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NUMERICAL SIMULATION OF GRAIN GROWTH IN
LIQUID PHASE SINTERED MATERIALS

by

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Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

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May, 1995
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GRADUATE STUDIES

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*We also certify that written approval has been obtained for any proprietary material contained therein.
NUMERICAL SIMULATION OF GRAIN GROWTH IN LIQUID PHASE SINTERED MATERIALS

Abstract

by

VEENA TIKARE

Grain growth in liquid phase sintered materials occurs by Ostwald ripening and has been modeled extensively by both analytical and numerical techniques starting with the LSW theory. However, all models make simplifying approximations to make the problem tractable and the approximations used in these models make them most accurate at low solid fractions. A Monte Carlo simulation technique based on the Potts model which makes no assumptions about solid fractions, grain shapes or diffusion fields around grains has been developed, characterized, and used to study grain growth in liquid phase sintered materials.

The Potts model presented in this work utilized a two dimensional, square lattice similar to that developed by Stolovitz and coworkers to digitize the microstructure. The two-phases, solid grains in a liquid matrix, were achieved by populating the lattice with a two component, canonical ensemble where the two components were designated as A and B. Component A, which constitutes the solid grains, could assume one of 100 degenerate states, and component B, the primary constituent of the liquid phase, could assume only one state. Bond energies between all first and second nearest-neighbors were assigned. The sum
of all the bond energies between neighboring sites defined the Hamiltonian for the simulation. Solution and reprecipitation was simulated by allowing exchanges between neighboring A- and B-sites using the classical Metropolis algorithm.

The simulation technique was used to study isotropic grain growth in a fully wetting system. It was found that the set simulation parameters gave diffusion-controlled grain growth for solid contents ranging from 30 to 90%. The grain size distribution was found to vary with solid fraction, becoming broader and more peaked with increasing solid fraction. The skewness was near zero at solid fraction of 0.41% and shifted to larger grain sizes with increasing solid fraction. This shift in the skewness of grain size distribution is not predicted by previous analytical or numerical models; however, it is consistent with experimental data collected by Fang and Patterson in the W-Ni-Fe system.
To

Sneha, Satya, Seema, and Ray
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SURVEY OF LITERATURE

Liquid phase sintering plays an important role in processing of ceramics. Almost all traditional ceramics such as pottery, bricks, porcelain, etc were, and still are, sintered using a liquid phase. Liquid phase sintering continues to play an important role in the processing of many recently developed engineering ceramics. A few examples are silicon nitrides for aircraft and automobile engine components, armor materials and heat exchangers, alumina substrates for packaging silicon chips, barium titanate electrical capacitors, and tungsten carbide for cutting tool applications. Thus, it is important to understand evolution of microstructural features generated by processes such as grain growth in the presence of a liquid phase so that such materials can be engineered for their respective applications.

Liquid phase sintering may be defined as the densification of packed powder by application of heat so as to induce the formation of liquid phase which promotes densification and bonding of solid particles at the elevated temperatures. The presence of the liquid phase generally increases the rate of sintering. Solid state diffusion rates are often slow making solid state sintering difficult in many cases and impossible in others such as silicon nitride. Diffusion rates through a liquid phase are at least two or three orders of magnitude higher than diffusion through solids, although; a few exceptions exist such as O₂ diffusion in ZrO₂ or Na diffusion in β-Al₂O₃. Therefore, liquid phase sintering is utilized in materials which would take too long, require much higher temperatures or not sinter at all by solid state sintering. Beyond making diffusion faster, the presence of the liquid minimizes the need for diffusive transport. At very high liquid contents, > 30 vol% liquid,
it is possible to get full densification without any diffusion. The liquid can simply fill all the interstitial space between the solid particles grains.

The liquid present during sintering is usually formed from a mixture of different powders. The interaction of the powders at elevated temperatures forms a two phase mixture which, at equilibrium, would consist of solid particles which have a composition defined by the appropriate solidus and a liquid of the composition given by the liquidus. Often, however, non-equilibrium conditions exist where the solid and liquid phases are not of the composition given by the liquidus and solidus. Liquid phase sintering is generally described as occurring in three stages.

1. Rearrangement
2. Solution - reprecipitation
3. Microstructural Coarsening

Rearrangement leads to very rapid densification in the early stages and contributes little in the later stages of sintering; thus, it is typically thought of as occurring in the first stage. The second mechanism, solution - reprecipitation, occurs throughout the sintering cycle, but is generally considered as occurring in the second stage of sintering as it dominates densification after rearrangement has ceased. What is often termed the third stage of liquid phase sintering, microstructural coarsening, occurs predominantly after densification is complete. In fully wetting systems, grain growth occurs by the solution-reprecipitation mechanism and is therefore appropriately considered in the context of Ostwald ripening. Ostwald ripening is the increase in average grain size driven by the reduction in interfacial energy between the grains and surrounding matrix by diffusion through the matrix phase. If some residual microporousity exists, Ostwald ripening of the porosity may also occur.
Modeling grain growth in the third stage of liquid phase sintering is the focus of this investigation. Prior analytical models, numerical simulations and experimental studies in the area of Ostwald ripening will be reviewed as a basis for this work.

**Analytical Models of Grain Growth**

Greenwood⁴ was the first to consider diffusion-controlled grain growth by Ostwald ripening, but the approach of Lifshitz and Slyozov⁵ as well as Wagner⁶ is the basis of modern studies of this subject. Their combined work is generally known as the LSW theory. In this model, the driving force for grain growth is assumed to be the reduction in interfacial energy between the grain and the surrounding liquid matrix. The mechanism of grain growth is Ostwald ripening. Ostwald ripening is the transport of matter from smaller to larger grains through a continuous matrix driven by the reduction of interfacial energy. The local solubility in the matrix at the surface of a particle is given by the Gibbs-Thomson relationship:

\[
C_R = C_0 \exp \left( \frac{2 \gamma_{sl} V_m}{kR_g T} \right)
\]  \hspace{1cm} (1)

where \( C_R \) is the solubility in the liquid of a spherical particle of radius \( R \), \( C_0 \) is the solubility of an infinitely large particle, \( \gamma_{sl} \) is the solid-liquid interfacial energy, \( V_m \) is the molar volume, \( R_g \) is the gas constant and \( T \) is absolute temperature. For small values of the argument, a series expansion of eq. (1) allows the solubility difference between two particles of different sizes to be written as:
\[
C_{e_1} - C_{e_2} = \frac{2Y_{g_1}V_mC_0}{R_gT}\left(\frac{1}{R_1} - \frac{1}{R_2}\right)
\]  

where \(R_1\) is the radius of grain 1 and \(R_2\) is the radius of grain 2. Grain growth occurs by dissolution of smaller grains, transport through the matrix and precipitation on to larger grains. One of two different steps can control the kinetics of transport from smaller grains to larger ones; diffusion of the solid in the liquid matrix or the interfacial reaction at either the receding or growing interface. Lifshitz and Slyozov modeled only the first case, diffusion-controlled grain growth; whereas, Wagner considered both. Both will be briefly reviewed here.

The derivation consists of two sections. The first considers the growth of a single grain in a random dispersion and the second considers the continuity equations for all the grains.

The growth of an individual particle by diffusion is modeled as a response to a random population of grains which are all far removed. The diffusion equation may be written as:

\[
D\nabla^2 C(x) = \frac{\partial C}{\partial t}
\]  

where \(D\) is the diffusion coefficient, \(r\) is the radial distance and \(t\) is time. The LSW theory solves the diffusion equation by first assuming the steady-state condition, \(\partial C/\partial t = 0\) or equivalently

\[
\nabla^2 C(x) = 0
\]
with boundary conditions:

$$C(x) |_{x=-} = \langle c \rangle$$

(5)

where $\langle c \rangle$ is the average solution concentration in a system of particles of different sizes or equivalently the concentration in equilibrium with the mean curvature of different sized particles and

$$C(x) |_{x=R} = C_R$$

(6)

where $C_R$ is given by eq. (1). The solution to the diffusion eq. (4) with the stated boundary conditions is:

$$C(x) = \langle c \rangle + \frac{[C_R - \langle c \rangle] R}{x}$$

(7)

The boundary condition given in eq. (5) makes the assumption that the distance between grains is large compared to the diffusion length in the matrix phase or stated differently the volume fraction of the grains is very small.

LSW then considers the molar flux, $J$, to a spherical grain of radius, $R$, through its surface area, $4\pi R^2$, which may be written as

$$J = -4\pi R D (C_R - \langle c \rangle)$$

(8)

where $\langle c \rangle$ is the average solution concentration in moles per unit volume and $(C_R - \langle c \rangle)/R = \partial C/\partial r$ evaluated at $r = R$. The molar mass gain rate, $dn/dt$, can be expressed in terms of
the rate of change of the radius of a spherical grain, $dR/dt$:

$$\frac{dn}{dt} = \frac{4\pi R^2}{V_m} \frac{dR}{dt} \tag{9}$$

Recognizing that $J = dn/dt$ and solving for $dR/dt$ gives

$$\frac{dR}{dt} = -\frac{DV_m}{R} (C_R - C) \tag{10}$$

the growth rate of grains with radius, $R$, in a polydispersed system with diffusion-controlled kinetics.

The second case of interfacial reaction-controlled grain growth occurs when the solution or the precipitation reaction at the interface between the precipitate and the liquid is much slower than the diffusion through the liquid. The driving force for the interfacial reaction is the difference between the equilibrium concentration at the surface, $C_R$, and the actual concentration in the liquid immediately adjacent to the surface. Since the diffusion rate is much slower than the interfacial reaction rate, the actual concentration in the liquid at the surface is assumed to be $<C>$. The molar flux, $J$, to a spherical grain of radius, $R$, through its surface area, $4\pi R^2$, is therefore

$$J = -4\pi R^2 k (C_R - <C>) \tag{11}$$

where $k$ is the interfacial reaction rate constant. Equating the molar flux in eq. (11) to the molar mass gain rate given in eq. (9) and solving for $dR/dt$ gives
\[
\frac{dR}{dt} = -v_wk(C_R - \langle C \rangle) \tag{12}
\]

the growth rate of all grains of radius, R, for interfacial reaction-controlled kinetics.

The average grain growth rate and grain size distribution is addressed in the second portion of the derivation. LSW theory uses a grain size distribution function, \( f(r, t) \), defined as:

\[
f(r, t) = \lim_{\Delta r \to 0} \frac{N(r, r+\Delta r, t)}{\Delta r} \tag{13}
\]

where \( N(r, \Delta r, t) \) is the number of particles with radii between \( r \) and \( r+\Delta r \) per unit volume at any given time \( t \). The continuity equation, a mass conservation equation\(^7\), is applied to the grain size distribution function given by eq. (13). The change in number of grains which reach and exceed a given grain size, \( r \), with respect to time is the product of the distribution function and grain growth rate of the individual grain, \( fdr/dt \). The change in number of grains of size, \( r \), with time is the negative derivative of \( fdr/dt \) or:

\[
\frac{\partial f}{\partial t} + \frac{d}{dr} \left( f \frac{dr}{dt} \right) = 0 \tag{14}
\]

Using eqs. (13) and (14) which relate grain size to time and eqs. (10) and (12), the growth rate of individual grains, both Lifshitz & Slyozov, and Wagner derived the average grain growth rate and the steady state particle size distribution. They reported that for the diffusion-controlled case, the time evolution of the average grain size is third order in \( R \):
\[ \bar{R}_t^3 - \bar{R}_0^3 = \frac{8}{9} \frac{D_{a1} V_a C_t}{R_g T} \quad (15) \]

and for the interface reaction-controlled case is second order in \( R \):

\[ \bar{R}_t^2 - \bar{R}_0^2 = \frac{64}{81} \frac{k_{a1} V_a C}{R_g T} \quad (16) \]

At long times, when \( R_0 \ll R_t \), eq. (15) and (16) reduce to:

\[ \bar{R}_t^3 = Kt \quad (17) \]

and

\[ \bar{R}_t^2 = Kt \quad (18) \]

respectively. The magnitude of the error introduced by the simplified grain growth equation for the diffusion-controlled case, at \( R_t = 2R_0 \), is 12.5% and at \( R_t = 2R_0 \), 1%. For the interfacial reaction-controlled case, at \( R_t = 2R_0 \), the error introduced by using the eq. (18) instead of eq. (16) is 25% and at \( R_t = 2R_0 \), 10%. Thus, diffusion-controlled grain growth is less sensitive to the simplified grain growth equation. The exponent of the grain growth equation is used to experimentally identify the rate controlling mechanism in materials.

The grain size distribution functions for the diffusion-controlled case is

\[ f(\rho) = \rho^2 \left( \frac{3}{3+\rho} \right)^{11/2} \exp \left( -\frac{3}{2} \rho \right) \quad \text{for} \quad \rho = \frac{R}{\bar{R}} \leq \frac{3}{2} \quad (19) \]
\[ f(\rho) = 0 \quad \text{for } \rho = \frac{R_3}{R} \geq \frac{3}{2} \quad (20) \]

The grain size distribution for the interfacial reaction-controlled case:

\[ f(\rho) = \rho \left( \frac{2}{2-\rho} \right)^{\gamma} \exp \left( \frac{-3\rho}{2-\rho} \right) \quad \text{for } \rho = \frac{R_3}{R} < 2 \quad (21) \]

\[ f(\rho) = 0 \quad \text{for } \rho = \frac{R_3}{R} > 2 \quad (22) \]

The grain size distributions for diffusion- and interfacial reaction-controlled grain growth are graphically presented in figures 1a and b.

Many investigators have modified diffusion-controlled LSW theory to include finite volume fraction of grains using a variety of techniques. All have found that \( R^3 \propto t \) and broadening of the grain size distribution with increasing volume fraction solid. But the actual steady state grain size distributions vary albeit slightly with each of the techniques. The results of some of the analytical models will be reviewed briefly. Ardell\(^8\) modified the LSW theory to consider finite volume fraction of grain by assuming that the diffusion of solute to a growing grain will depend on the average interparticle distance for randomly dispersed spherical grains of the same size. Ardell’s method is increasingly accurate as the volume fraction of grains, \( \phi \rightarrow 0 \), since his assumption of a uniform cutoff distance around spherical grains is not realistic at higher \( \phi \). While Ardell’s modified LSW shows a trend in grain size distributions with increasing \( \phi \) that is qualitatively of the form observed in
experiments; direct comparison is not possible because the assumptions used in the model are not accurate for realistic volume fractions. The grain size distributions at finite volume fractions of grains are shown in figure 2. At $\phi = 0$, the grain size distribution is the same as that predicted by diffusion-controlled LSW theory. As $\phi$ increases, the grain size distribution broadens. At $\phi = 1$, the grain size distribution is that predicted by interfacial reaction-controlled LSW theory.

Variations of Ardell’s method have been studied by Tsumuraya and Miyata\textsuperscript{9}. They defined a radius of influence around each grain using six different methods and studied grain growth of all six. All six models gave slightly different grains size distributions. The grain size distributions of the two models which they found to be in closest agreement with experimental data available in the literature are shown in figure 3. The grain size distributions predicted by both models are very similar and broaden as $\phi$ increased. Although, they consider solid fractions as large as $\phi = 0.5$; their assumption of a sphere of influence around spherical grains renders their models accurate only at low volume fractions of grains.

Brailsford and Wynblatt\textsuperscript{10} used a chemical rate theory approach to model grain growth. Their model assumes that all grains are spherical and all grain of a given size behave identically with spherical symmetry. Thus, their model becomes less accurate as the size, shape and geometry of the grains deviates from uniformly spaced spherical grains which is inevitable as the volume fraction of the grains increase. The grain size distribution for their model is shown in figure 4. The grain size distribution peak shifted to lower $R/<R>$ with increasing $\phi$, but remained at $R$ greater than $<R>$ even at $\phi = 0.80$. 
Voorhees and Glicksman\textsuperscript{11,12} and later Yao et al.\textsuperscript{13} studied Ostwald ripening by applying numerical techniques to the multi-particle diffusion problem using an approach based on Ewald-summation. The solution to the diffusion equation they used assumes that all grains are spherical and the distances between grains is much larger than the grain radii. These assumptions make this numerical technique less accurate at high volume fraction of grains. Yao et al. did not even attempt to study grain volume fractions larger than $\phi = 0.06$ with this method. The grain size distribution obtained by Voorhees and Glicksman and by Yao et al. are given in figures 5 and 6, respectively. The grain size distributions predicted by Voorhees and Glicksman are the broadest of the ones reviewed here, with grains as large as $R = 2.24\langle R\rangle$ at $\phi = 0.5$.

Marqusee and Ross\textsuperscript{14} used a multiple scattering approach to consider Ostwald ripening with finite volume fractions of grains. The highest volume fraction of solid they considered was 0.10. The resultant grain size distributions, shown in figure 7, differ qualitatively from the others in that the peak shifts to the right with increasing $\phi$.

DeHoff\textsuperscript{15} developed a communicating neighbor model for diffusion-controlled grain growth based on the evolution of aggregate curvature of all grains. In sharp contrast to the other theories that have been considered so far, the communicating neighbor model recognizes that the local concentration gradients surrounding each grain are determined by neighboring grains which are not necessarily spherical. DeHoff calculated a steady state particle size distribution assuming that all grains will be spherical and that the curvature of neighboring grains and the diffusion lengths between them are uncorrelated. The spherical grain size distribution he obtained is identical to Wagner's interfacial reaction-controlled grain size distribution\textsuperscript{4} (see Figure 1b) and is not a function of $\phi$ as long as the grains
remain spherical and the diffusion lengths between are uncorrelated.

Fang et al.\textsuperscript{16} used a numerical technique to study grain growth by Ostwald ripening. They used finite differences to solve the continuity equation given in eq. 14 coupled with DeHoff's\textsuperscript{15} grain growth equation. They showed that differing initial grain size distributions approach a steady state grain size distribution as shown in figure 8. Unlike all previous models, theirs predicts a grain size distribution skewed to lower sizes.

**Grain Growth Simulation Techniques**

Grain growth theories have proven useful in understanding grain growth kinetics including the time dependence of the average grain size and the steady-state grain size distribution. However, they all make some simplifying assumptions about grain growth geometry or diffusion fields around the grains, so that the problem may be solved analytically. Motivated by a desire to eliminate these approximations, a variety of numerical simulation techniques have been developed to study grain growth in single phase, polycrystalline materials. These simulation techniques will be reviewed, and the limitation of most techniques in addressing the Ostwald ripening problem will be discussed. A couple of simulation techniques for liquid phase sintered materials have been developed and will also be reviewed.

The Voronoi method\textsuperscript{17} and variations\textsuperscript{18,19} of the Voronoi method are nucleation based techniques used to study the morphological features. The Voronoi technique simultaneously seeds the simulation space at random locations with the desired density of nuclei. These nuclei then grow isotropically until they impinge onto another grain. Once impingement occurs both grains stop growing at the impingement point, but continue to
grow in other directions until impingement. Variations of the Voronoi technique are the Johnson-Mehl technique\textsuperscript{18}, which uses a time dependent nucleation function to seed grain growth, and the Ito-Fuller technique\textsuperscript{19}, which uses both simultaneous and continuous nucleation with anisotropic growth rates. While, Voronoi techniques provide morphological information about systems which undergo a phase transformation or recrystallization; they cannot be used to study Ostwald ripening since they are non-conservative.

Other techniques depend on morphological features such as grain boundary curvature or grain edge length to drive grain growth. Curvature driven grain growth\textsuperscript{20,21,22} exploits the phenomenological relationship between grain boundary velocity, \( V \), and grain boundary curvature, \( \kappa \).

\[
V = \mu \kappa
\]  

(23)

where \( \mu \) is grain boundary mobility. Information about both grain growth kinetics and grain size distribution can be obtained from these types of simulations. Chaix et al.\textsuperscript{22} used a curvature-driven technique to simulate interfacial reaction-controlled Ostwald ripening. Theirs is a three-dimensional simulation which yielded information on average grain growth rate and limited information on grain size distribution at \( \phi = 0.2 \). Curvature-driven grain growth simulation, however, is not easily adapted to the study of diffusion-controlled grain growth, the focus of the present study.

Line tension-driven grain growth\textsuperscript{23,24,25} is similar to curvature-driven grain growth. All grains are assumed to have straight edges which meet at vertices. The sum of the line tensions of all lines meeting at each vertex determines the displacement of each vertex with a velocity, \( V \), given by:
\[ V = \mu \sum \sigma_i \]  \hspace{1cm} (24)

where \( \mu \) is the vertex mobility and \( \sigma_i \) is the line tension of line \( i \). The initial microstructure is a Voronoi network. Grain growth is simulated by displacing each vertex according to eq. (24). When a grain (triangle) becomes smaller than some critical value, the triangle is replaced with a vertex and grain growth continues. Line tension-driven grain growth assumes no contribution from grain boundary curvature, which is not entirely realistic and cannot be applied to the problem at hand.

