Nucleation and growth in materials and on surfaces: kinetic Monte Carlo simulations and rate equation theory

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A Dissertation
entitled
Nucleation and Growth in Materials and on Surfaces: Kinetic Monte Carlo Simulations and Rate Equation Theory

by
Feng Shi

As partial fulfillment of the requirements for the Doctor of Philosophy Degree in Physics

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College of Graduate Studies

The University of Toledo
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A variety of nanocrystals, nanoparticles or quantum dots are fabricated using nucleation and growth processes. Therefore, a fundamental understanding of nucleation and growth is crucial to materials science and engineering on the nanoscale. In this dissertation, we explore the fundamental characteristics of nucleation and growth in multiple dimensional systems using several different methods. One method which has been found to be particularly useful is the Monte Carlo (MC) method. In particular, the kinetic Monte Carlo (KMC) method has made MC simulations of complicated many body systems very efficient. In this dissertation, we use KMC simulations to study nucleation, growth, and coarsening in a variety of different systems. In addition, we have carried out a theoretical analysis using rate equations. We have also carried out investigations of the fundamental characteristics of the coarsening process using parallel methods based on a newly developed parallel KMC algorithm.

This dissertation is organized in two parts, the first part is about fundamental characteristics of multiple dimensional systems, the second part is about parallel
KMC calculation of coarsening process. In Part I, we first study the fundamental characteristics of nucleation and growth in 3 dimensional (3D) systems using a simplified model of nucleation and growth. One of the main goals of this work is to compare with previous work on 2D nucleation and growth in order to understand the effects of dimensionality. The scaling of the average island-size, island density, monomer density, island-size distribution (ISD), capture number distribution (CND), and capture zone distribution (CZD) are studied as a function of the fraction of occupied sites (coverage) and the ratio \( D/F \) of the monomer hopping rate \( D \) to the (per site) monomer creation rate \( F \). Our model may be viewed as a simple model of the early-stages of vacancy cluster nucleation and growth under irradiation. Good agreement is found between our mean-field (MF) rate-equation results for the average island and monomer densities and our simulation results. In addition, we find that due to the decreased influence of correlations and fluctuations in 3D as compared to 2D, the scaled CND depends only weakly on the island-size. As a result the scaled ISD is significantly sharper than obtained in 2D and diverges with increasing \( D/F \). However, the scaled ISD obtained in kinetic Monte Carlo (KMC) simulations appears to diverge more slowly with increasing \( D/F \) than the MF prediction while the divergence occurs at a value of the scaled island-size which is somewhat beyond the MF prediction. These results are supported by an analysis of the asymptotic CND.

The final goal for understanding the mechanism of nucleation and growth is to develop a theory to concisely and precisely disclose the law underlying the nucleation and growth process. From the theoretical point view, dimension can be taken as a variable to develop theory. In order to obtain the upper critical dimension corresponding to
MF theories, we compare the results of kinetic Monte Carlo (KMC) simulations of a point-island model of irreversible nucleation and growth in four-dimensions with the corresponding mean-field (MF) rate equation predictions for the monomer density, island density, island-size distribution (ISD), capture number distribution (CND), and capture zone distribution (CZD), in order to determine the critical dimension $d_c$ for mean-field behavior. The asymptotic behavior is studied as a function of the fraction of occupied sites (coverage) and the ratio $D/F$ of the monomer hopping rate $D$ to the (per site) monomer creation rate $F$. Excellent agreement is found between our KMC simulation results and the MF rate equation results for the average island and monomer densities. For large $D/F$, the scaled CND and CZD do not depend on island-size in good agreement with the MF prediction, while the scaled ISD also agrees well with the MF prediction except for a slight difference at the peak values. Coupled with previous results obtained in $d = 3$, these results indicate that the upper critical dimension for irreversible cluster nucleation and growth is equal to 4.

While most of this work focusses on the correlations between various quantities and the island-size, it is also interesting to study the dependence of global quantities, such as the global CZD on dimensionality. In order to compare with recent analytic theories for the global CZD we have also studied the dependence of the global CZD using KMC simulations as a function of dimensionality in, one, two, three, and four dimensions. In general, we find that while the CZD depends on the short-range interaction for finite $D/F$ (corresponding to the ratio of monomer hopping rate $D$ to deposition rate $F$) in the asymptotic limit of infinite $D/F$ there is no significant dependence. However, poor agreement is found between the asymptotic CZD and the
predicted Wigner distributions. Our results also indicate that for $d = 2$ and 3 the asymptotic CZD is independent of model details and dimension. However, for $d = 1$ and $d = 4$ the resulting distribution is significantly more sharply peaked. We also find that in contrast to the island-size distribution, for which mean-field-like behavior is observed in $d = 3$ and above, the asymptotic CZD is significantly broadened by fluctuations even in $d = 4$.

In addition to nucleation and growth, coarsening also plays a significant role in nano-particle fabrication and thin film growth. Therefore, in Part II, we explore the coarsening process using KMC simulations. Exploring the fundamental characteristics of coarsening process requires large-scale simulations which cover a large time scale. In this study, the results of parallel kinetic Monte Carlo (KMC) simulations of island coarsening based on a bond-counting model are obtained. Our simulations were carried out both as a test of and as an application of the recently developed semi-rigorous synchronous sublattice (SL) algorithm. By carrying out simulations over long times and for large system sizes the asymptotic coarsening behavior and scaled island-size distribution (ISD) were determined. Our results indicate that while cluster diffusion and coalescence play a role at early and intermediate times, at late times the coarsening proceeds via Ostwald ripening. In addition, we find that due to fluctuations which become important in 2D, the asymptotic scaled ISD is significantly narrower and more sharply peaked than the mean-field theory prediction. The dependence of the scaled ISD on coverage is also studied. Our results demonstrate that parallel KMC simulations can be used to effectively extend the time-scale over which realistic coarsening simulations can be carried out. These results also suggest
that the SL algorithm is likely to be useful in the future in parallel KMC simulations of more complicated models of coarsening.
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To my mother, Lina Kang.
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Chapter 1

Introduction

1.1 Nucleation and growth in materials and on surfaces

Cluster nucleation and growth by aggregation is the central feature of many physical processes, from polymerization and gelation in polymer science, flocculation and coagulation in aerosol and colloidal chemistry, percolation and coarsening in phase transitions and critical phenomena, agglutination and cell adhesion in biology, to island nucleation and thin-film growth in materials science [1]. In particular, many condensed matter processes such as nano-particle fabrication involve cluster nucleation and growth. Furthermore, in thin film fabrication, homogeneous nucleation and growth of islands during the initial submonolayer stage of film plays a significant role in determining the morphology and properties of the resultant multilayer film. Due to its broad technical importance, the homogeneous nucleation and growth of
islands during the initial submonolayer stage of film growth has been studied intensively for decades. [2] This field attracted immense interests from researchers in thin film device fabrications such as thin film solar cells. One of the remarkable examples is the growth of ultra-thin metal films on metal oxides [3]. Chambers et al were able to realize layer-by-layer growth of ultra-thin Co on $\alpha-Al_2O_3$ surface by manipulating the island nucleation and growth during the initial submonolayer stage. By changing the 3 dimensional nucleation and growth of islands into 2 dimensional layer-by-layer nucleation and growth, they successfully fabricated films only a few atomic layers thick. This is particularly important because of a proposed use in magnetoresistive random access memory.

In addition to nucleation and growth on a substrate, clusters can also nucleate and grow to form nanocrystals and and this can significantly alter the properties of the films. For instance, Plasma Enhanced Chemical Vapor Deposition (PECVD) is widely used to fabricate amorphous silicon solar cells, displays and imaging devices. The size of the nanocrystals determines the spectral absorption properties of the active layer of solar cells, since the band gap of the nanocrystals is determined by the quantum confinement effect. In addition, the performance of the nanocrystalline silicon solar cells is closely related to the volume fraction of nanocrystals embedded in the amorphous matrix. [4] The nucleation and growth of nanocrystals in bulk materials of the thin film solar cells can also affect the thickness of the thin films needed for absorption of incident sunlight. Therefore it is of interest to study the nucleation and growth of nanocrystals in thin film materials. Such quantities as the cluster size distribution, volume fraction of nanocrystals and atomic structure of the
nanocrystals are of particular interest.

Besides the important role played by nanocrystals in the performance of thin film amorphous silicon solar cells, nanocrystals generated in an amorphous matrix such as SiO$_2$ by ion implantation [5] are also attractive as building blocks of many novel optoelectronic devices. In the ion implantation process, silicon atoms are shot into the glass matrix to form precipitates, then the precipitates grow into nanocrystals during the subsequent annealing process. At present it is difficult to control the nanocrystal size sufficiently for the fabrication of regular optoelectronic devices. Therefore, experimental and theoretical investigation of the nucleation and growth of the clusters may be useful in developing novel nano scale devices.

Since these processes play an important role in thin-film growth and ion-implantation one of the main goals of this dissertation is to explore the statistical properties of cluster nucleation and growth and their dependence on substrate dimension. In order to do so, a variety of methods have been used, including kinetic Monte Carlo (KMC) simulations, rate equations, and scaling theory. Another important goal is to study the coarsening process over extended time- and length-scales after nucleation and growth. In order to achieve this goal we have developed methods for parallel KMC simulation and applied them to study the coarsening of 2D submonolayer islands.

1.2 The scope of this thesis

The thesis is organized as follows. In Chapter 2, we first introduce the Monte Carlo method and its applications with emphasis on the significance of this method and its
Wide applications and successes. In particular, the kinetic Monte Carlo method, which is a modified Monte Carlo method used to simulate the dynamic properties of systems is discussed. In order to improve our understanding, it is desirable to develop a systematic theory which can accurately describe non-equilibrium processes. Therefore, in Chapter 3 we introduce the rate equation theory used to describe the evolution of cluster nucleation and growth in material systems. In this Chapter the mathematical method used to solve rate equations for realistic material systems is introduced and its application for some practical cases is demonstrated. In Chapter 4 we first introduce the basic concepts used to describe cluster nucleation and growth, and then present our theoretical analysis and KMC simulation results for 3 dimensional (3D) systems. One of the main goals of this work is to compare with known results in 2D nucleation, in order to understand how the underlying dimensionality affects the nucleation and growth process. Since our 3D results indicate that the critical dimension for mean-field (MF) behavior is larger than 3, we have also studied the nucleation and growth process in 4 dimensions \((d = 4)\) as discussed in Chapter 5.

We note that most of the recent work on cluster nucleation and growth has focussed on the principal quantities of interest, e.g. the average cluster size and cluster-size distribution. However, evidence indicates that in some cases understanding such geometrical properties as the environment of clusters may be useful in understanding the physics underlying nucleation and growth. Therefore, in Chapter 6, we present an analysis of the capture-zone distribution during nucleation and growth and its dependence on dimensionality, and compare with recent theoretical predictions.

In the last part of this thesis, we study the coarsening process after cluster nu-
cleation and growth. In Chapter 7, we first review the background of coarsening processes and its applications while in Chapter 8 we review the synchronous sub-lattice algorithm used in our parallel KMC simulations. In Chapter 9, we present our parallel KMC simulation results and theoretical analysis for the coarsening of 2D islands. Finally, in Chapter 10, we summarize our results and give an outlook for future research work.
Chapter 2

Monte Carlo methods

2.1 Introduction

Monte Carlo methods are algorithms for solving various kinds of computational problems by using random numbers (or rather, pseudorandom numbers). While statistical sampling was well known long before it was named Monte Carlo it was the development of the first electronic computer ENIAC which made it practical. Shortly after this the Monte Carlo method was proposed by von Neuman, Ulam, and Metropolis for the Manhattan project of World War II. [7] Since then a large variety of different Monte Carlo methods have been developed. However, Monte Carlo simulations can generally be classified into four main types:

- Direct Monte Carlo, in which random numbers are involved to simulate the effects of complicated processes.
- Monte Carlo integration, which is a very efficient technique to calculate high dimension volume integrals using random numbers.
• Metropolis Monte Carlo, in which a sequence of distributions of a system with random states is generated in a so-called Markov chain. By the end of the simulation each state has occurred with the appropriate probabilities.

• Kinetic Monte Carlo.

The details of these topics are given in the remainder of the chapter.

2.2 Direct Monte Carlo

The time evolution of Monte Carlo methods proceeds according to a stochastic algorithm which is very simple, as below:

1. Generate a random number.

2. Accept or reject a new random step, depending upon the generation of a random number.

3. Repeat trial.

Direct Monte Carlo methods are powerful tools which have a variety of applications inside and outside physics. An example is the modeling of “Brownian motion”, where the bigger colloidal particle (Brownian particle) moves randomly, colliding with small solvent particles in solution.

2.3 Monte Carlo integration

Monte Carlo can also be used to evaluate definite integrals. Consider the integral below on the interval \([a, b]\) on the real axis:
\[ I = \int_{a}^{b} f(x)dx \quad (2.1) \]

An efficient numerical approach is to note that we can write Eq. 2.1 as,

\[ I = \int_{a}^{b} \rho(x)f(x)dx \approx \frac{b - a}{N} \sum_{i=1}^{N} f(x_{i}), \quad (2.2) \]

where the \( x_{i} \) are random numbers on the interval \((a, b)\) chosen with probability distribution \( \rho(x) \). If \( \rho(x) = \frac{1}{b - a} \) then the coordinates \( x_{i} \) are chosen randomly from a uniform distribution within the domain \([a, b]\). If \( N \) is sufficiently large, then estimates based upon 2.2 will converge to a result arbitrarily close to the exact integral. The variance in the result will be \([8]\):

\[ \sigma^{2} = \frac{1}{N} \left\{ \int_{a}^{b} \left( \frac{f(x)}{\rho(x)} \right)^{2} \rho(x)dx - \left[ \int_{a}^{b} \frac{f(x)}{\rho(x)} \rho(x)dx \right]^{2} \right\} \approx \left( \frac{b - a}{N} \sum_{i=1}^{N} f_i \right)^{2} - \left( \frac{b - a}{N} \sum_{i=1}^{N} f_i \right)^{2} \quad (2.3) \]

The angular brackets represent the average over all possible values of the sequence of randomly and uniformly distributed coordinates \( x_{i} \).

For simple one-dimensional integration, i.e. Eq. 2.1, the MC method is not competitive with standard numerical methods such as Simpson’s rule. However, for the multidimensional integrals of statistical mechanics, such as the canonical or (NVT) ensemble for a many-body system, or phase-space integrals, the MC method, with a suitable choice of \( \rho(x) \), is the only accessible solution. Furthermore, it is possible to speed up the convergence of MC integration in higher dimensions, by using quasi-
random numbers which fill a high-dimensional volume very homogeneously without attempting to achieve pseudo-random numbers [8].

2.4 Metropolis Monte Carlo

2.4.1 Markov chains

For many stochastic systems, the probability evolution can be described by a Markovian master equation such that the transition probability is independent of the system history or current time. Consider the probability $P(x, t)$ that a system is in state $x$ at time $t$. In the case of a Markovian master equation the evolution of $P(x, t)$ can be written,

$$\frac{\partial P(x_f, t)}{\partial t} = \sum_{x_i} W(x_i \rightarrow x_f) P(x_i, t) - \sum_{x_f} W(x_f \rightarrow x_i) P(x_f, t). \quad (2.4)$$

Here $W(x_i \rightarrow x_f)$ is the transition probability per unit time that the system will transit from state $x_i$ to state $x_f$.

The controlling factor in a Markov chain is the transition probability. The probability is a conditional probability for the system to transit or migrate to a particular new state, given the current state of the system. For many situations, such as the case in which the system at thermal equilibrium (steady state), the transition probability is weighted according to the Boltzman distribution:

$$W \propto e^{-\frac{E}{k_B T}}. \quad (2.5)$$
At steady state, the sum of all transitions into a particular state \( x \) equals the sum of all transitions out of the state. To be consistent with the Boltzmann distribution, the \textit{detailed-balance criterion} must be imposed on the MC transition probabilities. The detailed-balance criterion may be expressed as:

\[
W(x_i \rightarrow x_f)P(x_i, t = \infty) = W(x_f \rightarrow x_i)P(x_f, t = \infty).
\] (2.6)

However, the detailed-balance criterion does not uniquely determine the transition probability \( W(x_i \rightarrow x_f) \) but leaves an ambiguity in the choice of \( W \).

\subsection*{2.4.2 Metropolis algorithm}

To evolve a system towards equilibrium or evaluate thermodynamic averages of the system, one can apply MC methods with importance sampling. The desired importance sampling may be obtained by the Markov chain. This means that estimates can be quite efficient if the proper transition probabilities can be determined. There are many methods used to select the proper transition probabilities. One method which satisfies detailed balance is the \textit{Metropolis algorithm} given by:

\[
W(x_i \rightarrow x_f) = \begin{cases} 
\frac{1}{\tau}e^{-\frac{\delta E}{k_BT}} & : \delta E > 0 \\
\frac{1}{\tau} & : \text{otherwise}
\end{cases}
\]

For Metropolis, \( \tau \) is the usual MC step, and \( \delta E = E(x_i) - E(x_f) \) the energy difference.

The detailed procedure of the Metropolis algorithm may be outlined as:
1. Produce a new state from the current state by using a uniform random number.

2. Calculate the energy difference $\delta E$ between the new state to the current state.

3. if $\delta E \leq 0$, update to new state.

4. if $\delta E > 0$, then generate a uniform random number $\nu \in [0, 1]$.
   - if $e^{-\frac{\delta E}{k_BT}} > \nu$, update to new state.
   - else, no update.

5. Go to 1 and repeat.

### 2.5 Kinetic Monte Carlo

To evolve a system towards equilibrium, the Metropolis algorithm follows a Markov process, and makes all transitions of the system to states of lower or equal energy having uniform probability, regardless of the barrier to access this state, the process required or the transition rate. Thus, while Metropolis Monte Carlo (MMC) will lead to the correct equilibrium state, it does not necessarily have the correct dynamics. In addition, if a transition to a state with higher energy is attempted, then that transition is only accepted with the appropriate probability. Therefore, even in simulations in which the only goal is to reach equilibrium MMC simulations may be inefficient due to the existence of significant rejection of attempted events.

