous fluid system with respect to the appearance of a new phase. For example, in a single component system, taking (N, V, S) as the variables Equation 1.2.10 gives

$$(N, V, S) \Longrightarrow -\left(\frac{\partial P}{\partial V}\right) > 0.$$
 (1.2.12)

In the context of the gas liquid transition, Equation 1.2.12 shows that the gas phase remains metastable at volumes below the equilibrium point until the limit of stability (spinodal) is reached at the maximum in the Van der Waals equation of state. The same analysis can be carried out for other thermodynamic potentials, such as the Helmholtz (N, V, T) and Gibbs (N, P, T) free energies. A similar analysis also applies to other phase transitions, such as the liquid-crystal freezing transition, which is the focus of the current thesis. However, the existence of a spinodal-like limit of stability of the liquid phase is unlikely because the liquid and crystal phases have different fundamental symmetries.

In the metastable region, State A shown in Figure 1.2, the system is locally stable to small fluctuations, but large fluctuations will allow the system to find the stable energy minimum (State B). This implies that there is a barrier between the metastable and stable states that must be overcome. It also highlights the fact that metastable states must have a finite lifetime because a large enough fluctuation will eventually appear in the system as described in Figure 1.2.



Figure 1.2: Illustration of the evolution of a system from a metastable equilibrium state (State A), via an unstable equilibrium to a stable equilibrium state (State B). Adapted from figure 4 in reference [8].

1.3 Nucleation

Nucleation involves forming clusters of a new stable phase in the presence of a metastable mother phase. These clusters can be formed in both sub-saturated and supersaturated conditions. If the mother phase is sub-saturated, the clusters form but are unstable and disappear but if the mother phase is supersaturated, the clusters that are formed need to exceed a certain minimum size before they grow spontaneously into the new stable phase. The volume of the newly formed phase is proportional to the free energy decrease associated with moving material from the metastable phase to the more stable phase. On the other hand, forming a new phase implies the formation of an interface between the mother phase and the new phase. This proportionally increases the energy to the area of the interface. The first comprehensive study of thermodynamics of the nucleation process was by Gibbs [9], who revealed that the reversible work required to form a nucleus of a new phase comprises two terms, a bulk and a surface term. Becker and Doring [10] derived an expression for the rate of formation of critical clusters. Volmer and Weber [11] came up with the first nucleation rate expression, arguing that the nucleation rate should be proportional to the frequency of collisions between the critical clusters of the new phase and the vapour molecules. Zeldovich [12] and Frenkel [13] expanded on nucleation work done earlier. Their work together forms what is now known as classical nucleation theory (CNT). This has become the standard simple theory for nucleation of a new phase, such as a liquid or a crystal. Classical nucleation theory has excelled at describing simple materials but has failed to describe complex materials. For example, although CNT could estimate critical supersaturations in vapour-liquid systems, the nucleation rates are off by many orders of magnitude and CNT fails both quantitatively and qualitatively to describe binary nucleation in water-rich aqueous alcohol or acetone mixtures since the composition of the nucleus was incorrectly predicted [14].

1.3.1 Kinetic Model for Cluster Formation

For a cluster, E_n , formed from n molecules, it is assumed that adding or removing a single molecule, E_1 , causes the cluster to either grow or shrink in a series of bimolecular reactions:

$$E_{n-1} + E_1 \underbrace{\stackrel{k^+(n-1)}{\overleftarrow{k^-(n)}}}_{k^-(n)} E_n, E_n + E_1 \underbrace{\stackrel{k^+(n)}{\overleftarrow{k^-(n+1)}}}_{k^-(n+1)} E_{n+1},$$
 (1.3.1)

where $k^+(n)$ represents the rate of addition to an *n*-sized cluster, while $k^-(n)$ is the rate of single molecule loss. This process of monomer addition and loss to a cluster is represented in Figure 1.3.

Considering a system of coupled differential equations, the description of change in the population of an embryo of a given size, n, at time, t, may be written as,

$$\frac{\partial N(n,t)}{\partial t} = N(n-1,t)k^+(n-1) - N(n,t)(k^+(n) + k^-(n)) + N(n+1,t)k^-(n+1), \quad (1.3.2)$$

where N(n,t) is the number density of embryos having n-monomers at time t. The nucleation rate past a cluster size n, J(n,t), represents the time-dependent flux of clusters past that size and is written as,

$$J(n,t) = N(n,t)k^{+}(n) - N(n+1,t)k^{-}(n+1).$$
(1.3.3)

The nucleation rate in the above equation has dimensions of inverse time, and is proportional to the total number of molecules in the system.



Figure 1.3: Growth and decay of a cluster occurs through a series of bimolecular reactions.

In the context of vapour condensation, the forward rate of monomer addition to a cluster can be obtained from kinematic consideration of the gas phase, and is directly related to the vapour pressure. However, the rate constant associated with the loss of a monomer is independent of the pressure, and is a property of the cluster that is unknown. By assuming detailed balance, the backward rate can be obtained in terms of the equilibrium populations of the clusters and the forward rate. In crystal nucleation, both forward and backward rates are unknown. Nevertheless, the equilibrium hypothesis forms one of the essential assumptions in classical nucleation and can be described as follows. Consider a well defined problem like a chemical species A reacting to give a new species B, with a forward rate constant k_A^+ and for the reverse, k_B^- . The rate of change of A is given by,

$$\frac{dX_A}{dt} = -k_A^+ X_A + k_B^- X_B, (1.3.4)$$

where X_A and X_B are mole fractions of species A and B, respectively. For a closed system, X_A and X_B become constant after some time, so at equilibrium, $dX_A/dt = 0$. Having the forward rate and the equilibrium mole fractions of A and B makes it relatively simple to obtain the reverse rate,

$$k_B^- = k_A^+ \frac{X_A^{eq}}{X_B^{eq}}.$$
 (1.3.5)

By using the constrained equilibrium hypothesis, which states that the embryos evolving from the metastable phase cannot grow beyond a certain limit size, and assuming microscopic reversibility at equilibrium, the net rate must be zero. The backward rate for the cluster growth can therefore be expressed in terms of the forward rate as

$$k^{-}(n+1) = k^{+}(n) \frac{N^{eq}(n)}{N^{eq}(n+1)}.$$
(1.3.6)

where $N^{eq}(n)$, is the equilibrium cluster size distribution.

1.3.2 Classical Nucleation Theory

It is still necessary to obtain an expression for the equilibrium number of clusters before an expression for the rate can be obtained. The metastable state of a system contains thermal fluctuations. When the nucleation barrier is high enough compared to the thermal energy,

$$N^{eq}(n) \propto exp\left(-\frac{\Delta G_n}{k_B T}\right),$$
 (1.3.7)

where ΔG_n is the (minimum) reversible work needed to form an n-molecule embryo. Because in principle, there should be no work associated with the formation of a single molecule embryo, the proportionality constant should equal the number density of unassociated molecules in the bulk metastable phase. Therefore,

$$N^{eq}(n) = N_0 exp\left(-\frac{\Delta G_n}{k_B T}\right),\tag{1.3.8}$$

where N_0 is the number of the monomers, or isolated molecules.

Taking into account the sequential formation of embryonic liquid droplets in a supersaturated vapour, as described in Equation 1.3.1, the unimolecular steps resulting in the formation of these droplets are considered to be at equilibrium. The chemical potential for a droplet with n molecules, μ_n , can therefore be written as

$$\mu_n = n\mu_1, \tag{1.3.9}$$

where μ_1 is the chemical potential per molecule in the bulk vapour. The embryos are treated as distinct molecular species of an ideal gas mixture, because of this assumption, it follows that

$$\mu_n = \lambda_n(T, \upsilon) + k_B T \ln \frac{N^{eq}(n)}{\sum N^{eq}(n)},$$
(1.3.10)

where λ_n is the chemical potential of an n-sized embryo when it is the only species present, v is the bulk specific volume and $N^{eq}(n)$ is the concentration of n-molecule droplets. The concentration, $N^{eq}(n)$, becomes

$$N^{eq}(n) = \left[\sum N^{eq}(n)\right] exp\left[\frac{n\mu_1 - \lambda_n}{k_B T}\right].$$
(1.3.11)

Comparing Equation 1.3.11 with Equation 1.3.8 implies,

$$\Delta G_n = \lambda_n - n\mu_1, \tag{1.3.12}$$

where $\lambda_n = n\mu - A(n)\sigma$, and μ is the chemical potential of the stable phase and A(n) is the area of the cluster interface, and σ is surface tension. Classical nucleation theory assumes steady state conditions, where the distribution of clusters of different sizes is independent of time. The total steady state nucleation rate obtained by performing a recurrent summation over all embryo sizes present is given by,

$$J = N_{tot} \left[\sum_{n_{min}}^{n_{max}} \frac{1}{k_{(n)}^+ N^{eq}(n)} \right]^{-1}, \qquad (1.3.13)$$

where N_{tot} is the total number density of embryos, n_{min} and n_{max} are the smallest embryo size and largest embryo size in the cluster distribution, respectively.

Replacing the summation in Equation 1.3.13 by an integral and using Equation 1.3.8 gives,

$$J = k_{(n)}^{+} N_{tot} \left[\int_{n=n_{min}}^{n_{max}} \frac{1}{k_{(n)}^{+} N^{eq}(1)} exp\left(\frac{\Delta G(n*)}{k_B T}\right) dn \right]^{-1}.$$
 (1.3.14)

where n* is the critical nucleus. The major contribution to the integral comes from a narrow size range centred around the location of n*, where the distribution exhibits a sharp maximum. Approximating the free energy around the location of n* gives,

$$\Delta G(n) \approx \Delta G(n^*) + \frac{1}{2} \frac{d^2 \Delta G(n)}{dn^2} |_{n^*} (n - n^*)^2.$$
 (1.3.15)

The nucleation rate then becomes

$$J = k_{(n)}^{+} N_{tot} N^{eq}(1) exp\left(\frac{\Delta G(n*)}{k_B T}\right) \left[\int_0^\infty exp\left(\frac{\frac{1}{2}\frac{d^2 \Delta G(n)}{dn^2}|_{n*}(n-n*)^2}{2k_B T}\right) dn\right]^{-1}.$$
 (1.3.16)

Some of these fluctuations may reach and overcome the critical size, which leads to growth of the cluster to become more stable. Classical nucleation theory assumes the system reaches a steady-state whose nuclei appears at a rate described by evaluating the integral in Equation 1.3.16 to give,

$$J = k_{(n)}^+ Z N_{tot} exp\left(-\frac{\Delta G(n*)}{k_B T}\right), \qquad (1.3.17)$$

where Z is the Zeldovich factor, which is a function of the second derivative of the cluster formation free energy at the critical size,

$$Z = \sqrt{-\frac{1}{2\pi K_B T}} \frac{\delta^2 \Delta G}{\delta n^2}|_{n=n*}.$$
(1.3.18)

This factor was introduced by Becker and Doring [10] to describe the cluster fluctuations around the critical size. The number of critical clusters that reach a size that is large enough to grow continuously is given by $ZN_{tot}exp\left(-\frac{\Delta G(n*)}{k_BT}\right)$. Volmer and Weber [11] and Farkas[15] did not consider the Zeldovich factor in their work which resulted in an overestimation of the nucleation rate. The Zeldovich factor therefore characterizes the flatness of the energy profile around the critical size.