Srolovitz and coworkers have used a Monte Carlo-based technique to study a variety of solid state grain growth problems including normal polycrystalline grain growth\(^{26,27,28,29}\), abnormal grain growth\(^{30,31}\), grain growth with inert inclusions\(^{32}\) as well as grain growth in a two phase system\(^{33}\). This technique has the advantage of providing kinetics and topological information for a wide range of problems; however, it has been suggested\(^{34}\) that the use of discreet, digitized images may simulate migration of kinks and ledges yielding a grain growth exponent, \( n = 2.4 \) \(^{27,29,35}\), rather than \( n = 2.0 \) as predicted by solid state grain growth theory\(^{36}\).

Exact solutions by numerical simulation of grain growth in liquid phase sintered materials have also been used. Nikolic and Huppmann\(^{27}\) simulated chemically driven, diffusion-controlled grain growth during liquid phase sintering. The solution-rep Precipitation process is driven by reduction in free energy due to formation of a solid solution and a liquid solution from the initially pure solid component in a liquid solution. An initial configuration is defined and the general diffusion equations are solved numerically using the
finite differences method. Although, this technique can easily be modified to simulate
Ostwald ripening and has the advantage of incorporating a wide number of variables and
providing information on many aspects of the grain growth problem; it is computationally
intensive and to date has only been applied to simple geometries with 2 or 3 grains.
Primarily motivated by the computational tractability, it is an extension of the Monte Carlo
approach rather than a finite difference model that is developed in this work.

**Experimental Studies of Grain Growth**

Grain growth kinetics in liquid phase sintered materials has been studied in the ZnO-
Bi₂O₃⁴⁸. ZnO-BaO⁴⁰, UO₂-Al₂O₃⁴¹, MgO-V₂O₅⁴², MgO-CaO⁴³, Fe-Cu⁴⁴,⁴⁵, Co-
Cu⁴⁶,⁴⁷, Mn-Mg⁴⁸, Ti(C,N)-Ni⁴⁹ and many other metallic systems the results of
which have been summarized by German⁵⁰. The majority of these studies have shown the
grain growth exponent, n, is 2 or 3. Based on the grain growth exponent, most of the
investigators have inferred interfacial reaction- (n = 2) or diffusion-controlled (n = 3) grain
growth. Others, however, have reported n ranges from 2 to 8⁴⁴,⁴⁶,⁴⁸ depending on the
composition, liquid content and temperature during grain growth. Some investigators have
reported difficulty in determining the rate-controlling mechanism (i.e. if n = 2 or 3) for grain
growth from the time evolution of grain size and have examined grain size distributions as
a means of determining the rate controlling mechanism⁴⁹,⁵⁰,⁵¹,⁵². This, however, is not a
satisfactory solution as the different analytical models have given rise to several grain size
distributions. Distinguishing the rate controlling mechanism based on grain size distributions
is difficult, especially when one considers the grain size distribution predicted by interfacial
reaction-controlled LSW theory overlaps the grain size distributions predicted by diffusion-
controlled grain growth theories.

Fang and Patterson\textsuperscript{53} studied the effect of initial particle size distribution on kinetics and evolution of the grain size distributions during liquid phase sintering in the W-14Ni-6Fe system. They found $n = 3$ held most of the time, except during initial stages when the grain size distribution was changing rapidly. The steady state grain size distribution they obtained for solid fraction of 0.60 is shown in figure 9. Significantly, they also found that the quasi-steady state distribution was unaffected by the nature of the initial distribution. Specifically, they started with narrow and broad grain size distributions and promoted grain growth in both samples. They found that the grain size distribution in both samples approached a quasi-steady state distribution.

**Two-Dimensional Grain Growth**

The solution to the diffusion equation given by eq. (4) in two-dimensional space is:

$$C(r) = A + B \ln r$$

(25)

The boundary condition given in eq. (5) results in a divergence for eq. (25), since $\ln \infty = \infty$; thus, this approach cannot be used for the two-dimensional case. Several investigators have used various techniques to study Ostwald ripening in two-dimensions. Ardell\textsuperscript{54} used the mean free distance between neighboring grains as a cutoff distance to solve the diffusion equation. Marqusee\textsuperscript{55} and Zheng and Gunton\textsuperscript{56} used an effective medium approach. Yao et al.\textsuperscript{13} used numerical solution to the diffusion equation to study Ostwald ripening in two-dimensions. Rogers and Desai\textsuperscript{57} applied a numerical technique, finite differences to the Cahn-Hilliard equation of phase separation\textsuperscript{58}, to study this problem. All reported $R^3 \propto t$
except Rogers and Desai who reported $R^{3A} \propto t$, a value 12% higher than others', for their numerical method. Rogers & Desai\textsuperscript{57} and Ardell\textsuperscript{59} extended Lifshitz and Slyozov's theory to two-dimensions. The grain size distributions, shown in figures 10 to 14, are different from each other, but very similar to the three-dimensional distribution of corresponding technique. As in the three-dimensional case, broadening of the grain size distributions and increasing skewness (skewness becomes less negative) are predicted with increasing volume fraction grains; although, the distribution shapes and trends vary for each theory. The two-dimensional grain size distribution is slightly narrower and more peaked compared to the three-dimensional grain size distribution obtained by the same technique.

**MOTIVATION**

Although, Ostwald ripening has been the subject of many investigations, it is still not well understood. The analytical models are not accurate at realistic volume fraction of grains or for cases where the grain shapes deviate from spheres. DeHoff’s\textsuperscript{15} communicating neighbor model is capable of considering high solid fractions. Unfortunately, his model yields results in terms of the curvatures of the grains, a quantity which is not measurable by conventional stereological techniques. Chaix et al.\textsuperscript{22} simulated Ostwald ripening in the case of interfacial reaction-controlled grain growth at 20 vol% grains. Fang and Patterson\textsuperscript{16} used a numerical technique to study diffusion-controlled Ostwald ripening, also at 20 vol% grains. Simulations at higher volume fractions of solids during Ostwald ripening do not exist. Thus, a numerical simulation technique to study the kinetics and grain size distribution of two-dimensional, diffusion-controlled grain growth in liquid phase sintered materials is proposed.
OBJECTIVE

The objectives of this work were:

(a) to develop a Monte Carlo based model of grain growth in liquid phase sintered materials that gives accurate results at high solid fractions, and that places no restrictions on the spatial distribution of grains or grain shapes;

(b) to characterize the model by developing relations between the simulation parameters and macroscopic (continuum) expressions;

(c) to use the model to study the kinetics and shape of grain size distributions of two-dimensional, diffusion-controlled grain growth in an idealized liquid phase sintered material over a range of solid fractions;
Figure 1. Grain size distribution predicted by LSW for
(a) diffusion- and (b) interface reaction-controlled kinetics.
Figure 2. Grain size distribution predicted by Ardell

Figure 3. Grain size distributions predicted by Tsumuraya and Miyata
Figure 4. Grain size distribution predicted by Brailsford and Wynblatt

Figure 5. Grain size distributions predicted by Voorhees and Glicksman

Figure 6. Grain size distributions predicted by Yao et al.
Figure 7. Grain size distributions predicted by Marqusee and Ross

Figure 8. Grain size distribution predicted by Fang et al.'s simulation technique.
Figure 9. Grain size distribution experimentally determined by Fang and Patterson
Figure 10. Grain size distribution predicted by Ardell

Figure 11. 2-D grain size distributions predicted by Marqusee.
Figure 12. 2-D grain size distribution predicted by Zeng and Gunton

Figure 13. 2-D grain size distribution predicted by Yao et al.
Figure 14. 2-D grain size distribution predicted by Rogers and Desai.
Chapter 2

SIMULATION METHODOLOGY

The Monte Carlo method was developed by Metropolis and co-workers\textsuperscript{60,61} in the mid-1940's. Since then, it has been applied to many scientific and engineering problems. In materials science, Monte Carlo techniques have been used to study diffusion\textsuperscript{62,63}, ionic transport\textsuperscript{64}, magnetic properties\textsuperscript{65}, phase transitions\textsuperscript{66,67}, grain growth\textsuperscript{26} and many other phenomena. In this investigation, a simulation technique based on the Monte Carlo method was used to study grain growth in liquid phase sintered materials.

The Q-state, Potts, Monte Carlo simulation technique adapted by Srolovitz et al.\textsuperscript{26} to study grain growth was modified to simulate grain growth in liquid phase sintered materials. The Potts model is a discreet, statistical mechanical model with more than two states; Q is the number of states\textsuperscript{68}. The interaction energies between the various states were defined and used to determine the internal energy of that particular system. Detailed characteristics of the Potts model are presented in this chapter.

This technique was chosen for several reasons. It is easily adaptable to a two-phase system, i.e. solid grains in a liquid matrix. The technique is able to identify solid grains, a liquid matrix, the interface between solid and liquid phases and grain boundaries between grains. Furthermore, the simulation technique can simulate solution of the solid phase in the liquid phase and diffusion through the liquid phase. It also is sufficiently versatile to allow adaptation to more complex problems of microstructural evolution.

The microstructure was represented digitally on a two dimensional, square lattice with periodic boundary conditions in both the X- and Y- directions. The lattice size was at
least 200 x 200 sites and ranged up to 300 x 300 sites. The lattice was populated with a canonical ensemble of two types of entities. A canonical ensemble is a collection of a fixed number of entities which occupies a fixed volume at a constant temperature. The average energy of a canonical ensemble may fluctuate and its energy density is given by Boltzmann statistics. Entity A represented the solid phase and entity B, the liquid phase. The A-sites were allowed to assume one of a hundred degenerate states, \( q_A \in \{1, 2, \ldots, 100\} \). Each state, \( q_A \), can be considered to be a different crystallographic orientation where the orientation difference between consecutive integers, \( q_A \), is \( 2\pi/Q \). The B sites were allowed to assume only one state, \( q_B = -1 \). The negative number has no significance other than to make computation easier. A digitized microstructure consisting of a few solid grains surrounded by a liquid is shown figure 1. The grains are features consisting of contiguous sites of the same state, \( q_A \).

Conserved dynamics were used. While, A-sites could assume any value \( q_A \) between 1 and 100; the total numbers of A-sites and B-sites remained constant. The Hamiltonian, \( H \), for the simulation was the sum of the interaction energy between each site and each of its first and second nearest neighbors

\[
H = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{8} E(q_i q_j)
\]  

(1)

where \( N \) was the total number of sites, \( E \) was the bond energy between neighboring sites in arbitrary units of energy and was a function of the state of the two neighboring sites, and \( q_i \) was the phase and orientation of the entity occupying site \( i \). The Hamiltonian has units of energy, the same as that for \( E \), the bond energy. The bond energy, \( E \), was defined so that
only neighbors of different states have a bond energy; thus, only bonds between unlike neighboring sites contribute to the Hamiltonian. The solid-liquid (A-B) interfacial energy, $\gamma_{il}$, and the grain boundary energy between two solid grains (A$_{i}$-A$_{j}$) of different orientation, $\gamma_{ij}$, were defined by their respective bond energies. The liquid phase cannot have liquid-liquid interfaces in the simulations because only a fully miscible liquid is considered. Assigning only one state to the liquid sites insured that no liquid-liquid interfaces occurred, $\gamma_{il} = 0$. The interfacial energies, $\gamma_{il}$ and $\gamma_{ij}$, can be calculated as follows:

$$\gamma_{i\ell j} = \frac{E(q_{i}, q_{j}) N_{i\ell j}}{L}$$  \hspace{1cm} (2)

where $E$ is the bond energy and is a function of neighboring phases and states, $q_{i}$ and $q_{j}$, $N_{i\ell j}$ is the number of the unlike bonds at the interface, and $L$ is the length of the interface. The units of interfacial energy, $\gamma$, are in energy per unit length rather than energy per unit area because a two-dimensional space is being used for this simulation. A consequence of eq. (2) is that the ratio of $\gamma_{il}$ to $\gamma_{ij}$ can be varied by the varying $E(A,A)$ and $E(A,B)$.

The use of a square lattice to digitize the microstructure introduces some anisotropy to the interfacial energies. Consideration of both first and second nearest-neighbors interactions minimizes lattice anisotropy effects as shown by Holm et al.\textsuperscript{71} The Wulff plots of a grain surrounded by the liquid with nearest neighbor interactions only as well as with first and second nearest neighbors interactions were calculated using eq. (2). The effectiveness of using second nearest neighbors to reduce the anisotropic effects is evident in figure 2.

The pathway for material transport was dissolution of the solid in the liquid phase, diffusion of the solid through the liquid and precipitation of the solid. No solid state
diffusion was permitted in the simulation. This is justified as diffusion in actual solids is typically several orders of magnitude lower than in a liquid.

The step-by-step simulation technique used is reviewed below. The choice of this particular sequence of steps is discussed in chapter 4, Simulation Technique.

1. The two-dimensional, square lattice was populated with the desired composition (fraction of A-sites, \( X_A \), and B-sites, \( X_B \)). The lattice was initialized by placing the A- and B- entities at randomly selected lattice sites.

2. A lattice site was chosen at random and one of the neighboring sites was chosen at random from its eight first and second nearest neighbors.

3. If one site was an A-site and the other a B-site, then the simulation continued to step 4; if not, then to step 7. If both were A-sites, the exchange was not permitted because solid state diffusion was not permitted. If both sites were B-sites, the exchange does not result in a change to the microstructure; therefore this exchange was unnecessary.

4. A new orientation for the A-site was chosen at random from \( Q (=100) \) possible orientations.

5. The new configuration, A- and B-sites exchanging places with the A-site assuming the new orientation, was considered. If the exchange resulted in the A-site going directly from one grain to the next grain, the exchange was rejected and the simulation jumped to step 7 (see chapter 4); if not, it continued to step 6.

6. The Metropolis\(^{6}\) algorithm was used to determine if the new configuration was accepted or rejected. The Metropolis algorithm used the Hamiltonian given in equation (1) as the equation of state in conjunction with Boltzmann statistics to determine the microstructural evolution. The exchange probability, \( w \), is given by
\[ w = \exp\left(-\frac{\Delta H}{k_b T}\right) \text{ for } \Delta H > 0 \quad (3a) \]

\[ w = 1 \text{ for } \Delta H \leq 0 \quad (3b) \]

where \( k_b \) is the Boltzmann constant, and \( T \) is absolute temperature and has units of bond energy divided by the Boltzmann constant. In this work, all temperatures will be given as \( k_b T \) with units of energy rather than \( T \).

7. The time is incremented by \( 1/N \), where \( N \) is the total number of sites and then the program returned to step 2. Note: time was given in units of Monte Carlo step, MCS. At time = 1 MCS, the number of attempted exchanges was equal to the total number of sites in the simulations.

Periodically the microstructure was examined for grains close to each other which had the same orientation, \( q \). The orientations of such grains were reset to prevent coalescence (two or more grains of same \( q \), merging to form one large grain). This subject is discussed in detail in chapter 4, Simulation Technique.
Figure 1. A digitized microstructure of several grains in a liquid matrix. B-sites are -1 and A-sites are all integers > 0.
Figure 2. Wulff plot for 2-D lattice.

- □ 1st nearest neighbor interaction
- ○ 1st & 2nd nearest neighbor interaction
Chapter 3

SIMULATION THERMODYNAMICS

The statistical-mechanical nature of the canonical ensemble coupled with the Hamiltonian given in equation (1) of chapter 2 results in certain thermodynamic behavior. These will be reviewed in this section before proceeding to the grain growth simulations.

WETTING

The first thermodynamic feature was wetting of the solid by the liquid as a function of the interfacial energies. It has been shown both analytically and experimentally that the wetting of the solid phase by the liquid phase and the continuity of the solid phase in the final microstructure is controlled by the relative magnitudes of the solid-solid and solid-liquid interfacial energies, $\gamma_s$ and $\gamma_l$. A set of simulations was run to verify that the algorithm reproduced expected behavior. In these simulations, the ratio of $\gamma_s$ to $\gamma_l$ was varied and the effect on wetting of the solid by the liquid and continuity of the solid were observed. Microstructures generated with different interfacial energies at composition, $X_A = 0.50$, $Q = 100$, and temperature, $k_B T = 1.1$ are shown in figure 1. For the case with $\gamma_s > 2\gamma_l$, the liquid completely surrounded and wetted the solid grains. At $\gamma_s = 2\gamma_l$, few grains share a grain boundary. As the ratio $\gamma_s/\gamma_l$ increased, wetting continued to decrease and the continuity of the solid increased.

DISSOLUTION

For the purposes of this simulation, dissolved sites were defined as single sites with no neighbors of the same state. For example, an A-site surrounded by B-neighbors, is considered to be dissolved in the liquid matrix. Likewise a B-site surrounded by A-sites is
considered to be dissolved in the solid grains. Dissolution is a thermally activated process with an associated enthalpy and entropy of dissolution. This section will consider the thermally activated nature of dissolution in the simulation and discuss the enthalpy of dissolution. The entropy of dissolution will be discussed in a later section in this chapter.

A set of simulations was run to determine solubility as a function of temperature at constant mole fraction A and B ($X_A = X_B = 0.5$). In these simulations, the solid was permitted to assume only one state, $Q = 1$. The bond energies were $E_{AA} = 0$ because the A component could only assume one state, $E_{AB} = 1.0$ and $E_{BB} = 0$. A single, solid, circular grain was allowed to come to equilibrium with the liquid surrounding it at a given temperature. The concentration of the liquid solution at $k_B T$ was determined for such a system. It is plotted in figure 2a on an Arrhenius plot, logarithmic solution concentration versus reciprocal temperature. The slope of such a plot is the enthalpy of dissolution. The enthalpy of dissolution was expected to be, $\Delta H_D = 8.0$, since each dissolved site must have eight A-B bonds with an energy, $\Delta E = 8E_{AB} = 8.0$. The line corresponding to enthalpy, $\Delta H = 8.0$ is also plotted on figure 2a. The agreement between the data and the $\Delta H = 8.0$ curve is good.

The Arrhenius plot of dissolution and the enthalpy of dissolution will be addressed again in a later section. It was also found that in this symmetric system (i.e. $Q = 1$ for both A and B) the solubility of the B-sites, in the solid, A, was exactly the same as that of A-sites in the liquid as shown by figure 2b.

GIBBS-THOMSON RELATION

Grain growth by the Ostwald ripening mechanism occurs in systems exhibiting behavior formalized by the Gibbs-Thomson relationship,

$$C_r = C_w \exp \left( \frac{\Delta G_f}{RT} \right)$$  \hspace{1cm} (1)
where $\Delta G_r$ is the interfacial energy contribution to the molar free energy. For small values of the exponent, $\Delta G_r/RT \ll 1$, eq. (1) can be approximated as

$$C_r = C_e \left( 1 + \frac{\Delta G_r}{RT} \right)$$  \hspace{1cm} (2)

The derivation of Porter and Easterling\textsuperscript{75} for three dimensional space is reproduced here. For a spherical grain, the molar interfacial free energy, $\Delta G_r$, is

$$\Delta G_r = \frac{dE_f}{dn} = \gamma \frac{dA}{dn} = \gamma \frac{2V_m}{r}$$  \hspace{1cm} (3)

where $E_f$ is interfacial energy, $A$ is interfacial area of a spherical grain of radius $r$, $n$ is the number of moles in the grain and $V_m$ is the molar volume. Substituting $\Delta G_r$ from eq. (3) into eq. (2) gives the more familiar form of the Gibbs-Thomson relationship

$$C_r = C_e \left( 1 + \frac{2\gamma V_m}{rRT} \right)$$  \hspace{1cm} (4)

In order to accurately simulate Ostwald ripening, the Gibbs-Thomson relationship must hold in the simulations. This was tested by determining the solubility as a function of grain size.