One solution to this problem is the kinetic Monte Carlo method. In particular, kinetic Monte Carlo (KMC), sometimes called dynamic MC [6], is an extremely efficient
method for carrying out dynamical simulations of a wide variety of stochastic and/or thermally activated processes when the relevant atomic-scale processes are known. Serial KMC simulations have been used to model a variety of dynamical processes ranging from catalysis to thin-film growth. In this section, we first introduce the basic algorithm of KMC, and then deal with models of crystal growth using KMC.

### 2.5.1 KMC algorithm

The KMC algorithm is based on the so called “n-fold-way” also known as the Bortz-Kalos-Lebowitz or residence-time algorithm. This algorithm may be outlined as follows:

1. Set the start time $t = 0$.

2. Update list of all possible events (transitions) that can occur and rates for each event in the system: assume each event $i$ has rate $R_i \propto e^{-\frac{E_i}{k_b T}}$, where $E_i$ is the barrier energy.

3. Calculate the partial cumulative event rates (partial sums)

$$S_i = \sum_{j=1}^{i} R_j \quad (2.7)$$

4. for $i = 1, \cdots, N$ where $N$ is the total number of events. Denote $S_0 = 0$ and the total event rate $R_T = S_N$.

5. Generate a uniform random number $p \in [0, 1]$. 
6. Select event $j$ using the partial sums:

$$S_{j-1}/R_T < p \leq S_j/R_T.$$  \hspace{1cm} (2.8)

7. Perform event $j$.

8. Update time $t = t - \ln(r)/R_T$ where $0 < r < 1$ is a uniform random number

9. Go to 2 and repeat.

This algorithm scales as $O(N)$, since at least step 3 has a sum over $N$ elements. As discussed in the next section, it is possible to reduce the scaling below-$N$, even down to $O(\log_2 N)$ or $O(N^{1/K})$ using a binary-tree or K-level search algorithm.

2.5.2 K-level Search Algorithm

One important application of kinetic Monte Carlo is simulations of growth by molecular beam epitaxy (MBE), where the surface is directly bombarded by atoms. In typical MBE growth models, there are only a limited number of kinds ($g$) of possible events, such as adatom adsorption, adatom hopping, adatom exchange, dimer desorption, dimer diffusion and so on. Therefore, the following procedure using the K-level search algorithm may be used to improve the scaling of a kinetic Monte Carlo simulation:

1. Set the start time $t = 0$.

2. Update list of all possible event types (transitions) that can occur and rates for
each event type in the system: assume each event type $i$ has event number $n_i$ with rate $R_i$.

3. Calculate the k-level recursive binning

$$S_i^{(k)} = \sum_{j=2i-1}^{2i} S_i^{(k-1)}$$  \hspace{1cm} (2.9)

for $i = 1, \cdots, G$, where $G$ is the integer of $(0.99 + g/2^k)$, $k = 1, \cdots, K$, $K = \text{int}(0.99 + \log_2 g)$, and $S_i^{(0)} = n_i R_i$, $S_0^{(0)} = 0$.

4. Get a uniform random number $P_j \in [0, 1]$.

5. Recursively search the k-level binning

$$S_{j-1}^{(k)} < P_j < S_j^{(k)}$$  \hspace{1cm} (2.10)

from $k = K$ to $k = 0$, then select that kind event $j$ to occur with probability

$$S_{j-1}^{(0)} < P_j < S_j^{(0)}$$  \hspace{1cm} (2.11)

6. Get another uniform random number $u \in [0, 1]$.

7. Perform the event $i$ by finding the $i$ in $j$ for which

$$n_{j-1} \leq u \leq n_j$$  \hspace{1cm} (2.12)

8. Find those event kinds $i$ that have changed as a result of event $j$ and update
\( n_i \); update only corresponding \( S'(0) \) and any data structure related \( S^{(k)} \).

9. Update time \( t = t - \ln(r)/RT \) where \( 0 < r < 1 \) is a uniform random number.

10. Go to 4 and repeat.

The \( k \)-level search algorithm is more efficient than the \( n \)-fold way algorithm in large systems with many different kinds of objects and possible events. KMC with \( k \)-level search can quickly find and implement data structures in this case.

While KMC simulations can be very useful, they can only be carried out if all the parameters, such as the event rates \( R_i \), are known in advance. Since the method itself can do nothing to predict them, they must be obtained from experimental data, or derived using other techniques such as MD simulations or \textit{ab initio} calculations.
Chapter 3

Rate equation theory

3.1 Rate equations

Rate equations provide a useful tool for understanding the nucleation and growth of clusters and the early stages of epitaxial growth. We note that two of the key processes in epitaxial growth are random deposition (with per-site deposition rate $F$) and diffusion of atoms on the substrate. If we denote the rate of single-atom or monomer hopping on the surface by $D$, then a key parameter is the ratio $D/F$ of the diffusion rate $D$ to the deposition rate $F$. Using these parameters, in this case of irreversible growth (e.g. no detachment of monomers from clusters) the following rate-equations for the evolution of the monomer density $N_1(\theta)$ and island-size distribution $N_s(\theta)$, where $N_s$ is the number of islands of size $s$ at coverage $\theta$ may be written,

$$\frac{dN_1}{d\theta} = 1 - 2(D/F)\sigma_1 N_1^2 - (D/F)N_1\sum_{s=2}^{\infty} \sigma_s N_s - \kappa_1 N_1 - \sum_{s=1}^{\infty} \kappa_s N_s \quad (3.1)$$
\[
d\frac{N_s}{d\theta} = (D/F)\sigma_s N_{s-1} - (D/F)\sigma_s N_s + \kappa_s N_{s-1} - \kappa_s N_s \{s = 2, \cdots, \infty\} \tag{3.2}
\]

where \(\sigma_s\) is the capture number for an island of size \(s\) and \(\kappa_s\) corresponds to direct impingement of an atom on an island of size \(s\). We note that the capture number, \(\sigma_s\), is a measure of how effectively an island of size \(s\) competes for the available monomers on the surface.

The first term on the right-hand side of Eq. 3.1 results from the flux of atoms onto the surface. The second and third terms account for the loss of monomers to dimer formation and attachment to islands, respectively. The factor of 2 in the second term is present because dimer formation results in the loss of two monomers. The fourth term accounts for the loss of diffusing monomers due to direct capture of the deposited flux, and the fifth term is the loss of flux to the direct impingement onto existing islands and monomers. Similarly, the first (second) term on the right-hand side of Eq. 3.2 is the rate at which diffusing monomers are added to an islands of size \(s - 1(s)\) multiplied by the total density of islands of that size. This process increases (decreases) the number of islands of size \(s\). The third and fourth terms account for the direct capture of deposited atoms by an island of size \(s - 1\) and \(s\) respectively. For compact islands in the quasistatic approximation \(\kappa_s \simeq s\).

We note that all information about island structure and the spatial correlations between islands is contained in the time-dependent capture number \(\sigma_s\). Complete information about the correlations is not contained in the average quantities \(N_s(\theta)\).
The system of equations given by Eqs. 3.1 and 3.2, therefore, are not complete without further information or assumptions. In general, the dependence of the $\sigma_s(\theta)$ on coverage and island-size is not known and ad-hoc assumptions for this dependence are used when using rate-equations. As a first step to resolve this problem, for the case of growth on a 2D substrate Bales and Chrzan [30] developed a self-consistent method for calculating the capture numbers $\sigma_s(\theta)$ which involves solving the diffusion equation surrounding each island self-consistently along with the mean-field assumption that at large distances from an island, the distribution of islands is the same for all islands. While this method is effective in predicting the average capture number $\sigma_{av} = \sum \sigma_s N_s / \sum N_s$ as well as the average island density $N = \sum N_s$ and average monomer density $N_1$, because of the neglect of correlations it does not correctly predict the capture number distribution $\sigma_s(\theta)$ or the island-size distribution $N_s(\theta)$.

Consider an island of radius $R_s$ (assumed to be circular) embedded in an ensemble average system of islands and monomers. The local density of monomers, $n_1(r, \theta)$, responds to the presence of this island. In particular, if adatoms attach irreversibly, the density of monomers vanishes at the edge of the island: $n_1(R_s, \theta) = 0$. The simplest possible diffusion equation which describes the spatial variation of $n_1$ is

$$\frac{\partial n_1}{\partial \theta} = (D/F) \nabla^2 n_1 + J - (D/F) \xi^{-2} n_1,$$  \hspace{1cm} (3.3)

The quantities $J$ and $\xi$ can be obtained by averaging Eq. 3.3 over all space, using the fact that $\langle n_1 \rangle = N_1$, and comparing with Eq. 3.1. This yields the following
expressions for $J$ and $\xi$:

$$J = 1 - \sum_{s=1}^{\infty} \kappa_s N_s$$ (3.4)

and

$$\xi^{-2} = 2\sigma_1 N_1 + \sum_{s=2}^{\infty} \sigma_s N_s + (F/D)\kappa_1,$$ (3.5)

where $\xi$ is the average distance a monomer travels before being captured by an island or another monomer and $J$ is the fraction of the flux, which lands on the bare substrate. Implicit in this approach is the mean-field assumption that at every point outside of the island, the local densities $n_s(r, \theta)$ take on their average value $N_s(\theta)$ (for $s \geq 2$).

Despite its deceptively simple form, Eq. 3.3 is difficult to solve due to its complicated time dependence [$\xi = \xi(t)$] and the growth of the island, i.e., the boundary is moving. An approximate solution can be found, however, by assuming that the rate of adatom diffusion is large compared to the growth rate of the island (a good approximation). It is sufficient, then, to fix the radius of the island and solve for the instantaneous concentration of monomers. One must be careful to assure that the boundary condition at large $r$ is satisfied; hence, it is not appropriate to simply neglect the left-hand side of Eq. 3.3. One cannot satisfy Eq. 3.2 as $r \to \infty$ if the coverage (time) derivative of the more general $n(r, \theta)$ is neglected. Instead, subtract Eq. 3.2 from Eq. 3.3 and neglect deviations of the coverage derivative from its average value:
\[
\frac{F}{D} \left( \frac{\partial n_1}{\partial \theta} - \frac{dN_1}{d\theta} \right) = \nabla^2 n_1 - \xi^{-2} - \xi^{-2}(n_1 - N_1) \approx 0. \tag{3.6}
\]

In 2D, Eq. 3.6 may be re-written in circular coordinates. Assuming no angular dependence, the resulting equation has the straightforward solution

\[
n_1(r, \theta) = N_1 \left[ 1 - \frac{K_0(r/\xi)}{K_0(R_s/\xi)} \right] \tag{3.7}
\]

with \( K_j \) a modified bessel function of order \( j \). From this, one can readily obtain the capture numbers,

\[
\sigma_s = \frac{2\pi R_s}{N_1} \frac{\partial n_1}{\partial r} \bigg|_{r=R_s} = \frac{2\pi R_s}{\xi} \frac{K_1(R_s/\xi)}{K_0(R_s/\xi)} \tag{3.8}
\]

Since the capture numbers can be written as functions of the average densities, Eqs. 3.1, 3.2, 3.5, and 3.8 form a complete set of equations that must be solved self-consistently for the island size distribution function. Calculation of \( \sigma_s \) with Eq. 3.8 is accomplished easily using an iterative scheme.

### 3.2 Application of self-consistent RE method

Fig. 3-1 shows the results obtained by Bales and Chrzan [30] using this method for the case of island-growth without edge diffusion (fractal islands) along with results from KMC simulations. Plots of the monomer density, \( N_1 \), and total number density of islands \( N \) versus coverage are shown for three different values of \( D_F \); (a) \( 10^5 \), (b) \( 10^7 \), and (c) \( 10^9 \). The coverage ranges from 0.0 to 0.4 monolayers. The dashed lines are solutions to the rate equations and the solid lines are KMC results. The agreement
between the mean-field rate equations and the KMC simulations is striking. Similar agreement is obtained for conditions yielding compact islands.

At large coverages, however, the island size distribution function $N_s(\theta)$ is not reproduced very well by the mean-field rate equations. Figure 3-2 shows the distribution at three different coverages for $\frac{D}{T} = 10^8$. Hence, the rate equations are seen to reproduce average quantities by not the distribution function. This is not surprising, since the mean-field approximation does not properly include island-island correlations.
Figure 3-1: Monomer density $N_1$ and total density of islands $N(\theta)$ versus coverage for ramified islands at (a) $DF = 10^5$, (b) $DF = 10^7$, (c) $DF = 10^9$. The solid lines are measured from KMC simulations, and the dashed lines are numerical solutions of the rate equations. Obtained from [30]
Figure 3-2: Island size distribution $N_s(\theta)$ versus $s$ at three different coverages. The solid lines are measured from KMC simulations, and the dashed lines are numerical solutions of the rate equations. Obtained from Ref. [30]
Chapter 4

Cluster nucleation and growth in three dimensional systems

4.1 Introduction

After decades of rapid development, the research in the central area of science and engineering nano-materials has approached to a stage in which the fabrication of novel devices in nano-materials is possible. The breakthrough happen due to the significantly progress in fabricating nano-materials in a controllable manner. The invention of the bottom-up assembly of nanoscale building blocks into complex structures [9] offers the potential to produce devices with novel function since it is possible to combine in a general way materials with distinct chemical composition, structure, size, and morphology. With semiconductor nanowires[10] and carbon nanotubes [11] as building blocks, field-effect and single electron transistors, and electrically driven single nano-wire laser [12] are assembled. These sparked the interests in the fabrica-
tion of nanocrystals as promise building blocks for novel technological applications in opto-electronic devices, in particular, the silicon nanocrystals for fabrication of electrically driven laser. In contrast to nanowires of other semiconductor materials, silicon nanocrystals as quantum dots are more attractive in assembly of laser as light source compatible to silicon photonic integrated circuits for signal processing.

Nanocrystals have ever been fabricated via number of different techniques including wet chemistry, and co-sputtering. Recently, it has been demonstrated that nanocrystals can be fabricated using ion beam synthesis (IBS) [13]. In this technique, energetic ions are implanted into a matrix. The ion/matrix combination is chosen to insure a strong segregating tendency for the implanted species. Subsequent annealing leads to the formation of nanocrystals embedded within the matrix. This processing route is technologically appealing, as ion implantation is already a commonly applied semiconductor processing route. However, IBS presently lacks the size control believed necessary for many of applications. Towards this end, quantitative and accurate models of the nucleation, growth and coarsening of nanocrystals via IBS are desirable.

As initials, the techniques for exploring the nucleation and growth in bulk materials must be developed to understand the physical processes happen in three dimensional systems. Consequently we start to employ KMC to study the fundamental properties of cluster nucleation and growth in bulk materials by using simplified model.

The nucleation and growth of islands in submonolayer epitaxial growth has been studied intensively both experimentally ([14] - [23]) and theoretically ([24] - [43])
since the structures formed in the submonolayer regime can strongly influence the morphology and properties of the resultant multilayer film. For example, recently considerable theoretical effort has been carried out towards an understanding of the scaling properties of the island-size distribution $N_s(\theta)$ (where $N_s$ is the number of islands of size $s$ at coverage $\theta$) in submonolayer growth ([24] - [43]). In the pre-coalescence regime the island size distribution satisfies the scaling form [27, 28],

$$N_s(\theta) = \frac{\theta}{S^2} f \left( \frac{s}{S} \right),$$  \hspace{1cm} (4.1)

where $S$ is the average island size, and the scaling function $f(u)$ depends on the critical island size and island morphology [31].

One of the standard tools used in these studies is the rate-equation (RE) approach [24, 25, 44]. In this approach the coverage-dependence of the island-size distribution (ISD) is calculated through a set of deterministic reaction-diffusion equations which involve a set of rate-coefficients usually called capture numbers. [24, 25] For the irreversible growth of point islands, rate-equations valid in the pre-coalescence regime may be written in the form

$$\frac{dN_1}{d\theta} = 1 - 2R\sigma_1 N_1^2 - RN_1 \sum_{s=2}^{\infty} \sigma_s N_s - \kappa_1 N_1 - \sum_{s=1}^{\infty} \kappa_s N_s$$  \hspace{1cm} (4.2)
\[
\frac{dN_s}{d\theta} = R\sigma_{s-1}N_{s-1}N_s - R\sigma_sN_1N_s \\
+\kappa_{s-1}N_{s-1} - \kappa_sN_s
\]  

(4.3)

where the capture numbers \(\sigma_s (\sigma_1)\) correspond to the average capture rate of diffusing monomers by islands of size \(s\) (monomers), \(R = D/F\) is the ratio of the monomer diffusion rate to the deposition rate, and the terms with \(\kappa_s\) (\(\kappa_s = 1\) for point-islands) correspond to direct impingement. We note that the central problem in the RE approach is the determination of the size- and coverage-dependent capture numbers \(\sigma_s(\theta)\).

The simplest possible assumption for the capture-number distribution (CND) is the mean-field assumption \(\sigma_s(\theta) = \sigma_{av}\). While such an assumption may be adequate to describe the scaling of the average island density \(N\) and monomer density \(N_1\) with coverage and \(D/F\), it is not adequate to describe the ISD. For example, using 2D kinetic Monte Carlo (KMC) simulations, Bartelt and Evans [32] showed that even for point-islands there is a non-trivial dependence of the capture number on the island-size due to the correlation between island-size and capture zone. In addition, they showed that in the asymptotic limit of large \(D/F\), the scaled ISD is related to the scaled CND as,

\[
f(u) = f(0) \exp \left[ \int_0^u dx \frac{2z - 1 - C''(x)}{C(x) - z} \right],
\]

(4.4)

where \(C(s/S) = \sigma_s/\sigma_{av}\) is the scaled CND, \(z\) is the dynamical exponent describing the dependence of the average island size on coverage \((S \sim \theta^z)\), and \(f(0)\) is determined by the normalization condition \(\int_0^\infty du \ f(u) = 1\). We note that for irreversible growth
of point-islands as is considered here, one has $z = 2/3$. As can be seen from Eq. 4.4, if $C(u) > zu$ then no divergence will occur. However, if $C(u)$ crosses $zu$ at some value $u_c$ then a divergence in the asymptotic ISD will occur if $C'(u_c) < 2z - 1$.