The key feature of classical nucleation theory is that it uses the constrained equilibrium hypothesis, involving detailed balance, to transform the nucleation rate from a kinetic problem into one that is amenable to thermodynamic analysis. The minimum reversible work of forming a cluster can then be calculated in a number of different ways, including simple classical thermodynamics or computer simulation.

1.3.3 Thermodynamics to Nucleation Free Energy Barrier

The free energy barrier to nucleation can be estimated by treating the droplet of the new phase as being composed of a bulk core surrounded by an interface [7]. At constant temperature, pressure, and number of particles, the Gibbs free energy is the appropriate thermodynamic potential for the reversible work of a process. The change in free energy associated with the formation of a nucleus is the sum of a bulk term and a surface term,

$$\Delta G(n) = \Delta \mu n + \sigma A(n), \qquad (1.3.19)$$

where $\Delta \mu$ is the chemical potential difference between the two phases involved, n is the size of the cluster, A is the surface area of the embryo and σ is the surface tension of the interface. The first term is equivalent to the total free energy associated with the formation of the nucleus of the new phase, while the second represents the free energy gain due to the formation of the new interface. It is usually assumed that the cluster is a sphere of radius, r, because this is the shape that minimizes the surface area of the cluster, and that the new phase is a uniform density, ρ , with a sharp interface between the cluster and the surrounding mother phase. Equation 1.3.19 then becomes,

$$\Delta G(r) = \frac{4}{3}\pi r^3 \rho \Delta \mu + 4\pi r^2 \sigma. \qquad (1.3.20)$$

Figure 1.4: Classical Nucleation Theory. The solid line represents $\Delta G(r)$, given by equation 1.3.20, which is the sum of the surface term (dashed line) and the volume term (dash-dot line).



Figure 1.4 shows the free energy of nucleation as a function of the nucleus radius, r, as envisioned by classical nucleation theory. The positive term is the cost of forming the new phase, and is proportional to the surface area of the new phase. The surface area for a spherical nucleus is given by $4\pi r^2$. To obtain the surface free energy, this is multiplied by the surface tension of the new phase, assuming it is a sharp interface with the surface tension of a flat bulk liquid-vapour interface at the coexistence. The negative term is related to the lower free energy of the most stable phase with respect to the metastable phase. This term is obtained by multiplying the number of particles in the nucleus with the difference in chemical potential between the two phases and noting $n = \frac{4}{3}\pi r^3 \rho$.

The competition between the negative and positive terms leads to the formation of a critical barrier with a critical cluster size, and it highlights how the metastable state is stabilized. Fluctuations that lead to the formation of clusters smaller than the critical size lower their free energy by shrinking back into the uniform mother phase. If a cluster greater than the critical size is formed, it lowers its free energy by spontaneously growing into a droplet of the new stable phase. The nucleation rate is then the rate at which clusters pass over the nucleation barrier and is usually measured as the number of clusters formed per

unit time per unit volume.

Classical nucleation theory is based on several assumptions that may be violated under certain circumstances. It assumes nucleation is a one step process, where only one free energy barrier is relevant, and the nucleus forming in the metastable phase consists of only a small piece of the thermodynamically stable phase. It has been known that during crystallization, the structural composition of crystalline clusters changes as they become larger. The chemical potential difference is assumed constant in classical nucleation theory but it may be a function of crystal size, depending on the structure of the small cluster, although the exact relation is not known. The formation of intermediate phases during crystallization has also been noticed for many systems including small molecules, proteins and ice. Also, the spherical nucleus is a good approximation for the gas liquid phase, but crystals have facets, with different surface free energies, etc. This leads to the need to use the Wulff [16] construction, where the surface free energy term involves a sum over the facets with the equilibrium shape of the crystal. However, despite these draw backs, CNT remains the most widely used approach to study nucleation.

1.4 Molecular Monte Carlo Simulation Methods

The Monte Carlo method was originally developed by von Neumann, Ulam and Metropolis, at Los Alamos [17], to study the diffusion of neutrons in nuclear materials, and has since become one of the essential computer simulation methods used to study a wide range of molecular systems [18, 13], including many spins systems [19, 20]. The method gets its name from the extensive use of random numbers that help evaluate integrals, such as the partition function found in statistical mechanics. However, rather than the direct evaluation of an integral, the Metropolis MC algorithm focuses on producing a trajectory in phase space that samples from a particular statistical mechanics ensemble and allows for the calculation of average properties of a system.

In a classical system, the canonical partition function for a system of N identical particles, in a volume V, at a temperature T, can be written as

$$Q = c \int dp^{N} dr^{N} exp[-\hat{H}(r^{N}, p^{N})/k_{B}T], \qquad (1.4.1)$$

where r^N represents the particle coordinates, p^N represents their corresponding momenta,

 $c = 1/h^{3N}N!$, *h* being Planks constant, and $H(p^N, r^N) = K(p^N) + E(r^N)$ is the Hamiltonian for the system with kinetic energy, *K*, and potential energy, *E*. The kinetic energy is a quadratic function of the momenta, and independent of the position of the particles, so it is possible to integrate over these degrees of freedom to obtain

$$Q = (1/N!)Z/\Lambda^{3N},$$
 (1.4.2)

where $\Lambda = (2\pi m kT/h^2)^{1/2}$ is the de Broglie wavelength and Z is the configurational integral,

$$Z = \int dr^N exp[-\beta E(r^N)]. \qquad (1.4.3)$$

An average quantity in statistical mechanics is then given by,

$$\langle A \rangle = \frac{\int dr^N exp[-\beta E(r^N)]A(r^N)}{Z}.$$
(1.4.4)

The metropolis method provides an efficient method for the evaluation of two integrals in Equation 1.4.4 by using importance sampling. The goal of importance sampling is to draw a sample from a proposal distribution and re-weight the integral using importance weights so that the correct distribution is targeted. In this case, the method samples regions of the distributions with a large Boltzmann factor. If the configurations of the system are sampled with the correct distribution, then the average of a property can simply be calculated as

$$< A >= (1/N_s) \sum_{i=1}^{N_s} A_i,$$
 (1.4.5)

where N_s is the total number of configurations sampled and A_i is the value of the property in the i^{th} configuration.

The challenge in molecular simulation is to sample the distribution to obtain the average even when Z is not known in advance and only $\exp[-\beta E]$ is known. To achieve this, the Metropolis method uses an acceptance probability for moving from an old configuration (o)to a new configuration (n), as shown in Figure 1.5, that is based on the need for equilibrium and detailed balance between the old and new states.

Acceptance probability
$$(old \rightarrow new) = min(1, \exp[-\beta \Delta E]),$$
 (1.4.6)

where ΔE is the energy difference between the new configurational state and the old, and kT is the Boltzmann's constant times the absolute temperature. Equation 1.4.6 shows that

any MC move that results in a decrease in the energy is automatically accepted. If the move results in an increase in the energy, the move that is accepted has a probability that decreases exponentially with increasing ΔE . To test if such a move is accepted, a random number between 0 and 1 is generated. If the random number is below the acceptance probability, given by Equation 1.4.6, the move is accepted, otherwise, it is rejected and the system is returned to the old configuration.

One advantage of this technique is that only a small fraction of the states of the system need to be sampled in order to get accurate estimates of physical quantities, assuming the system is able to access the equilibrium states. The presence of metastable states, that trap the system in sub-regions of configuration space can influence the ability of the Monte Carlo methods to provide good equilibrium averages.



Figure 1.5: Acceptance ratio plot as a function of energy difference.

Figure 1.6: Periodic boundaries used in simulation. The shaded portion represents the system while the arrow shows the interaction.



In order to simulate bulk phases, it is important to choose boundary conditions that show the presence of the bulk surrounding for an N-particle model system rather than a wall. This is achieved by employing periodic boundary conditions. The system cell volume of Nparticles is treated as a primitive cell of a periodic lattice of identical cells, as shown in Figure 1.6. This allows the particles to interact with the closest particles in any of the cells. Periodic boundary conditions [15] have proven to be an effective method for simulating homogenous bulk systems [21]. It is important to note that this can lead to artificial correlations that are not present in a true bulk system, and it is important to consider only interactions that span half the cell width to avoid artificial interactions. It is worthwhile stating that the boundary of the periodic box itself has no special significance thus, the origin of the periodic lattice of primitive cells may be chosen anywhere and will not affect any property of the model system under study.

The importance sampling Monte Carlo method provides good estimates of average quantities in equilibrium because it samples the states where the Boltzmann factor is high. However, it is often interesting to know the properties of the system away from the equilibrium, where the probability of sampling is small. For example, in nucleation, the states associated with the critical nucleus appear at the top of a free energy barrier so these states are rarely sampled in MC simulation. Umbrella sampling was introduced by Torrie and Valleau [22], to overcome this problem and is designed to sample configurations along an arbitrary reaction coordinate. The method works by adding a bias in the form of an additional energy term to the interaction energy that forces the system to sample regions of configuration space that usually have low probabilities of appearance. The average properties are then calculated by reweighing the bias to ensure the correct probability is obtained. The method has been used extensively to study nucleation and is very effective in studying systems with high barriers [72]. However, this study will not use umbrella sampling because the barriers are low enough to allow nucleation to occur on the simulation time scale. Instead, this work will use the mean first passage time as a way of obtaining the free energy barrier.

1.5 Mean First Passage Time

The mean first passage time (MFPT) method for analyzing simulations of activated processes was presented by Wedekind et. al. [23]. The method is based on the concept of mean first passage times and has many advantages to it. It is simple and straightforward to implement in a simulation, it can be used to determine the rate, and also facilitates the location of transition states, i.e, finding the critical nucleus, solely from the kinetic data. It differentiates activation from the subsequent growth of the system and has the possibility to infer more valuable information, such as the thermodynamics of the activation barrier, including the height of the barrier, as well as growth curves and lag times. The parameter of interest in nucleation is the rate at which the barrier is crossed and this method makes this relatively simple to determine.

The dynamics of many non-equilibrium and activated processes can be described in terms of a Fokker-Planck equation,

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[D_0 e^{-\beta U(x)} \frac{\partial}{\partial x} (P(x,t) e^{\beta U(x)}) \right]$$
(1.5.1)

where P(x,t) is the probability distribution function, D_0 the diffusion coefficient, U(x) the free energy barrier, $\beta = 1/kT$, k the Boltzmann constant and T the temperature. The reaction coordinate x is the cluster size. Figure 1.7a shows a typical one-dimensional free energy surface for an activated process with a domain [a, b] that has a barrier located at x^*

Figure 1.7: Free energy barrier and corresponding mean first passage time.



(a) A Plot showing the free energy of formation of a cluster. The MFPT arises from a narrow size range close to x*.



passage time of Figure 1.7a.