First, the Gibbs-Thomson relation is derived for a two-dimensional square lattice. The interfacial energy, $E_f$, is:

$$E_f = N_{AB} F_{AB}$$  \hspace{1cm} (5)
where $N_{AB}$ is the number of A-B bonds and $E_{AB}$ is the bond energy. The molar free energy due to the interface, $\Delta G_r$, is

$$\Delta G_r = \frac{dE_r}{dn} = E_{AB} \frac{dN_{AB}}{dn} = E_{AB}N_A \frac{dN_{AB}}{da}$$  \hspace{1cm} (6)$$

where $n$ is the number of moles inside the grain, $a$ is the grain area given in the number of sites in the grain and $N_A$ is Avogadro’s number. The function $dN_{AB}/da$ for circular grains was determined numerically. Circular grains of component A with radii ranging from 4 to 40 surrounded by component B were digitized. The number of A-B bonds, $N_{AB}$, at the perimeter of the grain was determined as a function of grain area, $a$. The results are presented in figure 3. It was found that the function:

$$N_{AB} = 10.8 \sqrt{a}$$  \hspace{1cm} (7)$$

fits the data given in figure 3. The derivative of this function is easily calculated

$$\frac{dN_{AB}}{da} = \frac{5.4}{\sqrt{a}}$$  \hspace{1cm} (8)$$

By comparing eq. (7) and (8), one can see that

$$\frac{dN_{AB}}{da} = \frac{N_{AB}}{2a}$$  \hspace{1cm} (9)$$

Substituting eq. (9) and (6) in (1) gives the Gibbs-Thomson relationship for a square lattice
\[ C_r = C_0 \exp \left( \frac{N_A E_{AB} N_{AB}}{2aRT} \right) \]  \hspace{1cm} (10)

Since \( N_A/R = 1/k_b \), eq. (10) becomes

\[ C_r = C_0 \exp \left( \frac{E_{AB} N_{AB}}{2a k_b T} \right) \]  \hspace{1cm} (11)

The quantities \( N_{AB} \) and \( a \) are easily determined to verify the Gibbs-Thomson relationship.

A set of simulations was run in which a single circular grain of varying size was allowed to come to equilibrium with the liquid at temperature, \( k_b T = 1.4 \). Once equilibrium was attained, the solubility was measured as a function of surface free energy, \( E_{AB} N_{AB}/2a \). The surface free energy was measured rather than size, \( a \), because thermal fluctuations gave grains which were not perfectly circular. The A-component could only assume one state, \( Q = 1 \). The simulation was run at \( k_b T = 1.5 \) for 20,000 MCS. Then the temperature was reduced to \( k_b T = 1.4 \) and the system was allowed to equilibrate by running the simulation for 50,000 MCS. Once, equilibrium was attained, the solution concentration, \( C \), and molar interfacial energy, \( \Delta G_r \), were calculated at intervals of 2 MCS for 100 configurations. The average values of these 100 configurations are presented in figure 4, a plot of solution concentration as a function of molar interfacial energy. The solubility did increase with increasing surface free energy and the measured solubilities were in good agreement with that predicted by eq. (11) for \( C_0 = .0027 \), i.e. \( C_r \) is plotted as a function of \( E_{AB} N_{AB}/2a \) at \( k_b T = 1.4 \). Thus, the Gibbs-Thomson relationship was validated for the discreet two-dimensional simulation used in this investigation.
THE EFFECT OF Q ON SOLUBILITY

One set of experiments were run to determine solubility as a function of the total number of orientations the A-sites could assume, Q, at constant temperature, $k_B T = 1.4$. Fully wetting conditions were used ($\gamma_{AA} = 2.5$ and $\gamma_{AB} = 1.0$), and Q was varied from 1 to 200. A single solid grain was allowed to reach equilibrium with the surrounding liquid before measuring solubility in the same manner described before.

The liquid solution concentration increased with increasing Q as shown in figure 5. In an attempt to understand the origin of this behavior, the free energy of mixing is considered as a function of Q. The solution concentration, C, is proportional to the free energy of mixing, $\Delta G_m$, as:

$$ C = \exp \left( -\frac{\Delta G_m}{k_B T} \right) $$

(12)

where $\Delta G_m$ is

$$ \Delta G_m = \Delta H_m - T \Delta S_m $$

(13)

and $k_B$ is the Boltzmann constant, T is absolute temperature, $\Delta H_m$ is the enthalpy of mixing and $\Delta S_m$ is the entropy of mixing. For an ideal solution, the configurational entropy of mixing is given by the Boltzmann equation

$$ S = k_B \ln \omega $$

(14)

where $\omega$ is a measure of randomness. The randomness of a mixture is the number of distinguishable ways that the constituents can be arranged on a lattice and is given by
\[ \omega = \frac{N!}{N_1! N_2! \ldots N_n!} \]  

(15)

where \( N \) is the total number of sites, \( N_i \) is the number of sites occupied by component \( i \) and \( n \) is the total number of components. Substituting eq. (15) into eq. (14) and using Stirling’s approximation, \( \ln N! = N \ln N - N \), yields

\[ \Delta S_m = -N K_B \sum_i x_i \ln x_i \]  

(16)

where \( x_i = \frac{N_i}{N} \). The entropy of mixing for the simulation can be calculated using eq. (16).

For a liquid solution of concentration \( C \), the mole fraction of component B is \( (1-C) \). Since the A component can assume one of \( Q \) different states with equal probability, the mole fraction of each state is \( \frac{C}{Q} \). Substituting these mole fractions into eq. (16) yields the entropy of mixing for the liquid solution

\[ \Delta S_m = -N K_B \left( (1 - C) \ln(1 - C) + \sum_{i=1}^{Q} \frac{C}{Q} \ln \left( \frac{C}{Q} \right) \right) \]  

(17)

and

\[ \sum_{i=1}^{Q} \frac{C}{Q} = C \]  

(18)

so

\[ \Delta S_m = -N K_B \left( (1 - C) \ln(1 - C) + C \ln \left( \frac{C}{Q} \right) \right) \]  

(19)
The enthalpy of mixing, $\Delta H_m$, is

$$\Delta H_m = N_{AB}E_{AB}$$  \hspace{1cm} (20)$$

where $N_{AB}$ is the number of A-B bonds and $E_{AB}$ is the bond energy for A-B neighbors. For a solution of concentration $C$, $N_{AB} = 8CN$ and eq. (20) becomes

$$\Delta H_m = 8CNE_{AB}$$  \hspace{1cm} (21)$$

since each dissolved A-site has eight B-neighbors with the bond of energy, $E_{AB} = 1.0$. Substituting the enthalpy and entropy terms into eq. (21) gives

$$\Delta G_m = 8CNE_{AB} + Nk_BT\left[(1-C)\ln(1-C) + C\ln\left(\frac{C}{Q}\right)\right]$$  \hspace{1cm} (22)$$

The equilibrium concentration, $C$, will occur at the minima in $\Delta G_m$ or at

$$\frac{\partial \Delta G_m}{\partial C} = 0$$  \hspace{1cm} (23)$$

The equilibrium solution concentration at various $Q$, were obtained by substituting eq. (22) into eq. (23)

$$C = \frac{Q\exp\left(\frac{-8\Phi}{k_BT}\right)}{1 + Q\exp\left(\frac{-8\Phi}{k_BT}\right)}$$  \hspace{1cm} (24)$$
The measured solution concentration and eq. (24) are plotted in figure 5. The calculated solution concentrations at low Q are in good agreement with those observed in the simulations. While the trend in the calculated solution concentration with increasing Q is similar to that observed in the simulations; the calculated concentrations are higher than those observed in the simulations. This discrepancy is attributed to the assumptions made in the calculations. The entropy of mixing was estimated assuming an ideal solution. Clearly, the solution in the simulation is not an ideal solution, since $\Delta H_m > 0$. Furthermore, at the solution concentration increases, the A-sites in solution start to interact with each other. These interactions will increase $\Delta H_m$. These factors lead to some ordering which would yield a lower entropy and thus, a lower solution concentration.

Earlier in this chapter, the Arrhenius behavior for the Q = 1 case was presented. It was stated that the slope of the Arrhenius plot ($\ln C$ vs $k_B T^{-1}$) was expected to be 8.0, since the enthalpy was expected to be, $\Delta H_m = 8.0$. The temperature dependence of solution given by eq. (24) shows this is not so. The quantity $C/(1-C)$

$$\frac{C}{1-C} = Q \exp\left(-\frac{8\phi}{k_B T}\right)$$  \hspace{1cm} (25)

is the one that exhibits Arrhenius behavior. However, $C/(1-C) = C$ because $1 >> C$ at $Q = 1$. The Arrhenius plot presented in figure 2a is almost identical to one plotted as $C/(1-C)$ versus $k_B T^{-1}$ as shown in figure 6.

As Q increases, the configurational entropy of the system also increases resulting in higher solubility of the solid in the liquid. The solubility of the B component, in the solid phase remained constant and was not a function of Q. This feature permits the simulator to
vary the solubility of the of the A component in the liquid by varying Q; while, keeping the B component virtually insoluble in the solid grains.

**LIQUIDUS TEMPERATURE**

Dissolved sites are defined as single sites with no neighboring sites of the same state. At high temperatures, all the A-sites are single sites surrounded by B-sites or A-sites of different q. This complete disordering of A- and B-sites can be considered to form only one phase, the liquid phase. The temperature at which this occurs will be defined as the liquidus temperature, $T_c$, since it is analogous to the liquidus temperature in an actual two-component system.

The liquidus temperature was determined as a function of composition. Fully wetting conditions were used with $Q = 100$. The simulations were initialized with a single grain of component A surrounded by component B. The composition was varied by varying the size of the single grain. The grain was allowed to come to equilibrium with the surrounding liquid at different temperatures. The equilibrium concentration of the liquid was determined as function of temperature using the following relationship

$$C = \frac{A1S}{A1S + BS}$$  \hspace{1cm} (26)

where $A1S$ is the number of single A-sites in the liquid and $BS$ is the number of B-sites in the liquid. These experiments were run in temperature increments of $k_B T = 0.1$. The results of these simulations are presented in figure 7, a plot of the liquidus temperature as a function of composition. As component A decreased, the liquidus temperature decreased in a manner similar to that typically observed for a two-component system.
While the solubility of component A in the liquid phase increased drastically with temperature, the solubility of component B in the solid phase was negligible ($\leq 1\%$) over the entire range of compositions and temperatures studied. This is a consequence of allowing the A component to assume one of 100 different states while allowing the B component to assume only 1 state, i.e. $Q >> 1$. This situation is desirable to study grain growth by Ostwald ripening as the solid phase is soluble in the liquid phase, but the liquid phase is virtually insoluble in the solid phase.
Figure 1. Microstructure of grain wetting and contiguity at $k_B T = 1.3$, $X_A = 0.50$, and $\gamma_{AB}/\gamma_{SL} = (a) 1.3$ and (b) 1.8 (continued, page 54)
Figure 1. Microstructure of grain wetting and contiguity at $k_B T = 1.3$, $X_A = 0.50$, and $\gamma_{SS}/\gamma_{SL} = (c) 2.0$ and (d) 2.5.
Figure 2b. Microstructure showing solubility in liquid and solid are the same at $Q = 1$. 
Figure 3. The number of broken bonds as a function of grain size

Figure 4. Solution concentration of grains of different molar interfacial energies
Figure 6. Arrhenius plot of modified solution concentration at \( Q = 1 \).

\[ (C-1)/C \]

Temperature, \( k_B T^{-1} \)
Figure 7. Disordering temperature as a function of composition for $Q = 100$
The definitions of parameters measured from the simulations are presented before proceeding with the discussion of the simulation technique.

**Grain area**, $a$, is the number of contiguous A-sites of the same orientation, $q_A$, i.e. the number of sites forming a grain.

**Average grain size**, $<R>$, is the linear mean of all grain sizes, $R$,

$$<R> = \frac{\sum_{i=1}^{m} R_i}{m}$$

(1)

where $R = \sqrt{a}$ and $m$ is the total number of grains.

**Solution concentration**, $C$, is defined by eq. (26) of chapter 3 as the fraction of liquid sites which are of component A.

**Composition**, $X_A$, is the overall composition of the system and is the fraction of A-sites in the system,

$$X_A = \frac{AS}{AS + BS}$$

(2)

where AS and BS are the number of A- and B-sites in the simulation space.

**Solid fraction**, $\phi$, is the mass fraction of sites in grains,

$$\phi = \frac{ASG}{AS + BS}$$

(3)

where ASG is the number of A-sites in grains and AS is the total number of A-sites.

**Grain growth exponent**, $n$, is the exponent of $<R>$ in the grain growth equation.
\[ \langle R \rangle^a = Kt \] (4)

where \( K \) is the grain growth constant and \( t \) is time. It is determined by calculating the inverse of the slope of the logarithm \( \langle R \rangle \) versus logarithm \( t \) curve. Now, that the reader is familiar with the terms used in presenting and analyzing results, the discussion of simulation technique will begin.

The objective of this investigation was to simulate grain growth by the solution-precipitation mechanism. The solid grains must dissolve in the liquid matrix, be transported through the liquid, and finally precipitate onto existing grains. This section presents the results of experiments carried out to insure that grain growth occurred by the solution-precipitation mechanism in the simulations.

Three variants of the simulation were examined. Each of these will be described and the results of critical tests will follow. Although, the simulation technique described here is very similar to the one outlined in chapter 2, Simulation Methodology; the complete step by step description of the first variant will be given for clarity.

**Variant 1.**

In the first variant, all exchanges between A- and B-sites were considered to simulate the solution-precipitation mechanism.

1. The 2-D, square lattice was populated with the desired composition. The initial condition was a random distribution of A and B components. The B-sites were all of one state, \( q = -1 \). The A-sites were assigned one of \( Q (=100) \) states, \( q \in \{1,2,\ldots,Q\} \), at random.
2. A lattice site and a neighboring site were chosen at random.
3. If one site was an A-site and the other a B-site, then the simulation continued to step 4; if not, then to step 7.
4. An orientation for the A-site was chosen at random from Q possible orientations.

5. The new configuration, the A- and B-sites exchanging places with the A-site assuming the new orientation, was considered.

6. The Metropolis\textsuperscript{71} algorithm was used to determine if the new configuration was accepted or rejected. The Metropolis algorithm used the Hamiltonian given by eq. (1) of chapter 2 in conjunction with Boltzmann statistics to determine the microstructural evolution. The exchange probability was given by

\[ w = \exp\left(-\frac{\Delta H}{k_B T}\right) \text{ for } \Delta H > 0 \quad (1a) \]

\[ w = 1 \text{ for } \Delta H \leq 0 \quad (1b) \]

where \( k_B \) is the Boltzmann constant, and \( T \) is absolute temperature.

7. The time was incremented by \( 1/N \), where \( N \) was the total number of sites in the simulation and return to step 2.

The grain growth results of Variant 1 are shown in figure 1 as average grain size, \( <R> \), versus time on logarithmic scales for a composition of 70\% component A. The slope of the latter portion of the grain growth curves is the inverse of the grain growth exponent, \( n \), given by eq. (4).

The grain growth exponent increased with increasing temperature over the range of temperatures investigated. The grain growth exponent, \( n \), was not expected to be a function of temperature as long as the grain growth mechanism did not change with temperature. Rather, the temperature dependence of the grain growth equation is incorporated in the pre-
exponential term $K$. Examination of images of the simulated microstructures at several times revealed that grain growth by coalescence occurred occasionally. Coalescence is the mechanism by which two or more grains of the same orientation come into contact with each other to form one large grain. Figure 2 illustrates this mechanism. Furthermore, coalescence was more common at higher temperatures because grains grew much larger and were more likely to encounter other grains of the same orientation. Coalescence is a different mechanism from solution-precipitation and may lead to the temperature dependence of the grain growth exponent, $n$. Although, it is possible to imagine physical situations in which this might take place; for the purposes of the simulations being considered here it is an artifact and the simulation procedure was modified to prevent it.

To further understand coalescence, one set of grain growth simulations was run to determine the influence of the number of orientations, $Q$, on grain growth simulations. Coalescence was not explicitly prevented in these simulations. Only the fully wetting case ($\gamma_\omega = 2.5\gamma_{\text{ad}}$) with the solution-precipitation mechanism for grain growth was considered. The composition in these simulations was 70% A - 30% B, temperature was 1.4 and the total number of orientations, $Q$, ranged from 5 to 100.

At low $Q$, grain growth by coalescence was the dominant grain growth mechanism. Grain growth by coalescence gave rise to long meandering grains as seen in figure 3a, a microstructure generated for $Q = 5$. At higher $Q$, the probability of two neighboring grains having the same orientation, $q$, was low; thus, coalescence was less frequent. Grain growth occurred primarily by each solid site dissolving in the liquid (either detaching from a grain or assuming an orientation that is not the same as any of its neighboring solid sites), diffusing through the liquid and precipitating out on a grain (attaching itself to a grain). The
microstructure generated for Q = 100 is shown in figure 3b. The grain shape for this case has the expected equiaxed shape, since anisotropy was deliberately minimized in these simulations.

The grain growth exponent, n, was determined as a function of the total number of orientations, Q. The results for these simulations are shown in figure 4, a plot of the grain growth exponent, n, as a function of the total number of orientations, Q. The grain growth exponent, n, increased with increasing Q over the entire range of Q = 5 to 100. At Q > 40, this increase was slow, but significant. At Q = 5, coalescence was the primary grain growth mechanism. As Q increased, the probability of coalescence decreased, but continued to influence n.

**Variant 2**

To prevent coalescence, the simulations were run with the same procedure described in Variant 1, with one change. Periodically, the microstructure generated by the simulation was examined for grains in close proximity to each other with the same orientation. The orientation of such grains were reset so that they had an orientation different from that of any other grains close to them. This effectively prevented grains from coalescing without affecting the Hamiltonian of the system. The grain growth results of Variant 2 are shown in figure 5. The grain growth exponent, n, remained constant with temperature. Based on these data it was concluded that coalescence gave rise to the temperature dependence of the grain growth exponent, n, in Variant 1.

To ensure that coalescence was the cause of the observed dependence of n on Q, a second set of simulations was run to determine the grain growth exponent, n, as a function of Q, but this time coalescence was prevented. Again, fully wetting conditions were used
with temperature, $k_B T = 1.4$. The results of these simulations, presented in figure 6, reveal that when coalescence was prevented the grain growth exponent was not a function of the number of orientations, $Q$.

Preventing coalescence did give constant grain growth exponent, $n$, with temperature and $Q$; however, figure 7 shows that $n$ did change with composition. This result was also contrary to expectation, since the grain growth exponent, $n$, was not expected to be a function of composition unless the grain growth mechanism changed with the composition. Examination of the simulation revealed that it was possible for an A-site to go directly from one grain to the next if the two grains were close to each other. At higher mole fraction of B, $X_B$, when grains were separated by several liquid sites, the direct exchange mechanism was not possible and most A-sites had to detach completely from the first grain, diffuse through the liquid, and then attach themselves to the next grain. The solution-precipitation method is illustrated in figure 8a. As component B decreased and grains moved closer together, many solid sites could go directly from one grain to the next in a single exchange without ever being a single solid site (i.e. being dissolved in the liquid) as illustrated in figure 8b. This is a distinctly different grain growth mechanism than diffusion controlled solution-precipitation, as the solid site was never dissolved in, and did not diffused through the liquid. The relative contribution of this mechanism was a function of composition, since grains are closer together at lower mole fraction of B.

**Variant 3**

Grain growth by a solid site jumping directly from one grain to the next was prohibited in variant 3 of the simulation by changing step 5 to the following:

5. The new configuration, the solid and liquid domains exchanging places with the
solid site assuming the new orientation, was considered. If the exchange resulted in the solid sites going directly from one grain to another, the exchange was rejected and the simulation jumped to step 7; if not, it continued to step 6.

This insured that each solid site had to detach completely from the first grain (solid had to dissolve in the liquid) before attaching itself to the second grain. This mechanism is illustrated in figure 8c. Coalescence of neighboring grains was also prevented in variant 3. The results of these simulations are shown in figure 9. The grain growth exponent, n, remained constant as a function of composition and temperature as predicted by grain growth theory. Variant 3 was the simulation technique chosen for further study. Appendix A contains the source code used for these simulations.
Figure 1. Grain growth curves for Variant 1 at composition, $X_A = 0.70$. 

- $T = 1.5$, $n = 2.9$
- $T = 1.4$, $n = 3.1$
- $T = 1.3$, $n = 3.3$
Figure 2. Diagram illustrating the coalescence mechanism.
Figure 3. Microstructure for Variant 1 at $Q = (a) \ 5$ and (b) 100.
Figure 4. Grain growth exponent as a function of $Q$ for simulation when coalescence was permitted.
Figure 5. Grain growth curves for Variant 2 at constant composition.
Figure 6. Grain growth exponent as a function of $Q$ for simulation when coalescence was permitted and prevented.
Figure 7 Grain growth curves for Variant 2 at constant temperature.
Figure 8a. Diagram illustrating simulation of the solution reprecipitation mechanism
Figure 8b. Diagram illustrating the direct exchange mechanism
Figure 8c. Diagram illustrating the solution-reprecipitation mechanism.
Figure 9. Grain growth curves for Variant 3 at constant (a) composition and (b) temperature.
Chapter 5
Grain Growth Kinetics

The simulation technique discussed in the previous chapter was used to study grain growth by the solution-reprecipitation mechanism. All grain growth experiments were carried out under fully wetting conditions ($\gamma_m = 2.5\gamma_a$) and $Q = 100$. The composition ranged from mole fraction of component A, $X_A = 0.30$ to $0.90$. The temperature ranged from 0 to $k_B T$ the liquidus temperature, i.e. the temperature at which all the solid is dissolved in the liquid. The kinetics of grain growth simulations will be presented in this chapter.