This result highlights the importance of understanding the capture-number distribution in order to understand the scaling behavior of the ISD. For example, using this expression Bartelt and Evans were able to show[32] that the usual mean-field (MF) assumption that the capture number is independent of island size leads to a divergent ISD. On the other hand, by measuring the CND for various models in two-dimensional submonolayer island growth, they showed that due to correlations, the actual CND is not mean field but depends strongly on the island size. Accordingly, the scaled ISD for 2D nucleation and growth does not diverge in the asymptotic limit.

While the scaling behavior of the ISD and CND are now well understood for the case of two-dimensional nucleation and growth, the corresponding behavior has not been studied in three-dimensions. This is of interest from a theoretical point of view, since we would like to understand to what extent fluctuations play a role in determining the scaled ISD and CND, and a comparison with 3D simulations would be quite useful in providing such understanding. In addition, the scaling behavior of the ISD in simple models of 3D nucleation and growth may also be important in understanding a variety of important processes. For example, the nucleation and growth of islands in bulk materials has attracted tremendous interest in recent years, as these processes create nano-particles which as quantum dots are promising in fabricating light emission devices [45, 46, 47].

Here we present results for the scaled island-size distribution and capture-number
distribution obtained from KMC simulations of a simple point-island model of 3D nucleation and growth. For completeness, we also present the results of a self-consistent RE calculation which leads to good agreement with KMC simulations for the coverage dependence of the average island density \( N(\theta) \) and monomer density \( N_1(\theta) \). We find that, due to the decreased role of fluctuations and correlations in three-dimensions, the scaled ISD in 3D is significantly sharper than in 2D, and appears to diverge with increasing \( D/F \), while the asymptotic CND depends only weakly on island size. However, the asymptotic scaled ISD and CND still appear to deviate from the MF prediction. We attribute this deviation to the existence of geometric effects and correlations which, although reduced in 3D, still appear to play a role in three-dimensions.

This chapter is organized as follows. In Sec. II we first describe our simulations and point-island model. In Sec. III we describe a self-consistent rate-equation approach to the calculation of the capture numbers. In Section IV we first present a comparison between our self-consistent RE results and KMC results for the average island and monomer densities. We then present our KMC results for the ISD and CND along with a comparison with the corresponding RE results. Results for the scaled capture zone distribution (CZD) are also presented. Finally, we discuss and summarize our results in Section V.
4.2 Model and Simulations

In order to study the scaling behavior of the ISD and CND in 3D nucleation and growth, we have studied a simple point-island model of irreversible nucleation and growth on a cubic lattice. Our model is a straightforward analog of the corresponding point-island model previously studied in two-dimensions. [32] However, it may also be considered to be a simple model of vacancy cluster nucleation and growth in solids. We note that a more realistic model would take into account the increase of the lateral dimension of an island with island size. However, in the asymptotic limit of large $D/F$ the point-island approximation is appropriate for extended islands up to a finite coverage ($\theta \leq 0.01$) since over this coverage range the average island separation is still significantly larger than the average island radius. [39]

In our model, monomers are randomly created throughout the lattice with creation rate $F$ per site per unit time, and then hop randomly in each of the 6 nearest-neighbor directions with hopping rate $D_h$. If a monomer lands on a site already occupied by another monomer or is created at such a site, then a dimer island is nucleated. Similarly, if a monomer lands on or is created at a site already occupied by an island then that monomer is captured by that island and the island size increases by 1. As for 2D nucleation and growth the key parameter in this model is the ratio $R_h = D_h/F$ of the monomer hopping rate to the (per site) monomer creation rate, or equivalently the ratio $R = D/F = R_h/6$.

In order to study the asymptotic scaling behavior corresponding to large $D/F$, we have carried out simulations over a range of values of $R_h$ ranging from $10^5$ to $10^{10}$. 
(We note that in epitaxial growth on a two-dimensional substrate such large values are actually quite typical due to the relatively high growth temperatures and low deposition rates used.) To avoid finite-size effects, simulations were carried out over a range of different values of the system size $L$ ranging from $L = 160$ to $L = 450$. In addition, our results were typically averaged over 200 runs to obtain good statistics. For each set of parameters the scaled ISD, CND, and capture-zone distribution (CZD) were obtained for coverages up to $\theta = 0.4$, while the average island density $N(\theta)$ and monomer density $N_1(\theta)$ were also measured. We note that in order to measure the capture-number distribution, the method outlined in Ref. [32] was used. In particular, the capture number $\sigma_s(\theta)$ was calculated using the expression $\sigma_s(\theta) = n_s^c/(R\Delta\theta N_1 N_s L^3)$ where $n_s^c$ is the number of monomer capture events corresponding to an island of size $s$ during a very small coverage interval ($\Delta\theta \simeq 0.001$). As in Ref. [32] the island size $s$ at the beginning of the coverage interval was used when incrementing the counter $n_s^c$ in order to obtain good statistics. We also note that in our capture-zone distribution calculations, the capture zone of an island was defined as corresponding to all monomer sites or empty sites which are closer to that island than any other island. If such a site was equally close to several islands, than that site’s contribution to the capture zone was equally distributed between the islands.
4.3 Self-consistent rate-equation calculation

As in Ref. [30] we consider a quasistatic diffusion equation for the monomer density \( n_1(r, \theta, \phi) \) surrounding an island of size \( s \) of the form,

\[
\nabla^2 n_1(r, \theta, \phi) - \xi^{-2}(n_1 - N_1) = 0
\]  

(4.5)

where \( N_1 \) is the average monomer density and \( \xi \) corresponds to an overall average capture term. For consistency with the RE’s (4.2) and (4.3) we require \( \xi^{-2} = 2\sigma_1 N_1 + \sum_{s=2}^{\infty} \sigma_s N_s \). We note that if we assume that \( \sigma_s = \sigma_1 = \sigma \), then this self-consistency condition may be written more simply as,

\[
\xi^{-2} = \sigma(N + 2N_1).
\]  

(4.6)

Assuming spherical symmetry Eq.4.5 may be written,

\[
\frac{1}{r^2} \frac{d}{dr} (r^2 \frac{d\tilde{n}_1}{dr}) - \xi^{-2}\tilde{n}_1(r) = 0
\]  

(4.7)

where \( \tilde{n}_1(r) = n_1(r) - N_1 \). The general solution is given by,

\[
\tilde{n}_1(r) = A \frac{\sinh(r/\xi)}{r} + B \frac{\cosh(r/\xi)}{r}.
\]  

(4.8)

Using the boundary condition \( n_1(R_s) = 0 \) (where \( R_s \) is the island radius) corresponding to irreversible growth, along with the asymptotic boundary condition \( n_1(\infty) = N_1 \),
we obtain,
\[ n_1(r) = N_1[1 - (R_s/r) e^{-(r-R_s)/\xi}]. \] (4.9)

Equating the microscopic flux of atoms near the island \( 4\pi R_s^2 D[\partial n_1/\partial r]_{r=R_s} \) to the corresponding macroscopic RE-like term \( DN_1\sigma_s \), we obtain for the capture number,
\[ \sigma_s = \frac{4\pi R_s^2}{N_1} (\frac{\partial n_1}{\partial r})_{r=R_s} = 4\pi R_s(1 + R_s/\xi). \] (4.10)

We note that this result agrees with that of Talbot and Willis [48] who carried out an analysis of the mean “sink” strength of voids in a random array of voids in an irradiated material.

For the point-island model the island-radius \( R_s \) is independent of island-size (i.e. \( R_s = R_0 \)) which implies
\[ \sigma_s = \sigma = 4\pi R_0(1 + R_0/\xi) \] (4.11)

where \( R_0 \) is a model-dependent constant of order 1. Substituting the self-consistency condition (4.6) for \( \xi \) leads to the result,
\[ \sigma \simeq 4\pi R_0[1 + \chi(1 + \sqrt{1 + 2/\chi})] \] (4.12)

where \( \chi = (N + 2N_1)2\pi R_0^2 \) and \( N = \sum_{s=2}^{\infty} N_s \) is the average island density. Using this result the contracted rate-equations for the monomer and island densities may be written,
\[ \frac{dN_1}{d\theta} = 1 - 2N_1 - N - 2(D/F)\sigma N_1^2 - (D/F)\sigma N_1N \] (4.13)
\[
\frac{dN}{d\theta} = N_1 + (D/F)\sigma N_1^2.
\]

(4.14)

We note that for large \(D/F\), Eq. 4.12 implies a capture number \(\sigma \approx 4\pi R_0\) which does not depend on coverage or \(D/F\).

### 4.4 Results

Fig. 4-1 shows a comparison between our KMC simulation results for the average monomer and island densities and the corresponding RE results obtained by numerically integrating Eqs. 4.12 - 4.14. The KMC results for \(D_h/F = 10^5, 10^7\) and \(10^9\) are shown, while the value of \(R_0\) (\(R_0 = 1/3\)) was chosen to give the best fit to the KMC data. As can be seen, there is excellent agreement between the RE and KMC results over all coverages and for all values of \(D_h/F\). Thus, as was previously found in two-dimensions, [30] the self-consistent RE approach can be used to accurately predict average quantities such as the monomer and island density in three-dimensions. We now consider the scaled island-size distribution (ISD).

Fig. 4-2 shows the corresponding results for the scaled ISD obtained from KMC simulations (symbols) at coverage \(\theta = 0.2\). As can be seen, the peak of the scaled ISD increases with increasing \(D/F\) while the island-size distribution becomes sharper, thus indicating a divergence in the asymptotic limit of infinite \(D/F\). Also shown in Fig. 4-2 are the corresponding self-consistent RE results (solid curves). The asymptotic MF result\([26, 31]\) \(f(u) = \frac{1}{3}(1 - \frac{2u}{3})^{-\frac{1}{2}}\) corresponding to infinite \(D/F\) is also shown (dashed curve). As expected, the self-consistent MF RE results for the ISD approach
the asymptotic MF prediction with increasing $D/F$. However, there are significant differences between the KMC results and the RE results. In particular, while there is good agreement between the KMC and RE results for small $D/F$, for large $D/F$ the KMC results for the scaled ISD are significantly lower than the RE predictions.

These differences are more dramatically indicated in Fig. 4-3 which shows the peak values of the scaled ISD obtained from both KMC simulations and RE calculations as a function of $D/F$. As can be seen, in both cases the peak value $f_{pk}(D/F)$ of the scaled ISD increases as a power-law i.e. $f_{pk} \sim (D/F)^{\phi}$ thus indicating a divergent ISD in the asymptotic limit. However, the value of $\phi$ obtained from the KMC simulations ($\phi \simeq 0.06$) is significantly smaller than the value ($\phi \simeq 0.08$) obtained from our RE calculations.

In order to understand these differences, we have also measured the scaled capture number distribution $C(s/S)$ in our KMC simulations for $D_h/F = 10^5 - 10^{10}$ as shown in Fig. 4-4. The MF prediction corresponding to the horizontal dashed line $C(u) = 1$ is also shown. As can be seen, there are significant deviations between the KMC results and the MF prediction. In particular, $C(u)$ is less than 1 for $u < 1.3$ while it increases rapidly with $u$ for $u > 1.3$. We note that the MF prediction corresponds to an asymptotic divergence in the scaled ISD at the point $u_{c}^{MF} = 3/2$ where the MF CND crosses the line $2u/3$. On the other hand, for large $D/F$ the scaled CND curves obtained from the KMC simulation appear to “pivot” with increasing $D/F$ around a fixed point at $u_{c} \simeq 1.55$ which is also the point at which they cross the line $2u/3$.

As indicated by Eq. 4.4, a divergence in the asymptotic ISD will only occur if $C''(u_c) < 2z - 1 = 1/3$. For all values of $D/F$ considered here, the slope $C''(u_c)$ of the
scaled CND at the crossing point $u_c \simeq 1.55$ is lower than the critical value $2z-1 = 1/3$ required to avoid a divergence. Furthermore, for large $D/F$ the slope is well described by the expression $C'(u_c) = (1/3) \exp[-a/(D/F)^{0.2}]$ where $a = 23.6$. Thus $C'(u_c)$ is less than the critical value of $1/3$ for all finite $D/F$ although it approaches the critical value asymptotically. These results are consistent with the observed divergence in the scaled ISD with increasing $D/F$. However, the asymptotic divergence appears to occur at a point, $u_c \simeq 1.55$, which is somewhat beyond the point $u_c^{MF} = 3/2$ at which the MF ISD diverges.

In order to better understand the asymptotic behavior we have also studied the dependence of the peak position $u_{pk}$ of the scaled ISD obtained from our KMC simulations as a function of $D/F$. In order to extrapolate the asymptotic behavior, the peak position $u_{pk}(D/F)$ was fit to the form $u_{pk}(D/F) = u_{pk}(\infty) + c (D/F)^{-\gamma}$ while the value of $\gamma$ was varied to find the best fit. A similar fit was used to extrapolate the MF RE results. Fig. 4-5 shows the corresponding results for the KMC simulations (filled circles, $\gamma \simeq 1/9$) as well as for the MF RE results (open circles, $\gamma \simeq 1/5$). As expected, for the MF RE results we find $u_{pk}^{MF}(\infty) \simeq 3/2$. However, for the KMC simulation results we find $u_{pk}(\infty) \simeq 1.55$ which is in good agreement with our results for the scaled CND. We note that the value of $\gamma$ ($\gamma \simeq 1/9$) obtained in our fits to the KMC results may be partially explained by noting that $(D/F)^{1/9}$ corresponds to the ratio of the island separation to the island size. However, we have no similar explanation for the value of $\gamma$ ($\gamma \simeq 0.20$) obtained in our fits to the MF RE calculations.

We have carried out a similar analysis of the crossing point $u_{cr}$ corresponding to
the position at which the tails of successive ISD curves (corresponding to values of $D/F$ varying by a factor of 10) cross. In this case a fit similar to that used for the peak position, i.e. $u_{cr}(D/F) = u_{cr}(\infty) + c (D/F)^{-\gamma}$, was used and again the value of $\gamma$ was varied to find the best fit. The corresponding results are also shown in Fig. 4-5. We note that the best-fit value of $\gamma$ ($\gamma \simeq 0.24$) used for the KMC crossing points (upper filled symbols) is significantly different from that used to fit the scaling of the KMC peak position ($\gamma \simeq 1/9$) and is much closer to that used for the MF RE results (upper open symbols). However, the asymptotic value of the crossing point $u_{cr}(\infty) \simeq 1.55$ is still in good agreement with the asymptotic value for the peak position. Similarly, for the MF RE results we again find $u_{cr}^{MF}(\infty) \simeq 3/2$ and $\gamma \simeq 1/5$. Thus these results confirm that, as already indicated in Figs. 2-4, although the asymptotic scaled ISD diverges with increasing $D/F$ it is significantly different from the MF prediction.

For completeness, we have also measured the scaled capture-zone distribution (CZD) as shown in Fig 4-6. The shape of the scaled CZD is similar to that of the scaled CND. In particular, it is relatively “flat” for $u < 1.3$, while for $u > 1.3$ it increases rapidly with island-size for large $D/F$. However, just as for the case of 2D submonolayer nucleation, [32] the scaled CZD is quite different from the scaled CND. This difference is most likely due to the effects of geometry as well as fluctuations which imply that an adatom in the capture zone of a given island is not necessarily captured by that island.
4.5 Discussion

In order to understand the role of fluctuations and geometry in irreversible nucleation and growth, and also to compare with results obtained in two-dimensions, we have carried out simulations of a simple point-island model of irreversible island nucleation and growth in three-dimensions. We have also presented a self-consistent RE calculation similar to that previously carried out by Bales and Chrzan[30] in two-dimensions. In contrast to the case of island nucleation and growth in 2D, we find that the peak of the scaled ISD increases and the distribution becomes sharper with increasing $D/F$, thus leading to a divergence in the asymptotic limit. However, while good agreement is found between the self-consistent RE results for the average island and monomer densities and our simulation results, there is poor agreement between the MF RE results for the scaled ISD and simulations. In particular, the scaled island-size distribution obtained in KMC simulations diverges more slowly than the MF prediction. By directly measuring the scaled capture-number distribution for different values of $D/F$ we have found that, in contrast to the MF assumption, the scaled CND depends weakly on island-size. In addition, our analysis of the dependence of the scaled CND on $D/F$ clearly indicates that the asymptotic CND is also different from the MF prediction. In particular, the asymptotic CND appears to cross the line $2u/3$ at a value $u_c \simeq 1.55$ which is significantly larger than the MF prediction $u_c = 3/2$. As indicated by Eq. 1, this leads to a divergence of the ISD at a value $u_c \simeq 1.55$ which is somewhat larger than the value $3/2$ predicted by MF theory. These results are further supported by our analysis of the asymptotic behavior of the
ISD peak position and crossing-point which indicate that in both cases there is an asymptotic divergence at a scaled island-size \( u_c \approx 1.55 \) which is somewhat beyond the MF prediction. This “bending” of the CND away from the MF value \( C(u) = 1 \) for large \( u \) also leads to a decreased value of the numerator in Eq. 1, thus explaining the “decrease” in the peak of the ISD compared to the MF prediction. Thus, we conclude that although the scaled ISD and CND in 3D are significantly closer to the MF prediction than in 2D, in the asymptotic limit of large \( D/F \) the scaled CND is still not completely independent of island-size as predicted by MF theory. We believe that this is due to the effects of fluctuations and geometry, which still appear to play a significant role in 3D.