The MFPT for the nucleation event described by Equation 1.5.1 is given by the expression

$$\tau(x_0; a, b) = \int_{x_0}^{b} \frac{1}{D_0} dy \exp[\beta U(y)] \int_{a}^{y} dz \exp[-\beta U(z)].$$
(1.5.2)

The MFPT is analyzed based on a starting position, x_0 , in the Figure 1.7a. The boundary conditions reflect at point a and absorb at point b. The average time it takes the system to reach x^* for the first time is given by $\tau(b = x^*)$ and the barrier crossing rate is,

$$J = \frac{1}{2\tau(x^*)},$$
 (1.5.3)

where the factor 1/2 arises from the fact that the system has an equal chance of falling to either side at the top of the barrier. The location of the transition state can also be obtained from the behaviour of the MFPT. The first derivative of Equation 1.5.2 with respect to b yields

$$\frac{\partial \tau(b)}{\partial b} = \frac{1}{D_0} \exp[\beta U(b)] \int_a^b \partial z \exp[-\beta U(z)].$$
(1.5.4)

Taking the second derivative gives,

$$\frac{\partial^2 \tau(b)}{\partial b^2} = \frac{1}{D_0} + \beta U'(b) \frac{\partial \tau(b)}{\partial b}, \qquad (1.5.5)$$

where the prime (') denotes the first derivative. At the top of the barrier $\beta U'(x^*) = 0$, which gives the size of the critical nucleus at the top of the barrier,

$$\frac{\partial^2 \tau(b)}{\partial b^2}|_{b=x*} = \frac{1}{D_0}.$$
(1.5.6)

Activation rates are determined accurately only when the nucleation barrier is high, i.e when $\beta U(x^*) \gg 1$. The MFPT has a characteristic sigmoidal shape as shown in Figure 1.7b, and the rate is given by the inverse of the value of the MFPT at the plateau, τ_J , and is relatively insensitive to the initial conditions [23]. The inflection point of the MFPT curve gives x^* , which indicates the size of the critical nucleus at the top of the barrier. Near the critical nucleus size, x^* , the MFPT expression is given by Equation 1.5.2 and can be evaluated by the method of steepest descent to give,

$$\tau(b) = \frac{\tau_J}{2} (1 + erf((b - x^*)c)), \qquad (1.5.7)$$

where x^* is the critical size at the transition state, $erf(x) = 2/\sqrt{\pi} \int_0^x e^{-x^2} dx$ is the error function, and

$$c = \sqrt{\frac{|U''(x^*)|}{2kT}},$$
(1.5.8)

which is related to the Zeldovich factor $Z = c/\sqrt{\pi}$ and the local curvature around the top of the barrier, U''(x*). The MFPT at the plateau,

$$\tau_J = \frac{1}{J},\tag{1.5.9}$$

represents the inverse of the transition rate. By fitting MFPT results to Equation 1.5.7, many of the important parameters can be obtained.

The free energy barrier, which refers to the minimum amount of free energy that must be procured by a chemical entity in order to undergo a given activated process, controls the dynamics of many systems such as phase transitions and chemical reactions. There are different equilibrium techniques used to study activation barriers and free energy landscape from simulations. An example is the umbrella sampling [6]. Equilibrium techniques however are mostly not sufficient because the process of interest does not occur at equilibrium. Nonequilibrium techniques have also recently been developed where the system is forced by an external influence.

The method developed by Wedekind and Reguera [23] presented above allows the calculation of the nucleation rate and size of the critical cluster, directly from non equilibrium trajectories of the nucleation process. The method also allows for the reconstruction of the equilibrium free energy barrier [6]. This method is easy to implement and can be used in stochastic simulations. The dynamics of many non-equilibrium and activated processes described in terms of a Fokker-Planck equation is presented in Equation 1.5.1. When the barrier is relatively high for an activated process, the system reaches a steady state after a short transient time, where $\frac{\partial P(x,t)}{\partial t} = 0$. This steady state is characterized by a timeindependent probability distribution, P(x), and a constant current reaction rate, J, given by,

$$J = -D(x)e^{-\beta U(x)}\frac{\partial}{\partial x} \left(P(x)e^{\beta U(x)}\right), \qquad (1.5.10)$$

that is independent of x as $\frac{\partial P(x)}{\partial t} = \frac{-\partial J}{\partial x} = 0$. Integrating this equation yields,

$$\beta U(x) = -\ln P(x) - J \int \frac{dx'}{D(x')P(x')} + C, \qquad (1.5.11)$$

where C is a constant. It is worthwhile noting that in an equilibrium situation, Equation 1.5.11 reduces to $\beta U(x) = -\ln P(x)$. This equation shows that the free energy landscape from the knowledge of the steady state probability can be reconstructed as long as the value of the steady state rate and the diffusion coefficient are known. These parameters are not accurately obtained easily in a simulation however, the steady state rate is related to the mean first passage time which is given by Equation 1.5.2. Taking the second derivative of Equation 1.5.2 gives,

$$\frac{\partial \ln(A(x)D(x))}{\partial x} = \frac{1}{D(x)A(x)} + \frac{\partial(\beta U(x))}{\partial x},$$
(1.5.12)

where $A(x) = \frac{\partial \tau(x)}{\partial x}$. Integrating this equation gives,

$$\beta U(x) = \ln(B(x)) - \int \frac{dx'}{B(x')} + C.$$
(1.5.13)

Combining Equation 1.5.11 and Equation 1.5.13 gives,

$$\frac{\partial(B(x)P(x))}{\partial x} = P(x) - JA(x). \tag{1.5.14}$$

Integrating this then gives,

$$B(x) = \frac{1}{P(x)} \left[\int_{a}^{x} P(x') dx' - \frac{\tau(x)}{\tau(b)} \right],$$
(1.5.15)

where $J = 1/\tau(b)$ has been used. As long as the steady state is reached, the equations are valid. The method is valid only for high and symmetrical nucleation barriers, where the simulation data are well described by Equation 1.5.7. The analysis has been proved to work fairly well although it is more involved for transitions in which the time scales of nucleation and growth are not well separated [24, 25]. Wedekind et. al. [26] used the method to investigate the thermodynamics of the crossover from a nucleation-growth process to spinodal decomposition in a condensing Lennard-Jones vapour and to reconstruct the free energy barrier for cluster formation. Wedekind et. al. [27] report six nucleation rate isotherms for vapour-liquid condensation in argon using the MFPT method and also calculates the critical cluster size. Although the results obtained deviated from CNT by two to seven orders of magnitude, they are consistent with rates obtained by other simulation methods. The method has been extensively used to determine the rate, cluster sizes and to estimate free energy barriers in different vapour-liquid transitions [28]. It has also been used to study crystallization in Lennard-Jones nano-droplets [29] and liquids [30], and is found to be an effective method in characterizing crystal nucleation. One of the challenges of using the method is that the nucleation events must take place within the time scale of simulation, which generally restricts the analysis to the study of nucleation involving barriers lower than 15kT.

1.6 Favoured Local Structures

1.6.1 Local structure in liquids

Crystals have both well defined local structures and long-range periodic order. In a simple crystal, such as the face centred cubic (FCC) crystal, all the individual atoms share the same local order, which is then propagated in all three axial directions. The individual atoms in

more complex crystals may exhibit different local structures that are then organized on a longer length scale into a large unit cell able to be replicated over a long-range. On the other hand, while liquids do not exhibit long-range ordering, even the simplest model liquid, such as the hard sphere fluid or liquid argon [31, 32], show significant short-range ordering as indicated by the short-ranged peaks in their radial distribution functions (see Figure 1.8).



Figure 1.8: Radial distribution functions for liquid argon and solid argon obtained from simulation [32] reproduced with permission.

There is growing evidence to suggest that the presence of local structure within the liquid phase has important implications for their properties. Local ordering in systems with directional bonding is well known. For example, water has been known to form local tetrahedral order stabilized by hydrogen bonding [33, 34]. This was already recognized by Rontgen [35], leading to the famous mixture model of water [36]. The local tetrahedral order in liquid Si and SiO_2 [7] is almost identical to that of the crystal, but the long order is disrupted by the orientational disorder of the tetrahedra, leading to the formation of what is known as a random tetrahedral network. The number density of such tetrahedral

local structures may play a critical role in water-like anomalies, such as the liquid density maximum [37] and possible liquid-liquid phase transitions between high and low density liquid [38], observed in these systems. Local order has also been observed in metallic liquids [39].

Local order in simple liquids is more difficult to characterize, but mesoscopic structural order, which can be characterized by bond orientational order parameters, have been identified [36]. There is growing evidence that local structure in liquids may assume a vital role in crystallization, quasicrystal formation, and the liquid-glass transition. One approach to understanding liquid behaviour, particularly below the freezing temperature where the liquid is expected to thermodynamically freeze to the stable crystal, is to consider the formation of favoured local structures (FLS) that have a low energy. The idea was first suggested by Frank [39] and has been developed into a more general theory of frustration in liquids and glass forming by Tarjus [40]. The main focus is on the formation of local structures that frustrate the formation of the crystal phase. The icosahedron is one example of a structure that is energetically favourable but is unable to fill space and has been linked to glass forming [41]. However, recent studies have begun to examine the role of a wide range of different FLS that can be identified as small polyhedral packing units [42] involving small clusters (see Figure 1.9). Figure 1.9: Topological clusters [43] reproduced with permission. The structures detected by the topological cluster classification [44]. The letters correspond to local structures found in different models/systems, while the numbers identify the number of atoms in the cluster. K is the Kob-Andersen model [45], W is the Wahnstrom model [46]. The locally favoured structures for the Kob-Andersen model (11A), Wahnstrom model (13A) and hard spheres (10B) are highlighted by boxes. Other letters correspond to the variable-ranged Morse potential. Letters at the start of the alphabet refer to long-ranged interactions and later letters refer to short-ranged interactions, following Doye et al. [47]. Common crystal structures are also shown.



The local order formed in the liquid state does not necessarily have to frustrate crystal formation, and some liquids show evidence of the formation of FLS that favour crystal formation [48]. In the absence of frustration, ordering is likely to proceed through a continuous or weakly first-order transition. Competition between bond orientational order parameters compatible with the crystal symmetry, and those that are incompatible, leads to strong frustration effects against crystallization and transitions that are strongly first order.
1.6.2 Lattice Models

Favoured local structures (FLS) describe long lived and energetically favourable structures that appear in the liquid. Some FLS are related to the crystal states that the system can form, and they promote nucleation. Other FLS frustrate nucleation and can lead to glass formation. These structures have been identified and are known to gain significant concentration as temperature is lowered by various studies. However, FLS are difficult to identify in experiments or atomic models of liquids. Ronceray and Harrowell [49, 5] developed a new lattice spin model, where the FLS is explicitly specified. In this model, a spin is located at each lattice site on a two-dimensional triangular lattice, and it can take two possible orientations, up or down. The energy of a spin is determined by the up-down pattern of its neighbouring six spins. If the pattern matches the pattern of the FLS, then it is given a lower energy of -1, otherwise it has an energy of zero. The energy of the configuration is then the sum of the energies for all the spins. Figure 1.10 shows the different FLS structures possible in the model, along with their resulting crystal structures. The identity of a given FLS is denoted by indicating the number of down spins, followed by the length of the longest sequence of up spins in the FLS. For example, the $\{2,4\}$ notation indicates that the FLS has 2 down spins and 4 up spins following each other sequentially. The $\{1, 5\}$, however, is labeled $\{1\}$ because if there is 1 down spin then the remaining 5 are all up spins and will follow each other in the sequence. The $\{0, 6\}$ FLS is labeled $\{0\}$ for the same reason. In Figure 1.10, the symbol g is the multiplicity, Z is the unit cell size and E_o is the ground-state energy as shown in Figure 1.10.