The grain growth simulation run at composition, $X_A = 0.70$ will be used to present typical results. The microstructures generated for the composition, $X_A = 0.70$ at temperature, $k_B T = 1.3$, but increasing time during the simulation are shown in figure 1. The microstructure at constant time, $t = 100,000$ MCS, but increasing temperature, $k_B T = 1.2$, 1.3, 1.4 and 1.5, are shown in figure 2. As one can see grain growth does occur with increasing time and growth rates increase with increasing temperature.

Data obtained from such simulations are plotted as average grain size versus time on logarithmic scales for temperatures, $k_B T = 0.9$ and 1.3 in figure 3a. The detailed description of the average grain size calculation is given in Appendix B. Two features are immediately obvious from figure 3a. First, two distinct regions are apparent; the early stage of the simulation was characterized by a rapid nonlinear increase in grain size followed by a second stage characterized by a linear region which suggests a power law behavior. Second, the slope during the second stage increased with increasing temperature, that is, the
grain growth exponent increased with increasing temperature.

The origin of the two regions is considered first. Examination of the microstructures shown figures 1 and 2 revealed that component A was dissolved in B to form the liquid solution throughout the simulations. A plot of liquid solution concentration as a function of logarithmic time for the same simulations shown in figure 3a is shown in figure 3b for temperatures, $k_b T = 0.9$ and 1.3. The data in figures 3a and b are replotted in figures 3c and d on linear scales. The solution concentration was highly supersaturated at the start of simulation, since the simulation lattice was populated by random assignment of q at each lattice site. Thus, the initial microstructure consisted of virtually all solid sites being single solid sites, which were considered dissolved in the liquid. As the simulation progressed, the solution concentration decreased dramatically until it reached a plateau in the second region. A comparison of figures 3a and b reveals that the onset of the plateau in figure 3b occurred towards the end of the transition from the first region to the second region. The microstructures of the simulation at $k_b T = 1.3$ in figures 3a and b at time, $t = 0, 371, 1320,$ and 4914 MCS are shown in figure 3e. At time, $t = 0$, almost all the A was dissolved in B. At time, $t = 371$ MCS, some grains had nucleated, and the solution concentration decreased rapidly while grain size was growing. At time, $t = 1320$ MCS, the grains formed at time, $t = 371$ MCS had grown; a few new grains had formed; and the solution concentration continued to drop rapidly. By time, $t = 4914$ MCS, the solution concentration had almost reached its plateau and power law region of grain growth was about to start.

The nucleation event is depicted much more clearly by a case where the initial solution concentration was much lower. The simulation results of composition, $X_A = 0.30$

*The times chosen for presentation are at fairly regular intervals on a logarithmic scale.*
and temperature, $k_b T = 1.3$, are presented in figure 4. The grain growth plot, figure 4a, reveals that grains did not start growing until time, $t > 10,000$ MCS and the second stage, power law grain growth, was never attained. The solution concentration, shown in figure 4b, also did not decrease until time, $t > 10,000$ MCS. However at time, $t > 16,000$ MCS, grain growth occurred very rapidly and solution concentration also decreased rapidly. The corresponding microstructures shown in figure 4c, reveal a few nuclei had formed by time, $t = 16,464$ MCS. The larger nuclei continued to grow while the smaller ones redissolved, but grain growth occurred primarily due to precipitation not due to larger grains growing at the expense of smaller ones. By time, $t = 29,376$ MCS, a couple of new nuclei had formed. Again the larger ones grew and the smaller ones redissolved. Even at time, $t = 100,000$ MCS, there is no evidence to suggest that Ostwald ripening has occurred in this simulation. Grain growth occurred entirely by precipitation of A-sites from a supersaturated solution.

Based on the data presented in figures 3 and 4, it is concluded that nucleation of grains occurred at the beginning of the transition region followed by rapid precipitation of the A component on the these nuclei during the transition region. Grain growth by Ostwald ripening occurred in the second stage of the simulation where the solution concentration remained relatively constant.

The grain growth curves and the corresponding solution concentration curves of simulations over a range of compositions and temperatures are shown in figures 5a & b to 10 a & b. The grain growth exponents from these simulations are summarized in figure 11a, a plot of $n$ as a function of temperature for the various compositions. The grain growth exponent, $n$, decreased with increasing temperature up to temperature, $k_b T = 1.3$, and remained constant at $n = 3$ at temperatures, $k_b T \geq 1.3$. This temperature dependence of $n$
at lower temperatures is attributed to the lack of sufficient thermal energy at the lower temperatures. At higher temperatures, grain growth occurred with the expected kinetic behavior for diffusion-controlled grain growth.

By varying the temperature and composition, grain growth can be studied over a range of solid fractions. The grain growth exponents given in figure 11a are plotted as a function of solid fraction in figure 11b. Diffusion-controlled kinetics were obtained from 0.30 to 0.90 solid fraction.

Further examination of figures 3a and b revealed that the nucleation time and the mean grain size at nucleation increased with increasing temperature. Time to nucleation and the average grain size at nucleation as function of temperature for various compositions are given in figures 12a and b, respectively. Time to nucleation was defined as the time at the onset of the plateau in figure 3b. Both, nucleation time and average grain size at nucleation increased with increasing temperature.

The nucleation time was also found to be a function of composition. As component A decreased and B increased, the time to nucleation increased from 20% B and up. The supersaturation of the liquid solution decreased with increasing temperature and increasing component B. As the supersaturation decreased, the driving force for nucleation also decreases yielding longer nucleation times.

At very low mole fraction of B, around 10% B, the nucleation time increased with decreasing B. This behavior is attributed to the simulation technique used. Only neighboring sites occupied by different components are allowed to exchange places. When the mole fraction of B was very low, the probability of neighboring sites of different components is so low that, evolution of the microstructure was very slow.
At a given composition, as the liquidus temperature was approached, studying grain
growth became increasingly computationally demanding. The nucleation times were long,
t \geq 100,000 \text{ MCS}, and the mean grain sizes at the onset of grain growth were large. These
factors bounded the upper temperature region for grain growth simulations. While the lower
temperature bound of $k_B T > 1.2$ was constant for all compositions, the upper temperature
bound varied with composition.

At compositions of $X_A < 40\%$, meaningful grain growth simulation is not feasible.
For example, the nucleation time at composition, $X_A = 30\%$, and temperature, $k_B T = 1.3$, is
greater than 100,000 MCS as shown by figure 4. At lower temperatures, $k_B T < 1.3$, grain
growth by the solution-reprecipitation mechanism did not take place in the simulation. The
temperature and composition range for practical simulation is given in figure 13. This
imposes an additional constraint on the range of solid fraction which can be simulated. To
obtain grain growth results at low solid fractions ($<0.30$), the simulation must be run either
at high temperatures or at compositions of low $X_A$. Under these conditions, the time to
nucleation and the grain size at the end of nucleation is very large. Thus, the time necessary
to obtain grain growth and the simulation lattice size must be much larger than that used in
this investigation. Numerical computations on such a large scale are not practical on
workstation-class computers.
Figure 1. Microstructure of simulation at temperature, $k_b T = 1.3$, composition, $X_A = 0.70$, and time, $t = (a) 3,978$ and (b) $11,088$ MCS (continued, page 89)
Figure 1. Microstructure of simulation at temperature, $k_B T = 1.3$, composition, $X_A = 0.70$, and time, $t = (c) 35,532$ and (d) 100,000.
Figure 2. Microstructures of simulations at composition, $X_A = 0.70$, time, $t = 100,000$ MCS and temperature, $k_B T = (a) 1.2$, (b) 1.3 (continued, page 91).
Figure 2. Microstructures of simulations at composition, $X_A = 0.70$, time, $t = 100,000$ MCS and temperature, $k_B T = (c) 1.4$, and (d) 1.5.
Figure 3. (a) Grain growth curves and (b) corresponding solution concentrations.
Figure 3. (c) Grain size versus time and (d) solution concentration versus time for composition, $X_A = 0.70$, and temperature, $k_bT = 1.3$. 
Figure 3e. Microstructures illustrating nucleation at temperature, $k_B T = 1.3$, composition, $X_A = 0.70$, and time, $t = (1) 0, (2) 371$ MCS (continued page 95).
Figure 3e. Microstructures illustrating nucleation at temperature, $k_B T = 1.3$, composition, $X_A = 0.70$, and time, $t = (3) 1320$ and (4) 4914 MCS.
Figure 4. (a) Grain growth curve and (b) corresponding solution concentrations.
Figure 4c. Microstructures illustrating nucleation at temperature, $k_B T = 1.3$, composition, $X_A = 0.30$, and time, $t = (1) 0, (2) 16,464$ MCS (continued page 98).
Figure 4c. Microstructures illustrating nucleation at temperature, $k_B T = 1.3$, composition, $X_A = 0.30$, and time, $t = (3) 29,376$ and (4) 100,000 MCS.
Figure 5a. Grain growth curves for composition $X_A = 0.90$. 

- Composition: 90% A
- $T = 1.8$
- $T = 1.7$, $n = 2.94$
- $T = 1.6$, $n = 2.91$
- $T = 1.5$, $n = 3.00$
- $T = 1.4$, $n = 3.01$
- $T = 1.3$, $n = 3.02$
Figure 5b. Solution concentration during grain growth simulations.
Figure 6a. Grain growth curves for composition, $X_A = 0.80$. 

Composition: 80% A

- $T = 1.8$, $n = 2.98$
- $T = 1.6$, $n = 3.14$
- $T = 1.1$, $n = 3.08$
- $T = 1.1$, $n = 3.70$

Time, MCS

Grain Size, $R$
Figure 6b. Solution concentration during grain growth simulations.
Figure 7a. Grain growth curves at composition, $X_A = 0.70$. 
figure 7b. Solution concentration during grain growth simulations.
Figure 8a. Grain growth curves for composition, $X_A = 0.60$. 

Composition: 60% A

- $T = 1.5$, $n = 3.10$
- $T = 1.4$, $n = 3.03$
- $T = 1.3$, $n = 2.97$
- $T = 1.2$, $n = 3.01$
- $T = 1.1$, $n = 3.56$
Figure 8b. Solution concentration during grain growth simulations.
Figure 9b. Solution concentration during grain growth simulations.
Figure 10b: Solution concentration during grain growth simulations.
Figure 11. Grain growth exponent as a function of (a) temperature and (b) solid fraction.
Figure 12. (a) Time to precipitation as a function of temperature and (b) Avg. grain size at the end of precipitation.
Figure 13. Simulations can be run over the range of temperatures and compositions shown.
Chapter 6

Grain Size Distributions

The grain size distributions obtained from the simulations are presented in this chapter. A single simulation of size 300 x 300 did not generate sufficient grains to plot smooth grain size distribution histograms; therefore, multiple simulations under the same conditions were run to generate large numbers of grains. Five simulation conditions were chosen for further study. They were compositions, $X_A = 0.90, 0.80, 0.70, 0.60$, and $0.50 \text{ A}$, at temperature, $k_B T = 1.3$. At the composition, $X_A = 0.90$, four simulations were run; at $X_A = 0.80$, six simulations; and at $X_A = 0.70, 0.60$ and $0.50$, seven simulations for each composition. At time, $t = 100,000$ MCS, multiple simulations yielded a minimum of 788 grains for the compositions, $X_A = 0.50$, and a maximum of 2780 grains at $X_A = 0.90$.

The grain size distributions for compositions, $X_A = 0.90, 0.80, 0.70, 0.60$ and $0.50$ are presented in figures 1 to 5, respectively as a function of time. The data are presented as normalized frequency versus normalized grain size, so that the distributions at different times and compositions may be compared directly to each other. The solid grain fraction varied from 0.89 at $X_A = 0.90$ to 0.41 at $X_A = 0.50$.

Dynamic scaling of the grain size distribution was achieved for each of the five compositions at time, $t \geq 20,000$ MCS. The nucleation times for these simulations ranged from 9,000 MCS for $X_A = 0.90$ and 0.50 to 4,000 MCS for $X_A = 0.80$, (see figure 12a of chapter 5). At $t \geq 20,000$ MCS, all simulations were in the grain growth region.

The grain size distribution varied with the solid fraction. It became broader and more peaked with increasing solid fraction. The peak of the grain size distributions
remained at \( R \) just under \( R \langle \langle R \rangle \) for all the different compositions. The grain size
distribution was skewed to the right for solid fraction = 0.89. As the solid fraction
decreased, the skewness shifted to the left.

In order to quantitize these characteristics, the variance, skewness and kurtosis of
the grain size distributions were calculated. Skewness and kurtosis were calculated as,
\( \mu_3 / \mu_2^{3/2} \) and \( \mu_4 / \mu_2^2 - 3 \), respectively, where \( \mu_x \) is the \( x \)th moment of the grain size distribution.
Variance was normalized by the mean squared, \( \mu_2 / \mu_1^2 \), to compare variances of different
distributions directly to each other.

The variance increased slightly with increasing time and with decreasing solid
content. The small change in variance can be explained by the truncation of small grains
due to the digitized nature of the simulations. The small grains in a steady state grain size
distribution are produced by shrinking grains. In the simulations, there were two sources
of the small grains. One was from larger grains which had shrunk. The second and
predominant source of these small grains was the formation of subcritical nuclei which were
forming and redissolving constantly. Consider the grain size distribution of the grain growth
simulation at composition, \( X_\alpha = 0.70 \), and temperature, \( k_B T = 1.3 \). Some relevant grain size
data are tabulated in Table I at time, \( t = 20,000 \) and 100,000 MCS.
Table I - Average Grain Size and the Number of Grains between Size, $a = 2$ and 9 at Time, $t = 20,000$ and 100,000 MCS for Composition, $X_a = 0.70$, and Temperature, $k_B T = 1.3$.

<table>
<thead>
<tr>
<th>Grain Size (Area)</th>
<th>20,000 MCS, $&lt;R&gt; = 8.64$</th>
<th>100,000 MCS, $&lt;R&gt; = 15.28$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Number of Grains</td>
<td>$R/&lt;R&gt;$</td>
</tr>
<tr>
<td>2</td>
<td>1089</td>
<td>.164</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
<td>.201</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>.232</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>.259</td>
</tr>
<tr>
<td>6</td>
<td>9</td>
<td>.284</td>
</tr>
<tr>
<td>7</td>
<td>9</td>
<td>.306</td>
</tr>
<tr>
<td>8</td>
<td>13</td>
<td>.327</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>.347</td>
</tr>
</tbody>
</table>

Total number of grains: 4961

The number of grains of area, $a = 2$, at time, $t = 100,000$ MCS, was 878 out of a total of 2522, which is disproportionately high. Clearly, 878 grains had not shrunk to a size of $a = 2$; rather, they had precipitated out of solution and would redissolve as the simulation continued. Likewise, 61 grains of size, $a = 3$, was disproportionately high as were 1089 grains of size, $a = 2$, and 90 grains of size, $a = 3$, at time, $t = 20,000$ MCS. For this reason, all grains of size, $a < 4$, were not included in the grain size distribution analysis. This had the effect of truncating the grain size at $R/<R> < .131$ for the grain size distribution at time, $t = 100,000$ MCS and at $R/<R> < .232$ for time, $t = 20,000$ MCS. Since, the truncation occurred at a higher relative size, $R/<R>$, at 20,000 MCS than at 100,000 MCS, the variance was decreased slightly. To confirm this hypothesis, the grain size distribution at time, $t = 100,000$ MCS was truncated at $R/<R> < .232$ which corresponds to size, $a = 13$. The variance, $s$, of this distribution decreased from $s = 0.111$ to $s = 0.100$ and the variance at $t = 20,000$ MCS was $s = 0.090$. Thus, the small change in variance with time is attributed
primarily to the truncation of the small grains.

The small change in variance with solid fraction was also due to truncation of small grains. The average grain size increased with decreasing solid fraction. At high solid fractions, when the average grain size was small, variance was depressed due to truncation. The variance of the grain size distribution did not change much with time or with solid fraction.

The skewness remained constant with time, but increased with increasing solid fraction. The increase in skewness with increasing solid fraction was consistent with the grain size distributions shown in figures 1 to 5 and was due to the shifting of grain size distribution toward the right. The truncation of small grains increased skewness of grain size distributions with lower average grain size, <R>. Consider the example in Table I. The skewness of the grain size distribution at time, t = 100,000 MCS, was 0.090 and the skewness of the same data truncated at size, a < 13, was 0.140. This variation in skewness was small compared to the variation in skewness at different solid fractions. Thus, truncation had little effect on skewness.

The kurtosis also remained fairly constant with time, but increased with increasing solid fraction indicating that the grain size distribution was more peaked at higher solid fractions. This confirms the trend seen in figures 1 to 5. Truncation of small grains decreased the kurtosis slightly; however, like skewness the difference between kurtosis of different solid fraction was larger than the change in kurtosis due to truncation.
Figure 1a. Grain size distributions for solid fraction = 0.89
Figure 1b. Grain size distributions for solid fraction = 0.89.
Figure 2a. Grain size distributions for solid fraction = 0.78.
Figure 2b. Grain size distribution for solid fraction = 0.78.
Figure 3a. Grain size distributions for solid fraction = 0.66.
Figure 3b. Grain size distributions at solid fraction = 0.66.
Figure 4a. Grain size distributions at solid fraction = 0.53.
Figure 4b. Grain size distributions at solid fraction = 0.53.
Figure 5a. Grain size distributions at solid fraction = 0.41.
Figure 5b. Grain size distributions at solid fraction = 0.41.
Figure 6. (a) Variance, (b) skewness and (c) kurtosis of grain size distributions as a function of time.
Simulation Thermodynamics

Simulation of grain growth in liquid phase sintered materials necessitates a two phase system with solid grains dispersed in a liquid matrix. Furthermore, the solid phase had to consist of one component, A, and the liquid phase a solution of two components, A and B, with B as the primary component. A system with these characteristics was achieved by using the Potts model which sampled a two component, canonical ensemble consisting of A which could assume a hundred states and B which could assume only one state, coupled with a Hamiltonian which defined interfacial energies. This two component system had certain thermodynamic properties and phase equilibria characteristics which were presented in chapter 3. The two phases were a solid phase consisting almost entirely of the component A and a liquid phase consisting primarily of the component B with a significant amount of A dissolved in it.

Several options were considered to prevent dissolution of the B-component within grains. One was to simply prevent any B-sites from dissolving into the solid A grains. This proved to be difficult as many different events could lead to dissolution of B in A. Two different sequence of events which can lead to dissolution are illustrated in figures 1a and b. A grain boundary B-site can exchange places with an A-site to give dissolution of the same B-site as shown in figure 1a, or a similar exchange can lead to the dissolution of a second B-site which does not participate in the exchange itself as shown in figure 1b. Preventing dissolution of the B-site by these two methods involved checking all potential
neighbors of the B-site and of all the neighbors of the A-site participating in the exchange to insure that such an exchange was prevented. This proved to be computationally too expensive as several steps were added to each exchange.

Another option considered to prevent solution of B-sites within grains was to prevent any exchange which caused the B-site participating in the exchange from becoming a dissolved site. This prevented the formation of dissolved B-sites by the method illustrated in figure 1a, but not by that illustrated in figure 1b. The dissolved sites formed by the latter method were effectively frozen because any exchange resulting in a dissolved B-site was prevented. This method prevented diffusion in the grain although dissolution itself could still occur. This option also added several steps to each exchange as the potential neighbors of all B-sites had to be checked.

The dissolution of B in the solid grains was much less than the dissolution of A in the liquid matrix. At temperature, $k_B T = 1.3$, the solution concentration of A in the liquid, $C_A = 0.14$ and B in the solid, $C_B = .0005$. The difference was primarily due to the difference in entropies of solution of the solid and liquid solutions. The entropy of solution for B-sites dissolved in solid grains was much lower than that of A-sites in the liquid matrix. A secondary contribution to solution suppression in the grains was the Gibbs-Thomson effect. The convex curvature of the grain suppressed solution of B-sites in the solid grains. The negligible solubility of B-sites in the solid grains satisfied the desired characteristics.