We note that since we have been primarily interested in the asymptotic behavior of the point-island model, the results shown here have primarily focussed on the behavior at a relatively high coverage i.e. \( \theta = 0.2 \). While at higher coverages the differences between our KMC results and the MF prediction are even larger, we have also examined the behavior at significantly lower coverage \( \theta \approx 0.05 \). In this case, we found that a similar discrepancy between the KMC results and the MF prediction also occurs, although it is significantly smaller for the same value of \( D/F \). We conclude that at lower coverages, much higher values of \( D/F \) are needed to clearly see the asymptotic behavior. Finally, we note that for a more realistic model with 3D islands, the dependence of the capture number on island size is likely to be even stronger than for the point-island model studied here. Based on these results, we expect that the “critical dimension” \( d_c \) for mean-field behavior for the point-island model is larger than 3 and is possibly equal to 4. In the future we plan to carry out parallel KMC
simulations in four-dimensions in order to see if this is the case.
Figure 4-1: Comparison between KMC results (symbols) and the corresponding RE results (solid lines) for the monomer density $N_1$ and island density $N$ as a function of coverage for $D_h/F = 10^5$ (circles), $10^7$ (triangles) and $10^9$ (diamonds).
Figure 4-2: Scaled island-size distributions for $D_h/F = 10^5, 10^7$ and $10^9$. KMC simulation results (symbols), RE results (solid lines), and asymptotic MF limit (dashed curve).
Figure 4-3: Log-log plot of peak value of scaled ISD as function of $D_h/F$. 

\[
\theta = 0.2
\]

slope = 0.08

- KMC
- RE

slope = 0.06
Figure 4-4: KMC simulation results for scaled CND $\sigma_s/\sigma_{av}$ versus scaled island size for $D_h/F = 10^5 - 10^{10}$. Horizontal dashed line corresponds to MF CND, solid line corresponds to $(2/3)(s/S)$. 
Figure 4-5: Plot of $u_{pk}(D/F)$ and $u_{cr}(D/F)$ as a function of $(Dh/F)^{-\gamma}$ for $Dh/F$ ranging from $10^5$ to $10^{10}$. Lines are fits as described in text while values of $\gamma$ correspond to best fits.
Figure 4-6: KMC simulation results for scaled capture zone $z_s/Z$ versus scaled island size $s/S$ for $D_h/F = 10^5 - 10^9$. 

\[ \theta = 0.2 \]
Chapter 5

Upper critical dimension for irreversible cluster nucleation and growth

5.1 Introduction

Our KMC simulations of a point-island model of irreversible growth in three-dimensions ($d = 3$) carried out in the previous chapter indicate that while the scaled capture number distribution $C(u)$ is close to the MF prediction and as a result the asymptotic ISD diverges, for large $D/F$ both the scaled ISD and CND differ from the MF predictions. In particular, due to geometric effects in 3D, the scaled ISD diverges more slowly than the MF prediction while the asymptotic divergence occurs at a value of the scaled island-size which is somewhat larger than the MF prediction. These results suggest that the critical dimension $d_c$ for MF behavior is larger than 3.
Here we present the results of kinetic Monte Carlo simulations of a point-island model of irreversible growth carried out in $d = 4$ in order to compare with MF predictions. For comparison, the results of a self-consistent mean-field RE calculation are also presented and compared with the corresponding simulation results for the average island density $N$, monomer density $N_1$, island-size distribution, and capture number distribution. Our results indicate that, due to the decreased role of correlations in 4D, the asymptotic scaled ISD and CND, and CZD are in good agreement with the MF prediction in $d = 4$. These results confirm that the upper critical dimension for irreversible nucleation and growth is $d_c = 4$.

This chapter is organized as follows. In Sec. II we first describe our simulations. In Sec. III we present our self-consistent MF rate-equation approach. In Section IV, we present a comparison between our self-consistent MF RE calculations and KMC results for the average island and monomer densities. We then present our KMC results for the ISD, CND and CZD along with a comparison with MF theory. Finally, we discuss and summarize our results in Section V.

5.2 Model and Simulations

In order to study the scaling behavior of the ISD, CND and CZD in 4D, we have used a simple point-island model of irreversible nucleation and growth. Our model is a straightforward analog of the corresponding point-island model previously studied in two-dimensions [32]. In our model, monomers are created at random sites on a 4D cubic lattice with rate $F$ per site per unit time, and then hop randomly in each
of the 8 nearest-neighbor directions with hopping rate $D_h$. If a monomer lands on a site already occupied by another monomer or is created at such a site, then a dimer island is nucleated. Similarly, if a monomer lands on or is created at a site already occupied by an island then that monomer is captured by that island and the island size increases by 1. The key parameter in this model is the ratio $R_h = D_h/F$ of the monomer hopping rate to the (per site) monomer creation rate, or equivalently the ratio $R = D/F = R_h/8$.

In order to study the asymptotic scaling behavior, we have carried out simulations over a range of values of $R_h$ ranging from $10^5$ to $10^{10}$ and with system sizes ranging from $L = 40$ to $L = 100$. Our results were typically averaged over 200 runs to obtain good statistics. For each set of parameters the scaled ISD, CND and CZD were obtained for coverages ranging from $\theta = 0.1$ to $\theta = 0.4$, while the average island density $N(\theta)$ and monomer density $N_1(\theta)$ were also measured. We note that in order to measure the capture-number distribution, the method outlined in Ref. [32] was used. In particular, the capture number $\sigma_s(\theta)$ was calculated using the expression $\sigma_s(\theta) = n_s^c/(R\Delta\theta N_1 N_s L^4)$ where $n_s^c$ is the number of monomer capture events corresponding to an island of size $s$ during a very small coverage interval ($\Delta\theta \simeq 0.001$). As in Ref. [32] the island size $s$ at the beginning of the coverage interval was used when incrementing the counter $n_s^c$ in order to obtain good statistics. We also note that in our capture-zone distribution calculations, the capture zone of an island was defined as corresponding to all monomer sites or empty sites which are closer to that island than other island. If such a site was equally close to several islands, then that site’s contribution to the capture zone was equally distributed between the islands.
5.3 Self-consistent rate-equation approach

For the point-island model the island radius $R_s$ is independent of island-size $s$, i.e. $R_s = R_0$. Accordingly, within the MF RE approach the capture numbers are assumed to be independent of island-size $s$ and may be written as $\sigma_s = \sigma$. The coupled rate-equations for the average monomer density $N_1$ and island-density $N$ (where $N = \sum_{s=2}^{\infty} N_s$) may then be written,

\[
\frac{dN_1}{d\theta} = 1 - 2N_1 - N - 2(D/F)\sigma N_1^2 - (D/F)\sigma N_1 N \tag{5.1}
\]

\[
\frac{dN}{d\theta} = N_1 + 2(D/F)\sigma N_1^2. \tag{5.2}
\]

In order to solve Eqs. (5.1) and (5.2), one has to obtain an expression for the capture numbers $\sigma$. As in Ref. [30] in which a self-consistent RE approach to 2D irreversible nucleation and growth is discussed, we consider a quasi-static diffusion equation for the monomer density $n_1(r, \theta, \phi)$ surrounding an island of size $s$ of the form

\[
\nabla^2 n_1(r, \theta, \phi) - \xi^{-2}(n_1 - N_1) = 0, \tag{5.3}
\]

where $N_1$ is the average monomer density and

\[
\xi^{-2} = \sigma(N + 2N_1). \tag{5.4}
\]
Assuming spherical symmetry Eq. (5.3) may be written in 4D,

\[
\frac{1}{r^3} \frac{d}{dr} (r^3 \frac{d\tilde{n}_1}{dr}) - \xi^{-2}\tilde{n}_1(r) = 0
\] (5.5)

where \(\tilde{n}_1(r) = n_1(r) - N_1\). The general solution is given by,

\[
\tilde{n}_1(r) = \left( \frac{\xi}{r} \right) \frac{d}{d(r/\xi)} \left[ b_1 I_0(r/\xi) + b_2 K_0(r/\xi) \right],
\] (5.6)

where \(b_1\) and \(b_2\) are constants. Since \(\tilde{n}_1(r) \to 0\) as \(r \to \infty\), one has \(b_1 = 0\) which implies that \(\tilde{n}_1(r) \sim (\frac{1}{r}) \xi K_1(r/\xi)\). The irreversible growth boundary condition \(n_1(R_s) = 0\) then leads to

\[
n_1(r) = N_1 \left[ 1 - \frac{R_s}{r} \frac{K_1(r/\xi)}{K_1(R_s/\xi)} \right].
\] (5.7)

Equating the microscopic flux of atoms near the island \(S_v D[\partial n_1/\partial r]_{r=R_s}\) (where \(S_v = 2\pi^2 R_s^3\) is the surface area of a sphere of radius \(R_s\) in 4D) to the corresponding macroscopic RE-like term \(DN_1 \sigma_s\), we obtain an equation for the capture number,

\[
\sigma_s = \frac{S_v}{N_1} \left( \frac{\partial n_1}{\partial r} \right)_{r=R_s} = 4\pi^2 R_s^2 \left[ 1 + \frac{R_s}{2\xi} \frac{K_0(R_s/\xi)}{K_1(R_s/\xi)} \right].
\] (5.8)

Since for the point-island model considered here \(R_s = R_0\), the corresponding capture numbers may be written

\[
\sigma_s = \sigma = 4\pi^2 R_0^2 \left[ 1 + \frac{R_0}{2\xi} \frac{K_0(R_0/\xi)}{K_1(R_0/\xi)} \right]
\] (5.9)
where \( R_0 \) is a model-dependent constant of order 1 and \( \xi \) is defined in Eq. (5.4). In the limit of infinite \( D/F \) one has \( R_0/\xi = 0 \), which implies \( \sigma = 4\pi^2 R_0^2 \), i.e. the capture numbers have no coverage-dependence.

### 5.4 Results

Fig. 5-1 shows a comparison between our KMC simulation results for the average monomer and island densities and the corresponding self-consistent mean-field RE results obtained by numerically solving Eqs. (??) and (5.2) along with Eqs. (5.4) and (5.9). Results are shown for \( D_h/F = 10^5, 10^7, \) and \( 10^9 \), while the value of \( R_0 \) \((R_0 = 0.407)\) was chosen to give the best fit to the KMC data. As can be seen, there is excellent agreement between the RE and KMC results over all coverages and for all values of \( D_h/F \). Thus, as was previously found in \( d = 2 \) [30] and \( d = 3 \) [49], the self-consistent RE approach provides an accurate description for average quantities such as the monomer and island density. We now compare our simulation results for the ISD and CND with the corresponding MF rate-equation results.

Figure 5-2 shows the scaled capture number distribution \( C(s/S) \) obtained in our KMC simulations for \( D_h/F = 10^5 - 10^{10} \). The MF prediction \( C(u) = 1 \) is also shown (horizontal dashed line). As can be seen, in contrast to the significant deviations between the KMC results and the MF prediction observed in \( d = 1 \) [36], \( d = 2 \) [32], and \( d = 3 \) [49], the KMC results in 4D approach the MF prediction with increasing \( D_h/F \). In particular, \( C(u) \) for \( D_h/F = 10^{10} \) is approximately equal to 1 for \( u < 1.5 \) while it increases slightly with \( u \) for \( u > 1.5 \). As already noted, (see Eq. 4.4), the
MF prediction implies the existence of an asymptotic divergence in the scaled ISD at the point $u_{c}^{MF} = 3/2$ where the MF CND crosses the line $2u/3$. In order to find the corresponding asymptotic crossing point in our simulations, we have examined the point $u_{c}^{KMC}(D/F)$ at which the scaled CND crosses the MF prediction $C(u) = 1$ for $u > 3/2$ as a function of $D/F$. We find that the crossing point is well fit by the form $u_{c}^{KMC}(D/F) = u_{c}^{KMC}(\infty) + c(D/F)^{-\gamma}$ with $u_{c}^{KMC}(\infty) \simeq 1.50$ and $\gamma = 0.22$. This result indicates that the scaled CND exhibits pure MF behavior, i.e. $C(u) = 1$ for $0 < u < 3/2$, in the asymptotic limit of infinite $D/F$.

For completeness, we have also measured the scaled capture-zone distribution (CZD) as shown in Fig 5-3. The shape of the scaled CZD is similar to that of the scaled CND. In particular, it is relatively “flat” for $u < 1.3$, while for $u > 1.3$ it increases rapidly with island-size for large $D/F$. And, for large $D/F$ the scaled CZD curves obtained from the KMC simulation appear to “pivot” with increasing $D/F$ around a fixed point at $u_{c} \simeq 1.5$ which is also the point at which they cross each other. In order to understand the asymptotic behavior better, we plot the slope of each of the curves at the crossing point as function of $D/F$. As shown in Fig 5-4, the slope has a good power law relation with $D/F$. This indicates that as $D/F$ reach infinity, the CZD approaches MF prediction.

Figure 5-5 shows a comparison between our KMC results (symbols) and the corresponding self-consistent mean-field RE results (solid curves) for the scaled ISD at coverage $\theta = 0.2$. The asymptotic MF result $f(u) = \frac{1}{3}(1 - 2u/3)^{-1/2}$ [26, 31] corresponding to infinite $D/F$ is also shown (dashed curve). As can be seen, the island-size distribution becomes sharper and the peak of the scaled ISD increases with increas-
ing $D/F$, thus indicating a divergence in the asymptotic limit of infinite $D/F$. In contrast to the 3D case [49], in 4D the KMC results are in very good agreement with the corresponding self-consistent MF RE results and approach the asymptotic MF prediction with increasing $D/F$. However, there is a small difference for large $D/F$ between the peak values of about 3.3% between the KMC results and MF RE predictions. While the origin of this small difference is not entirely clear, we speculate that it may be due to weak fluctuations during the very early stages of nucleation and growth.

In order to understand this difference, we have plotted in Fig. 5-6 the peak values of the scaled ISD obtained from both KMC simulations and RE calculations as a function of $D/F$. As can be seen, in both cases the peak value $f_{pk}(D/F)$ of the scaled ISD increases as a power-law with $f_{pk} \sim (D/F)^\phi$, thus indicating a divergent ISD in the asymptotic limit. In addition, in contrast to our previous results in $d=3$ [49], the value of $\phi$ obtained from the KMC simulations ($\phi = 0.081 \pm 0.001$) for $D_h/F \geq 10^7$ is in excellent agreement with the value obtained from our MF RE calculations ($\phi = 0.083 \pm 0.001$). Thus in the asymptotic limit the scaled ISD obtained from KMC simulations is essentially the same as the MF prediction.

Additional evidence supporting the asymptotic MF behavior of the KMC results is given in Fig. 5-7 which shows the dependence of the peak position $u_{pk}$ of the scaled ISD obtained from our KMC simulations as a function of $D/F$. In order to extrapolate the asymptotic behavior, the peak position $u_{pk}(D/F)$ was fit to the form $u_{pk}(D/F) = u_{pk}(\infty) + c (D/F)^{-\gamma}$ while the value of $\gamma = 1/5$ was used for the best fit. A similar fit was used to extrapolate the MF RE results. Figure 5-7 shows the
corresponding results for the KMC simulations (open circles) as well as for the MF RE results (filled circles). As can be seen, there is excellent agreement between the KMC and MF RE results. For the MF RE and KMC results we find $u_{pk}^{MF}(\infty) = 1.502$ and $u_{pk}^{KMC}(\infty) = 1.50 \pm 0.02$, respectively. In contrast to the corresponding KMC simulation results in 3D [49], the asymptotic peak position of the KMC simulation result in 4D is in excellent agreement with the MF RE result.

5.5 Discussion

In our previous study of irreversible nucleation and growth in 3D [49], we found that due to the existence of (weak) correlations, the asymptotic scaled CND depends weakly on the island-size while the asymptotic scaled ISD also differs somewhat from the MF prediction. In particular, we found that the scaled ISD diverges more slowly than the MF prediction while the asymptotic divergence occurs at a value of the scaled island-size which is somewhat larger than the MF prediction. Based on these results we concluded that the critical dimension for mean-field behavior is higher than 3, and is possibly equal to 4.

The results presented here appear to confirm this prediction since in general we have found excellent agreement between our KMC simulation results in $d = 4$ and the predictions of our self-consistent MF RE calculations. In particular, our results for the exponent describing the divergence of the peak height of the scaled ISD as a function of $D/F$ are in excellent agreement with the MF RE results, while an analysis of the $D/F$ dependence of the peak position indicates an asymptotic divergence at a
scaled island-size $u = 3/2$ in good agreement with the MF prediction. While there is a small discrepancy for large $D/F$ between the peak height obtained in simulations and the MF RE prediction, we believe that this may be due to fluctuations in the early-stages of growth. This is supported by the fact that our KMC results indicate that at finite coverage the scaled CND approaches the mean-field result $C(u) = 1$ for $0 < u < 3/2$ in the asymptotic limit of large $D/F$. Thus, we conclude that the critical dimension for irreversible nucleation and growth of point-islands is equal to 4.

Finally, we note that it would also be interesting to compare our results with those obtained for a more realistic extended island model in $d = 4$. For such a model, the corresponding explicit size-dependence of the capture number and direct impingement terms is likely to lead to modified scaling behavior for the ISD and CND. However, even in this case there should still be a significant range of coverage over which the point-island model is a good approximation. Accordingly, the scaled ISD is still expected to diverge in the asymptotic limit of large $D/F$. 
Figure 5-1: Comparison between KMC results (symbols) and the corresponding self-consistent MF RE results (solid lines) for the monomer density $N_1$ and island density $N$ as a function of coverage for $D_h/F = 10^5$ (circles), $10^7$ (squares) and $10^9$ (diamonds).
Figure 5-2: KMC simulation results for scaled CND for $D_h/F = 10^5 - 10^{10}$. Horizontal dashed line corresponds to MF CND.
Figure 5-3: KMC simulation results for scaled CZD for $D_h/F = 10^5 - 10^9$. Horizontal dashed line corresponds to MF CZD.
Figure 5-4: Slope of scaled CZD curves at crossing point $u_c \simeq 1.5$ for $D_h/F = 10^5 - 10^9$. 

slope = 0.18
Figure 5-5: Scaled island-size distributions for $D_h/F = 10^5, 10^7, 10^9$ and $10^{10}$. KMC simulation results (symbols), RE results (solid lines), and asymptotic MF limit (dashed curve).
Figure 5-6: Log-log plot of peak value of scaled ISD as function of $D_h/F$. 