	FLS	Ground State Crystal		FLS	Ground State Crystal \boldsymbol{a}		Ground State Crystal b	
	{0}	Z = 1		{23}	Z = 9		Z = 9	
	20	$E_0 = -1$		2	$E_0 = -2/3$		$E_0 = -2/3$	
	00	g = 1	20000000000000000000000000000000000000	ŌŎ	g = 6			
	{1}	$\mathcal{Z}=7$		{24}	$\mathcal{Z} = 9$	* * * * * *	$\mathcal{Z}=3$	
	00	$E_0 = -6/7$		•	$E_0 = -2/3$		$E_0 = -2/3$	
	00	g=6		00	g=6			
	{22}	Z = 4		{31}	$\mathcal{Z} = 3$		$\mathcal{Z}=3$	
	00	$E_0 = -3/4$		2	$E_0 = -2/3$		$E_0 = -2/3$	•••••
	00	g = 3		00	g = 2	*****		
	{32}	$\mathcal{Z}=20$		{33}	$\mathcal{Z} = 6$			
	•	$E_0 = -4/5$			$E_0 = -2/3$			
	00	g=12		00	g = 6			

Figure 1.10: Distinct locally favoured structures and their ground-states in the two dimensional spin lattice model [5]. Reproduced with permission from authors.

FLS accumulate in liquids upon cooling for a given interaction potential between particles because of their stability. The model produces various crystals with different sized unit cells that exhibit different symmetries and geometries. The properties of this FLS model make it a good choice for study, as it is possible to study nucleation as a function of crystal complexity and unit cell size, and it is relatively simple to simulate these lattice spin models. In addition, several FLS models show interesting freezing phenomena. For example, two FLS, the $\{2,3\}$ and $\{2,4\}$ FLS in Harrowell's [5] paper usually freezes into the groundstate crystal structure *a* in figure 1.10, even though there are two ground-state structures of the same energy. The $\{3,1\}$ FLS, on the other hand, freezes into either of the two possible structures indicating a variety of nucleation mechanisms. The work in this thesis focuses on the nucleation behaviour of the $\{1,5\}$ and the $\{3,3\}$ FLS systems. These were chosen because they show significant differences in their freezing behaviour. They also show significant differences in their symmetry.

1.7 Scope of Thesis

This work is going to address two key questions:

- What is the difference in the nucleation mechanism for strong and weak first order phase transitions?
- How do differences in the symmetry of the FLS affect the nucleation mechanisms?

To address these two questions, this thesis will use the lattice FLS model developed by Ronceray and Harrowell [5], and will focus on the study of the $\{3,3\}$ FLS and $\{1,5\}$ FLS models because they exhibit a strong and weak first order phase transitions, respectively. The two models have similar sized unit cells. The $\{3,3\}$ FLS model has a unit cell of 6, while the unit cell of the $\{1,5\}$ FLS model is 7, which should rule out unit cell size as a factor influencing the nucleation process. However, the two models have different symmetries. The $\{1,5\}$ FLS model belongs to the C_s point group, with two symmetry operations, while the $\{3,3\}$ FLS belongs to the C_{2h} point group that has 4 symmetry operations.

Monte Carlo simulations will be used to study both the freezing behaviour and the nucleation behaviour of the two FLS models. In particular, the MFPT method, developed by Wedekind et al [6], will be used to calculate the nucleation rates, critical cluster size and nucleation free energy barriers for a range of temperatures below the equilibrium freezing point. The nucleation of the two models will then be compared.

To complete this study, it is necessary to perform the following:

- 1. Develop a Monte Carlo simulation code to model the FLS systems.
- 2. Characterize the equilibrium fluid and crystal structures in terms of the probability of finding a given FLS.
- 3. Develop a cluster criteria for identifying nuclei in the fluid state.
- 4. Calculate nucleation barriers and nucleation rates, and identify crystal embryos for each crystal.

The remainder of the thesis is organized as follows. Chapter 2 describes the simulation model (Section 2.1), as well as the simulation method used to calculate the equilibrium properties (Section 2.2), the cluster criteria (Section 2.3) and the Mean First Passage Time is described in Section 2.4. The results of the study are described in Chapter 3, starting with the $\{3,3\}$ FLS model (Section 3.1) and followed by the $\{1,5\}$ FLS model in Section 3.2. The discussion of the results and future outlook for the work are contained in Chapter 4.

CHAPTER 2

SIMULATION DETAILS

2.1 Model

The systems under study contain spins organized in a two dimensional triangular lattice, with periodic boundary conditions. Each site has a single degree of freedom called the spin value that can be either up or down. The local environment comprises the spin states of the nearest six neighbours. Each site is given an energy of 0 if its environment is not in the FLS and $E_i = \varepsilon = -1$, if its environment is in the FLS and ε is the energy scale. Thus,

$$E_i = \begin{cases} -1, \text{ neighbours in FLS} \\ 0, \text{ neighbours not in FLS}, \end{cases}$$
(2.1.1)

and the total energy of the system is,

$$E = \sum_{i}^{N} E_i, \qquad (2.1.2)$$

where the sum is over all N spins in the configuration.

As mentioned earlier, this model has 13 distinct FLS. For clarification purposes, the system under study will be termed the Favoured Local Structure (FLS) and the remaining 12 configurations will be referred to as Local Structures (LS). The total energy per particle is obtained by adding up all the energy per site and dividing by the total number of particles.

This thesis work will examine the nucleation behaviour in two of the FLS models, the $\{3,3\}$ FLS model, and the $\{1,5\}$ FLS model, shown in Figure 2.1. The purple particle represents a down spin, while the green particle represents an up spin. The identity of a spin is denoted by indicating the number of down spins followed by the longest sequence of up spins. It is worthwhile to note that the particles identity has no relation to its own spin

orientation. The overall identity of the system is indicated by the favoured local structures which will dominate the system in the crystal state but will not necessarily be the only local structure observed in a configuration.

Figure 2.1: An example of the $\{1, 5\}$ and $\{3, 3\}$ FLS configuration. Purple represents down spins, while green represents up spins.



In Figure 2.1, spin *a* has six neighbours, which defines its identity as $\{1, 5\}$ FLS. The identity of the FLS is obtained by indicating the number of down spins (1 purple for this particular particle) and the longest sequence of up spins (5 up spins following each other sequentially here) leading to the labelling $\{1, 5\}$ FLS. Spin *b* has 3 green particles, which represents up spins and 3 purple particles which are down spins. The 3 up spin neighbours follow each other sequentially. The labeling of this will therefore be 3 down spins and 3 longest sequence of up spins, thus referred to as the $\{3, 3\}$ FLS.

Figures 2.2a and 2.2b show the spin arrangements in the ground-state crystal for the $\{1,5\}$ and $\{3,3\}$ FLS models. The $\{1,5\}$ FLS crystal contains the $\{1,5\}$ FLS itself, as well as the $\{0,6\}$ LS. The $\{3,3\}$ crystal also contains additional local structures, the $\{2,2\}$ LS and the $\{4,1\}$ LS. Figure 2.3 shows some spins organized in a triangular lattice. The values are their respective energies, which are determined solely from the organization of the neighbours. The system under study is the $\{3,3\}$ FLS system in this example.

Figure 2.2: Ground-state crystal of the $\{1, 5\}$ and $\{3, 3\}$ FLS configuration. Purple represents down spins, while green represents up spins.



Figure 2.3: Example of energy assignment for a configuration of spins in the $\{3,3\}$ FLS system. Purple represents down spins, while green represents up spins.

The total energy per spin of this system is obtained by adding up all the energies per site and dividing by the total number of spins.

2.2 Equilibrium Properties

The equilibrium properties of the two FLS models were studied using the standard Metropolis Monte Carlo simulation method. A Monte Carlo cycle has flip attempts equal to the total number of spins. Each flip attempt involves selecting a spin at random, with the old energies of the neighbours calculated, the spin is flipped and the new energy is also calculated, considering the fact that the spin flip changes the energy of neighbours. If the new energy is less than the old, we accept the move, but if not, the move is accepted with a probability:

Acceptance probability
$$(old \rightarrow new) = min(1, \exp[-\beta \Delta E]),$$

where $\Delta E = E_{new} - E_{old}$, is the difference in energy between the configurations, E_{old} is the energy before the spin was flipped and E_{new} is the energy as a result of the spin flip, $\beta = \frac{1}{k_B T}$. To test the acceptance probability, a random number generator is used to generate a random number between 0 and 1. If the result is less than $\exp[-\beta \Delta E]$, then the move is accepted, otherwise the move is rejected and the spin is returned to its original state.

The temperature of the system is reported in dimensionless reduced units, scaled by ε/k_B , where k_B is the Boltzmann's constant. The system consists of N = 3600 spins, arranged in the 60 × 60 triangular lattice. The system was equilibrated and at a high temperature, T = 1.6. The system's temperature is then varied with 0.05 decrements till it reaches a temperature T = 0.3. At each fixed temperature, 100 flips per site is used to reach equilibrium and data is collected over the next 100 flips per site. The simulation continues till a temperature of 0.3 is reached then, the process is reversed and the system is heated in increments of 0.05 to a final temperature of T = 1.6, measuring equilibrium data at each temperature.

During the equilibrium simulations, the following properties are measured:

- The average energy.
- The probability of observing a given local structure surrounding a spin.

2.3 Cluster Criteria

The size of a cluster of the growing embryo is the key order parameter used to describe nucleation. In a simulation, it is necessary to develop a criteria that identifies which particles have the characteristics of the new phase and then identify how these particles are clustered together to form a physical cluster. In the case of the freezing transition, it is necessary to distinguish solid-like particles from liquid-like particles based on their local environment, then identify which solid-like particles belong to the same cluster. In chapter 3, the description of how the solid-like spins are identified in the $\{3,3\}$ and $\{1,5\}$ FLS models are explained in detail. In the current work, two solid-like spins that are neighbours in the lattice are considered to be in the same solid cluster and the algorithm developed by Sevick et. al. [50], is used to identify clusters.

2.4 Mean First Passage Time and Nucleation Events

To examine individual nucleation events, the simulation code developed for the lattice spin models was used. The system contained spins organized in a triangular lattice. The mean first passage time analysis, described in Section 1.5 of the introduction chapter (chapter 1), is the main tool used in this thesis to study nucleation. This method involves the calculation of the time to the first appearance of the largest cluster of size, n, in the system during a dynamic nucleation event, which is then averaged over an ensemble of trajectories. An individual nucleation trajectory is simulated in the following way using the same basic MC code, described in Section 1.4, for the study of the equilibrium properties. The system is initially equilibrated for 100 MC moves per site at a high temperature, T = 1.6, that is above the equilibrium freezing temperature for the model. After equilibration, the temperature of the system is then instantaneously quenched to a temperature below the equilibrium freezing temperature, where nucleation occurs on a reasonable simulation time scale. For the $\{3,3\}$ FLS model, this occurs in the range T = 0.6 - 0.7. For the $\{1, 5\}$ FLS, this occurs in the range T = 0.4 - 0.5. If the quench temperature was lower than these ranges, nucleation occurred too rapidly, and it was not possible to sample the clusters sizes in the metastable liquid region. If the quench temperature was higher than these ranges, nucleation did not occur on the simulation time scale.