The liquid solution concentration, $C_A$, was defined as the fraction of dissolved sites, single A-sites (1AS), in the liquid

$$C_A = \frac{1AS}{1AS + BS}$$

(1)
where BS is the number of B-sites in the liquid. The definition of solution concentration, however, is not as unambiguous as it would seem. When the solution concentration was high, dissolved A-sites were continuously forming and redissolving grain of 2- and 3-sites. These 2- and 3-site grains were considered to be subcritical nuclei and were not included in the calculation of solution concentration. A more rigorous analysis might show that the liquid solution concentration is some function of 2-site grains, 2AS, and 3-site grains,

\[ C = C(1AS, 2AS, 3AS, BS) \]  

(2)

and not just a simple function of 1AS as given by eq. (1). Determination of the more rigorous definition of solution concentration was not pursued as it is only peripherally related to the simulation of grain growth in liquid phase sintered materials.

The driving force for grain growth in real systems is the reduction in solid-liquid interfacial energy. In the simulations, the bond energies between neighboring A_i-A_j, A_i-A_j, B-B, and A-B sites lead to a solid-liquid interfacial energy and a grain boundary energy as shown in chapter 2. As grain growth occurred, both total interfacial length and interfacial energy decreased, decreasing the free energy of the system. Thus, the driving force for grain growth in the simulations was the decrease in interfacial energy.

Grain growth by Ostwald ripening occurs in systems which exhibit the Gibbs-Thomson behavior. The Gibbs-Thomson relationship for the two-dimensional, discreet, square lattice used in the simulation has been derived. The experimental data collected from simulations agreed with the derivation as shown in chapter 3. The same effect which permits grain growth in actual liquid phase sintered materials was operating in the simulations.
Simulation Technique

The transport mechanism for grain growth is solution of the solid grains in the liquid, diffusion through the liquid and reprecipitation of the solid from the liquid. In this section, it will be shown that the simulation technique did simulate a system with these characteristics.

Transport was simulated by allowing neighboring A- and B-sites to exchange places. Diffusion through the liquid matrix occurred by the dissolved A-sites exchanging places with neighboring B-sites. Simultaneously, diffusion through the solid grains also occurred by dissolved B-sites exchanging places with A-sites.

In real liquid phase sintered materials, diffusion through the liquid matrix leads to grain growth. Diffusion in the solid grains is limited if it occurs at all and it does not contribute to grain growth. As an example consider MgO grains in a CaO-SiO$_2$ liquid. Magnesia is highly soluble in the CaO-SiO$_2$ liquid forming montecellite liquid, but almost no SiO$_2$ or CaO is dissolved in the MgO grains$^{26}$. Likewise, Al$_2$O$_3$ grains in an MgO-SiO$_2$ liquid$^{27}$ and Si$_3$N$_4$ grains in a Y$_2$O$_3$-SiO$_2$ liquid$^{28}$ have negligibly small solubility of the liquid components in the solid grains. In the simulations, solubility of B-sites in the solid was very low. Diffusion of these few B-sites did not result in a net diffusion of B-sites from one side of the grain to the other because diffusion in the simulations was curvature driven and the average curvature within the grain was constant for all directions. The diffusivity of B-sites in the solid was much slower than diffusivity of A-sites in the liquid. Consider a dissolved B-site in a grain as shown in figure 2. The probability, P, of this site exchanging sites with one of its neighbors is
\[ p = \frac{1}{Q} + \frac{Q-1}{Q} e^{\left( \frac{-17.5}{k_B T} \right)} \]  

(3)

The first term in eq. (3) corresponds to a dissolved B-site exchanging places with an adjacent A-site and assuming \( q = q_{\text{grain}} \). The second to an exchange where the A-sites assume a \( q \neq q_{\text{grain}} \). In the temperature range where grain growth can be simulated, the exponential term in eq. (3) is much lower than the first term; thus, the exchange probability is \( 1/Q = 0.01 \). Using similar reasoning it can be shown that the probability of a dissolved A-site exchanging places with one of its neighboring B-sites is 1. Thus, this combination of low solubility of B-sites in the solid grains, the lower diffusivity of these few dissolved B-sites and no net transport in any one direction insured that diffusion in the solid grains did not contribute to grain growth.

Exchanges between two neighboring A-sites were not permitted. This was to simulate the case where solid state diffusion was much slower than diffusion through the liquid phase. Figure 3 illustrates how exchanges between two neighboring A-sites can result in grain growth by solid state diffusion. Not permitting exchanges between two A-sites was to avoid such occurrences. In actual liquid phase sintered systems, the activation energy for solid state diffusion, \( \Delta E_s \), is generally higher than the activation energy for diffusion in a liquid, \( \Delta E_L \). \( \Delta E_s \gg \Delta E_L \). The kinetics of diffusion are controlled by the activation energies since the transition probabilities \( w = \exp(-\Delta E/k_B T) \). The Metropolis algorithm used in this simulation does not consider activation energies, only the net change in configurational energy, \( \Delta E \). Rollett et al.\(^{31}\) used a method to incorporate the activation energy into the transition probability by assigning grain boundary mobilities, \( \mu \), to the
different possible events. Thus, the transition probability is

$$w = \mu \exp\left(-\frac{\Delta F}{k_B T}\right)$$  \hspace{1cm} (4)

In the notation used here, $\mu = \exp(-\Delta E/k_B T)$. In this manner Rollett et al. were able to incorporate kinetics factors into their simulations. In simulations presented in this work, a similar concept was used to prevent solid state diffusion. For all A-B and B-B exchanges, the activation energy, $\Delta E_s$, was assumed to be $\Delta E_s = 0$; thus, $\exp(-\Delta E/k_B T) = 1$. As stated earlier, the activation energy for solid state diffusion, $\Delta E_s^S >> \Delta E_s^L$; therefore $\exp(-\Delta E_s^S/k_B T)$ $<< \exp(-\Delta E_s^L/k_B T)$ and the transition probability for solid diffusion (A-A exchange), $w^S << w^L$. Instead of allowing exchanges between two A-sites with a probability of $w^S = \exp(-\Delta E_s^S/k_B T)\exp(-\Delta E/k_B T)$; the quantity $\exp(-\Delta E_s^S/k_B T)$ was taken to be $= 0$, since $\exp(-\Delta E_s^S/k_B T) << \exp(-\Delta E_s^L/k_B T) = 1$. Not permitting any A-A exchanges rather than permitting a few A-A with the appropriate exchange probability reduced computational time considerably without compromising the objective of this work.

Grain growth by the coalescence mechanism had to be explicitly prevented to obtain grain growth by a single growth mechanism, solution-precipitation. The physical phenomenon analogous to coalescence in real systems would be two neighboring grains of exactly the same orientation coming together so that the grain boundary between them disappears. This is possible, but highly improbable in real systems. Thus, preventing coalescence, a comparatively frequent occurrence in the simulations, was justified.

The other possibility is that special, low energy, grain boundaries between two grains exist which are not wet by the liquid phase. By chance when two grains encounter
each other with the special grain boundary, the two grains coalesce, but remain separate grains with a grain boundary separating them. This configuration is stable and persists because the dihedral angle stabilizes this configuration. A plot of the grain boundary energies and the corresponding grain boundary configuration is shown in figure 4. This type of coalescence is encountered in some systems\cite{79,80,81,82} and has been the topic of some models\cite{83,84}. The difference between special grain boundary coalescence and the one seen in the simulations is that in the simulations after coalescence the formerly two grains became one. Furthermore, after a few MCS the coalesced grain became fairly equiaxed with significantly less curvature than the two separate grains. In contrast, special grain boundary coalescence does not make the two grains one nor does it change the curvature of the two grains as much. The curvature difference was significant because Ostwald ripening is curvature driven. A couple of different methods for preventing coalescence were considered. The first was to increase the total number of orientations, Q, to a very large number. This would decrease the probability of having neighboring grains of the same orientation to the point that coalescence hardly ever occurred. The solubility of the A in B increases with increasing Q; thus, using very large Q would limit the temperature and composition range in which grain growth simulations could be run. The other method considered for preventing grain growth was to track all the grains and check before each exchange if the exchange would result in coalescence. This method was computationally very expensive as it added a number of steps to each exchange. The method chosen to prevent coalescence was to periodically examine the microstructure for grains close to each other of the same orientation. The orientation of such grains were reset so that they had an orientation different from that of all other nearby grains.
In simulations where coalescence was not explicitly prevented, the grain growth exponent, \( n \), increased with increasing number of orientations, \( Q \), over the entire range of \( Q \) studied, 5 to 100. This change in \( n \) with \( Q \) was attributed to coalescence. As \( Q \) increased, the probability of coalescence decreased, but was significant even at \( Q = 100 \). Anderson et al.\textsuperscript{27} reported the grain growth exponent, \( n \), in single phase grain growth simulations to be constant with \( Q \) at \( Q > 30 \). They attributed this behavior to the fact that at \( Q > 30 \), the occurrence of coalescence was sufficiently infrequent so that coalescence did not influence \( n \). This discrepancy between the two simulations in spite of their similarity is puzzling. A possible explanation may be that in single phase system such as the one studies by Anderson et al., each grain had an average of six neighboring grains.\textsuperscript{71,28} In the two-phase system such as the one studied in this investigation, grains had many more than six grains, which were nearby. While, the grains did remain equiaxed throughout the simulations, fluctuations in shape did occur. These fluctuations often brought grains close to each other in contact with each other. If the two such grains happened to be of the same orientation they coalesced. Fluctuations of these types are not possible in single phase grain growth simulations because the surrounding grains constrain shape changes. Grain must grow through one another to come into contact with each other.

Grain growth by the direct exchange mechanism (see figure 8 in chapter 4) was also explicitly prevented to assure grain growth occurred by the solution-precipitation mechanism alone. The direct exchange mechanism was found to be composition dependent. At high \( X_A \), where solid fraction was high many grains were separated by a thin liquid layer as shown in figure 8b of chapter 4. In this type of configuration, the direct exchange mechanism was energetically more favorable than the solution-precipitation mechanism.
Consider the examples given in figure 8a-c of chapter 4. The change in energy for the solution exchange in figure 8a $\Delta E = 8.5$; for the direction exchange in figure 8b, $\Delta E = -2.5$; and for the solution exchange in figure 8c, $\Delta E = 7.5$. The corresponding probabilities for each of these exchanges once they are selected at temperature, $k_B T = 1.3$, are 0.0014, 1.0, and 0.0031, respectively. The direct exchange in figure 8b had the lowest energy change of the three and the highest probability of occurring; therefore, it was the dominant mechanism when grains were close to each other.

In real liquid phase sintered systems, the liquid content can be as low as 10 vol% or less. At these liquid contents, the liquid grain boundary phase separating neighboring grains is at least a few atoms in width\textsuperscript{45,46,47}. Under these conditions, it is not possible for a grain boundary atom from the first grain to jump across several atoms of the liquid phase to the next grain. The atom must first dissolve or become part of the liquid and then precipitate out on a grain.

The digitized microstructure used by the simulation did not accurately model the complexity of the thin liquid layer in between grains. At a composition of $X_A = 0.90$, there were too few B-sites to completely surround each individual grain, let alone form several layers of liquid sites between neighboring grains. The B-sites which did exist are overwhelmingly between grains with a thickness of one site. Unless explicitly prevented, grain growth in such a system occurred almost entirely by the direct exchange mechanism.

It is noteworthy, that the grain growth exponent, $n = 2.4$, at composition, $X_A = 0.90$, for simulation which permit direct exchange (see figure 7 in chapter 4) is identical to that obtained for single phase grain growth by Anderson et al.\textsuperscript{47} The grain growth mechanism in the single phase Potts model was migration of kinks and ledges yielding a grain growth
exponent, \( n = 2.4^{27.34} \), rather than \( n = 2^{36} \). At composition, \( X_A = 0.90 \), grain growth occurred almost exclusively by direct exchange. This similarity between the grain growth exponent obtained for the single phase system and for composition, \( X_A = 0.90 \), suggests that the direct exchange mechanism was similar to the migration of kinks and ledges seen in the single phase grain growth simulations.

**Simulation Grain Growth Kinetics**

The starting condition was a randomly populated lattice of the desired composition. This configuration is analogous to a supersaturated solution in a real system. As the temperature decreased below the liquidus or the mole fraction of A-component, \( X_A \), and supersaturation increased. Thus, the driving force for precipitation of the solid from the supersaturated liquid increased with decreasing temperature and increasing \( X_A \). This was reflected by the increase in time to precipitation and the average grain size at the end of precipitation with increasing temperature and increasing A-component as shown in figures 12a and b of chapter 5.

In order to understand the driving force for precipitation, the probability that grains of various sizes will grow and the probability that they will shrink were calculated. These probabilities were calculated for the most compact grain configuration at each size, since these have the lowest internal energy. As an example, consider a grain of size, area = 4, in its most compact configuration as shown in figure 5. The probability that this grain will shrink is the sum of the probabilities that each of the four sites will detach from the grain. Each site can jump to the position shown in figure 5a assuming any orientation, \( q \), and become completely detached from the grain. The probability that one of the four sites will be chosen is 4/36. The probability of the particular neighboring site shown being chosen
is 1/8. The probability of that neighbor being a B-site is (1-C_A), where C_A is the solution concentration of the A-component in the liquid. The A-site will form 3 new A-B bonds in the exchange gaining an energy, ΔE = 3E_{AB} = 3. The A-site in its new position will have 5 new neighbors each of which maybe another A-site increasing the energy by ΔE = 5*C_A*1.5. Thus, the probability that the grain will shrink by this method is:

\[ P_1 = \frac{4}{36} \frac{1}{8} (1-C_A) e \left( \frac{-3-5C_A}{k_B T} \right) \]  \hspace{1cm} (5)

The second method by which the same grain can shrink is by one of the A-sites jumping to one of the positions shown in figure 5b and assuming an orientation, q ≠ q_{grain}. Consider the jump labeled 1 in figure 5b. Each of the four A-sites in the grain can make this jump, 4/36, to two neighboring positions, 2/8, by assuming an orientation q ≠ q_{grain}, (Q-1)/Q = 99/100 = 1. Each jump will result in two new A-B bonds and one A_i-A_j bond with an increase in energy, ΔE = 2E_{AB} + E_{AA} = 2 + 2.5. The jump will result in three new neighbors; each of which may be an A-site with an energy increase, ΔE = 3*C_A*1.5. The probability that the grain will shrink by this method is:

\[ P_2 = \frac{4}{36} \frac{2}{8} (1-C_A) e \left( \frac{-2.5-3C_A}{k_B T} \right) \]  \hspace{1cm} (6)

Consider the jump labeled 2 in figure 5b. It can be shown that this type of jump will occur with a probability given by:
\[ P_3 = \frac{4}{36} \frac{2}{8} (1 - C_A) e^{\left(\frac{-2-2.5-5C_A}{k_B T}\right)} \]  

(7)

The probability that the grain shown in figure 5 will shrink is the sum of all three:

\[ P_S = P_1 + P_2 + P_3 \]  

(8)

The probability of this grain growing is the sum of the probabilities of A-sites from the surrounding liquid matrix precipitating out on the existing grain. Figure 5c illustrates how an A-site, labelled 1, can jump to a neighboring site assuming an orientation, \( q = q_{\text{grain}} \), and become part of the original grain. An A-site, labelled 3, can also jump to three different neighboring sites to become part of the grain. All the possible exchanges resulting in the grain growing are shown in figure 5d. The numbers at each site are the number of neighboring sites that an A-site occupying that particular site can jump to in order to become part of the grain. Consider the site labelled 1 in figure 5c. The probability of that site being chosen is 1/36, the probability that it is occupied by an A is \( C_A \), the probability that the neighboring site will be chosen is 1/8 and the probability it is occupied by a B is \( 1 - C_A \). The probability that the orientation chosen for the A-site will be \( q = q_{\text{grain}} \) is 1/9. Summing over all the possible exchanges resulting in the grain growing yields the probability of the grain growing is

\[ P_G = \frac{1}{36} C_A \frac{1}{8} (1 - C_A) \frac{1}{Q} (4 \ast 1 + 12 \ast 2 + 16 \ast 3) \]  

(9)

In this manner, the probability of a grain growing or shrinking at any solution concentration
and temperature can be calculated. The probability of growing and shrinking of grains of various sizes were calculated using the method shown above. These probabilities are tabulated in Appendix C.

The net growth probability, $P_g - P_s$, as a function of the grain size is plotted in figure 6 for temperature, $k_bT = 1.2$ to $1.6$ for solution concentration, $C_A = (a)\ 0.9$, (b) $0.5$, (c) $0.4$, (d) $0.3$ and (e) $0.2$. At solution concentration, $C_A = 0.9$, all precipitates will grow at all temperatures, although they will grow a little faster at higher temperatures. As the solution concentration decreases to $C_A = .5$, again all precipitates will grow. At solution concentration, $C_A = .4$, at temperature, $k_bT < 1.6$, all precipitates will grow but at $k_bT = 1.6$, precipitates of size, $A < 5$, will shrink. At solution concentration, $C_A = .3$, at $k_bT > 1.4$, all precipitates considered ($A < 65$) will shrink and as solution concentration further decreases to $C_A = .2$, all precipitates considered at $k_bT > 1.1$ will shrink.

As an example, these growth probabilities will be applied to the case of composition, $X_A = 0.7$ at temperature, $k_bT = 1.3$, shown in figure 3a and 3b of chapter 4. Figure 3b of chapter 4 shows that the solution concentration, $C_A = 0.60$ at time, $t = 100$ MCS. The growth probability diagrams shown in figure 6 of this section show that between solution concentration of $C_A = 0.9$ and $0.5$, precipitates of all sizes grow. Figure 3a of chapter 4 shows that precipitates were growing. As solution concentration continued to drop to $C_A = 0.3$, figure 6d shows that precipitates of larger sizes should be growing faster than the smaller ones. As the solution concentration further decreases to $C_A = 0.2$, precipitates of size $A < 37$ should shrink and the larger ones should grow. When the solution concentration has decreased just below $C_A = 0.2$, it continued to decreases slowly and grain growth occurred almost exclusively at the expense of other grains rather than by
precipitation from a supersaturated solution.

As noted before, the nucleation time increased with decreasing A-component except at composition, $X_A = 0.9$. This was a result of the simulation technique. Each A-site could only exchange places with a B-site; thus, at very low mole fraction of A, the probability of having neighboring A-B sites was small and exchanges were less likely. Figure 6 supports this conclusion and predicts that at a solution concentration of $C_A = 0.9$, all precipitates should grow, but the growth probability will be approximately half of that at solution concentration of $C_A = 0.5$ and an order of magnitude less than at $C_A = 0.3$.

After nucleation, before the power law region, there was a transition zone. The grain growth curve for composition, $X_A = 0.7$, and temperature, $k_BT = 1.3$, is shown in figure 7a with the transition zone marked on the graph. The line on figure 7a was obtained by using least squares best fit of the data on logarithmic scales. This line yields lower grain sizes than that observed in the simulation in the transition region. The grain growth equation predicts $<R>^3 \propto t$; thus, the data shown in figure 7a were plotted as $<R>^3$ versus time, $t$, in figure 7b. The least squares technique was used to calculate the best fit line as shown in figure 7b. This data and the line were replotted as grain radius, $<R>$, versus time, $t$, on logarithmic scales in figure 7c. This plot shows the deviation between the data and the best fit line is much smaller than seen in figure 7a. The higher deviation seen in figure 7a was attributed to the discrepancy between the grain growth equation and the simplified grain growth equation. The grain growth equation is

$$R^3 - R_0^3 = k't$$  \hspace{1cm} (10)$$

and the simplified grain growth equation is
\[ R^3 = KT \]  

(11)

It applies when the initial grain size, \( R_0 << R \). In the transition region, the initial grain size, \( R_0 \), was not negligibly small. The grain growth data for compositions, \( X_A = 0.9, 0.8, 0.7, 0.6 \) and \( 0.5 \), at temperature, \( k_BT = 1.3 \), is plotted with the best fit grain growth equation given by eq. (10) in figure 7d. The deviation between the data and the best fit line in each case was smaller than that between the same data and the simplified grain growth equation.

Several possibilities for the deviation were considered. One was that the precipitation was still occurring at a high rate in the transition zone. This hypothesis was tested by calculating the number of A-sites that precipitated out during the transition period. The average grain size was adjusted so that all the mass in the grains was equal to the actual mass in grains plus the mass of the A-component that precipitated out during the transition period. This did not explain the discrepancy as the adjusted average grain size was virtually identical to the actual grain size.