Slope = 0.08

$\theta = 0.2$
Figure 5-7: Plot of $u_{pk}(D/F)$ as a function of $(D_h/F)^{-\gamma}$ for $D_h/F$ ranging from $10^5$ to $10^{10}$. Solid line is a fit as described in text with $\gamma = 1/5$, and error bars are given for the KMC result.
Chapter 6

Capture-zone areas in submonolayer nucleation: effects of dimensionality and short-range interactions

6.1 Introduction

The organization and ordering of islands in the submonolayer regime of thin-film growth can play an important role in determining the multilayer growth behavior [50]. Consequently, island nucleation and growth has been the subject of much recent interest (for a recent review see Ref. [51]). One quantity of particular interest is the
island-size distribution (ISD) which may be written in the form,

\[ f(s/S) = N_s(\theta)S^2/\theta \]  

(6.1)

where \( N_s(\theta) \) is the density (per site) of islands of size \( s \) at coverage \( \theta \), \( S = \sum_{s \geq 2} sN_s/N_s \) is the average island size, and \( f(s/S) \) is the scaled ISD. In particular, simulations\[52\] have shown that the asymptotic scaled ISD corresponding to large values of \( D/F \) (where \( D \) is the monomer hopping rate and \( F \) is the deposition rate) in the pre-coalescence regime depends on the size \( i \) of the critical nucleus, which corresponds to one less than the size of the smallest stable cluster. While no exact analytical form exists even for the simplest case corresponding to irreversible growth \( (i = 1) \), a variety of approximate expressions and/or methods have been proposed\[52, 53, 54, 55, 56, 57, 58\] for calculating the ISD.

A related quantity \[53, 54\], which is indirectly linked to the scaled ISD is the scaled capture-zone size distribution (CZD). The capture-zone of an island coincides roughly with the island’s Voronoi polygon, and may be defined as the region surrounding that island in which a diffusing particle or monomer is more likely to attach to that island than to any other existing island. Since the size of an island’s capture zone is directly related to its capture number or propensity to capture diffusing particles, the ISD is indirectly related to the CZD \[54\]. As a result, determining the dependence of the CZD on the critical island size is a subject of some interest.

Recently, it has been suggested \[59\] that the scaled capture-zone size distribution
may be accurately represented using a Wigner distribution[60, 61] of the form,

\[ P_\beta(u) = a_\beta u^\beta \exp(-b_\beta u^2) \]  

(6.2)

where the parameter \( \beta \) depends on the substrate dimension \( d \) and critical island size \( i \), via the expression[62] \( \beta = (2/d)(i + 1) \) for \( d = 1, 2 \). We note that the critical island size \( i \) corresponds to one less than the number of atoms in the smallest stable cluster. Thus, for example in the case of irreversible growth considered here, the smallest cluster is a dimer and therefore the critical island size is 1. It was also suggested that for \( d > 2 \), the value of \( \beta \) is the same as for \( d = 2 \), i.e. one has \( \beta = i + 1 \). Using this expression, good agreement with simulation results was demonstrated[59] for the scaled CZD for compact islands with \( i = 0 \) and \( i = 1 \) and \( d = 2 \). However, poor agreement between simulation results and the predicted \( P_2(u) \) was found for the case of point-islands with \( i = 1 \) in \( d = 2 \), and instead much better agreement[63] was found with \( P_4(u) \). Therefore, it is of interest to study in more detail the asymptotic scaled CZD as well as the dependence on substrate dimension \( d \) in order to determine the true asymptotic behavior.

Here we present the results of extensive kinetic Monte Carlo (KMC) simulations carried out to obtain the asymptotic capture-zone size distribution for the case of irreversible growth \( (i = 1) \) of point-islands with \( d = 1 - 4 \). In order to determine the asymptotic distribution, results are presented for values of \( D/F \) ranging from \( 10^5 \) to \( 10^{10} \). In order to understand the dependence of the CZD on the short-range interaction, results are also presented for two different point-island models with somewhat
different short-range interactions.

This chapter is organized as follows. In Section II, we discuss the models used in our simulations while our results are presented in Sec. III. Finally, we discuss our results in Section IV.

6.2 Model and Simulations

To understand the dependence on substrate dimension we have studied the scaling of the capture-zone distribution on a one-dimensional lattice \((d = 1)\), as well as on square and triangular lattices \((d = 2)\), cubic \((d = 3)\) and hypercubic \(d = 4\) lattices for the case of irreversible growth \((i = 1)\) of point-islands. In our simulations, monomers were deposited randomly with a (per site) deposition rate \(F\), and were assumed to diffuse to nearest-neighbor sites with hopping rate \(D\). The size of an island’s capture zone was determined by counting the number of non-island sites corresponding to empty sites or sites occupied by monomers whose distance from the island is less than the distance to any other island. If a site is found to be equally distant to two or more closest islands, then its contribution to the capture zone is divided equally between those islands. This is essentially equivalent to a Voronoi construction around each island. Once the capture zone for each island was determined, the scaled capture-zone distribution \((CZD) C(z/Z)\) was calculated using the expression,

\[
C(z/Z) = ZN_z/\sum_z N_z
\]  

(6.3)
where $N_z$ is the number of capture zones of size $z$ and $Z$ is the average capture zone size.

We note that in previous point-island model simulations of the ISD and capture-number distribution (CND) for the case of irreversible growth in $d = 3$ and $d = 4$ carried out by Shi, Shim, and Amar (SSA Model) [49, 64], if a monomer is deposited on or hops onto an already occupied site then that monomer is irreversibly captured by the island. Similarly, if a monomer hops onto another monomer then a dimer island is nucleated at that site. However, in the 2D point-island simulations of the capture-zone distribution carried out by Evans and Bartelt [57] (EB) the short-range interaction was treated differently. In particular, in the EB point-island model (see also Ref. [65]) if a monomer is deposited at or diffuses to a site which is nearest-neighbor to an occupied site, then that monomer is immediately captured by the nearby monomer or island. Thus in the EB point-island model, the range of the short-range interaction between a monomer or island and another monomer is larger than in the SSA model, and is more similar to that for a compact or fractal island model (e.g. less point-island-like). Since these differences involve only the short-range interaction, we expect that in the asymptotic limit of large $D/F$ there will be no differences between the scaled CZD obtained for both models. However, for comparison in all cases we have carried out simulations using both the EB and SSA versions of the point-island model.

In order to determine the asymptotic behavior, simulations were carried for values of $D/F$ ranging from $10^5$ to $10^{10}$, and the CZD and ISD were calculated for coverages ranging from $\theta = 0.1$ to $\theta = 0.4$. Our simulations in $d = 1$ were carried out on systems
of size $L = 10^6$ with results averaged over $200 - 1000$ runs. Simulations in $d = 2$ were carried out for both square and triangular lattices with systems of size $L = 1024$, while for $d = 3$ and $d = 4$, simulations were carried out on cubic lattices of size 160 and 50 respectively. In order to obtain good statistics, our results for $d = 2 - 4$ were averaged over $40 - 200$ runs.

6.3 Results

6.3.1 Results for $d = 2 - 4$

We first consider the dependence of the scaled CZD on coverage and $D/F$ in $d = 2 - 4$. Fig. 6-1(a) shows typical results for the dependence on coverage for $d = 3$ ($D/F = 10^9$) for the SSA model, while Fig. 6-1(b) shows the corresponding results for the dependence on $D/F$ ($\theta = 0.1$). Similar results have been obtained in $d = 2$ and $d = 4$. As can be seen, while there is essentially no coverage dependence, in general the peak of the scaled CZD decreases with increasing $D/F$. This latter behavior indicates that the asymptotic scaled CZD distribution only occurs for significantly larger $D/F$. Accordingly, here we focus on the dependence of the scaled CZD on $D/F$ for $\theta = 0.1$ since there is essentially no coverage dependence.

We now consider the dependence of the CZD on the details of the short-range interaction. Fig. 6-2 shows a comparison between results obtained using the SSA model (filled symbols) and EB model (open symbols) in $d = 2$ for $D/F = 10^7$ and $\theta = 0.1$. As can be seen, for finite $D/F$ there is a clear disagreement between the
scaled CZD obtained using the two models. In contrast, as shown in Fig. 2 the ISD’s are in perfect agreement. These results indicate that for finite $D/F$ the scaled CZD depends more sensitively on the details of the short-range interaction than the scaled ISD. They also indicate that the connection between the CZD and the ISD is more indirect than might have previously been considered.

We now consider the dependence of the scaled CZD on dimension for large $D/F$. Fig. 6-3(a) shows our SSA model results for $d = 2 - 4$ for $D/F = 10^9$ and $\theta = 0.1$. As can be seen, the scaled capture-zone distribution for $d = 2$ is very close to that for $d = 3$, in good agreement with the prediction of Ref. [59] that for $i = 1$ the scaled CZD should be independent of dimension for $d \geq 3$. However, in both cases the scaled CZD is much closer to the Wigner distribution with $\beta = 3$ rather than the predicted value of $\beta = 2$ (dotted curve). Furthermore, for $d = 4$ the scaled CZD appears to be significantly different from the distribution for $d = 2$ and 3 and is instead close to the Wigner distribution with $\beta = 4$. Similar results for the EB model are shown in Fig. 6-3(b). While the peak values for the scaled CZD are somewhat higher than for the SSA model, we still find that the scaled CZD is approximately independent of dimension for $d = 2$ and 3 and is significantly closer to the Wigner distribution with $\beta = 3$ than the predicted distribution corresponding to $\beta = 2$.

To determine the asymptotic behavior of the scaled CZD we have also studied the dependence of the peak height on $D/F$. Fig. 6-4 shows our results for the CZD peak height as a function of $D/F$ for square, cubic, and hypercubic lattices in $d = 2, 3,$ and 4 respectively and for a triangular lattice ($d = 2$) for both the SSA and EB models, for values of $D/F$ ranging from $10^6$ to $10^{10}$. In order to extrapolate to the
Table 6.1: Simulation results for asymptotic peak heights for SSA and EB models, along with average $C_{\text{av}}(\infty)$ in different dimensions $d$. For comparison, predicted values for $\beta$ and peak height $P_{\beta}(x_{pk})$ from Ref. [59] are also shown. $P_d(x_{pk})$ is also shown for reference.

<table>
<thead>
<tr>
<th>$d$</th>
<th>$C_{\text{SSA}}(\infty)$</th>
<th>$C_{\text{EB}}(\infty)$</th>
<th>$C_{\text{av}}(\infty)$</th>
<th>$\beta$</th>
<th>$P_{\beta}(x_{pk})$</th>
<th>$P_d(x_{pk})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.31 ± 0.01</td>
<td>1.31 ± 0.01</td>
<td>1.31 ± 0.01</td>
<td>4</td>
<td>1.225</td>
<td>0.760</td>
</tr>
<tr>
<td>2</td>
<td>1.04 ± 0.04</td>
<td>1.08 ± 0.04</td>
<td>1.06 ± 0.03</td>
<td>2</td>
<td>0.937</td>
<td>0.937</td>
</tr>
<tr>
<td>3</td>
<td>1.04 ± 0.05</td>
<td>1.05 ± 0.04</td>
<td>1.05 ± 0.04</td>
<td>2</td>
<td>0.937</td>
<td>1.09</td>
</tr>
<tr>
<td>4</td>
<td>1.17 ± 0.04</td>
<td>1.13 ± 0.06</td>
<td>1.15 ± 0.04</td>
<td>2</td>
<td>0.937</td>
<td>1.225</td>
</tr>
</tbody>
</table>

asymptotic behavior, the CZD peak height $C_{pk}$ was fit to the form $C_{pk}(D/F) = C_{pk}(\infty) + a (D/F)^{-\gamma}$. The value of $\gamma$ ($\gamma \simeq 0.1$) was chosen which gives the best overall fit for both models for $d = 2 - 4$. For comparison, the peak heights for the Wigner distributions with $\beta = 3$ and $\beta = 4$ are also shown. A summary of our results is shown in Table 1.

As can be seen, due to the longer effective range of interaction, the dependence on $D/F$ is stronger for the EB model than for the SSA model. However, for a given value of $d$ the asymptotic values of the peak heights for both models agree within error-bars (see Table 1). In addition, for $d = 2$ and $3$ the extrapolated asymptotic value $C_{pk}(\infty)$ is roughly independent of dimension. Thus, our results indicate that for $d = 2$ and $3$ the asymptotic scaled CZD is independent of dimension and/or model details, in good agreement with the prediction of Ref. [59] that for $d \geq 2$ the scaled CZD should be independent of dimension. However, the asymptotic peak value of the CZD for $d = 2$ and $3$ is significantly higher than the predicted value corresponding to $\beta = 2$ ($P_2(x_{pk}) = 0.937$) and is somewhat lower than that corresponding to $\beta = 3$ ($P_3(x_{pk}) = 1.09$).

In contrast, for $d = 4$, we find that for both models the asymptotic peak value
is significantly higher. In particular, for the SSA model we find $C_{pk}^{SSA}(\infty, d = 4) = 1.17 \pm 0.04$ while for the EB model we find $C_{pk}^{EB}(\infty, d = 4) = 1.13 \pm 0.06$. Averaging over both models, we obtain $C_{pk}^{av}(d = 4) = 1.15 \pm 0.04$. We note that this value is in between the peak values corresponding to $\beta = 4 (1.225)$ and $\beta = 3 (1.09)$.

### 6.3.2 Results for $d = 1$

In order to get a more complete picture of the dependence on dimension, we have also carried simulations in $d = 1$ for both the EB and SSA models. Fig. 6-5(a) shows our results for the SSA model for different values of $D/F$. We note that for comparable values of $D/F$ these results are in relatively good agreement with previous results obtained in Ref. [53] using a similar point-island model. However, somewhat surprisingly we find that, in contrast to our results for higher dimensions, in $d = 1$ the peak of the CZD increases with $D/F$. In addition, we note that while the scaled CZD for $D/F = 10^7$ is relatively close to the prediction of Ref. [59] corresponding to $P_4(u)$, for $D/F = 10^9$ the peak of the scaled CZD is somewhat higher. In order to obtain the asymptotic peak height for both the EB and SSA models, we have plotted in Fig. 6-5(b) the peak-height as a function of $(D/F)^{-\gamma}$ (where $\gamma = 0.2$ was found to be the best fit for both models) for values of $D/F$ ranging from $10^5$ to $10^9$. As can be seen, while the peak height for the EB model tends to be lower than that for the SSA model for finite $D/F$, the asymptotic peak height for both models is essentially the same ($1.31 \pm 0.01$) and is significantly larger than the peak value corresponding to $\beta = 4 (1.225)$. Thus, our results indicate that although the predicted distribution
$P_4(u)$ is close, it is still significantly lower than the asymptotic CZD for point-islands in $d = 1$.

### 6.4 Discussion

We have carried out extensive simulations of point-island models of irreversible nucleation and growth in $d = 1 - 4$ for values of $D/F$ ranging from $10^5$ to $10^{10}$ in order to determine the asymptotic scaled CZD and compare with recent predictions based on random matrix theory. In addition, to determine the dependence on the short-range interaction and also check for universality, we have studied two different models with different short-range interactions, the EB model (in which any particle within a nearest-neighbor distance is automatically incorporated to an island) and the SSA model (for which only particles which land on an existing monomer or island are incorporated into the island). We have also carried out simulations on two different lattices in $d = 2$, a triangular lattice and a square lattice, in order to determine the dependence on lattice geometry. In each case, by extrapolating to infinite $D/F$ we have estimated the asymptotic peak height for the scaled CZD.

In general, we find good scaling as a function of coverage, i.e. the CZD is essentially independent of coverage for fixed $D/F$. However, we also find that the CZD depends on $D/F$ for finite $D/F$. In particular, for $d = 2 - 4$ we find that the peak height of the scaled CZD decreases with increasing $D/F$, while for $d = 1$ it increases. We also note that for $d = 2 - 4$, the dependence of the peak height on $D/F$ and lattice dimension tends to be stronger for the EB model than for the SSA model. This is
perhaps not surprising, since the range of the short-range interaction is larger for the
EB model than for the SSA model. However, somewhat surprisingly, for \( d = 1 \) the
dependence of the peak height on \( D/F \) is larger for the SSA model than for the EB
model.

When extrapolating to the asymptotic limit our results indicate that, for \( d = 2 \)
and 3 the asymptotic CZD is independent of model details and dimension, in good
qualitative agreement with the prediction of Ref. [59]. This behavior is in strong con-
trast to that of the scaled ISD which depends strongly on dimension and corresponds
to a finite distribution in \( d = 2 \) [57], while diverging with increasing \( D/F \) in \( d = 3 \)
[49]. We also note that our estimate for the asymptotic value of the peak of the CZD
in \( d = 2 \) and 3 \( (C_{pk}^{d=2,3} \simeq 1.06 \pm 0.03) \) is significantly lower than obtained in previous
2D point-island model simulations for finite \( D/F \) [57], but is still significantly higher
than the predicted peak value[59] \( (P_2(x_{pk}) = 0.937) \) corresponding to the Wigner dis-
bution with \( \beta = 2 \). However, it is relatively close to the peak value \( (P_3(x_{pk}) = 1.09) \)
corresponding to the Wigner distribution with \( \beta = 3 \). In contrast, for \( d = 1 \) the peak
height of the asymptotic CZD is significantly larger than for \( d = 2 \) and \( d = 3 \). For
this case, while our results for small \( D/F \) agree with previous results [53], for which
good agreement with the Wigner distribution with \( \beta = 4 \) was found [59], both the
peak height for larger \( D/F \) as well as the asymptotic peak height \( (C_{pk}^{d=1} \simeq 1.31 \pm 0.01) \)
are noticeably higher than the value \( (P_4(x_{pk}) = 1.225) \) corresponding to the Wigner
distribution with \( \beta = 4 \). We have also obtained results for \( d = 4 \). In this case, we
found somewhat surprisingly that the asymptotic peak height \( (C_{pk}^{d=4} \simeq 1.15 \pm 0.03) \)
is significantly higher than in \( d = 2 \) and \( d = 3 \). However, it is still somewhat lower
(e.g. outside the error-bars) than that corresponding to the Wigner distribution with \( \beta = 4 \) \( (P_4(x_{pk}) = 1.225) \). We note that while the system sizes in \( d = 4 \) were somewhat limited compared to our simulations for smaller \( d \), there was no evidence for a finite-size effect in this case, since the average island separation for the highest value of \( D/F \) studied \( (D/F = 10^9) \) was several times smaller than the system size \( L \).