A time step in the simulation consists of N MC attempts to flip a spin. In principle, this allows the possibility that every spin in the system could change during a single time step. However, since the spins are selected randomly for each MC attempted move, some particles may not be selected in a single time step and some may be selected more than once. The energy of the system and the cluster sizes are calculated at the end of each time step. The simulation runs for 100 time steps, which is usually much longer than the time for nucleation in the system. Three hundred trajectories are performed for each model, at each temperature.

The mean first passage time is calculated as the number of time steps for the first appearance of largest cluster of size, n, in the system, averaged over the ensemble of trajectories. It is calculated for all n. However, the stochastic nature of the MC moves, as opposed to a deterministic trajectory, means that a cluster may grow or shrink by the addition or loss of several spins during a single time step. For example, the cluster may grow from size n = 10to n = 14 in a single time step. To ensure all cluster sizes are sampled, the intermediate cluster sizes are assumed to have appeared at the same time, i.e., it is assumed that the cluster, size 14, appeared through the growth of the intermediate cluster sizes:n = 11, 12and 13, within the single time step.

The free energy barrier was calculated using Equation 1.5.13 along with Equation 1.5.15. The steady state probability of observing an *n*-sized cluster, P(n), was obtained by counting the total number of times an *n*-sized cluster appears in the ensemble of states sampled in the MC trajectories, and dividing by the total number of states sampled. The trajectories were truncated at sizes just above the critical cluster size to avoid including states associated with the stable crystal state.

CHAPTER 3 Results and Discussion

This chapter presents the results obtained for the entire work and discusses the findings. Section 3.1 looks at the findings for the $\{3,3\}$ FLS, while section 3.2 discusses the $\{1,5\}$ FLS. In both sections, the equilibrium system is characterized in terms of the energy and the probability of finding a given FLS as a function of temperature. These results are used to help develop the cluster criteria used to identify the growing embryos during a nucleation run. The results for the nucleation runs and MFPT analysis are also presented.

3.1 {3,3} **FLS**

3.1.1 Equilibrium properties

Figure 3.1 shows the equilibrium energy per spin of the $\{3,3\}$ FLS system, plotted as a function of temperature, for a cooling cycle followed by a heating cycle obtained using the equilibrium MC simulation method described in Section 2.2. This data is consistent with the results obtained by Ronceray and Harrowell [5] as they have the same energy variation as a function of temperature and melting/freezing temperatures. Together with results obtained for the $\{1,5\}$ FLS, which are presented in Section 3.2, this shows that the Monte Carlo simulation code that was developed is able to model the FLS systems accurately.

Figure 3.1: The Energy, E, per spin of the $\{3,3\}$ FLS model as a function of temperature, T. The symbols represent the data points for cooling (circles) and heating (squares). The solid line provides a guide to the eye.



The energy of the system is proportional to the fraction of states in the system that are in the FLS, because only those sites with the $\{3,3\}$ have a favourable energy, while all other local structures have no energy. In the high temperature limit, $T \to \infty$, all possible spin configurations become equally likely, so there are 2^6 possible configurations for the six neighbouring spins that surround a given site. The energy, $E(T = \infty)$, is then the fraction of these possible states that correspond to the FLS. This gives $E(T = \infty) = -g/2^6 = -6/2^6 =$ -0.09375, where the multiplicity, g, accounts for the number of ways the FLS can appear at the site and is equal to six for the $\{3,3\}$ FLS [49]. At the highest temperature studied here, T = 1.6, the energy E = -0.17, which is still well below the high energy limit and indicates the system has already developed FLS structure. As the temperature is decreased further, the energy decreases continuously until T = 0.65, where this drops significantly from E = -0.3 to E = -0.62, showing the system has frozen. It also shows that the system achieves most of its order during the phase transition, as observed by Ronceray and Harrowell [5]. The energy of the perfect crystal is $E_0 = -2/3$, so Figure 3.1 shows that the system does not freeze directly to a perfect crystal, but to one where there are defects. As the temperature is decreased further, the defects anneal out and the energy of the system approaches E_0 .

When the system is heated, the energy follows the same temperature dependence as the cooling curve, except that it remains a crystal until T = 0.70, where it then melts. This gives rise to a hysteresis loop, characteristic of a strong first order phase transition. Outside of the hysteresis, the energy, as a function of temperature of the cooling and heating cycles, are the same. This suggest that the system is in equilibrium on the time scale of the simulations. The existence of a hysteresis loop gives the upper and lower bounds on the equilibrium phase transition temperature, as they define the temperatures where the system can freeze and melt on the time scale of the simulation. The system has 13 distinct local structures, only one of which is the FLS. It is therefore important to understand how the populations of the different structures evolve as the system cools, then freezes. Figure 2.2b depicts that in the perfect crystal, there are two other local structures that are present, the $\{2, 2\}$ and the $\{4, 1\}$ local structures, although they are not energetically the most favoured structures. These two local structures are however, spin inversions of each other.

Figure 3.2 shows how the populations of the different local structures change with temperature for the $\{3,3\}$ FLS system . All the local structures start decreasing in the probability of finding them as the temperature decreases, with the exception of the $\{2,2\}$ and the $\{3,3\}$. The increase in the $\{3,3\}$ FLS is expected, because the lower energy states are favoured as the temperature is decreased. However, the $\{2,2\}$ local structure has no energetic advantage. To understand why the $\{2,2\}$ local structure increases, it is important to note that there are correlations between the local structure surrounding one site and the local structure surrounding a neighbouring site. For example, the presence of a $\{6,0\}$ local structure at a site, which has six down spins, reduces the probability of finding a neighbour with a long string of up spins because two neighbouring sites also share two additional neighbour sites (see Figure 3.3).

Figure 3.2: Probability distribution of FLS (P) as a function of temperature (T), for the $\{3,3\}$ FLS model for both cooling and heating cycles.



Figure 2.2b shows that in the $\{3,3\}$ FLS perfect crystal, the $\{2,2\}$ local structure appears next to a pair of neighbouring $\{3,3\}$ structures. This suggests that as the number of $\{3,3\}$ FLS structures increases in the equilibrium liquid state, the probability that two $\{3,3\}$ FLS become neighbours increase, then the correlation between the local structure around neighbouring spins increases the probability that the $\{2,2\}$ structure appears. This could account for the increase in the $\{2,2\}$, local structure in the equilibrium fluid, even though it is not energetically favourable. However, it should be noted that this hypothesis should also apply to the $\{4,1\}$ local structure, which decreases with increasing temperature. This suggests the possibility of additional correlations that suppress the $\{4,1\}$ local structure in the liquid state, but not the $\{2,2\}$ local structure. At the freezing transition, both the $\{2,2\}$, and the $\{4,1\}$ local structures increase to the same final value as expected for the crystal of this model. They follow the same trend till the temperature is close to the crystallization temperature. The probability of finding $\{2,2\}$ FLS and $\{4,1\}$ FLS both shoot up in the

system as the temperature decreases. After visualization of the crystal states of this system, it has been confirmed that the two local structures are present in the crystal of the $\{3,3\}$ FLS. This highlights the important role local structures other than the FLS may play in the freezing process. They will also play an important role in nucleation.



Figure 3.3: A diagram showing the correlation between configuration of neighbours. Purple represents a down spin, while green represents an up spin. The first neighbours around b, share the two sites on either side of the a - b lattice line. The second neighbours, a - c, share the two adjacent sites immediately between them

3.1.2 Cluster Criteria

The main goal of the cluster criteria is to identify physical clusters of local structures that can lead to the formation of the crystal phase. This means that it is necessary to be able to distinguish between spins that have a local environment that is solid-like from those that are liquid-like. It has been established from the characterization of the probabilities of finding a given FLS in equilibrium fluid (Figure 3.2), that there are only three local structures in the crystallized state, the $\{3, 3\}$, $\{4, 1\}$ and the $\{2, 2\}$ structures. This did not give insight into the identity of an FLS and its surrounding neighbours however. The system studied contained N = 3600 spins organized in a 60×60 triangular lattice. Starting at T = 1.6 to T = 0.3 with 0.05 decrements, the probability of each of the three local structures present in the $\{3, 3\}$ FLS crystal having any of the three local structures as neighbours over a set of temperatures was determined.

Figure 3.4 shows that the spins have all six neighbours being one of the local structures present below the freezing temperature. This implies that a spin with all neighbours being the same as the crystal local structures can be defined as a solid-like spin, since these environments appear in the liquid state with a very low probability. From the results obtained in Figure 3.4, there is a distinction between the liquid and the crystal-like spin in the liquid. The probabilities were further examined by looking at each of the local structures appearing in the crystal individually and the probabilities of finding each of them as neighbours, which is shown in Figure 3.5, 3.6 and 3.7. Results presented in Figure 3.5a clearly show a $\{2, 2\}$ spin is not likely to have itself, or a $\{4,1\}$ spin, as its neighbour in the crystal state. In the perfect crystal, the $\{2, 2\}$ and $\{4, 1\}$ local structures are never neighbours of the $\{2, 2\}$. However, this is also true in the liquid state. The same is true for a spin with $\{4, 1\}$ identity. However, all local structures present in the system have clear distinctions between the solid and liquid phases in reference to having the $\{3,3\}$ FLS as a neighbour, shown in Figure 3.7. The $\{2,2\}$ and $\{4,1\}$ spins have 6 of their neighbours having the $\{3,3\}$ configuration, while (Figure 3.5b and 3.7h) the $\{3,3\}$ spin has exactly 3 of its neighbours having the $\{3,3\}$ configuration beyond freezing, as shown in the Figure 3.6e. A spin with a $\{3,3\}$ configuration will have 1 or 2 of its neighbours with either the $\{2,2\}$ or $\{4,1\}$ configuration.



Figure 3.4: The probability of crystal FLS having (n) = 0 - 6 other crystal FLS neighbours





Figure 3.5: Cluster criteria for $\{3,3\}$ FLS. This shows how the local structures present in the crystal relate to each other over the set of temperatures.







Figure 3.6: Cluster criteria for $\{3,3\}$ FLS. This shows how the local structures present in the crystal relate to each other over the set of temperatures.







Figure 3.7: Cluster criteria for $\{3,3\}$ FLS. This shows how the local structures present in the crystal relate to each other over the set of temperatures.







A spin with a $\{2,2\}$ or $\{4,1\}$ local structure with 6 of its neighbours, all with $\{3,3\}$ configuration, can therefore be defined as a solid-like spin while a spin with the $\{3,3\}$ configuration having exactly 3 of its neighbours with the $\{3,3\}$ configuration can be termed a solid-like spin.

However, in addition to considering the local environment, it is necessary to examine the relative orientation of the local structures. Figure 3.8 shows one of the configurations of the $\{3,3\}$ FLS system during the nucleation process.