Another possible explanation for the deviation in the transition zone which was considered was the effect of excluding grains of size, \( A < 4 \), from the grain population (see Appendix B). The small grains were excluded because they were numerous and considered subcritical nuclei rather than grains. This time the average grain size was recalculated assuming an LSW\(^{56}\) distribution at the appropriate relative size, \( R/<R> \), for grains of size, \( A = 1, 2 \) and \( 3 \). This lowered the average grain size a little, but failed to explain the deviation from power law behavior. The discussion of the transition region will be continued later in this section after the discussion of other concepts.
The grain growth exponent, $n$, was constant at $n = 3$ at temperatures, $k_B T > 1.2$. As temperature decreased below $k_B T = 1.2$, the grain growth exponent, $n$, increased until at $k_B T = 0$, $n = \infty$. The increase in $n$ indicates that grain growth was increasingly inhibited with decreasing $T$. The process required for grain growth which was highly temperature dependent was dissolution. For solution to occur, an A site had to detach itself from a grain. This process was always accompanied by an increase in the Hamiltonian. Thus, sufficient thermal energy had be present to overcome this energy barrier. At $k_B T = 0$, no thermal energy was present in the system and solution could not occur; therefore, grain growth could not occur and $n = \infty$. At temperature $k_B T > 1.2$, there was enough thermal energy in the system to simulate grain growth by the solution precipitation method.

The two phase system studied in these simulations was characterized by a phase diagram shown in figure 7 of chapter 3. This phase diagram was generated by allowing a single grain to come to equilibrium with the surrounding liquid. In the grain growth simulations, the solution concentration changed slightly with varying composition as shown in figure 8a. The solution concentrations at time, $t = 100,000$ MCS, from the grain growth simulations were compared to the equilibrium concentration from figure 7 of chapter 3. At composition, $X_A = 0.9$, the solution concentration was slightly lower than that at equilibrium at temperatures, $k_B T < 1.8$. At temperature, $k_B T = 1.8$, the solution concentration was higher because precipitation was still occurring at time, $t = 100,000$ MCS (see figure 5b of chapter 5). Similarly, at composition, $X_A = 0.8$, the solution concentration was lower than the equilibrium solution concentration. The lower solution concentration at composition, $X_A = 0.9$ and 0.8, was due to the digitized nature of the simulations. Not all dissolved sites were of the same energy as illustrated in figure 9. The feature shown is a grain with surrounding
liquid sites. The liquid sites immediately surrounding the grain can be occupied by dissolved A-sites, but these dissolved sites would have between 1 and 5 A-A bonds with energy, $E_{AA} = 2.5$ as opposed to A-B bonds with energy, $E_{AB} = 1.0$. At composition, $X_A = 0.9$ and 0.8, there were many such near-grain sites, since the space between grains was small. Thus, solution was slightly suppressed. At compositions with lower A-component, $X_A = 0.7$, 0.6 and 0.5, the solution concentration was virtually identical to the equilibrium concentration. The fraction of near-grain sites, $X_{nag}$, were counted for simulations run at temperature, $k_B T = 1.3$. Table I lists these fractions. The fraction of near-grain sites, $X_{nag} = 0.076$ for the case of a single large grain in equilibrium with the liquid. For grain growth simulation run at composition, $X_A = 0.90$, and temperature, $k_B T = 1.3$, $X_{nag} = 0.995$. Despite the large difference in these special near-grain sites, the difference in solution concentration was small, ~2%.

The data given in figure 8a is solution concentration at time, $t = 100,000$ MCS. The grain sizes for the different composition at $t = 100,000$ MCS range form $<R> = 11$ at composition, $X_A = 0.90$ to $<R> = 17$ at $X_A = 0.50$; therefore, the relative contribution to the solution concentration from the Gibbs-Thomson effect was higher at the smaller grain sizes. To minimize the Gibbs-Thomson effect, the solution concentration at constant grain size, $<R> = 11$, for different compositions was plotted in fig. 8b. The solution concentrations for simulations which had not completed the precipitation event at $<R> = 11$ were not included in this figure. The solution concentration at the high $X_A$'s was lower than the equilibrium solution concentration. The difference in solution concentration between $X_A = 0.40$ and $X_A = 0.90$, ~4%, was marginally higher at constant grain size than at constant time, ~3%. At very long times, $t \to \infty$, when grain growth has progressed to the point that only large grains
are left, the solution concentration at all compositions is expected to approach the equilibrium solution concentration.

Table I - Fraction of Near-Grain Sites, $X_{\text{near}}$, at temperature, $k_bT = 1.3$, and time, $t = 100,000$ MCS and the corresponding solution concentrations.

<table>
<thead>
<tr>
<th>Composition $X_A$</th>
<th>Fraction Near-Grain Sites $X_{\text{near}}$</th>
<th>Solution Concentration $C_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>0.995</td>
<td>.126</td>
</tr>
<tr>
<td>0.80</td>
<td>0.825</td>
<td>.123</td>
</tr>
<tr>
<td>0.70</td>
<td>0.571</td>
<td>.137</td>
</tr>
<tr>
<td>0.60</td>
<td>0.376</td>
<td>.148</td>
</tr>
<tr>
<td>0.50</td>
<td>0.265</td>
<td>.152</td>
</tr>
<tr>
<td>single grain</td>
<td>0.076</td>
<td>.145</td>
</tr>
</tbody>
</table>

The grain growth curves for temperature, $k_bT = 1.3$, and compositions, $X_A = 0.9$, 0.8, 0.7, 0.6 and 0.5 are plotted in figure 7d. The grain growth constant $K$ given in the grain growth eq. (10) is the $y$-intercept of these curves. As one can see, $K$ increased with decreasing solid fraction. This increase in $K$ is contrary to that predicted by all grain growth theories. All theories which consider finite solid fractions predict increasing $K$ with solid fraction because diffusion distances between grains decrease. This counter intuitive result was an artifact of the simulation technique. Figure 10a, b and c are the microstructures at time, $t = 100,000$ MCS, for solid fraction, $\phi = 0.41$, 0.66 and 0.89, respectively. At solid fraction, $\phi = 0.89$, shown in figure 10c, many grains were in direct contact with each other with no B-sites separating them; thus, forming grain boundaries rather than solid-liquid interfaces. Grain growth in these areas could not occur until a B-site diffused to a position between these two grains. In areas where grain growth could occur, the grain growth rate was slower due to the suppression of the solution-reprecipitation mechanism by narrow liquid channels. Narrow liquid channels are liquid areas between grains which are only one
site thick. These narrow channels offered limited opportunity for dissolution as the existing sites were high energy sites. They also restricted precipitation because the dissolved A-sites were surrounded by many other A-sites in grains and A-A exchanges were prohibited. As the solid fraction decreased, the number of grains in direct contact with each other, fraction of interfacial length which forms grain boundaries, and the narrow channel area between grains decreased as given in Table II. Many more exchange events occurred as the grain boundary length and narrow channel area decrease which in turn leads to faster simulation rate.

Table II - The fraction of interfacial in grain boundary and the fraction of liquid in channels of single width at temperature, \( k_B T = 1.3 \) and time, \( t = 100,000 \) MCS.

<table>
<thead>
<tr>
<th>Composition ( X_A )</th>
<th>fraction of grain boundary</th>
<th>fraction of liquid in narrow channels</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>0.57</td>
<td>0.98</td>
</tr>
<tr>
<td>0.80</td>
<td>0.16</td>
<td>0.69</td>
</tr>
<tr>
<td>0.70</td>
<td>0.06</td>
<td>0.42</td>
</tr>
<tr>
<td>0.60</td>
<td>0.04</td>
<td>0.25</td>
</tr>
<tr>
<td>0.50</td>
<td>0.03</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Time in classical Monte Carlo simulations is not intrinsically defined\(^5\). It was first introduced by Limoge and Bocquet\(^8\) as a scaled time parameter in Monte Carlo simulations. Their technique for scaling time will be applied to these simulations. In real systems, the transport mechanism from state a to state b as shown in figure 11 would require time, \( t = t_{ab} \):

\[
t_{ab} = \frac{1}{w_{ab}}
\]  \hspace{1cm} (12)
where \( w_{ab} \) is the transition probability of transport from \( a \) to \( b \) given by:

\[
w_{ab} = v \exp\left(-\frac{\Delta E_a}{k_bT}\right) \exp\left(-\frac{\Delta E}{k_bT}\right)
\]  

(13)

where \( v \) is the jump attempt frequency, \( \Delta E \) is the difference in energy between state \( a \) and \( b \) as shown in figure 11, \( \Delta E_a \) is the activation energy, \( k_b \) is the Boltzmann constant and \( T \) is absolute temperature. The reverse jump, \( B \) to \( A \), has a transition probability given by:

\[
w_{ba} = v \exp\left(-\frac{\Delta E_a}{k_bT}\right)
\]  

(14)

Thus the net transition probability, \( w \), is given by

\[
w = w_{ab} - w_{ba}
\]  

(15)

In the simulations, the attempt frequency, \( v_* = 1/MCS \), since time was incremented by \( 1/N \) (\( N \) is the number of sites) after each attempted exchange. The argument of the exponential in eq. (13) and (14) which corresponds to the activation energy, \( \Delta E_a \), was not considered in the simulation. It was assumed to be constant for all possible transitions; therefore, the exponential was also constant at any given temperature, \( k_bT \). Time in a real system is
\[ t = \frac{1}{\nu} = \frac{1}{\nu} \frac{\exp\left(\frac{\Delta E_a}{k_B T}\right)}{\exp\left(\frac{-\Delta E}{k_B T}\right) - 1} \]  

(16)

and time in a Monte Carlo simulation is

\[ t_s = \frac{1}{\nu_s} = \frac{1}{\nu_s} \frac{1}{\exp\left(\frac{-\Delta E}{k_B T}\right) - 1} \]  

(17)

Since \( \nu_s = 1 \), the time parameter in the simulation, \( t_s \), is related to an equivalent time in a real system as:

\[ t_s = \frac{t \nu}{\exp\left(\frac{\Delta E_a}{k_B T}\right)} \]  

(18)

at any given temperature, \( T \).

The digitized nature of these simulations does not allow incorporation of a thin liquid layer in between grains at high solid fractions; rather, grain boundaries were created between grains as demonstrated by Table II and figure 12a. The only exchanges which contributed to microstructural evolution were exchanges between neighboring A- and B-sites. This introduced an additional factor in the simulation, the probability of an A-site at the grain perimeter being next to a B-site, \( P_{AB} \).
Another factor introduced by the digitized nature of the simulations was due the narrow channels between grains. As discussed before, the channels caused the dissolved sites in them to assume high energy configurations which are not expected in a real system. This caused the $\Delta E$ term in eq. (14) of dissolved site in a narrow channel to be higher than that in a larger region of liquid. Thus, $\Delta E$ was a function of configuration in the simulations, $\Delta E = \Delta E(\text{configuration})$ and an additional change to the Monte Carlo time parameter was introduced. The simulation time, $t_s$, for the simulation presented in this investigation is related to time in a real system, $t$, as:

$$t_s \propto \frac{t v P_{AB}}{\exp\left(\frac{\Delta E_g}{k_B T}\right) \exp\left(\frac{\Delta E(\text{config})}{k_B T}\right)}$$  \hspace{1cm} (19)

$P_{AB}$ and $\Delta E(\text{config})$ changed with composition, $X_A$, and with grain size, $<R>$.  

The effect of grain boundary length and narrow channels to lower the constant $K$ in eq. (11) also occurred as a function of grain size. At smaller grain sizes, the number of grains in contact with each other was larger and the narrow channels between grains were more numerous as shown in figures 12a and b. The change in these quantities with grain size at a given composition was far less than that between different compositions. This had the effect of increasing $K$ as grain growth progresses; however, the change in $K$ with grain size was small in the region where grain growth occurred. To put this in term of eq. (19), the change in $P_{AB}$ and $\Delta E$ with $<R>$ was small. Thus, power law behavior is obtained for constant composition, $X_A$, at larger grain sizes. The change in $P_{AB}$ and $\Delta E$ with composition was significant and did not allow one to obtain information about the constant $K$ in eq. (11)
as a function of solid fraction.

The physical phenomena which is the closest analogy to these nonwetted areas and narrow liquid channels in real systems are solid grain which are not fully wetted by the liquid phase\(^{40,79}\). In these non-wetted regions, grain growth is virtually non-existent because grain growth can occur only by solid-state diffusion and it is a much slower mechanism than solution-reprecipitation. Thus, the non-wetted regions effectively do not contribute to grain growth and this lowers the constant \(K\) in eq. (11) while the power law behavior still holds\(^{89}\).

The discussion of transition region after precipitation shown in figure 7 will be continued now. The transition region was due to the change in \(K\) with \(<R>\). The contact area between grains and narrow channel area decreased quickly at smaller grain sizes as shown in figure 12a and b. This higher rate of change may influence \(K\) more than at larger sizes.

The grain growth exponent, \(n = 3\), indicated that diffusion-controlled grain growth was simulated in this work. However, calculation of the magnitude of the diffusion coefficient, \(D\), and the interfacial reaction coefficient, \(k\), would suggest that grain growth kinetics in the simulations should have been mixed or interfacial reaction-controlled. The diffusion coefficient, \(D\), was estimated by using the formula

\[
D = \frac{3}{8} \lambda^2 \left( 1 - C_A \right) \tag{20}
\]

where \(\lambda\) is the lattice spacing, \(C_A\) is the solution concentration and \(3/8\) is obtained because eight nearest neighbors were considered.
The interfacial reaction coefficient, \( k \), can be estimated by calculating the flux from dissolution and precipitation at the interface. It was calculated to be

\[
k = \frac{3}{8} \lambda v \left( \frac{1}{Q} + \exp \left( -\frac{8E_{AB}}{k_b T} \right) \right)
\]  \hspace{1cm} (21)

The complete derivations of eq. (20) and (21) are given in Appendix D.

Wagner\(^d\) has shown that when the diffusion coefficient, \( D \), is much smaller than the interfacial reaction coefficient, \( k \), times the average grain size, \(<R>\), \( D \ll k <R> \), grain growth kinetics is controlled by diffusion, yielding a grain growth exponent, \( n = 3 \). When \( k <R> \ll D \), then grain growth kinetics is controlled by the interfacial reaction, yielding \( n = 2 \). At temperature, \( k_b T = 1.3 \), solution concentration, \( C_A = 0.20 \), and \( Q = 100 \), the ratio, \( D/k <R> \) ranged from 3 to 12, for average grain size, \(<R> = 20 \) to \( 5 \). Since \( D \) was estimated to be greater than \( k <R> \), the grain growth exponent, \( n \), obtained in these simulations, \( n = 3 \), indicating diffusion-controlled growth was unexpected.

In order to identify whether the kinetics of grain growth in the simulation were diffusion-controlled or interfacial reaction-controlled, several experiments were performed where the diffusion coefficient and interfacial reaction coefficient were varied with respect to each other. All experiments were carried out at composition, \( X_A = 0.70 \), temperature, \( k_b T = 1.3 \), and lattice size of \( 100 \times 100 \).

In the first experiment, the condition of interfacial reaction-controlled kinetics, \( k <R> \ll D \), was tested. It was assumed that the time for an interfacial exchange, dissolution or precipitation was infinitely larger than for a diffusive exchange, \( t_R \gg t_0 \). Using this assumption, the time in the simulations was incremented by 1 each time an interfacial event
(an A-site attaching to or detaching form a grain) was attempted. Time was not incremented for any other exchange event (not incremented for diffusive exchanges in the liquid). The grain growth exponent obtained from this experiment was $n = 2$ indicating grain growth was controlled by interfacial reaction-controlled kinetics.

The second experiment was performed at the other extreme of diffusion-controlled-kinetics, $D \ll k\langle R\rangle$. The time for a diffusive exchange in the liquid was assumed to be infinitely larger than the time for a interfacial exchange. In this simulation time was incremented for all diffusive events, but not for any others. The grain growth exponent from this simulation was $n = 3$ as expected for diffusion-controlled grain growth.

The two experiments just discussed apply to the two extremes where the ratio of $k\langle R\rangle/D = 0$ and $\infty$, respectively. To determine the relative magnitudes of $k\langle R\rangle/D$ in the simulations, another set of experiments were run. In this set, the relative magnitude of $k\langle R\rangle/D$ was varied by incrementing time for events at the interface, $t_{fr}$, by a different amount than for diffusive exchanges, $t_{D}$. For example, to reduce $D$ by 10, 0.1D, time was incremented by $t_{D} = 10$ for all diffusive events, but by 1 for all other events. Conversely, to decrease $k$ by 10, 0.1k, time for interfacial events was $t_{fr} = 10$ and 1 for all other events. This was done over a range of $10^{4} D/k\langle R\rangle$ to $10^{3} D/k\langle R\rangle$. The results of these experiments are given in figure 13. At $D/k\langle R\rangle$, diffusion-controlled kinetics grain growth was simulated. As $D$ was reduced from $D$ to 0.001D, the grain growth exponent remained constant at $n = 3$. As $k$ was reduced from $k$ to $2 \times 10^{-4} k$, the grain growth exponent goes from $n = 3$ at 0.1k to $n = 2$ at 0.005k and remains constant for smaller $k$. These results indicate that the simulations as they are run in this investigation simulate diffusion-controlled grain growth. Furthermore, the interfacial reaction coefficient has to be reduced by at least
three orders of magnitude before the grain growth kinetics will become interface controlled in the simulations.

To verify that diffusion-controlled grain growth was simulated, another experiment was performed. The diffusion coefficient, \( D \), was actually changed by reducing the probability of a diffusive event by 10. The transition probability, \( w_D \), of a diffusive exchange was changed to 0.1\( w_D \). This resulted in a grain growth exponent, \( n = 3 \), which was as expected, since the reducing \( D \) should result in diffusion-controlled grain growth. The complimentary experiment of reducing \( k \) was not practical as the transition probability must be reduced by 1000 which made the computation time of such a simulation prohibitively long.

**Grain Size Distributions**

The grain size distributions were determined for solid fraction ranging from 0.41 to 0.89 and presented in chapter 6. The simulation results were in agreement with grain growth theories on the trend in the spread of grain size distributions. As solid fraction increased, the grain size distribution broadened because a few grains grew larger. The largest grain size increased from 1.9\( <R> \) at 41% solid to 2.2\( <R> \) at 89% solid. This spread was larger than grain size distributions predicted by all grain growth theories except for Voorhees and Glicksman's\textsuperscript{12}. Thus, the overall spread in the grain size distribution was approximately in the range predicted by grain growth theories.

In the simulation, skewness of the grain size distribution at 41% solid was almost zero and increased gradually to 0.3 at 89% solid. This is very different from the predictions of grain growth theories. At 0% solid, the LSW\textsuperscript{5,6} theory predicts a grain size distribution with negative skewness. The theories which consider finite solid fractions, predict an
increase in skewness with increasing solid fraction, but none predict a change from negative to positive skewness as observed in the simulations.

Another significant difference between the simulations and grain growth theories was that the grain size distributions obtained by simulation were more peaked (higher kurtosis) at higher solid fractions. All grain growth theories predict a flattening of the peak (decreasing kurtosis) with increasing solid fraction.

The grain size distribution obtained from the simulation at 53% solid was compared to that predicted by Voorhees and Glicksman\textsuperscript{12} in figure 14. While the spread in grain sizes from the simulations was in agreement with that predicted by Voorhees and Glicksman, the skewness was quite different.

The simulation grain size distribution at 89% solid was compared to that obtain by Holm\textsuperscript{90} for grain growth in a single phase system in figure 15. Holm used the Potts model developed by Srolovitz et al.\textsuperscript{26} to study normal grain growth. Her simulation of a single phase system may be considered for the purposes of the simulations used in this investigation to occur at the limit as solid fraction, $\phi \rightarrow 1$. The broadening in grain size distribution was greater than that observed for the solid fraction of 0.89; the largest grain was $3.26\langle R \rangle$. The skewness was also larger (skewed to larger grain sizes) than that observed at solid fraction of 0.89. The trends observed in spread and skewness with increasing solid fraction continued as solid fraction, $\phi \rightarrow 1$.

The simulation grain size distribution at 66% solid was compared to experimental data collected by Fang and Patterson\textsuperscript{53} for the W-14Ni-6Fe system at 60% solid in figure 16. They allowed the grain size distribution to reach the steady state distribution and measured grain sizes by image analysis of two-dimensional cross-sections. The simulation grain size
distribution was in good agreement with the experimental data. The grain size ranged up
2.0<R> in the simulations. The largest grain size reported by Fang and Patterson was
2.1<R>. The skewness in both distributions was toward larger grain sizes and they both
peak at approximately <R>. The simulation grain size distribution was more peaked than
the experimental grain size distribution. This difference was consistent with the grain size
distributions predicted by two-dimensional and three-dimensional grain growth theories. The
two-dimensional theories predict a slightly narrower, more peaked grain size distribution
than the corresponding three-dimensional grain growth theories do.