In summary, our results indicate that while the scaled CZD depends strongly on \( D/F \) as well as on the short-range interaction for finite \( D/F \), the asymptotic CZD is relatively independent of model details such as the short-range interaction. In addition, we find good agreement between the asymptotic CZD in \( d = 2 \) and \( d = 3 \) as suggested in Ref. [59]. However, in general we do not find good agreement between the Wigner distribution using the predicted value of \( \beta \) \( (\beta = (2/d)(i + 1)) \) given in Ref. [59] and our asymptotic simulation results. In particular, in \( d = 2 \) and \( 3 \) we find better agreement with the Wigner distribution with \( \beta = 3 \), than the predicted value of \( \beta = 2 \). Similarly, the peak height of the asymptotic CZD in \( d = 1 \) is noticeably higher than the Wigner distribution with \( \beta = 4 \).

Finally, it is interesting to discuss in somewhat more detail our results for the dimensionality dependence of the scaled CZD, and compare with previous results obtained for the scaled ISD. We note that we have previously shown[49, 64] that for the point-island model the ISD diverges in \( d = 3 \) and above, due to the fact that both the average capture zone and average capture number for a given island size become independent of island size. These results also indicate[64] that \( d = 4 \) is the critical dimension for pure mean-field (MF) behavior for the ISD as well as for the capture-number distribution (CND).
In contrast, the results presented here indicate that the asymptotic scaled CZD in $d = 3$ and 4 does not diverge with increasing $D/F$, and thus does not correspond to pure MF behavior, for which a delta-function like CZD would be expected. The difference in the behaviors is due to the effects of fluctuations, which tend to “broaden” the CZD even for large $d$, but which tend to “cancel out” when calculating quantities such as the average capture zone or capture-number for a given island-size. Thus, our results further underline the fact that, as indicated in Ref. [54], the connection between the CZD and the ISD is indirect, since for example one can have a MF ISD in $d = 4$ while the CZD does not exhibit MF behavior.
Figure 6-1: Scaled CZD $C(z/Z)$ (where $Z$ is the average capture zone size) obtained from simulations of SSA model in $d = 3$. (a) coverage-dependence (b) dependence on $D/F$. 
Figure 6-2: Comparison of scaled CZD $C(z/Z)$ and ISD $f(s/S)$ obtained for SSA and EB point-island models in $d = 2$ for $D/F = 10^7$ and $\theta = 0.1$ along with Wigner distributions $P_3(u)$ and $P_4(u)$. 
Figure 6-3: Scaled CZD for SSA model (a) and EB model (b) for $D/F = 10^9$ and $\theta = 0.1$ for $d = 2$ (filled circles), $d = 3$ (open triangles) and $d = 4$ (open squares) along with Wigner distributions for $\beta = 2, 3, 4$.
Figure 6-4: Peak height of scaled CZD as function of $D/F$ for SSA model (a) and EB model (b) in $d = 2 - 4$. Upper and lower $\times$‘s on y-axes correspond to $P_4(x_{pk}) = 1.225$ and $P_3(x_{pk}) = 1.09$ respectively.
Figure 6-5: (a) $D/F$ dependence of scaled CZD obtained from simulations of SSA model in $d = 1$. (b) Asymptotic peak heights for both EB and SSA models. Arrow indicates peak height for $P_4(u)$. 
Chapter 7

Coarsening process and its applications

7.1 Introduction

Whenever a single phase system is quenched into a metastable state nucleation of a second phase lowers the free energy of the system. Following this nucleation event, in solid state transformations, the second phase typically grows by the diffusion of mass either into or from the matrix. When the composition of the matrix is nearly at its equilibrium value coarsening occurs. In this process the matrix is no longer a source or sink of solute, but the majority of the mass transport is from small to large particles. This process is driven by the decrease in interfacial energy per unit volume and results in an increase in the size scale of two-phase mixture. The first to observe this coarsening process was Ostwald in 1900 who reported that the solubility of small HgO-particles is a function of the radius of the particle. The phenomenon has come
to bear his name: Ostwald ripening. Ostwald ripening can occur in virtually any two-phase mixture in which there is significant diffusion. It is thus observed in two-phase mixtures ranging from liquid-vapor mixtures, such as droplets in clouds, to solid-liquid mixtures both during and following solidification. Understanding the dynamics of this ripening process and its surprising self-organizational nature has been at the center of the field since the seminal papers of Lifshitz and Slyozov, and Wagner appeared in the early 60’s. From a more applied view, the Ostwald ripening process has a significant impact on manner in which materials are processed, e.g. age hardening of metallic alloys, grain refining, grain growth during recrystallisation, liquid and solid state sintering, and the deoxidation of steel melts [66]. Ostwald ripening regain considerable interests respect to clusters at surfaces, which are important in both fundamental and applied fields of research including epitaxial layer growth and nanostructuring of surfaces. And in particular, coarsening process becomes into core technique of many nano-crystal fabrication technologies.

7.2 Nanocrystal fabrication in 3D system through Coarsening

Due to the promise of nanocrystal as building blocks for novel technical applications in opto-electronic devices, chemical sensors and markers, and as single electron memory devices, nano-crystal fabrication attracts great deal of interests. As core technique to fabricate nano-crystal, coarsening process plays key role in formation of
nano-crystals. Nanocrystals in 3D systems have been fabricated via two basic techniques co-sputtering and ion beam synthesis (IBS). Following the fabrication processes, the samples with nanocrystals will be annealed at high temperature. During annealing process, the systems undergo Ostwald ripening and the nanocrystals grow.

Sputtering system is widely used in thin film deposition due to its simplicity and reliability. Variety of nanocrystals are fabricated by using co-sputtering technique. Fujii et al [67] grow Ge nanocrystals in $SiO_2 - Ge$ mixture films by using an RF co-sputtering method. In co-sputtering, small pieces of Ge wafers ($0.5 \times 5 \times 15mm^3$) were placed on a pure $SiO_2$ target ($10cm$ in diameter) and they were co-sputtered in Ar gas of 2.7 Pa with an rf power of 300 W. Thin films of the mixture of Ge and $SiO_2$ were deposited onto Si wafers. During the deposition the substrates were not intentionally heated and no trace of crystallites is detected by TEM observations for as-deposited films, as shown in Fig 7.1. As shown in Fig 7.2, detectable Ge nanocrystals are grown only when the films are annealed. For this particular sample, the thermal annealing was performed in vacuum of the order of $10^{-5}$ Pa for 30 min at 800°C.

During annealing process, the system undergoes nucleation and growth process and the coarsening process plays the key role in forming nanocrystals and determining the shape, size and physical properties.

IBS has been demonstrated an effective mean to fabricate nanocrystals in 3D systems. In this technique, energetic ions are implanted into matrix. The ion/matrix combination is chosen to insure a strong segregating tendency for the implanted species. Subsequent annealing leads to the formation of nanocrystals embedded within the matrix. The versatility of this method arises because ion implantation
can be used to inject virtually any impurity into the matrix. White, et al [13] have synthesized a variety of encapsulated nanocrystals by IBS method. Sequential implantation of various combinations of ions have been used to create various compound semiconductor or alloy nanocrystals in several host matrices. Fig 7.3 shows silicon nanocrystal formed in $\text{SiO}_2$ by the implantation of Si followed by annealing. Fig 7.4 shows CdS nanocrystal formed in $\text{SiO}_2$, which are not completely spherical.

After coarsening process the nanocrystals show pronounced optical absorption and very intense Photoluminescence.

### 7.3 Quantum dot fabrication in 2D system through Coarsening

Epitaxy technology is widely used to fabricate quantum dots on substrates, especially semiconductor quantum dots which are building blocks of many novel optoelectronic devices. A typical example is the novel SiGe quantum dots formed on Si substrate. Coherent island formation occurs to relieve strain associated with lattice mismatched heteroepitaxial growth. Coherent islands have been shown to self-assemble to produce a narrow distribution of sizes, and to self-order spatially onto two- or three-dimensional lattices. Floro, et al [68] have reported self-ordering of pyramidal islands (“hut clusters”) in $\text{Si}_{0.8}\text{Ge}_{0.2}$ films on $\text{Si}(001)$ during molecular beam epitaxy (MBE). Fig 7.5 shows the morphology of an example of a typical hut cluster array, both as-deposited, and after annealing in situ at the growth tempera-
This self-ordering process is intimately associated with coarsening during MBE growth, wherein some islands grow at the expense of others in order to minimize total surface energy.

7.4 Coarsening in thin film growth

The evolution and control of film morphology is of fundamental and technological interest. Typically, during deposition a film is driven far from equilibrium, and thus can be potentially "trapped" in a variety manifestly nonequilibrium configurations. While this allows control of morphology by intelligent manipulation of deposition parameters, one must recognize that a nonequilibrium structure is always prone to rearrangement. Understanding the mechanisms and kinetics of such rearrangement is necessary to predict film stability, and present a key challenge in nonequilibrium physics.

Below a critical temperature for two-dimensional (2D) phase separation, the equilibrium structure of a partially filled layer consists of a single large domain or "island" of a condensed phase coexisting with a dilute 2D gas phase. Since nucleation and growth of islands during deposition produces a distribution of "smaller" islands, subsequent temporal evolution toward the equilibrium state involve coarsening. Current discussions of coarsening in adlayers primarily invoke Ostwald ripening (OR), at least for low coverages, $\theta$. During OR, atoms tend to detach from smaller islands and reattach to larger islands, driven by a gradient in the vapor pressure of the surrounding 2D gas.
Wen, et al [69] use Scanning Tunneling Microscopy (STM) to determine the mechanism of coarsening of thin film growth. As shown in Fig 7.6, evaporation of submonolayer coverages, with sample held at room temperature, generates the ”initial” nonequilibrium 2D structures, whose features are then monitored quantitatively as a function of time, to observe coarsening over a period of several hours.

7.5 Theory of coarsening

Due to the significance of coarsening to a variety of processes, theoretical study of coarsening process is indispensable, therefore various theoretical approaches are developed to explore coarsening process. During the coarsening, the system tries to minimize its interfacial free energy by nonlocal diffusion. As time involves, the small clusters are shrinking, while the large ones growing. With assumption of sphere or round clusters, the total number of clusters decreases and the average cluster radius increases, but the volume fraction of clusters $\phi$ does not change with time.

The theory of coarsening determines how the clusters evolve with time. Important quantities of interest are the cluster-distribution function $f(R, t)$, the average cluster radius $\bar{R}(t)$, and the total number of clusters, $N(t)$. The classic coarsening theory is attributed to Lifshitz and Slyozov[70] (LSW), and Wagner [71], who studied the case in which the volume fraction of the minority phase tends to zero i.e. , $\phi \rightarrow 0$, in dimension $D = 3$.

The starting point of the LSW theory is the diffusion equation for the concentration $C$ in the steady-state limit:
\n\nnabla^2 C(r) = 0 \quad (7.1)

where \(\partial C/\partial t\) can be neglected. This determines the flow of material between clusters, subject to the Gibbs-Thomson boundary condition at the surface of cluster of radius \(R\):

\[
C(r)_{r=R} = C_\infty (1 + \frac{\nu}{R}), \quad (7.2)
\]

where \(\nu\) is the capillary length, defined below, and the boundary condition far from all clusters:

\[
\lim_{r \to -\infty} C(r) = \overline{C}, \quad (7.3)
\]

where \(\overline{C}\) is the mean concentration in the bulk. The capillary length is \(\nu = 2\gamma V_m C_\infty/(R_g T)\), where \(\gamma\) is the surface tension, \(V_m\) the molar volume, \(C_\infty\) the solute concentration at a flat interface, \(R_g\) the gas constant, and \(T\) the temperature. The mass balance

\[
\frac{d}{dt}\left(\frac{4\pi}{3} R^3\right) = 4\pi R^2 D \frac{dC(r)}{dr} \bigg|_{r=R^*} \quad (7.4)
\]

where \(D\) is the diffusion constant, ensures that the changes in volume of the clusters, which are assumed to be spherical, are due to a change in concentration. The cluster-distribution function \(f(R, t)\) determines averages by
\[
\overline{(...)} = \frac{\int dR f(R, t)(...)}{\int dR f(R, t)}, \tag{7.5}
\]

with convenient normalization

\[
\int dR f(R, t) = N(t), \tag{7.6}
\]

the total number of clusters. The distribution function obeys the continuity equation

\[
\frac{\partial f(R, t)}{\partial t} + \frac{\partial}{\partial R}[\dot{R} f(R, t)] = 0; \tag{7.7}
\]

thus there is no source of new clusters (nucleation has ceased), where the overdot denotes a time derivative, and the conservation law

\[
\Delta(t) + \frac{4\pi}{3} \int_0^\infty R^3 f(R, t) dR = Q, \tag{7.8}
\]

where \(\Delta(t) = \mathcal{C} - C_\infty\), is the supersaturation of the solution, which vanishes as \(t \to \infty\); \(Q = \phi V'\) is the initial concentration, and \(V'\) is the volume of the system. We shall consider this equation in the limit in which the minority phase (within the clusters) and majority phase (outside the clusters) are at their equilibrium concentrations, i.e. \(\Delta(t) = 0\). These equations above follow for all small volume fractions, provided a steady-state cluster picture is reasonable.

In the limit of \(\phi \to 0\), the solution of the steady-state diffusion equation is
\[ C(r) = \overline{C} - [\overline{C} - C(R)]R/r, \quad (7.9) \]

since one need only consider one cluster. With the equation for mass balance, this gives the growth law in that limit:

\[ \frac{dR}{dt} = \frac{D}{R}(\triangle - \frac{\nu}{R}), \quad (7.10) \]

where, evidently, clusters larger (smaller) than the time-dependent critical radius \( \nu/\triangle(t) \) grow (shrink). In an elegant calculation, LSW determined the asymptotic growth rate of the average cluster radius to be

\[ \bar{R}(t) = \left( \frac{4D\nu t}{9} \right)^{1/3}, \quad (7.11) \]

where the prefactor 4/9 is the dimensionless coarsening rate, and the overbar denotes and average. In addition to this prediction, an analytic form for the cluster distribution function is was obtained:

\[ f(R,t) \propto g(R/\bar{R})\bar{R}^4 \quad (7.12) \]

for late times. The explicit form of the scaled normalized distribution function is

\[ g(z) = \begin{cases} 
(3^4 e/2^{5/3})z^2 \exp[-1/(1 - 2^2z)]/[(z + 3)^{7/3} (3/2 - z)^{11/3}] & 0 < z < \frac{3}{2} \\
0 & otherwise 
\end{cases} \quad (7.13) \]
LSW is about the case where $\phi \to 0$. Earlier work on extending the theory of LSW to nonzero $\phi$ has been attempted by many groups, using both analytic and numerical methods. Yao, et al [72] developed a mean-field theory to deal with multiple cluster nonzero $\phi$ diffusion. They introduce screening effects among the clusters and approximate the many-cluster correlation effects. They obtained the expression

$$g(z) = \begin{cases} 
\frac{-D\lambda x_{av}}{w(x_{av}, \lambda)} \exp(D\lambda \int_{x_{av}z}^{x_{av}z} w^{-1}(z', \lambda) dz') & 0 < z < z_0 \\
0 & \text{otherwise}
\end{cases}, \quad (7.14)$$

where $z_0 = x_0/x_{av}$ and $x_{av} = \int_0^\infty xG(x)dx$. where

$$G(x) = \begin{cases} 
Cx^2 \exp(D/2)\frac{D/2}{x-3/2}/[(3/2 - x)^{2+5D/9}(x + 3)^{1+4D/9}] & 0 < z < \frac{3}{2} \\
0 & \text{otherwise}
\end{cases}, \quad (7.15)$$

$$w(x, \lambda) = x^{1-D}(\sigma - x^{-1})/V(x/\eta, x) - \lambda x, \quad (7.16)$$
Figure 7-1: Electron diffraction pattern (a) and high resolution electron micrograph (b) for as-deposited film. Obtained from [67]
Figure 7-2: Electron diffraction pattern, (a), and high resolution electron micrographs, (b) and (c), for Ge microcrystals embedded in SiO$_2$ thin film. (c) is an enlarged image of the area indicated in (b). Obtained from [67]
Figure 7-3: Cross-section TEM micrograph showing Si nanocrystals formed in SiO$_2$ by the implantation of Si(400kev, 6X10$^{17}$/cm$^2$, RT) followed by thermal annealing(1100°C/1h/Ar + H$_2$). Obtained from [13]
Figure 7-4: Cross-section micrograph showing CdS nanocrystals formed in SiO$_2$ by the implantation $10^{17}/cm^2$ of Cd(450kev) and S(164kev), followed by annealing (1000°C/1h). Obtained from [13]
Figure 7-5: Plan-view scanning electron micrographs of $Si_{0.8}Ge_{0.2}/Si(001)$ hut cluster arrays grown by MBE at 755°C. (a) As-deposited (100 A thick); (b) annealed for 40 min at the growth temperature (100 A thick). Obtained from [68]
Figure 7-6: STM images obtained following deposition of Ag on Ag(100) at room temperature. In each row, the left frame shows the starting point, and the right frame shows the surface several hours later. Full horizontal scale is 1500 Å. Bright areas are the deposited film, one atom deep; dark areas are substrate, except (b) where bunched steps are visible at the edges. Conditions are (a) 0.11 ML, $N_0 = 4.9 \times 10^{-5} \text{ Å}^{-2}$, $t_f = 520 \text{ min}$; (b) 0.69 ML, $t_f = 400 \text{ min}$; and (c) 0.87 ML, $N_0 = 1.5 \times 10^{-5} \text{ Å}^{-2}$, $t_f = 390 \text{ min}$. $N_0$ is the initial island density. Obtained from [69]
Chapter 8

Parallel Kinetic Monte Carlo

8.1 Introduction

While KMC is an extremely efficient method to carry out dynamical simulations of stochastic and thermally activated processes when the relevant activated atomic-scale processes are known, the standard KMC algorithm is inherently a serial algorithm since only one event can occur at each step and its next event time is determined by the total overall rate for all processes to occur. However, for some problems one needs to simulate larger length and time-scales than can be simulated using a serial algorithm. Thus, it would be desirable to develop efficient parallel kinetic Monte Carlo algorithms so that many processors can be used simultaneously in order to carry out simulations over extended time- and length-scales.