Figure 3.8: Configuration of the $\{3, 3\}$ FLS system containing multiple crystals with different orientations. Green dots represent up spins, while the purple dots represent down spins.

There appear to be multiple crystals formed with different orientations before the system freezes to a single crystal at later times. This is a factor that will need to be accounted for in the cluster criteria, because classifying a spin with a different orientation from the cluster as solid-like will lead to poor nucleation analysis.

The orientation of an FLS at a spin site can be defined by assigning a vector from the spin site itself to the spin site of the first down spin in the longest down spin chain of its neighbours counting in an anticlockwise direction (see Figure 3.9). To determine if two neighbouring FLS have the correct orientation, the dot product of the two orientational vectors is taken and compared to the dot product values allowed in the perfect crystal. For example two neighbouring $\{3,3\}$ FLS must have dot products of +1 or -1 to be considered as having the correct orientation.



Figure 3.9: Finding orientation for $\{3,3\}$ FLS.

Figure 3.10, shows a plot of the neighbour probabilities as a function number of neighbours at different temperatures, with their right orientations. It was established in Figure 3.5 that the combination needed for the description of a cluster is the local structures having $\{3,3\}$ FLS configuration as neighbour. The results shown in Figure 3.10 are therefore based on the $\{2,2\}$, $\{4,1\}$ or $\{3,3\}$ FLS configurations having a spin with $\{3,3\}$ FLS configuration as neighbours with the right orientations.

With orientation included, shown in Figure 3.10, it is evident that a spin with either $\{2, 2\}$ or $\{4, 1\}$ local structures having more than 5 of its neighbours with $\{3, 3\}$ FLS configuration, and with the right orientation, is described as a solid-like spin. A spin with $\{3, 3\}$ FLS configuration and right orientation also having exactly 3 of its neighbours with $\{3, 3\}$ FLS configuration and the right orientation is described as solid-like. Comparing the result with orientation included (Figure 3.10) to the results without orientation (Figure 3.5), it is evident that the cluster criteria in terms of numbers doesn't change much, however, it ensures only spins that are truly part of the same crystal are counted as being in the same cluster.

Figure 3.10: Cluster criteria for $\{3,3\}$ FLS with right orientation. This shows the local structures having the $\{3,3\}$ FLS as neighbour over the set of temperatures.







3.1.3 Mean First Passage Times

Before examining the MFPT properties of the system, which are obtained by taking averages over an ensemble of trajectories, it is useful to examine the general features of a nucleation trajectory. Figure 3.11 shows the energy as the temperature of the $\{3,3\}$ FLS system is dropped abruptly. The system was equilibrated at a temperature of T = 1.6 then quenched suddenly to T = 0.687, which is just below the freezing temperature. The simulation time is a measure of the full Monte Carlo cycles performed. The energy dropped immediately to a metastable state and fluctuated there for some time until the system finally nucleates. The system then dropped to a lower energy consistent with that of the crystal. Nucleation is a stochastic process, so while the nucleation event occurs near T = 0.687 for the trajectory shown in Figure 3.11, nucleation will occur at different times for each trajectory. Mathematica was used to visualize the configurations arising from the nucleation run. Figure 3.12 shows the configurations in terms of the spin states (up or down) for the system. The configuration number refers to the spin state after the specific number of Monte Carlo cycles have been completed following the temperature drop. The first two configurations, 3.12a and 3.12b of figure 3.12 are snapshots of the spins in the liquid state, which is consistent with energy before the drop, while configuration 3.12c is in the transition between the liquid and the crystal phase. The last configuration, Figure 3.12d, shows the spins after nucleation.

Figure 3.11: Energy (E) versus time (t) plot for the $\{3,3\}$ FLS nucleation run. This shows how the energy varies with time when the temperature of the system is dropped abruptly to a temperature T = 0.687, which is below freezing.



Figure 3.14, is a plot of cluster size (n) as a function of simulation time (t) as the temperature is dropped to 0.687 instantaneously, for the same trajectory. When the temperature is dropped, the cluster size fluctuates in the order of tens and a few hundreds for a considerable amount of time. Clusters that grow clearly shrink back to almost zero size, until the system forms a size known as the critical cluster, beyond which the cluster size keeps growing till the crystal is fully formed. This critical cluster is very important as the nucleus just grows after it is formed. The system has very small clusters as well as some isolated single solid clusters in the metastable state, (crystal 3.13a). Once the system nucleates, the solid cluster grows rapidly to span the entire system as seen in Figure 3.13c. Once the crystal is formed, only a few non-crystal sites remain, and these correspond to defects (Figure 3.13d).



Figure 3.12: Snapshots of spin configuration depicting the nucleation event for $\{3,3\}$ FLS. The green colour represents the up spins, while the purple shows the down spins.

Figure 3.13: Cluster dynamics during nucleation event for $\{3,3\}$ FLS system. The green colour represents the liquid-like spins, while the purple shows the clusters.



Figure 3.14: Cluster size (n) as a function of simulation time (t) when the temperature is dropped to 0.689.



To find the critical cluster, the simulation was run 300 times, quenching the system to the same temperature. The data was collected and analyzed by checking for the first time a cluster of a particular size was formed to obtain the MFPT. The MFPT provides a precise determination of the rate and location of transition states. There is the possibility of infering additional information like the activation barrier and lag times. The MFPT method yields a clear determination of the rate , the size of the critical embryo and the Zeldovich factor. This method therefore provides a direct way of determining all quantities necessary for characterizing the nucleation process. The Figure 3.15, is a plot of MFPT (τ) as a function of cluster size (n), after 300 runs all equilibrated at a temperature of 1.6 and dropped to a temperature of 0.687 for the {3,3} FLS system.

Figure 3.15: MFPT (τ) as a function of cluster size (n). The dark line is the MFPT curve, while the red line is the best fit of equation 3.1.1 to the data. The green area shows the error bars, measured as the standard deviation.



The MFPT data can be fit to the equation

$$\tau(n) = \frac{\tau_J}{2} (1 + erf((n - n^*)c)), \qquad (3.1.1)$$

where n is the cluster size, τ_J is the rate, n^* is the critical cluster size and c is related to the Zeldovich factor. τ_J , n^* and c were the fit parameters. The MFPT curve fits well with the equation. The rate JV, which is inversely related to τ_J , is found to be 9.4×10^{-5} clusters/(site . MC cycles). The critical cluster n^* is 396 and the Zeldovich factor, which is related to the local curvature around the top of the barrier Z is 0.00528. The error bars are obtained by calculating the standard deviations between the runs. The sigmoidal shape of the curve obtained in Figure 3.15 indicates the system has a well defined activation barrier.

To understand how changes in temperature affects nucleation, the system was equilibrated at a high temperature as before, and dropped to a set of different temperatures. The results obtained (Figure 3.16) were fitted with Equation 3.1.1 to obtain the parameters shown in Table 3.1. The critical cluster seems to be fluctuating around the same value for the different temperatures, indicating the size does not decrease with decreasing temperature, except for the very lowest temperature studied. According to classical nucleation theory, the critical size should decrease with decreasing temperature because the driving force for freezing increases. The rate of crystallization however increases as the temperature decreases, which is consistent with classical nucleation theory.



Figure 3.16: A Plot of MFPT as a function of cluster size for different temperatures.

Parameters	T=0.667	T=0.685	T=0.687	T=0.689	T=0.691
Rate(J)	1.5×10^{-3}	9.4×10^{-5}	5.2×10^{-5}	3.9×10^{-5}	3.2×10^{-5}
MFPT(n*)	260	396	418	391	390
Free energy (n^*)	-	330	328	301	303
Simulation(Δn)	243	378	401	377	377
Zeldovich factor (Z)	0.00245	0.00298	0.00287	0.00374	0.00321
Nucleation theorem(Δn^*)	-	382	383	383	384
$\Delta H/N$	0.273	0.276	0.278	0.281	0.281
ΔG^*	-	5.416	5.708	5.677	5.959
$\frac{\partial \Delta G}{\partial T}$	-	952.6	953.8	955.0	956.2

Table 3.1: Summary of nucleation parameters obtained for the $\{3,3\}$ FLS system.

3.1.4 Free Energy Barriers

The free energy barrier for nucleation was calculated using the MFPT analysis described by Equations 1.5.13 and 1.5.15, where the steady state probability of observing a cluster of a given size was obtained from the ensemble of configuration sampled in the nucleation trajectories. The barrier for the $\{3,3\}$ FLS system, presented in Figure 3.17, is found to be around 8.3kT, which is moderately high. The critical cluster sizes for the different temperatures are however found to be a little smaller in size compared to that given by the MFPT calculation (Table 3.1). Minor differences have been observed in previous comparisons [30]. The Figure 3.17, has a minimum at approximately n = 20 because there is a high probability that a cluster of this size can be found in the supercooled liquid. This is a system size effect associated with the translational degrees of freedom of the cluster. The classical nucleation theory free energy can be compared to the current data for cluster sizes greater than the minimum. The CNT barrier is given by

$$\Delta G(n) = -\Delta \mu n + A(n)\sigma, \qquad (3.1.2)$$

where A(n) is the surface area. Assuming the cluster is a 2D sphere, $A(n) = 2\pi r$, where $r = \sqrt{\frac{n}{\pi}}$. The data is fit with the classical nucleation theory (see Equation 3.1.2) using $\Delta \mu$

and σ as fit parameters. It is clear from Figure 3.17 that the fit is not good. The height of the barrier obtained from the fit is higher than that obtained from our analysis. The system plateaus earlier than the fit.

Figure 3.18 shows free energy barriers obtained for all temperatures studied. The barrier height ranges from 7.9kT to 8.6kT not showing very much differences and within 1kT of each other so it can be assumed the barrier height of the system is approximately same. The critical cluster sizes obtained from the barrier calculations are listed in Table 3.1.



Figure 3.17: A plot of free energy $(\beta \Delta G)$ as a function of cluster size (n) at T = 0.687

Figure 3.18: A Plot of Free Energy $(\beta \Delta G)$ as a function of cluster size (n) for different temperatures



3.1.5 The nucleation theorem

The nucleation theorem is usually expressed as,

$$\frac{\partial \Delta G^*}{\partial \Delta \mu} = -\Delta n^*, \tag{3.1.3}$$

where ΔG^* is the Gibbs free energy of forming a critical nucleus, $\Delta \mu$ is the chemical potential difference between the liquid and the solid, and Δn^* is the excess number of particles in the critical cluster. This excess is simply the difference in the number of spins in the critical cluster relative to the number of spins that would be present in the uniform metastable phase before the cluster is created. The theorem was originally derived by Anismov et al [51] and Kashchiev [52] to describe classical nucleation, but was later shown to be a general thermodynamic relation applicable to the formation of any inhomogeneity from a uniform fluid [53]. The nucleation theorem has been used to check the validity of different methods of free energy barrier calculation in the nucleation field [8]. Here the nucleation theorem will be used as a consistency check on the free energy calculations described in Section 3.1.4.