DeHoff’s¹⁵ communicating neighbor model predicts a single grain size distribution
for all solid fractions as long as the grains remain spherical and their interactions are
uncorrelated. The simulation results were not in agreement with DeHoff’s model. The grain
size distributions did change with solid fractions. The simulated microstructures show
considerable shape accommodation with increasing solid fraction as shown by figures 10a-c,
microstructures at time, t = 100,000 MCS for solid fractions, ϕ = 0.41, 0.66 and 0.89,
respectively. At solid fraction, ϕ = 0.41, all grains were fairly circular. As the solid fraction
increased to ϕ = 0.89, many of the grains had flat edges at the positions where they touched.
This shape accommodation, which yields a different aggregate curvature than spherical
grains would, may be the reason that the grain size distribution obtained from simulation
deviate from DeHoff’s predictions.

Grain growth in real systems occurs in three dimensions with the exception of a few
cases such as grain growth in thin films. The simulations, of course, used two-dimensional
space. The grain size distributions generated by the two-dimensional simulation were
thought to yield reliable data which can be used for investigating and predicting behavior
in three-dimensional systems for several reasons. The grain size distribution obtained from the two-dimensional simulations were in good agreement with Fang and Patterson’s experimental data. The grain size distributions predicted by two- and three-dimensional grain growth theories which use corresponding techniques have very similar spread, skewness and peakedness at any given solid fraction. The two-dimensional theories predict a slightly narrower, more peaked grain size distribution than their three-dimensional counterparts, but this difference is minor. The grain size distribution obtained by Srolovitz and coworkers for grain growth in a single phase system in two and three dimensions are in good agreement with each other.

The advantage of the simulation technique presented in this investigation over that of analytical models was the incorporation of spatial distribution of grains; grain shape accommodation and solute gradients between grains were inherent to the technique. Previous models and simulations of grain growth by Ostwald ripening did not consider the spatial arrangement of grains during the grain growth process. They assumed spherical grains, made no allowance for changes in size and shape of grains due to spatial arrangement and assumed a mean field solute concentration around grains. The exceptions who did consider spatial arrangement of grains were Voorhees & Glicksman and Yao et al. They considered diffusion gradients around spherical grains, but only at relatively low grain fractions where interactions were minimal. DeHoff’s communicating model was able to consider both deviation in curvature of grains and interactions of gradients between grains, but correlating curvature parameters and interaction parameters to nonspherical grain shapes has not been done. He did consider a special case where all grains are spherical and predicted a grain size distribution for this case; however, this does not yield accurate
information at high solid fractions where shape accommodation occurs.

This ability of the simulation to incorporate spatial features may be the reason it was able to predict the change in skewness from left to right with increasing solid fraction. Examination of figure 10a-c revealed that as solid fraction, $\phi$, increased, considerable grain shape accommodation occurred. At $\phi = 0.89$, figure 10c, many grains had flat edges and sharper corners in other regions. These features will modify both the local driving force for grain growth and the local solute gradients in the liquid matrix which in turn may influence the grain size distribution to give positive skewness at high solid fractions.

It has been shown, in the previous section, that as solid fraction increased, the contact area between grains increased modifying the kinetics of grain growth by influencing $K$ in eq. (11). However, the increase in contact area between grains was not expected to affect the grain size distribution. The system is energetically a fully wetting system. The lattice used to digitize the microstructure leads to non-wetted areas, but these areas do not remain non-wetted. The liquid matrix moves into these areas wetting them; while, simultaneously dewetting some formerly wetted areas.

**Simulation Capabilities and Limitations**

The Potts model simulation of grain growth in liquid phase sintered materials presented in this work was able to eliminate many of approximations and simplifications made by previous models. The Potts model made no assumptions about the solution gradients between grains; rather it relied on the ability of Monte Carlo technique to simulate random walk. Most of the previous models assumed grains were spherical at all solid fractions. The model presented here did not assume that the grains were of any specific shape and allowed the simulation to actually evolve a microstructure. Thus, it was able to
consider shape accommodation of grains as a function of solid fraction.

The simulation technique presented here did have some limitations. It simulated grain growth on a mesoscopic scale. It could not incorporate details of grain growth on an atomic level. On the other hand, it used a discreet lattice and could not simulate continuum characteristics on a macroscopic scale.

Liquid phase sintered materials were known to experience hydrodynamic flow to achieve the lowest energy configuration. This simulation was not capable of simulating movement of entire grains by rotation or translation. It could only simulate solution, diffusion and precipitation. Hydrodynamic flow is driven by two forces, interfacial energies and gravity, i.e. density differences between solid grains and liquid matrix. In fully wetting systems, such as the one considered in these simulations, once the liquid fully wets the grains, the lowest energy configuration was achieved and no further hydrodynamic flow driven by interfacial energies will occur. In most ceramics, the liquid matrix and the grains have similar densities and the liquid is usually quite viscous. This combination limits hydrodynamic flow. Although, hydrodynamic flow is not considered; the grain growth simulation presented here models grain growth well because hydrodynamic flow is not significant during grain growth in liquid phase sintered ceramics.

Lee et al. have shown that when a the liquid matrix is drawn out of a liquid sintered material by capillary forces, the grains in the liquid phase sintered material move closer to each other by hydrodynamic flow. This type of an experiment cannot be simulated, but grain growth with the liquid already distributed around grains can.

This inability to incorporate hydrodynamic flow makes the simulation more like coarsening by Ostwald ripening of solid precipitates in a solid matrix. Solid precipitates in
a solid matrix almost always have some strain energy due to elastic mismatch between the
two solid phases. The simulation presented here is not able to incorporate strain energy, but it can be modified to incorporate elastic mismatch.

The simulation is limited to study grain growth at higher solid contents, in range of 30% and higher. Lower solid contents simulations can be run, but the computational time required is large. It has also been shown that power law behavior was obtained at a fixed solid fraction, but when solid fraction changed drastically, limited kinetic information could be obtained.

CONCLUSIONS

The Potts, Monte Carlo model was adapted to simulate two-dimensional, isotropic grain growth in fully wetted liquid phase sintered materials. It has been shown that the simulation technique developed in this work had the ability to simulate a two phase system, solid grains in a liquid matrix. Furthermore, the solution composition of the liquid, C, as a function of Q was derived to be

$$C = \frac{Q \exp\left(\frac{-8\phi}{k_B T}\right)}{1 + Q \exp\left(\frac{-8\phi}{k_B T}\right)}$$

The model could also simulate the solution-reprecipitation mechanism. The driving force for grain growth in the simulations was the reduction in the interfacial energy and solution-reprecipitation was driven by the Gibbs-Thomson effect. The Gibbs-Thomson relation was derived for Q = 1 as
\[ C_x = C_0 \exp \left( \frac{E_{AB} N_{AB}}{2a k_B T} \right) \] (23)

where \( E_{AB} \) is the A-B bond energy, \( N_{AB} \) is the number of A-B bonds at the solid liquid interface and \( a \) is the grain area.

Unlike previous models, the simulation technique did not make any assumptions about grain size and shape or about diffusion gradients within the liquid matrix. It relied on the inherent ability of the simulation to accommodate spatial characteristics of the grains and to simulate diffusion by random walk in the liquid matrix.

Diffusion-controlled grain growth kinetics with power law behavior was obtained; however, the two constraints on the algorithm were necessary to insure that Ostwald ripening was simulated. First, coalescence of grains had to be prevented and second, exchanges resulting in an A-site going directly from one grain to the next had to be prevented. Grain growth at solid contents < 30% could not be simulated because the simulation space required to simulate grain growth was too large to run on a workstation-class computer.

Grain size distributions were characterized over a range of solid contents, 40 to 90% solid. Under isotropic, fully wetting grain growth conditions, the grain size distribution was found to vary with the solid fraction. The grain size distribution became broader and more peaked with increasing solid fraction. The grain size distribution was skewed to larger sizes for solid fraction = 0.89. As the solid fraction decreased, the skewness shifted toward smaller sized grains.
Figure 1a. Exchange leading to solution of a B-site, $q_B = -1$, in a grain.

Figure 1b. Exchange leading to solution of a B-site, $q_B = -1$, not participating in the exchange.
Figure 2. Schematic diagram illustrating diffusion within a grain.

Figure 3. Diagram of an exchange between two A-sites leading to grain growth by solid state diffusion. (↔ grain boundary before exchange, — grain boundary after exchange)
Figure 4. Diagram illustrating coalescence in materials due to special low energy grain boundaries. (a) interfacial energy as a function of orientation (b) Two grains before coalescence (c) after coalescence with low energy grain boundary and (d) after coalescence in simulations.
Figure 5. (a) Exchanges leading to grain shrinkage by complete detachment of A-sites from the grain. (b) Grain shrinkage by A-sites in grain assuming $q \neq q_{\text{grain}}$. (c) Grain growth by precipitation. The numbers correspond to the number of possible exchanges leading to precipitation if that particular site was occupied by an A-site. (d) The number of possible exchanges leading to grain growth if that particular site were occupied by an A-site.
Figure 6. (continued on next page)
Figure 6. Growth probabilities as a function of grain size at solution concentration of (a) 0.9, (b) 0.5, (c) 0.4, (d) 0.3, and (e) 0.2.
Figure 7. Grain growth data fitted with (a) simplified grain growth eq. (b) and (c) grain growth eq. for $X_A = 0.70$ and $k_B T = 1.3$. 
Figure 74: Grain growth data fitted by the grain growth eq. at $k_B T = 1.3$.
Fig. 8 Solution concentration as a function of temperature at (a) constant time (b) constant grain size
Figure 9. The sites immediately surrounding a grain are higher energy sites for dissolution. The numbers in sites adjacent to the grain correspond to the number of A-A bonds must be formed by a dissolved A occupying that particular site.
Figure 10a. Microstructure at temperature, $k_bT = 1.3$, time, $t = 100,000$ MCS and solid fraction, $\phi = 0.41$
Figure 10b. Microstructure at temperature, $k_BT = 1.3$, time, $t = 100,000$ MCS and solid fraction, $\phi = 0.66$. 
Figure 10c. Microstructure at temperature, \( k_B T = 1.3 \), time, \( t = 100,000 \) MCS and solid fraction, \( \phi = 0.89 \)
Figure 11. Diagram illustrating the free energy difference between states A and B, $\Delta E$, and activation energy, $\Delta E_a$, which must be overcome for transport from one state to the other.
Figure 12. (a) Fraction of interfacial sites which are in grain boundaries and (b) Fraction of liquid in narrow channels as a function of grain size.
Figure 13. The grain growth exponent as a function of adjusted $k<R>/D$, i.e. the simulations is scaled so that the ratio $k<R>/D$ is changed by the $x$-scale.
Figure 14. Grain size distributions predicted by Voorhees and Glicksman and obtained by simulations.
Figure 15. Grain size distributions obtained by Holm for single phase simulation and by Ostwald ripening.
Figure 16. Grain size distributions experimentally measured by Fang and Patterson and from simulations.


Appendix A

SIMULATION SOURCE CODE

S12Q3.c

#include <stdio.h>
#include <math.h>
#include <stdlib.h>
#include <sys/time.h>
#define iran(range) (lrand48() % (range)) /* returns a random integer between 0 and range-1 */
#define dran(range) (drand48() * ((double) range)) /* returns a real number between 0 and range */
#define xsize 200 /* defines size of simulation space in the X-direction */
#define ysize 200 /* defines size of simulation space in the Y-direction */
#define nbors 8 /* defines number of neighbor-interactions considered for the Hamiltonian */
#include "functions.c" /* file containing all the functions */

/* This program simulates grain growth in a liquid phase sintered material. */
/* declare all global variables */

int spin[xsize * ysize + 1]; /* matrix of q at each lattice site */
int neighs[xsize * ysize + 1][nbors+1]; /* matrix of the neighbors of each site */
int m, n; /* size of the simulation lattice */
int mcsps; /* simulation time */
int q; /* the total number of solid states */
int liqct; /* the fraction of component B */
int drawfreq; /* the frequency at which spin[] is saved */
int seed; /* seed for random number generator */
double temp; /* temperature */
double e[4][4][3]; /* the matrix which stores the interaction energies between neighbors */
double Esl_le, Esl_he, Esl_c, Ess_e, Ess_c, Ell; /* the interaction energy between neighbors */
void main()

{ /* initialize random_1 number generator and set parameters for simulation */
  m=xsize; n=ysize; temp=1.3; mcsp=100000; q=100; liqct=50; drawfreq = 20;
  Esl_le = 1.0; Esl_he = 1.0; Esl_c = 1.0; Ess_e = 2.5; Ess_c = 2.5; seed = init_random();

  fwrite(&m, sizeof(int), 1, stdout);
  fwrite(&n, sizeof(int), 1, stdout);

  ini(); /*initializes spins array*/
  popneighs(); /* initializes the neighs matrix */
  popintenr(); /* initializes the interr matrix */
  mcgrowth(mcsp); /* perform Monte Carlo grain growth until attfreq = (mcsp)(total # sites) */

  fwrite(&mcsp, sizeof(int), 1, stdout);
  draw(); /* draw the array */
  size(mcsp); /* returns mean grain size at time, t = mcsp */
}

FUNCTIONS.C

/* declare all functions */

extern double  eschange(int, int, int), probs(double);
extern void    mcgroth(int), prinr(), popneighs(), popintenr(), putpixel(int), size(int),
               draw(), respin(int, int);
extern int     init_random(), ingrain(int, int), innex(int, int, int);

int init_random()
/* returns a long integer based on the workstation time. */
{
    int seed;
    struct timeval time_value;
    struct timezone time_zone;

    gettimeofday(&time_value, &time_zone);
    srand48(seed = time_value.tv_usec);
    return seed;
}

void init()
/* initializes spin array with random spins of desired distribution. The index of the spin
array corresponds to the location of that site in the following manner for a 50 X 50
matrix:

                                 1  2  3  4  5
                                 48 49 50
                                 51 52 53 54 55
                                 ..........98 99  100
                                 .......
2451................................2500 */
{
    int x, y;
    for(y=0; y<n; y++)
        for(x=0; x<m+1; x++)
            spin[y*m+x] = -1;
    x = 1;
    while(x < (int) (m * m * (100 - liqct) / 100 + 1))
    {
        if(spin[y = iran(m*m+1)] == -1)
        {
            spin[y] = iran(q)+2;
            x++;
        }
    }
    return;
}
void popneighs()
/* populates the neighs matrix, which maintains the location of all neighbors of site. The
neighbors are located as illustrated with respect to the site and periodic boundary
conditions are introduced in this matrix.

6 2 5
3 site 1
7 4 8
*/
{
    int site, i, j;
    for(j=0; j<m*n; j=j+m)
        for(i=1; i<m+1; i=i+1)
        {
            site=j+i;
            neighs[site][1] = j + i%m + 1;
            neighs[site][2] = (j-m+m*n)%m + i;
            neighs[site][3] = j + (i-2+m)%m + 1;
            neighs[site][4] = (j+m)%m + i;
            neighs[site][5] = (j-m+m*n)%m + i%m + 1;
            neighs[site][6] = (j-m+m*n)%m + (i-2)%m + 1;
            neighs[site][7] = (j+m)%m + (i-2)%m + 1;
            neighs[site][8] = (j+m)%m + i%m + 1;
        }

    return;
}

void popintra()
/* populates the interaction energy matrix, e. The first index of the e matrix specifies the
spin of site given by [spin[site]%2+2] being considered, the second index is spin of
neigh given by [spin[neighs]%2+2], and the third index specifies the location of neigh
with respect to site given by [location%2] [0] and [1] for edge sites, and [2] for corner
sites of neigh. */
{
    int c1, c2, c3;
    for(c1=0; c1<4; c1++)
        for(c2=0; c2<4; c2++)
            for(c3=0; c3<3; c3++)
                e[c1][c2][c3]=0;

    e[1][2][1] = e[2][1][1] = e[1][3][0] = e[3][1][0] = Esl_le;
    e[1][2][0] = e[2][1][0] = e[1][3][1] = e[3][1][1] = Esl_he;
    e[1][2][2] = e[2][1][2] = e[1][3][2] = e[3][1][2] = Esl_c;
    e[2][3][1] = e[3][2][1] = e[2][3][0] = e[3][2][0] = Ess_c;
    e[2][2][0] = e[2][2][1] = e[3][3][0] = e[3][3][1] = Ess_c;
    e[2][3][2] = e[3][2][2] = Ess_c;
    e[2][2][2] = e[3][3][2] = Ess_c;

    return;
}
void mcgrowth(int mcsps)
/* performs exchange of an A and B site via a classical Metropolis algorithm with conserved dynamics. */
{
    int site, neigh, newspin, c, c1, c2, c3, tm;
    double attfreq, de;

    attfreq = 0; c = 0; c1 = 200; c2 = 1; c3 = 2;

    while(attfreq <= (double) mcsps*m*n) /* perform simulation for time, t = mcsps */
    {
        site = iran(m*n)+1;  /* choose site at random */
        neigh = neighs[site][iran(nbors)+1];  /* choose a neighbor of site at random */
        if(spin[site] != spin[neigh]) /* if spin of the two neighbors is not the same */
        {
            if (spin[site] == -1 || spin[neigh] == -1)  /* if one is a liquid site */
            {
                newspin = iran(q)+2; /* choose new spin at random */
                if(ingrain(site, neigh) == 0 || innext(newspin, site, neigh) == 0) /* this prevents a site from going directly from one grain to the next */
                {
                    de=exchange(site, neigh, newspin); /* calculate Hamiltonian */
                    if(dran(1) <= probs(de)) /* perform Metropolis algorithm */
                    {
                        if (spin[site] == -1) /*perform exchange*/
                        {
                            spin[site] = newspin;
                            spin[neigh] = -1;
                        }
                        else
                        {
                            spin[site] = -1;
                            spin[neigh] = newspin;
                        }
                    }
                }
            }
        }
    }
}
if(attfreq/(drawfreq*m*n) == c) /* save image at specified intervals */
{
    fprintf(stderr, " %f ", log(attfreq/(double) (m*n)));
    tm = (int) (attfreq/(m*n));
    fwrite(&tm, sizeof(long int), 1, stdout);
    draw();
    size(tm);
    c++;
    drawfreq += (int) (drawfreq/6);
}

attfreq += 1; /* increment time */
}

return;
}

double exchange(int site, int neigh, int newspin)
/* calculates the energy of exchanging site with neigh */
{
    int lsite[4], c1, c2, c3, sitespin, neighspin, coeff;
    double de;

    sitespin = spin[site]; neighspin = spin[neigh]; coeff = -1;

    for(c1 = 0; c1 < 4; c1++)
        for(c2 = 1; c2 < nbors + 1; c2++)
        {
            int lsite_temp;
            int neighs_temp;
lsite_temp = lsite[c1];
neighs_temp = neighs[lsite_temp][c2];

if(spin[lsite_temp] != spin[neighs_temp])
{
    if (c2 < 5)
        de += coeff * e[spin[lsite_temp]%2+2][spin[neighs_temp]%2+2][c2%2];
    else if (c2 > 4)
        de += coeff * e[spin[lsite_temp]%2+2][spin[neighs_temp]%2+2][2];
}
if(c1 == 1)
{
    if(spin[site] == -1)
    {
        spin[site] = newspin;
        spin[neigh] = -1;
    }
    else
    {
        spin[neigh] = newspin;
        spin[site] = -1;
    }
    coeff = 1;
}
else if(c1 == 3)
{
    spin[site]=sitespin;
    spin[neigh]=neighspin;
}
return de;
double probs(double de) /* calculates the probability of an exchange occurring based on the Hamiltonian, de */
{
    return (de <= 0.0 ? 1.0 : (temp != 0.0 ? exp(-1.0*de/temp): 0.0));
}

void draw() /* saves the resulting microstructure */
{
    int x;
    int site;

    for(site=1; site<m*n+1; site++)
    {
        putpixel(spin[site]+1);
    }
    return;
}

putpixel(z)
int z;
{
    fwrite(&z, sizeof(int), 1, stdout);
}

int ingrain(int site, int neigh) /* determines if the solid site participating in an exchange is in a grain */
{
    int i;
    int solid;

    if(spin[site] != -1) solid = site;
    else solid = neigh;
    for(i=1; i<nbors+1; i++)
    {
        if(spin[neighs[solid][i]] == spin[solid]) return 1;
    }
    return 0;
}

int innext(int newspin, int site, int neigh) /* determines if the solid site participating in an exchange will become part of a grain after the exchange */
{
    int i;
    int newsite;
if (spin[site] == -1)
  {
    newsite = site;
    if (spin[neigh] == newspin) return 0;
  }
else
  {
    newsite = neigh;
    if (spin[site] == newspin) return 0;
  }
for (i=1; i<nbors+1; i++)
  if (spin[neighs[newsite][i]] == newspin) return 1;
return 0;