Unlike KMC, the attempt time in Metropolis Monte Carlo (MMC) is independent of system configuration and thus, an asynchronous ”conservative” algorithm may be used. In such an algorithm all processors whose next attempt time is less than
their neighbor's next attempt times are allowed to proceed. Unfortunately such a "conservative" algorithm does not work for kinetic Monte Carlo. Since fast events may "propagate" across processors, the time for an event already executed by a processor may change due to earlier events in nearby processors, thus leading to an incorrect time evolution. One may also consider a hybrid version of the conservative asynchronous algorithm which has been developed by Lubachevsky [73] in the context of Ising simulations. In this algorithm, "n-fold way" simulations are carried out in the interior of each processor, while Metropolis Monte Carlo simulations are carried out at the boundary. Although the presence of the boundary regions leads to a correct time evolution in a processor, because of the possibility of significant rejection of boundary events, the parallel efficiency may be very low for problems with a wide range of rates for different processes. In addition, due to the asynchronous nature of the algorithm, the parallel efficiency is further reduced by the complexity involved in date taking.

In order to address these problems, Shim and Amar [74] developed a simple synchronous sublattice (SL) algorithm for parallel kinetic Monte Carlo simulations. While the SL algorithm is not rigorous, they found that using certain reasonable assumptions on the cycle length and processor size, the results obtained are identical to those obtained in serial simulations and in particular, the algorithm is very efficient. They also found that the parallel efficiency was essentially independent of the number of processors in the large \( N_p \) limit, thus leading to linear scaling.
8.2 Synchronous Sublattice Algorithm

In the synchronous sublattice (SL) algorithm, different parts of the system are assigned via spatial decomposition to different processors. However, in order to avoid conflicts between processors due to the synchronous nature of the algorithm, each processor's domain is further divided into different regions or sublattices (see the following Fig). At the beginning of a cycle each processor's local time is initialized to zero. One of the sublattices is then randomly selected so that all processors operate on the same sublattice during that cycle. Each processor then simultaneously and independently carries out KMC events in the selected sublattice until the time of the next event exceeds the time interval $T$. As in the usual serial KMC, each event is carried out with time increment $\nabla t_i = -\ln(r_i)/R_i$ where $r_i$ is a uniform random number between 0 and 1 and $R_i$ is the total KMC event rate. Each processor then communicates any necessary changes (boundary events) with its neighboring processors, updates its event rates and moves on to the next cycle using a new randomly chosen sublattice. Sublattice selection can be carried out by seeding all processors with the same random number generator so that they all independently select the same sublattice for each cycle. By picking the cycle length $T$ less than or equal to the average time for the fastest possible activated event we do indeed obtain results which are identical to those obtained in serial KMC except for very small sublattice sizes.
Figure 8-1: Two possible methods of spatial and sublattice decomposition. (a) square sublattice decomposition (9 processors) and (b) strip sublattice decomposition (3 processors). Solid lines correspond to processor domains while dashed lines indicate sublattice decomposition. Dotted lines in (a) and (b) indicate "ghost-region" surrounding central processor. Obtained from [74]
Chapter 9

Parallel Kinetic Monte Carlo

simulation of 2D island coarsening

Kinetic Monte Carlo (KMC) is an extremely efficient method to carry out dynamical simulations of stochastic and/or thermally activated processes when the relevant activated atomic-scale processes are known. KMC simulations have been successfully used to model a variety of dynamical processes ranging from catalysis to thin film growth. The basic principle kinetic Monte Carlo is that in order to efficiently simulate a dynamical system with a variety of different rates or processes, at each step in the simulation one picks the next process to occur with a probability proportional to the rate for that process. The time of the next event is determined by the total overall rate for all processes to occur, and after each event the rates for all processes are updated as necessary.

The standard KMC algorithm is a serial algorithm since only one event can occur at each step. However, for some problems one needs to simulate larger length and
time scales than can be simulated using a serial algorithm. For these problems it would be desirable to develop efficient parallel kinetic Monte Carlo algorithms so that many processors can be used simultaneously to carry out realistic computations over extended time and length scales.

Coarsening is a process for non-equilibrium system to approach to equilibrium state, it usually happen in a large system and last for a long time. The prominent features of coarsening process often appear in its long time course, so its asymptotic behavior is more important in understanding its mechanisms and properties. Parallel kinetic Monte Carlo algorithm provides the possibility to explore the coarsening process in large length and time scales.

9.1 Introduction

Coarsening plays an important role in a wide variety of processes ranging from grain growth in alloys [75], to soot formation [76], to the formation of galaxies[77]. One example of particular current interest is the coarsening of two-dimensional (2D) or three-dimensional (3D) islands on a surface [78], since the coarsening process determines the nanoscale ordering and surface structure. As a result, island-coarsening has recently been the subject of a large amount of experimental and theoretical work [78, 79, 69, 80, 81, 82, 83, 84, 85, 86, 87].

For the case of 2D clusters on a surface, it is useful to consider two particular limiting regimes in which the coarsening is dominated by diffusion - Ostwald ripening [88, 89] and cluster diffusion and coalescence [79, 69, 80, 81, 82, 83, 84, 85, 86]. In the
case of Ostwald ripening the islands are assumed to be immobile, while the coarsening is mediated by a background density of diffusing atoms such that islands bigger than a critical island-size grow while smaller islands shrink or evaporate. This results in power-law growth of the average island size $S(t)$ corresponding to the average number of atoms in an island, i.e. $S(t) \sim t^{2n}$ where $n = 1/3$ for the case of 2D clusters on a 2D substrate [90, 91]. It also leads to a scale invariant island-size distribution at late-time. In the case of cluster diffusion and coalescence, power-law growth of the average island-size and a scale-invariant island-size distribution are also observed. In particular, if the cluster diffusion coefficient $D(s)$ decays as a power-law with island-size $s$, i.e. $D(s) \sim s^{-x}$, then $n = 1/2(1 + x)$ [79]. Three different limiting cases have been considered to be of particular interest [69, 80, 81, 82, 83, 84, 85] - cluster diffusion due to periphery diffusion ($x = 3/2, n = 1/5$), cluster diffusion due to correlated evaporation/condensation ($x = 1, n = 1/4$), and finally cluster diffusion due to uncorrelated evaporation-condensation ($x = 1/2, n = 1/3$). Although asymptotically, one might expect one of these processes to dominate for a particular case, in general one might expect all these processes to play a role.

Besides the coarsening exponent, one quantity of particular interest is the asymptotic scaled island-size distribution. In particular, if $N_s(t)$ is the density of islands of size $s$ at time $t$ (where $s$ is the number of atoms in an island) then one may write [26],

$$f(s/S) = S^2N_s(t)/\theta$$  \hspace{1cm} (9.1)

where $S(t) = \sum sN_s/\sum N_s$ is the average island-size and $\theta$ is the coverage and
\( f(u) \) is the scaled island-size distribution (ISD). At late-time one expects that \( f(u) \) will be independent of time. We note that there have been a number of theoretical efforts to determine the asymptotic scaled ISD and its dependence on coverage. For example, for the case of Ostwald ripening the mean field theory of Lifshitz-Slyozov-Wagner (LSW) leads to an analytical expression for the scaled ISD which is valid in the limit \( \theta \to 0 \). However, for finite coverage one expects that correlations may play a significant role. As a result, there have also been a number of theoretical attempts [92, 93, 94, 95, 72] to extend the LSW theory to finite coverage in two- and three-dimensions, although these efforts have focussed primarily on the low-coverage limit in which islands may be treated as isolated droplets. For the case of 2D island coarsening, a number of numerical simulations have also recently been carried out [96, 97, 98, 99]. However, because of the role of correlations as well as the relatively slow convergence to the asymptotic distribution, determining the asymptotic scaled ISD remains a challenging problem.

Here we present the results of parallel kinetic Monte Carlo (KMC) simulations of 2D island coarsening which were carried out using our recently developed synchronous sublattice (SL) algorithm [100]. We note that in contrast to a variety of other algorithms for parallel KMC via domain-decomposition which are rigorous and which require global communications [101, 102, 103, 6], the SL algorithm only requires local communications with nearest-neighbor processors. As a result it is both relatively simple to implement and in general significantly more efficient. In particular, for a fixed processor size, we have demonstrated [100] that it exhibits linear scaling as a function of the number of processors, i.e. the parallel speed-up is proportional to the
number of processors. On the other hand, it is only semi-rigorous [100]. Therefore, it is of interest to examine the accuracy and efficiency of the SL algorithm in simulations of coarsening, since we have so far only applied it to parallel KMC simulations of growth. In addition we would like to use it to compare the asymptotic island-size distribution with the predictions of theories of Ostwald ripening. As discussed in more detail below, we find that the SL algorithm can indeed be used to accurately and efficiently carry out parallel KMC simulations of island coarsening, and in contrast to previous work on a similar model [96], we are able to reach the asymptotic scaling regime corresponding to $n = 1/3$. Our results also indicate that the asymptotic scaled island-size distribution is significantly different from the prediction of a recent mean-field theory of Ostwald ripening at finite coverage developed by Yao et al [72]. We believe that this is due to the existence of correlations as well as cluster diffusion which are not taken into account in Ref. [72].

The organization of this chapter is as follows. In section II, we describe the bond-counting model used in our coarsening simulations and then briefly review the SL algorithm. In section III, we present a comparison between parallel and serial results for the average island size and island-size distribution at early and intermediate times in order to validate our long-time simulation results. We then present our parallel KMC results for the evolution of the average island-size and island-size distribution at much longer times along with a comparison with the theory of Yao et al [72] for two different coverages $\theta = 0.1$ and 0.2. We also study the efficiency of the SL algorithm and its dependence on the number of processors and cycle-time. Finally, in section IV, we discuss our results.
9.2 Model and Simulations

Since one of the main goals of this work is to carry out a first test of the accuracy and efficiency of the SL algorithm when applied to coarsening, we have considered the simplest possible model, corresponding to “bond-counting” on a square-lattice. In particular, in our model atoms are assumed to diffuse in all four possible nearest-neighbor directions with a configuration-dependent hopping rate $D_n$ given by,

$$D_n = \nu_0 e^{-E_a/k_B T}$$

(9.2)

where the prefactor $\nu_0 = 10^{12} \text{s}^{-1}$, $E_a = E_0 + nE_b$ is the configuration-dependent activation energy, $E_0$ corresponds to the activation energy for monomer diffusion, $n = 0 - 4$ is the number of in-plane nearest-neighbors, and $T$ is the substrate temperature. In our simulations a value $E_0 = 0.4 \text{ eV}$, which is a typical value for metal (100) surfaces, was assumed along with a moderate “bond-strength” $E_b = 0.1 \text{ eV}$, while our coarsening simulations were carried out at a temperature $T = 250 \text{ K}$. We note that Lam et al [96] have recently carried out KMC simulations of island coarsening at 700 K using a similar bond-counting model, but using larger values for the activation energies for diffusion ($E_0 = 1.3 \text{ eV}$ and $E_b = 0.3 \text{ eV}$) which are more typical of semiconductors. However, once the higher coarsening temperature is taken into account, the effective parameters ($E_0/k_B T$ and $E_b/k_B T$) are close to those used in the model previously studied by Lam et al [96].

In order to study the asymptotic coarsening behavior, as well as the coverage
dependence, we have carried out simulations of coarsening at two different coverages, \( \theta = 0.1 \) and \( \theta = 0.2 \). In each case, the initial island distribution was prepared by depositing particles with deposition rate \( F = 1 \text{ ML/s} \) at \( T = 250 \text{ K} \) up to the desired coverage. Starting at this point (\( t = 0 \)) coarsening simulations were then carried out over times ranging from \( 10^3 \) s to \( 10^5 \) s while periodic boundary conditions were assumed. For the very short time simulations, system sizes of \( L = 256 \) and \( L = 512 \) were used while for the much longer time simulations systems of size \( L = 1600 \) were used to avoid finite-size effects. In order to obtain good statistics, the short-time results were typically averaged over 500 runs while the longer time results were averaged over 78 runs. In all of our simulations the island-size distribution \( N_s \) (where \( N_s \) is the density of islands of size \( s \)) was measured along with the total island density \( N = \sum_{s \geq 2} N_s \), monomer density \( N_1 \), and average island size \( S = \frac{1}{N} \sum_{s \geq 2} sN_s = (\theta - N_1)/N \).

While serial KMC simulations were used for comparison and for testing, in order to reach longer times, most of our simulations were carried out using the recently-developed semirigorous synchronous sublattice (SL) parallel KMC algorithm [100] with strip geometry. In this algorithm, different parts of the system are assigned via spatial decomposition to different processors. However, in order to avoid conflicts between processors due to the synchronous nature of the algorithm, each processor’s domain is further divided into different regions or sub-lattices. In particular, for the case of strip-geometry considered here our square system was divided into \( N_p \) strips (where \( N_p \) is the number of processors) of width \( N_x = L/N_p \) with each strip corresponding to a different processor. Each strip was then divided into two halves - one
corresponding to an $A$ sublattice and the other corresponding to a $B$ sublattice. A complete synchronous cycle corresponding to a time interval $\tau$ is then as follows. At the beginning of a cycle, each processor’s local time is initialized to zero. One of the sublattices is then randomly selected so that all processors operate on the same sublattice during that cycle. Each processor then simultaneously and independently carries out KMC events in the selected sublattice until the time when the next event exceeds the time interval $\tau$. As in the usual serial KMC, each event is carried out with time increment $\Delta t_i = -\ln(r_i)/R_i$, where $r_i$ is a uniform random number between 0 and 1 and $R_i$ is the total event rate for that sublattice. Each processor then communicates any necessary changes (boundary events) with its neighboring processors, updates its event rates, and moves on to the next cycle using a new randomly chosen sublattice.

We note that in the standard SL algorithm the cycle time $\tau$ must be smaller than the inverse of the fastest possible single-event rate in the system [100]. This ensures that for example particles near the processor or sublattice boundary will only move once (on average) before moving on to the next cycle and so will not be “trapped” in the “ghost” region just outside the boundary. Accordingly, in most of our parallel simulations a value $\tau = 1/D_0$ was used for the cycle time. In our previous tests of this algorithm using a variety of models of epitaxial growth [100] it was found that using such an upper bound on the cycle-time led to results which were identical to serial KMC results - except for extremely small processor sizes ($N_x \leq 8$) when the sublattice size was less than a “diffusion length”. However, we have also carried out additional test simulations of coarsening with a larger cycle time since this may
increase the parallel efficiency. As our results demonstrate, in the case of coarsening, the cycle time can be significantly increased without affecting the accuracy.

In order to study the asymptotic coarsening behavior while avoiding finite-size effects, our long-time parallel KMC simulations \((t = 10^5 \text{ s})\) were carried out using large system sizes \((L = 1600)\) with \(N_p = 8\). However, in order to validate our parallel KMC results we have first carried out short and intermediate time tests \((t = 10^2 - 10^3 \text{ s})\) in which we have compared serial and parallel simulation results for different numbers of processors \(N_p\). In these tests systems of size \(L = 256\) and 512 were used, while the number of processors ranged from \(N_p = 1\) (serial) to \(N_p = 64\). We note that the processor width \(N_x\) ranged from \(L\) (serial runs) to very small values \((N_x = 4)\) for the case of \(L = 256\) with \(N_p = 64\).

### 9.3 Results

Fig. 9-1 shows typical results for the system morphology as a function of time up to \(t = 10^5 \text{ s}\) for \(\theta = 0.1\) and 0.2, for the case \(L = 1024\). As can be seen, while the islands are initially very small and somewhat irregular, with increasing time the average island-size increases while the islands become smoother and appear to approach a “square-like” shape with rounded corners. We now present results for the comparison between serial and parallel simulations before studying in more detail the quantitative evolution of the average island-size and island-size distribution.
9.3.1 Comparison of serial and parallel results

As a first test of the accuracy of our parallel KMC simulations, we have compared serial results for the monomer and island densities as a function of time up to \( t = 10^3 \) s at coverage \( \theta = 0.1 \) (system size \( L = 256 \)) with the corresponding parallel results obtained with the SL algorithm with cycle time \( \tau = 1/D_0 \) and the number of processors ranging from \( N_p = 4 \) \((N_x = 64)\) to \( N_p = 64 \) \((N_x = 4)\). As can be seen in Fig. 9-2(a), both the island and monomer densities decrease with time although the island-density appears to be decreasing more quickly. The small value of the monomer density also indicates that to a good approximation the average island size \( S \) is directly related to the island density \( N \), i.e. \( S \approx \theta/N \). In addition, we find that for all values of \( N_p \) there is excellent agreement between the parallel and serial results for the island density even for extremely small processor sizes, thus indicating that there is a negligible finite processor-size effect. Similar agreement is obtained for the monomer density \( N_1 \) (see Fig. 9-2) although for the very smallest processor size \((N_x = 4, N_p = 64)\) there is a small finite processor size for the monomer density, i.e. the monomer density obtained in the parallel simulations is slightly higher than the serial result. Fig. 9-2(b) shows similar results for the scaled ISD at \( t = 100 \) s for a slightly larger system size \((L = 512)\) with the number of processors ranging from \( N_p = 1 \) (serial) to \( N_p = 64 \). As can be seen, there is essentially no difference between the serial and parallel KMC results for the scaled ISD. These results indicate that, somewhat surprisingly, the finite processor-size effect in island coarsening is significantly weaker than during submonolayer island growth [100]. We attribute this
to the fact that the process of coarsening is somewhat closer to equilibrium than nucleation and island growth.