To evaluate Equation 3.1.3, it is necessary to obtain an expression for the difference in chemical potential between the metastable liquid and the solid below the freezing temperature. The chemical potential is the molar Gibbs free energy, $\mu = G/N$. Thermodynamics defines the following relation,

$$\left(\frac{\partial G_l}{\partial T}\right)_p - \left(\frac{\partial G_s}{\partial T}\right)_p = -S_l + S_s = \frac{-H_l}{T} + \frac{-H_s}{T},\tag{3.1.4}$$

where S is the entropy, H is the enthalpy and the subscripts l and s refer to the liquid and solid phases, respectively. The Gibbs free energy can be obtained as

$$\Delta G = -\Delta H \int_{T_m}^T \frac{\partial T}{T} = -\Delta H \ln\left(\frac{T}{T_m}\right), \qquad (3.1.5)$$

where $\Delta H = H_l - H_s$ is assumed to be constant over the temperature range considered, T_m is the melting temperature and it is noted that $\Delta G = 0$ at the equilibrium phase transition temperature. If the temperature range considered below T_m is small, the log term in Equation 3.1.5 can be expanded using a Taylor expansion to yield,

$$\Delta \mu = \frac{\Delta H}{N} \left(1 - \frac{T}{T_m} \right), \qquad (3.1.6)$$

where the molar quantity is obtained by dividing by the number of spins, N. Finally to make use of the free energy barriers obtained in Section 3.1.4, it is necessary to transform 3.1.3 into a temperature dependent form. Taking the derivative of equation 3.1.6 with respect to T gives,

$$\frac{\partial \Delta \mu}{\partial T} = -\frac{\Delta H}{N} \frac{1}{T_m},\tag{3.1.7}$$

and substituting this into 3.1.3 gives

$$\left(\frac{\partial\Delta G}{\partial T}\right)_{P} = -\frac{N}{\Delta H}T_{m}\Delta n. \tag{3.1.8}$$

The enthalpy difference, $\Delta H = E_l - E_s + P(V_l - V_s) = E_l - E_s$, where E_l and E_s are the energies in the metastable liquid and solid respectively, because there is no volume difference between the phases in a lattice model. The energy of the solid phase is obtained directly from the equilibrium measurements of the crystal energy performed in Section 3.1.1 (see Figure

3.1). The estimate of E_l is obtained by averaging the energy over the metastable region of the dynamic trajectories, i.e, the time the temperature is decreased to the time where the critical nucleus is observed. The energies are averaged over all 300 trajectories for each temperature. The enthalpy per particle, $\Delta H/N$, for each temperature is tabulated in Table 3.1. There is a small temperature dependence but the values are essentially constant within error. Averaging over all the temperatures gives $\Delta H/N = 0.278$. The melting temperature is estimated as the average temperature within the hysteresis limits (see Figure 3.1), which yields $T_m = 0.693$. The temperature derivative of the Gibbs Free energy barrier is obtained by fitting the values of ΔG^* as a function of T, obtained in Section 3.1.4, to a second order polynomial (see Figure 3.19). This data is used to obtain values for the excess number of spins in the critical nucleus and these are listed in Table 3.1.



Figure 3.19: A plot of free energy (ΔG) as a function of temperature (T). The points represent the data, and are joined by solid lines to guide the eye. The dashed line represents the polynomial fit.

It is also possible to estimate the excess number of spins directly from the simulation results as $\Delta n = n^* - n^* p(n)$, where p(n) is the probability that a site in the metastable fluid is a solid-like spin, so that $n^* p(n)$ represents the background solid spins that occupied the cluster sites before the cluster was formed. Configurations of the metastable state (Figure 3.13a) suggest that most of the solid-like spins are contained in the largest cluster, so $p(n) \approx <$ n > /N is the average cluster size in the metastable state divided by N. This definition obviously underestimates the background because some solid-like spins are not in the largest cluster, but it should provide a reasonable estimate. The excess obtained by simulation is listed in Table 3.1, for comparison with the values obtained from equation 3.1.8.

This FLS model system has some ordering even in the equilibrium liquid, so it is suspected that the critical clusters obtained from the MFPT fitting does not reflect the true critical sizes because of the background clusters present in the equilibrium liquid. The excess (Δn) is obtained by subtracting the background crystal from the critical clusters (n^*) obtained from MFPT fitting.

3.2 {1,5} **FLS**

3.2.1 Equilibrium properties

Figure 3.20 shows the cooling and heating cycles for the $\{1, 5\}$ FLS model, that is, when the temperature is being decreased and increased, respectively, with 0.05 increments. The $\{1, 5\}$ system accumulates lots of order while remaining liquid, as indicated by the low energy of the liquid phase. In contrast, the $\{3, 3\}$ achieves most of the local ordering as a phase transition, which is evident from the plot of average energy per site, E, against the temperature. It should also be noted that while the energy shows a sharp drop at the freezing temperature, there is no hysteresis, and the cooling and heating curves follow the same behaviour for all temperatures. This is characteristic of a weak first order phase transition.



Figure 3.20: The energy per spin, E, of the $\{1, 5\}$ FLS model as a function of temperature, T. The symbols represent the data points for cooling (circles) and heating (squares). The solid line provides a guide to the eye.

Looking at the probability distribution for the $\{1,5\}$ FLS system shown in Figure 3.22, all the local structure probabilities decrease as a function of temperature, with the exception of the $\{0,6\}$ and the $\{1,5\}$, which make up the perfect crystal. The $\{0,6\}$, $\{2,4\}$ and $\{1,5\}$ local structures still remain in the frozen state. It is interesting to note that the $\{2,4\}$ FLS appears in the crystal with low percentage, but it actually appears in greater percentage in the liquid state. This might be related to the fact that the perfect $\{1,5\}$ FLS crystal can be achieved without the $\{2,4\}$ configuration. However, the $\{2,4\}$ local structure appears in the system as a defect (see Figure 3.21).



Figure 3.21: Ground-state crystal for the $\{1,5\}$ FLS model with $\{2,4\}$ configuration as defects. The green colour represent the up spins, while the purple shows the down spins.
Figure 3.22: Probability distribution of FLS (P) as a function of temperature (T) for the $\{1,5\}$ FLS model for both cooling and heating cycles.



3.2.2 Cluster Criteria

In order to fully understand how this crystal structure forms, a cluster criterion needs to be developed for the system. This is to ensure a solid-like spin can be distinguished from a liquid-like one. The $\{1, 5\}$ FLS system is known to have two other local structures from the equilibrium studies. A solid-like spin in this system can only be defined by its neighbours for this system. The results presented in Figure 3.23 show the probability of each of the local structures present in the crystal structure of the $\{1, 5\}$ FLS system having any of the crystal local structures as neighbours. For example, it shows the probability of a $\{1, 5\}$ particle having either $\{0, 6\}$ FLS, $\{1, 5\}$ FLS or $\{2, 4\}$ FLS spin as neighbour. Below freezing the crystal local structures are surrounded by six of the other crystal local structures, but there are also a significant number of spins in the liquid phase that have the same local environment. This makes it difficult to distinguish a liquid-like spin from a solid-like spin. Figure 3.23: Initial Cluster criteria for $\{1, 5\}$ FLS. This shows how the local structures relates to each other over a set of temperatures.









Figure 3.24: Cluster criteria for $\{1, 5\}$ FLS.







Figure 3.25: Cluster criteria for $\{1, 5\}$ FLS.







Figure 3.26: Cluster criteria for $\{1, 5\}$ FLS.





The local structures probabilities do not show significant differences between the liquid and the crystal structure except for the probability of the $\{0, 6\}$ FLS spin having $\{1, 5\}$ FLS spin as neighbours and the $\{1, 5\}$ FLS having $\{1, 5\}$ FLS as neighbours as shown in figure 3.24b and 3.25e, respectively. Because the $\{2, 4\}$ FLS is part of the local structures that appears in the crystal, it was expected that it would be required for the cluster criteria but it appears to be a defect in the system and not required for the formation of the crystal structure. In conclusion, a spin with a $\{0, 6\}$ FLS configuration having six neighbouring spins with a $\{1, 5\}$ FLS configuration is termed solid-like. A spin with a $\{1, 5\}$ FLS configuration having five neighbouring spins with a $\{1, 5\}$ FLS configuration is also termed solid-like for this system. A cluster for this system therefore comprises spins that are immediate neighbours and fulfil the cluster criteria. In principle, it is possible to assign an orientation to the $\{1, 5\}$ FLS, as was done with the $\{3, 3\}$ system. However, all orientations of the FLS appear in the local environment around a given $\{0, 6\}$ local structure. As a result, there is no correct orientation.

3.2.3 Mean First Passage Time

The MFPT is obtained by averaging an ensemble of nucleation trajectories, but it is also useful to examine the properties of the individual trajectories. The system was equilibrated at a temperature of T = 1.6. The temperature was abruptly dropped to a temperature of T = 0.51, which is directly below freezing. The energy was recorded for each Monte Carlo cycle. The Figure 3.27, shows how the energy changes with simulation time after the temperature of the system has been dropped. The energy of the system rapidly drops to a metastable state, where it fluctuated around E = -0.77, which is an energy very close to that of the ground-state crystal. The energy difference between the metastable phase and the crystal is not large. Figure 3.27: Energy (E) versus time (t) plot for $\{1,5\}$ FLS system after temperature has been dropped to 0.51.



The spin configuration for each time step was saved, and using Mathematica, these were visualized (see Figure 3.28). The configuration numbers correspond to the simulation time. Figures 3.28a and 3.28b show the arrangement of the spins when the system's energy is consistent with the liquid, while Figures 3.28c and 3.28d are snapshots of the spins after the drop to an energy consistent with that of the crystal. The system started becoming ordered to attain the desired ground-state crystal structure once the temperature was dropped.

The Figure 3.29, shows the cluster evolution as a function of time. The purple represents solid spins, while the green represents liquid spins in Figure 3.29. Even before the freezing transition, the metastable liquid configuration at time 32410 (Figure 3.29b) has a large number of solid-like clusters, proving the system organizes itself above the freezing temperature. Figure 3.28: Spin configuration for nucleation in the $\{1,5\}$ FLS system. The green colour represents the up spins, while the purple shows the down spins.



Figure 3.29: Cluster dynamics for the nucleation event in the $\{1, 5\}$ FLS system. The green colour represents the liquid-like spins, while the purple shows the solid-like spins.







The Figure 3.30 shows a plot of cluster sizes as a function of simulation time after the temperature has been dropped from T = 1.6 to T = 0.51. The system fluctuates around a large cluster size presented in Figure 3.30. The cluster size goes a little over a 1000 and still does not nucleate, indicating the critical cluster is likely to be over a 1000 spins, which is more than half the number of particles in the system. This system already has a lot of order before freezing, which confirms that the system has very little ordering to do. It is also clear that the system has a large equilibrium cluster, that is, the cluster size does not decay to zero.

The MFPT data fits well with Equation 3.1.1. The rate JV, which is inversely related to τ_J , is found to be 4.6×10^{-5} clusters/(site.MC cycles). The critical cluster, n^* is 1036, and the Zeldovich factor, Z, which is related to the local curvature around the top of the barrier, is 0.00495295. The MFPT analysis is carried out over a range of temperatures as described earlier. The data is plotted in Figure 3.32, and parameters extracted from the fitted plots are listed in Table 3.2. The rate for this system increases as the temperature decreases, as

shown in Table 3.2, however, the critical cluster size seems to change very little, or even grows with decreasing temperature. It is expected that as temperature decreases, critical size decreases.