9.3.2 Asymptotic coarsening behavior and scaled island-size distribution

Based on these results, we have carried out parallel KMC simulations over much longer times \( t = 10^5 \) s and much larger system sizes \( L = 1600 \) with \( N_p = 8 \) \( (N_x = 200) \) in order to determine the asymptotic behavior. We note that the processor width \( N_x = 200 \) in these simulations is significantly larger than the largest processor width \( N_x = 4 \) for which a noticeable finite-processor size effect was observed. In order to obtain good statistics our results were averaged over 78 runs. Fig. 9-3 shows the corresponding simulation results for the average island size \( S \) as a function of time for \( \theta = 0.1 \) and 0.2. As can be seen, after an initial “transient” period, there is an “intermediate” period from \( t = 10 - 10^3 \) s during which an effective slope of \( 1/2 \) corresponding to a coarsening exponent \( n \approx 1/4 \) is obtained. We note that this value corresponds to the correlated evaporation-condensation mechanism for cluster diffusion [80] and is also consistent with the observation of significant cluster diffusion and coalescence during this period. However, at later times \( t > 10^3 \) s the slope approaches the asymptotic value of \( 2/3 \) corresponding to a coarsening exponent \( n = 1/3 \). While such an exponent is consistent with both cluster diffusion due to uncorrelated evaporation-condensation and Ostwald ripening, we have observed that there is significantly less cluster diffusion and coalescence during this late-time
period. Instead, what is observed is that the smaller clusters evaporate while the larger clusters grow, as in Ostwald ripening. Such a scenario is also consistent with the fact that, as indicated by the inset in Fig. 9-3, at late-time the island density is smaller than the monomer density. Thus, at late time the islands are essentially in quasi-equilibrium with a “gas” of monomers as is assumed in Ostwald ripening. We now consider the time evolution of the scaled ISD as well as the dependence of the asymptotic ISD on coverage.

Fig. 9-4 shows our results for the scaled island-size distribution,

\[ f(s/S) = N_s(t)S^2/\theta \]  

at early and intermediate times \((t = 150 - 10^3 \text{ s})\) along with the initial scaled ISD at \(t = 0\) (dashed curve). We note that these simulations were carried out using \(L = 1600\) with \(N_p = 16\). Also shown is the prediction of the mean-field theory of Yao et al [72] (solid curve) for 2D Ostwald ripening and \(\theta = 0.1\), which was obtained by numerically solving the system of self-consistent equations given in Ref. [72]. We note that in 2D the theory of Yao et al [72] is based on the assumption of circular islands, and leads to a prediction for the “scaled droplet distribution function” \(g(r/R)\) where \(r\) is the cluster radius, \(R\) is the average island radius, and \(S = \pi R^2\). In order to convert this result to a scaled ISD we have used the relation \(f(u) = g(\sqrt{u})/(2\sqrt{u})\). As can be seen in Fig. 9-4 our simulation results exhibit good scaling over a relatively large range of times, thus indicating that the scaled ISD is approaching its asymptotic behavior. However, there are significant deviations between the simulation results.
and the asymptotic mean-field theory prediction of Yao et al [72]. In particular, the scaled ISD obtained from our KMC simulations is narrower and higher than the Yao model prediction.

Fig. 9-5 shows our parallel KMC results for the scaled ISD at much longer times (approximately 100 times longer) for system-size $L = 1600$ and $N_p = 8$. As can be seen, at late times the peak of the scaled ISD is slightly lower and is also slightly shifted to the right compared to the ISD at intermediate times but is still significantly different from the mean-field (MF) prediction of Yao et al. In particular, the peak of the distribution is still significantly higher and narrower than the Yao et al [72] prediction while the peak position corresponds to a scaled island-size close to 1, in contrast to the prediction of Yao et al. In addition, both the small $s/S$ portion of the distribution as well as the tail ($s/S > 2.0$) deviate even more strongly from the MF prediction than at intermediate times. We believe that these deviations are due to the existence of correlations which are not taken into account in the MF theory.

In order to study the coverage dependence of the scaled ISD we have also carried out simulations of coarsening at coverage $\theta = 0.2$, as shown in Fig. 9-6. As can be seen, our simulation results for the scaled ISD at $\theta = 0.2$ are very similar to those obtained at $\theta = 0.1$, thus indicating a relatively weak coverage dependence. We note that for comparison, also shown in Fig. 9-6 (solid and dashed curves) are the predictions of Yao et al [72] for the asymptotic scaled ISD for coverages $\theta = 0.1$ and $\theta = 0.16$. We note that while these results were obtained by numerically solving the system of self-consistent equations given in Ref. [72], for values of $\theta$ larger than 0.16 it appears that there are numerical instabilities in the solution of the self-consistent
equations used by Yao et al [72]. As a result, this theory could not be used to obtain a prediction for $\theta = 0.2$. In any case, a comparison between our scaled ISD results for $\theta = 0.2$ with the MF predictions for $\theta = 0.1$ and 0.16 indicates that at larger coverage the discrepancy between the simulation results and the MF prediction increases. This may be due in part to the fact that this theory is only applicable at relatively small coverage such that the “screening length” (corresponding roughly to the distance between islands) is significantly larger than the island radius.

9.3.3 Dependence of parallel efficiency on $N_p$ and cycle time $\tau$

We now consider the parallel efficiency obtained in our parallel KMC simulations. We note that in our simulations, the parallel efficiency was calculated using the expression,

$$PE = \frac{t_{\text{serial}}}{N_p t_{\text{parallel}}}$$

(9.4)

where $t_{\text{serial}}$ corresponds to the time for a serial simulation and $t_{\text{parallel}}$ corresponds to the time for a parallel simulation of the same system with $N_p$ processors. The solid lines in Fig. 9-7 indicate our results for the parallel efficiency obtained from test runs of length $t = 10^3$ s as a function of the number of processors $N_p$ for different system sizes $L = 512, 1024, \text{ and } 1600$ using a cycle-time $\tau = 1/D_0$. As expected, for fixed system size $L$ the parallel efficiency decays with increasing $N_p$ due to the decrease in the processor size and number of events per cycle. This leads to an increase in the relative communications overhead as well as in the relative fluctuations in the
number of events per processor which implies a decreased utilization per processor. However, for fixed $N_p$ the parallel efficiency increases with increasing $L$ since this leads to an increased processor size. We note that for the parameters used in most of our simulations ($L = 1600, N_p = 8$) the parallel efficiency is slightly larger than 80%.

We now consider the effects of increasing the cycle-time $\tau$ on the accuracy and efficiency of our parallel KMC simulations. We note that in previous work on parallel KMC simulations of submonolayer and multilayer growth using the SL algorithm [100], we found that a “conservative” cycle time corresponding to the inverse of the fastest possible single-event rate was required to maintain the accuracy of the parallel simulation. Accordingly all of the coarsening results presented so far were obtained using such a “conservative” cycle-time $\tau = 1/D_0$. However, it is of interest to investigate the effect of increasing the cycle-time $\tau$ since this may increase the parallel efficiency of the simulations by decreasing the relative fluctuation in the number of events in each processor as well as the communications overhead. In addition, we expect that since coarsening is a “slow” process which is close to equilibrium, there should be less dependence on the cycle time than in the previously studied cases of submonolayer and multilayer growth [100].

Fig. 9-8 shows the island and monomer densities during coarsening ($\theta = 0.1$) obtained in parallel simulations with $L = 1600$ and $N_p = 8$ for different values of the cycle time ranging from $\tau = 1/D_0$ to $\tau = 50/D_0$. As can be seen there is essentially no dependence of the island-density on the cycle-time for all values of $\tau$, while the monomer density agrees within error bars for all values of $\tau$ up $10/D_0$. However, for longer cycle times ($\tau \geq 20/D_0$) there are noticeable deviations in the monomer...
density. This relatively weak dependence on the cycle time $\tau$ is in striking contrast to our previous results for simple non-equilibrium growth models and is due, we suspect to the fact that coarsening is much closer to equilibrium. The corresponding results for the parallel efficiency are shown in Fig. 9-7 (dashed lines). As can be seen, using $\tau = 5/D_0$ leads to a significant increase in the parallel efficiency for the case of $L = 1600$ with $N_p = 8$, while using a significantly longer cycle-time ($\tau = 20/D_0$) does not further improve the parallel efficiency. We also note that for $N_p = 2$, using $\tau = 5/D_0$ leads to a parallel efficiency which is slightly larger than 1. This is due to the existence of cache effects which have a stronger effect in serial simulations than in parallel simulations due to the larger processor size [103].

9.4 Discussion

We have presented the results of parallel kinetic Monte Carlo simulations of 2D island coarsening using our recently developed semi-rigorous synchronous sublattice (SL) algorithm. Our results indicate that parallel simulations can be used to effectively extend the time-scale over which realistic coarsening simulations can be carried out. In particular, using a conservative cycle time $\tau = \tau_0 = 1/D_0$ corresponding to the inverse of the fastest possible single event-rate, we have demonstrated that the SL algorithm leads to results which are identical to those obtained using serial KMC except for extremely small processor sizes. In addition, for system sizes which were not too small the parallel efficiency was found to be relatively large. In particular, for our simulations of the late-stages of coarsening with system size $L = 1600$ and
$N_p = 8$, a parallel efficiency of larger than 80% was obtained.

We have also used the SL algorithm to carry out parallel KMC simulations of the asymptotic coarsening behavior for our bond-counting model, which is similar to that previously studied by Lam et al [96]. We note that, in part because of the longer simulation times available via our parallel simulations, our coarsening exponents are significantly larger than obtained previously by Lam et al [96], and so we were able to observe the asymptotic coarsening behavior. In particular, an asymptotic growth exponent $n \simeq 1/3$ was obtained for both $\theta = 0.1$ and $\theta = 0.2$.

In addition, our results indicate that while cluster diffusion and coalescence play a role at early and intermediate times up to about $10^3 \text{s}$, at late times the coarsening proceeds via Ostwald ripening.

By carrying out simulations of coarsening over long times and for large system sizes we have also studied the asymptotic behavior of the scaled ISD. For both $\theta = 0.1$ and 0.2, we find that the asymptotic scaled ISD is reached fairly quickly, i.e. there are only small changes in the scaled ISD for $t > 10^3 \text{s}$. However, the scaled ISD’s obtained in our simulations are significantly narrower and more sharply peaked than the mean-field theory predictions. As already noted, we believe that these deviations are primarily due to the existence of correlations which are not taken into account in the MF theory. However, other factors such as the existence of significant cluster diffusion for small islands in our model (due to evaporation-condensation), as well as the shape of our islands (which are square rather than circular) might also play a role.

Finally, we have also compared the results of parallel KMC simulations of coarsen-
ing carried out using cycle-times larger than the maximum “conservative” cycle-time \( \tau_0 \) with the corresponding serial results. Somewhat surprisingly, we found that for cycle times as large as 10 \( \tau_0 \) our results for the island and monomer densities are identical to the serial results. Interestingly, for larger cycle-times the island-density is still unaffected, although there are noticeable deviations in the monomer density. This is in contrast to our previous studies of submonolayer and multilayer nucleation and growth using the SL algorithm [100, 104], in which a cycle time significantly longer than the inverse of the fastest possible single-event rate led to results for the island density which deviate from the serial results. We believe that this relative insensitivity to the cycle time is due to the fact that coarsening is closer to equilibrium than nucleation and growth.

In conclusion, we have used the recently developed SL algorithm to carry out parallel kinetic Monte Carlo simulations of a simple bond-counting model of 2D island coarsening. Our results for this model indicate that while cluster diffusion via correlated evaporation-condensation and coalescence play a role at early and intermediate times, at late times the coarsening proceeds via Ostwald ripening. In addition, we found that the asymptotic scaled ISD is significantly narrower and more sharply peaked than the mean-field theory prediction of Yao et al [72]. Our results also indicate that the SL algorithm can be used to effectively extend the time-scale over which realistic coarsening simulations can be carried out. Based on these results we expect that the SL algorithm will be useful in the future in parallel KMC simulations of more complicated models of coarsening.
Figure 9-1: System morphology at different times for $\theta = 0.1$ and 0.2. Pictures correspond to $256 \times 256$ portions of $1024 \times 1024$ system.

Figure 9-2: Comparison of serial and parallel coarsening results at short and intermediate times for different values of $N_p$ ($N_x = L/N_p$) at $\theta = 0.1$. All results are averaged over 500 runs. (a) Monomer and island densities ($L = 256$). (b) Scaled ISD at $t = 100$ s for system size $L = 512$. 
Figure 9-3: Average island size $S$ as function of time for coverages $\theta = 0.1$ and 0.2 (system size $L = 1600$). Inset shows corresponding results for island and monomer densities.
Figure 9-4: Comparison between parallel KMC simulation results for scaled ISD at early and intermediate time ($\theta = 0.1$) and mean-field (MF) prediction of Yao et al [72].
Figure 9-5: Comparison between parallel KMC simulation results for scaled ISD at late-time ($\theta = 0.1$) and mean-field (MF) prediction of Yao et al [72].
Figure 9-6: Comparison of KMC simulation results for the scaled ISD at late-time ($\theta = 0.2$) and the mean-field (MF) predictions of Yao et al [72] at $\theta = 0.1$ (solid curve) and $\theta = 0.16$ (dashed curve).
Figure 9-7: Parallel efficiency $PE$ as function of number of processors $N_p$. Solid lines corresponds to results obtained using $\tau = 1/D_0$, while dashed lines correspond to results for $L = 1600$ using a larger value of $\tau$ (see text).
Figure 9-8: Evolution of monomer and island densities obtained using SL algorithm with different values of cycle time $\tau$ ($L = 1600$ and $N_p = 8$).
Chapter 10

Conclusions and future work

In this Thesis we have used a variety of techniques, including kinetic Monte Carlo simulations, rate-equations, and analytical methods to study the processes of nucleation, growth, and coarsening and their dependence on dimensionality. One of the central themes of this work has been the effects of fluctuations and how they lead to deviations from mean-field behavior. In particular, for the case of irreversible growth of point-islands in 3D, we found that due to the decreased influence of correlations and fluctuations in 3D as compared to 2D, the scaled CND depends only weakly on the island-size. As a result the scaled ISD is significantly sharper than obtained in 2D and diverges with increasing $D/F$. However, the scaled ISD obtained in kinetic Monte Carlo (KMC) simulations appears to diverge more slowly with increasing $D/F$ than the MF prediction while the divergence occurs at a value of the scaled island-size which is somewhat beyond the MF prediction. These results are supported by an analysis of the asymptotic CND. In addition, in 4D we found that for large $D/F$, the scaled CND and CZD do not depend on island-size in good agreement with the
MF prediction, while the scaled ISD also agrees well with the MF prediction except for a slight difference at the peak values. Coupled with previous results obtained in \( d = 3 \), these results indicate that the upper critical dimension for irreversible cluster nucleation and growth is equal to 4.

We have also studied the dependence of the scaled CZD on deposition rate \((D/F)\) and dimensionality in order to obtain the asymptotic CZD. While we found no dependence on coverage, there is a noticeable dependence on \( D/F \). In this case, we found that while the CZD depends on \( d \) due to fluctuations there is no MF behavior in \( d = 4 \). Poor agreement with Wigner distribution predicted in Ref. [59] is found. Interestingly, in this case fluctuations play a more important role and are still important in \( d = 4 \) while the CZD depends on the short-range interaction for finite \( D/F \) (corresponding to the ratio of monomer hopping rate \( D \) to deposition rate \( F \)) in the asymptotic limit of infinite \( D/F \) there is no significant dependence. Our results also indicate that for \( d = 2 \) and 3 the asymptotic CZD is independent of model details and dimension. However, for \( d = 1 \) and \( d = 4 \) the resulting distribution is significantly more sharply peaked. We also find that in contrast to the island-size distribution, for which mean-field-like behavior is observed in \( d = 3 \) and above, the asymptotic CZD is significantly broadened by fluctuations even in \( d = 4 \).

In addition to studying nucleation and growth, we have also studied the coarsening of two-dimensional islands on a surface and compared with recent sophisticated mean-field theories of Yao, Grant. As for the case of nucleation and growth we find that fluctuations play an important role, and can significantly affect the island-size distribution. However, the coarsening behavior corresponding to the average island-
size is in good agreement with MF theories. We note that as part of this work we have also tested the synchronous sublattice (SL) algorithm for parallel kinetic Monte Carlo. Our results indicate that this algorithm is well suited for parallel KMC simulation of coarsening, and is both efficient and accurate. One of the reasons for this is that in coarsening the system is typically ‘closer to equilibrium’ than during nucleation and growth. These results indicate that in the future it would useful to use this method to study more realistic systems. While we have focussed primarily on simplified models, we note that our 2D and 3D results are likely to have implications for a number of more complex systems such as ion-implantation, vacancy clusters formed during irradiation, general coarsening problems. However, in the future it would be interesting to study more complex models which take into account such details as cluster shape and geometry as well as energetics. Thus, a number of obvious extensions of this work present themselves. These include the study of more sophisticated models of cluster growth in 2D and 3D (we note that some of these studies are currently being carried out) as well as the application of parallel KMC methods to more sophisticated models of coarsening.
Bibliography


[62] The constants $a_\beta$ and $b_\beta$ are determined by normalization, e.g. $a_\beta = 2\Gamma(\frac{\beta+2}{2})^{\beta+1}/\Gamma(\frac{\beta+1}{2})^{\beta+2}$ and $b_\beta = [\Gamma(\frac{\beta+2}{2})/\Gamma(\frac{\beta+1}{2})]^2$.