Figure 3.31: A Plot of MFPT (τ) as a function of cluster size (n) for the $\{1,5\}$ FLS at T = 0.51. The red curve is the fitted data, while the green is the error bar.

Figure 3.32: A Plot of MFPT (τ) as a function of cluster size (n) for different temperatures.



Table 3.2: Summary of the nucleation parameters obtained for the $\{1, 5\}$ FLS system

Parameters	T=0.48	T=0.49	T=0.50	T=0.505	T=0.51	T=0.52
Rate(J)	1.4×10^{-4}	1.3×10^{-4}	8.9×10^{-5}	5.9×10^{-5}	4.6×10^{-5}	3.1×10^{-5}
MFPT (n^*)	1117	1073	1038	1067	1036	985
Free energy (n^*)	-	-	-	742	796	858
Zeldovich factor (Z)	0.00196	0.00210	0.00241	0.00242	0.00279	0.00309
$\operatorname{Excess}(\Delta n)$	692	707	725	767	776	789

3.2.4 Free Energy Barrier

Figure 3.33 shows the free energy barrier obtained from the barrier reconstruction analysis for the $\{1, 5\}$ FLS at a temperature, T = 0.51, which is just below the freezing temperature

for the model. The minimum at $n \approx 200$ indicates the presence of a large equilibrium cluster in the system. This is consistent with observations made by examining the individual trajectories and configurations. The minimum is also very broad and shallow, which would allow for large fluctuations in the equilibrium cluster size. The critical size appears to be approximately 800 sites, which represents a significant fraction of the system. This could lead to potential problems associated with system size effects, where large clusters interact with themselves through the periodic boundary conditions.

Figure 3.34 shows the free energy barriers for a range of temperatures. The minimum associated with the equilibrium practical cluster shifts to larger sizes as the temperature is decreased and the barrier seems to slowly disappear. At T=0.50, the free energy surface decreases monotonically as a function of cluster size. This suggests that the clusters are able to increase without having to cross an activation barrier. However, this is potentially also a system size effect [54, 55, 56]. Unfortunately, it was not possible to get the simulation code to work for larger system sizes to check this effect.



Figure 3.33: Plot of free energy $(\beta \Delta G)$ as a function of cluster size (n) for the $\{1, 5\}$ FLS system at T = 0.51.

Figure 3.34: The free energy $(\beta \Delta G)$ as a function of cluster size (n) for the $\{1,5\}$ FLS system at different temperatures.



3.2.5 Nucleation Theorem

In section 3.1.5 the nucleation theorem was used to examine the excess number of spins associated with the critical cluster for the $\{3,3\}$ FLS model. In principle, the same approach can be used to study the $\{1,5\}$ FLS system, but as Figure 3.34 shows, there is no systematic evolution of the barrier height, or the critical cluster size as a function of temperature. This makes it impossible to use Equation 3.1.8. However, it is possible to estimate the excess from the computer simulation by calculating the background and subtracting this from the critical size obtained from the MFPT analysis. The background is obtained by calculating the probability that a spin in the metastable liquid is solid-like, as in Section 3.1.5, and the excess is tabulated in table 3.2. As can be seen, the excess number of particles decreases as the temperature decreases, which is consistent with the expectations of classical nucleation theory, while the critical size calculated directly from the MFPT increases with decreasing temperature.

To explain this, it should be noted that the equilibrium cluster within the metastable liquid of the $\{1, 5\}$ FLS system increases in size as the temperature is decreased, as indicated by the location of the free energy minimum in Figure 3.34. Lower temperatures enhance the local order in the metastable liquid. This causes the background to increase. When this background is removed from the size of the critical cluster, the expected CNT trend is recovered. This highlights the importance of calculating the excess cluster size in problems of crystal nucleation rather than just focusing on the critical cluster size.

CHAPTER 4

DISCUSSIONS, CONCLUSIONS AND FUTURE WORK

4.1 Discussion

The goal of this thesis was to explore the difference in nucleation mechanisms between systems undergoing strong or weak first order phase transitions. The lattice spin favoured local structure models, developed by Ronceray and Harrowell [5], provide ideal systems for exploring the effects of local structure on the properties of liquids and solids. By assigning a low energy to the different possible spin arrangements surrounding a lattice spin, the models display a wide range of freezing behaviour, which include strong and weak first order phase transitions, as well as second order phase transitions. The types of crystals formed also exhibited a wide variety of structures, with unit cell sizes ranging from 1 through to 20, while some FLS models also display the ability to freeze into multiple crystal forms. This work is focused on studying the nucleation behaviour of the $\{3,3\}$ FLS and the $\{1,5\}$ FLS models, because they undergo strong and weak first order transitions, respectively.

The equilibrium cooling and heating curves (Figures 3.1 and 3.20) clearly show the strong and weak freezing behaviour. The $\{3,3\}$ FLS system has a large decrease in its energy as the system freezes and it exhibits a clear hysteresis loop. The energy of the $\{1,5\}$ FLS system only decreases by a small amount at freezing and exhibits no hysteresis. The local structure probabilities also highlight clear differences between the two systems. In the $\{3,3\}$ FLS model, the $\{3,2\}$ local structure is the most probable at high temperatures and its probability changes very little as a function of temperature until the freezing temperature is reached. The $\{3,3\}$ FLS becomes the most probable as the temperature decreases because it is energetically favoured. The only other local structure to increase in probability is the $\{2,2\}$ local structure, which appears as part of the crystal. Surprisingly, the $\{4,1\}$ local structure, which also appears in the crystal, decreases with decreasing temperature until the freezing point is reached. All the other local structures rapidly disappear upon freezing. Most importantly, the large energy drop at freezing shows that the system gains most of its order during the freezing process.

In contrast, the liquid phase of the $\{1,5\}$ FLS model contains a large amount of order right from a high temperature, T = 1.6. The $\{1,5\}$ FLS is the most probable structure and has a significant amount even at T = 1.6 and by the time freezing occurs, it has reached 70% of its crystal structure, only gaining another 10% when it freezes. The $\{0,6\}$ FLS, which also appears in the perfect crystal, increases in probability as the temperature is decreased. It is interesting to note that the $\{2,4\}$ structure does not disappear on freezing, even though it is not part of the perfect crystal, and creates defects in the crystal.

The nucleation studies also reveal significant differences between the two systems. The nucleation trajectories of the $\{3,3\}$ FLS system appear classical in nature. Small clusters grow, but they then shrink again to almost zero until they reach the critical cluster size. However, the CNT fit to the free energy barrier does not provide a proper fit. The $\{1,5\}$ system exhibits a large equilibrium cluster that is stable in the metastable liquid phase. This is consistent with the large degree of order that the liquid develops before freezing occurs. The cluster size fluctuates around the equilibrium cluster before nucleation occurs. The presence of the large cluster is also apparent in the free energy curve for the system. The equilibrium cluster also increases in size as the temperature is dropped.

The MFPT analysis generally worked well for both systems. The rate of nucleation increased with decreasing temperature for both systems. This is the expected behaviour because the drive force for nucleation, which is the difference in chemical potential between the liquid and the crystal, increases as the temperature moves further below the equilibrium freezing temperature. According to CNT, the critical cluster size is expected to decrease with decreasing temperature. The critical cluster sizes predicted by MFPT and the size of the excess number of spins predicted by the nucleation theorem were approximately the same for the $\{3,3\}$ FLS system. This may be because the temperature range studied was small and the error bars on the MFPT curves are relatively large. The lowest temperature studied did

show a decrease in the critical cluster size. However, as the temperature is decreased further, the nucleation occurs more rapidly and it becomes difficult to establish the metastable liquid state, which is a necessary feature of the MFPT analysis.

The MFPT analysis showed that the critical cluster size actually increased with decreasing temperature for the $\{1, 5\}$ FLS model. Some non-classical theories of nucleation predict that this is possible as the system approaches a spinodal limit of stability because the fluctuation in the system begins to diverge. However, spinodals are not expected to occur in liquid-crystal phase transitions. Subtracting the background from the cluster size to calculate the excess number of spins in the critical nucleus made the critical sizes decrease as expected . This work suggests that accounting for the background is important in crystal nucleation, particularly when the metastable liquid can develop so much order before freezing.

The free energy barrier calculations for the $\{1,5\}$ FLS model appear to be in error and show no consistent behaviour. This is probably due to the large size of the critical nucleus, which grew to be larger than half the system size. This means that the cluster would interact with itself across the periodic boundary conditions. This would also affect the MFPT calculations so the current results should be tested at both a smaller and larger system size to check for system size effects. Unfortunately, the current simulation code could not be made to work for larger systems.

The symmetry of the FLS and LS involved in the crystal, along with the correlations the FLS impose on their environment, may play an important role in the ability of the liquid phase to develop structural order before freezing occurs, which then affects nucleation. The $\{3,3\}$ FLS belongs to the C_{2h} point group and causes the other local structures to adopt specific orientations in order to form a crystal nuclei. This makes it difficult to develop order in the liquid phase without growing a crystal nucleus. This leads to the strong first order phase transition. The $\{1,5\}$ FLS has just the identity and reflection operations, but the $\{0,6\}$ local structure, which also appears in the perfect crystal, is the most symmetric structure. The $\{1,5\}$ FLS can adopt any orientation when it is next to the $\{0,6\}$ local structure, that is, the structural correlations are not as restrictive in this model. The number $\{1,5\}$ FLS structures can therefore grow in the liquid without necessarily forming the crystal structure. This leads to the weak first order transition behaviour.

4.2 Conclusion

The $\{3,3\}$ FLS model exhibits a strong first order transition and the nucleation behaviour is characterized by the fluctuations in cluster sizes that grow and shrink from small clusters in the metastable liquid. The $\{1,5\}$ FLS model exhibits a weak first order phase transition and nucleation involves growth from a large fluctuating cluster that forms in the metastable liquid. This work also highlights the need to focus on the excess number of spins in the system, obtained from the nucleation theorem rather than the absolute critical cluster size, where significant order exists in the metastable phase. The differences in freezing and nucleation behaviour may be understood in terms of the structural correlations the FLS impose on their environment.

4.3 Future Work

This work focused on studying the $\{1, 5\}$ FLS and the $\{3, 3\}$ FLS models. Nucleation studies on the remaining distinct FLS will be crucial to fully understanding these FLS systems and could help our understanding of nucleation in more complex systems occurring in nature. The MFPT method could be used to study systems where nucleation occurs on the time scale of simulations, but umbrella sampling Monte Carlo simulations could also be used. The system size effects also need to be checked.

While the spin lattice FLS models provide ideal systems for studying the effect of local structure on nucleation, the results and observation obtained in this model need to be examined in more realistic models of liquids and crystals. This remains a challenge because the FLS in these liquids are difficult to identify. The experimental identification of FLS also remains a significant challenge, but this may be possible in some colloidal systems where confocal microscopy allows the structure of the liquid state to be imaged directly.

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