void size(int time_step)
/* calculates size of grains */
{
  int nucl, spinnucl, neigh, liqarea, gnum, gsite, i1, i2, i3, i4, x, y, xi1, xi2, yi1, yi2,
  largest, newspin;
  int burn[xsize*ysize+1], area[xsize*ysize], grain[xsize*ysize], gmbors[xsize*ysize][200],
  numgmbors[xsize*ysize], lknn[4000];
  double avgsize_2;
  for (nucl=1; nucl<m*n+1; nucl++) burn[nucl] = spin[nucl];
  nucl=1; liqarea=0; gnum=0; gsite=1;
  while (nucl < m*n+1)
    {
      if (burn[nucl] == -1)
        {
          liqarea++;
          burn[nucl]=0;
        }
      else if (burn[nucl] > 1)
        {
          spinnucl = burn[nucl]; burn[nucl]=0;
          i1=0; i2=0; lknn[1]=nucl; gsite=1; gnum++;
          area[gnum]=1; grain[gnum]=nucl;
          while (i1 <= i2)
            {
              for (neigh=1; neigh<nbors+1; neigh++)
                {
                  if (spinnucl == burn[neighs[lknn[i1]][neigh]])
                    {
                      burn[neighs[lknn[i1]][neigh]] = 0;
                    }
                }
            }
        }
  }
}
area[gnum]++; gsite++; i2++; lknn[i2]=neighs[lknn[i1]][neigh];
}
}
i1=i1+1;
}
}
nucl++;

i2 =i3 = 0; largest = area[1];
for(i1 = 1; i1 < gnum+1; i1++)
{
  if(area[i1] > 2)
  {
    i3 += area[i1]; i2++;  
    if(area[i1] > largest) largest = area[i1];
  }
}
avgsize = (double)i3/(double)i2;
fprintf(stderr, " %f \n", log(avgsize));

for(i1=1; i1<gnum+1; i1++) numgmbors[i1] = 0;

if(time_step > 0)
{
  for(i1 = 1; i1 < gnum+1; i1++)
  {
    if(area[i1] > 20)
    {
      i3 = 0;
      for(i2 = 1; i2 < gnum+1; i2++)
      {
        if(i1 != i2 && area[i2] > 10)
        {
          xi1 = (grain[i1] - 1) % xsize + 1;  
          xi2 = (grain[i2] - 1) % xsize + 1;  
          yi1 = grain[i1] / xsize;
          yi2 = grain[i2] / xsize;
          if((sqrt((xi1-xi2)*(xi1-xi2) + (yi1-yi2)*(yi1-yi2))) < 3*sqrt(largest))
          {
            i3++; if(i3 >= 200) fprintf(stderr, "Error num oF grain neighbors has exceeded 200");
            gmbors[i1][i3] = i2;
          }
        }
      }
    }
  }
}
numgmbors[i1] = i3;
}
}

i3 = 0;
for(i1 = 1; i1 < gnum+1; i1++)
{
    i4 = 1;
    if(area[i1] > 20)
    {
        for(i2 = 1; i2 < numgmbors[i1]+1; i2++)
        {
            if(spin[grain[i1]] == spin[grain[gmbors[i1][i2]])
            {
                i3++; newspin = iran(q) + 2;
                while (i4 <= numgmbors[i1])
                {
                    if(newspin == spin[grain[gmbors[i1][i4])]
                        
                    newspin = iran(q) + 2;
                    i4 = 1;
                        
                    else i4++;
                }
            nucl=grain[i1];
            respin(newspin, nucl); 
            i2 = numgmbors[i1]+2;
        }
    }
}

fprintf(stderr, "#number of grains respined = %d\n", i3);
return;
}

void respin(int newspin, int nucl)
/* reassigns spin of grains which are close to each other and have the same spin */
{
    int i1, i2;
    int lkn[5000];
    int spinnucl;
    int lneigh;
    i1=0; i2=0; lkn[i1]=nucl;
    spinnucl = spin[nucl];
    spin[nucl] = newspin;

    }
while(i1 <= i2)
{
    for(Ineigh=1; Ineigh<nbors+1; Ineigh++)
    {
        if(spinnucl==spin[neighs[lknn[i1]][Ineigh]])
        {
            spin[neighs[lknn[i1]][Ineigh]]=newspin;
            i2++;  
            lknn[i2]=neighs[lknn[i1]][Ineigh];
        }
    }
    i1++;
}
return;
A grain was a feature which had contiguous sites occupied by A's of the same state, q. The grain size was the number of these contiguous sites. The grain size reported was square root of the average grain size and was proportional to the radius of the size of the equivalent circular grain by the quantity √π. The method used to calculate the mean grain size is discussed in this section.

The mean grain size was determined by taking the average of all grains which were larger than one site. Single A-sites were considered to be dissolved in the liquid phase. The grain growth curves calculated in this manner for the composition 70% A at $k_b T = 1.3$ and 1.4 are shown in figure 1. The corresponding microstructures at time = 100,000 MCS are shown in figure 2. This method of calculating mean grain size did not yield the power law behavior for grain growth. Furthermore, the calculated mean grain size at 100,000 MCS and temperature, $k_b T = 1.4$ was smaller than that at $k_b T = 1.3$. This was clearly incorrect.

Examination of the various grain sizes revealed that many grains of just two and three sites were present throughout the simulations. Anderson et al.27 observed similar behavior. They defined a grain and calculated mean grain size the same way as is done here. They too observed the presence of a few very small grains (1 or 2 sites) which changed the grain growth curves. To circumvent this problem, they quenched (ran simulation for a short time at temperature, $k_b T = 0$) the microstructure before determining the grain size. This insured that most of the small grains were absorbed by larger grains by grain growth. They calculated mean grain size from the quenched microstructures, but continued the simulation with the pre-quenched microstructure.
Quenching the microstructure before measuring grain size could not be used for these simulations. The grain growth curves of the same simulations presented in figure 1 were recalculated after quenching for 500 MCS. The results are presented in figure 3 and the corresponding microstructures at $t = 100,000$ MCS are shown in figure 4. Quenching the microstructure, caused component A which was dissolved in the liquid to precipitate on to existing grains and to form new grains in between the existing one. Clearly, calculating the mean grain size of a quenched microstructure did not accurately reflect the grain size as new grains were formed and existing ones were enlarged.

Further examination of the simulations revealed that these tiny grains were constantly forming and dissolving in the liquid phase. This behavior was analogous to the constant formation and dissolution of subcritical nuclei in an actual system with a saturated liquid solution.

Grains consisting of one site were considered to be dissolved in the liquid and grains of two or three sites were considered to be subcritical nuclei. The mean grain size was calculated by taking the square root of the average of all grains larger than three sites and plotted in figure 5. The latter method of calculating mean grain size was accurate and was used for all the grain growth results presented in this investigation.
Figure 1. Grain growth curves calculated by considering all grains of size, $A > 1$
Figure 2. Microstructures at time, $t = 100,000$ MCS, composition, $X_A = 0.70$, and temperatures, $k_B T = (a) 1.3$ and (b) 1.4.
Figure 3. Grain growth curves calculated after quenching microstructure for 500 MCS
Figure 4. Microstructures after quenching for 500 MCS for simulations run at composition, $X_A = 0.70$, for time, $t = 100,000$ MCS and temperature, $k_B T = (a) 1.3$ and (b) 1.4.
Figure 5. Grain growth curves calculated by averaging all grains of size, $A > 3$. 
Appendix C

GROWTH PROBABILITIES OF PRECIPITATES

The growth and shrinkage probabilities of grains of various size at different solution concentrations, \( C_A = 1 - C_B \), are listed in this section. The method used to calculate these quantities is described in Chapter 7 in the section titled Simulation Kinetics. The growth probability is denoted as \( P_G \) and the shrinkage probability is \( P_S \) with

\[
P_S = \sum_i P_{Si}
\]

where \( P_{Si} \) are the different exchanges which can lead to grain shrinkage. The net growth probability is \( P_G - P_S \).

Size = 2

\[
P_{S1} = \frac{2}{30} \left( \frac{1}{8} \right) C_A e^{-3 \frac{k_B T}{k_B T}} \left( 2 e^{-5C_A^{1.5} \frac{k_B T}{k_B T}} + e^{-3C_A^{1.5} \frac{k_B T}{k_B T}} \right)
\]

\[
P_{S2} = \frac{2}{30} \left( \frac{2}{8} \right) C_B e^{-3.5 \frac{k_B T}{k_B T}} \left( e^{-3C_A^{1.5} \frac{k_B T}{k_B T}} + e^{-5C_A^{1.5} \frac{k_B T}{k_B T}} \right)
\]

\[
P_G = \frac{1}{30} \left( \frac{1}{8} \right) Q C_A C_B (4 + 12 * 2 + 10 * 3 + 2 * 4)
\]

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\[ P_{s1} = \frac{1}{35} \frac{1}{8} C_B e^{-\frac{2}{k_s T}} \left( 3e^{-\frac{5C_{A1.5}}{k_s T}} + 2e^{-\frac{3C_{A1.5}}{k_s T}} \right) \] (5)

\[ P_{s2} = \frac{1}{35} \frac{1}{8} C_B e^{-\frac{3C_{A1.5}}{k_s T}} \left( 2e^{-\frac{7}{k_s T}} + 6e^{-\frac{4.5}{k_s T}} \right) \] (6)

\[ P_{s3} = \frac{1}{35} \frac{1}{8} C_B e^{-\frac{5C_{A1.5} - 7}{k_s T}} \] (7)

\[ P_g = \frac{1}{35} \frac{1}{8} \frac{1}{Q} C_A C_B (5 + 12 \ast 2 + 12 \ast 3 + 3 \ast 4) \] (8)

Size = 4

\[ P_{s1} = \frac{4}{36} \frac{1}{8} C_B e^{-\frac{3-5C_{A1.5}}{k_s T}} \] (9)

\[ P_{s2} = \frac{4}{36} \frac{2}{8} C_B e^{-\frac{4.5}{k_s T}} \left( e^{-\frac{3C_{A1.5}}{k_s T}} + e^{-\frac{5C_{A1.5}}{k_s T}} \right) \] (10)

\[ P_g = \frac{1}{36} \frac{1}{8} \frac{1}{Q} C_A C_B (4 + 12 \ast 2 + 16 \ast 3) \] (11)

Size = 5

\[ P_{s1} = \frac{1}{41} \frac{1}{8} C_B e^{-\frac{2}{k_s T}} \left( e^{-\frac{5C_{A1.5}}{k_s T}} + e^{-\frac{3C_{A1.5}}{k_s T}} + 2e^{-\frac{4C_{A1.5}}{k_s T}} \right) \] (12)
\[ P_{S2} = \frac{1}{41} \frac{1}{8} C_B e^{-\frac{3}{k_5 T}} \left( 6 e^{-\frac{-5 C_{1.5}}{k_5 T}} + e^{-\frac{-4 C_{1.5}}{k_5 T}} \right) \]  
(13)

\[ P_{S3} = \frac{1}{41} \frac{1}{8} C_B e^{-\frac{4}{k_5 T}} \left( e^{-\frac{-4 C_{1.5}}{k_5 T}} + 2 e^{-\frac{-3 C_{1.5}}{k_5 T}} + 3 e^{-\frac{-5 C_{1.5}}{k_5 T}} \right) \]  
(14)

\[ P_g = \frac{1}{41} \frac{1}{8} \frac{1}{Q} A C_A C_B (5 + 15 \times 3 + 14 \times 2 + 2 \times 4) \]  
(15)

Size = 6

\[ P_{S1} = \frac{4}{42} \frac{1}{8} C_B \left( e^{-\frac{-3 - 5 C_{1.5}}{k_5 T}} + e^{-\frac{-4.5}{k_5 T}} \left[ 2 e^{-\frac{-3 C_{1.5}}{k_5 T}} + e^{-\frac{-5 C_{1.5}}{k_5 T}} \right] \right) \]  
(16)

\[ P_{S2} = \frac{2}{42} \frac{1}{8} C_B \left( 2 e^{-\frac{-6 - 4 C_{1.5}}{k_5 T}} + 2 e^{-\frac{-6.5 - 5 C_{1.5}}{k_5 T}} + e^{-\frac{-8 - 3 C_{1.5}}{k_5 T}} \right) \]  
(17)

\[ P_g = \frac{1}{42} \frac{1}{8} \frac{1}{Q} A C_A C_B (4 + 12 \times 2 + 20 \times 3) \]  
(18)

Size = 9

\[ P_{S1} = \frac{4}{49} \frac{1}{8} C_B \left( e^{-\frac{-3 - 5 C_{1.5}}{k_5 T}} + 2 e^{-\frac{-4.5 - 3 C_{1.5}}{k_5 T}} + 2 e^{-\frac{-6 - 4 C_{1.5}}{k_5 T}} \right) \]  
(19)

\[ P_{S2} = \frac{4}{49} \frac{2}{8} C_B \left( 2 e^{-\frac{-6.5 - 5 C_{1.5}}{k_5 T}} + 2 e^{-\frac{-8 - 3 C_{1.5}}{k_5 T}} \right) \]  
(20)
\[ P_s = \frac{1}{49} \frac{1}{8} C_A C_B (4 + 16 \times 2 + 20 \times 3) \] (21)

Size = 16

\[ P_{S1} = \frac{4}{64} \frac{1}{8} C_A \left( e^{\frac{-3 \times 5 C_A 1.5}{k_s T}} + 2e^{\frac{-4.5 \times 3 C_A 1.5}{k_s T}} + 2e^{\frac{-6.5 \times 5 C_A 1.5}{k_s T}} \right) \] (22)

\[ P_{S2} = \frac{4}{64} \frac{2}{8} C_B \left( e^{\frac{-6 \times 4 C_A 1.5}{k_s T}} + e^{\frac{-8 \times 3 C_A 1.5}{k_s T}} + e^{\frac{-8 \times 4 C_A 1.5}{k_s T}} \right) \] (23)

\[ P_s = \frac{1}{64} \frac{1}{8} C_A C_B (4 + 20 \times 2 + 24 \times 3) \] (24)

Size = 25

\[ P_{S1} = \frac{4}{81} \frac{1}{8} C_B \left( e^{\frac{-3 \times 5 C_A 1.5}{k_s T}} + 2e^{\frac{-4.5 \times 3 C_A 1.5}{k_s T}} + 2e^{\frac{-6 \times 4 C_A 1.5}{k_s T}} \right) \] (25)

\[ P_{S2} = \frac{4}{81} \frac{1}{8} C_B \left( 2e^{\frac{-6 \times 5 C_A 1.5}{k_s T}} + 3e^{\frac{-8 \times 3 C_A 1.5}{k_s T}} + 4e^{\frac{-8 \times 4 C_A 1.5}{k_s T}} \right) \] (26)

\[ P_s = \frac{1}{81} \frac{1}{8} C_A C_B (4 + 24 \times 2 + 28 \times 3) \] (27)
\[ P_{S1} = \frac{4}{100} \frac{1}{8} C_B \left( e^{\frac{-3.5 C_1.5}{k B T}} + 2e^{\frac{-4.5 - 3 C_1.5}{k B T}} + 2e^{\frac{-6.4 C_1.5}{k B T}} \right) \] (28)

\[ P_{S2} = \frac{8}{100} \frac{1}{8} C_B \left( e^{\frac{-6.5 - 5 C_1.5}{k B T}} + 2e^{\frac{-8 - 3 C_1.5}{k B T}} + 3e^{\frac{-8 - 4 C_1.5}{k B T}} \right) \] (29)

\[ P_G = \frac{1}{100} \frac{1}{8} C_A C_B \left( 4 + 28 \times 2 + 32 \times 3 \right) \] (30)

\[ P_{S1} = \frac{4}{144} \frac{1}{8} C_B \left( e^{\frac{-3.5 C_1.5}{k B T}} + 2e^{\frac{-4.5 - 3 C_1.5}{k B T}} + 2e^{\frac{-6.4 C_1.5}{k B T}} \right) \] (31)

\[ P_{S2} = \frac{8}{144} \frac{1}{8} C_B \left( e^{\frac{-6.5 - 5 C_1.5}{k B T}} + 3e^{\frac{-8 - 3 C_1.5}{k B T}} + 4e^{\frac{-8 - 4 C_1.5}{k B T}} \right) \] (32)

\[ P_G = \frac{1}{144} \frac{1}{8} C_A C_B \left( 4 + 12 \times 3 + 64 \times 3 \right) \] (33)
Appendix D

DERIVATION OF THE DIFFUSION AND INTERFACIAL

REACTION COEFFICIENTS

Diffusion coefficient

The derivation of the diffusion coefficient, $D$, by Shewmon is reproduced here. The flux of A-sites across a line is calculated and substituted into Fick's first law. The forward flux in a 2-D plane from line 1 to line 2, $J_{12}$, is the number of A-sites which hop from line 1 to line 2 and the backward flux, $J_{21}$, is vice versa. The flux, $J_{12}$, is proportional to the number of A-sites on line 1, $n_1$, the attempt frequency, $\Gamma$, the success rate, $(1-C_A)$ and the fraction of neighbors in the forward direction, 3/8. Thus, $J_{12}$ is

$$J_{12} = \frac{3}{8} (1-C_A) \Gamma n_1$$

(1)

Similarly, the backward flux, $J_{21}$, is

$$J_{21} = \frac{3}{8} (1-C_A) \Gamma n_2$$

(2)

The net flux across the interface, $J$, is

$$J = J_{12} - J_{21}$$

(3)

Substituting eq. (1) and (2) into (3) and recognizing that

$$n_1 - n_2 = \lambda c_1 - c_2$$

(4)
where $\lambda$ is the lattice spacing yields

\[ J = \frac{3}{8} \Gamma \lambda (1-C_\lambda) (c_1-c_2) \]  \hspace{1cm} (5)

Fick's first law is

\[ J = -D \frac{\partial c}{\partial x} \]  \hspace{1cm} (6)

Equation the flux in eq. (6) to that in eq (5) with

\[ \frac{\partial c}{\partial x} = \frac{c_1-c_2}{\lambda} \]  \hspace{1cm} (7)

and solving for $D$ gives

\[ D = \frac{3}{8} \Gamma \lambda^2 (1-C_\lambda) \]  \hspace{1cm} (8)

where $D$ has units of length square per time.

**Interfacial reaction coefficient**

The interfacial reaction coefficient, $k$, can be obtained by calculating the flux of A-sites at the interface. The net flux of A-sites at the interface, $J$, may be calculated by determining the difference between the flux due to dissolution, $J_\text{d}$, and the flux due to precipitation, $J_\text{p}$, as
\[ J = J_D - J_P \]  

The flux due to dissolution is the probability of A-sites detaching from a flat interface in a given time interval per unit length of the interface, \( \lambda \). An A-site at a flat interface can exchange sites with 3 B-neighbors out of 8 total neighbors, 3/8. The probability that these 3 site will be occupied by a B-site is \( (1 - C_A) \), where \( C_A \) is the concentration of A-sites in the liquid. The probability that the exchange will occur is the attempt frequency, \( \Gamma \), times the success probability, \( \exp(-8E_{AB}/k_BT) \) since on average 8 A-B bonds must be broken for dissolution. Thus, \( J_D \) is

\[ J_D = \frac{3}{8} \Gamma \lambda (1 - C_A) \exp\left(\frac{-8E_{AB}}{k_BT}\right) \]  

where \( \lambda \) is the distance that an A-site must jump, i.e. the lattice spacing.

The flux due to precipitation is the probability of a dissolved A-site precipitating onto a flat interface of length, \( \lambda \), during a given time interval. The probability of a site at the interface being occupied by an A is \( C_A \). This A-site exchanging with 3 out of 8 neighbors, 3/8, will result in precipitation. The attempt frequency of these exchanges is \( \Gamma \) and the success rate is 1/Q since the A-site must chose the correct orientation for precipitation. Thus, \( J_P \) is

\[ J_P = \frac{3}{8} \Gamma \lambda \frac{C_A}{Q} \]  

The net flux at the interface, \( J \), is
\[ J = J_D - J_F = \frac{3\Gamma\lambda}{8} \left( (1 - C_A) \exp\left(\frac{-8E_{AB}}{k_BT}\right) - \frac{C_1}{Q}\right) \]  \hfill (12)

The flux at the interface, \( J \), is also a function of the interfacial reaction coefficient, \( k \),

\[ J = k \left( C_A - C_{eq} \right) \]  \hfill (13)

where \( C_{eq} \) is the equilibrium concentration of A-sites in the liquid. It has been derived in chapter 3 and is given by eq. (24) of chapter 3. Equating the flux, \( J \), in eq. (12) and (13) to each other and solving for \( k \) gives

\[ k = \frac{3\Gamma\lambda}{8} \left( \frac{1}{Q} + \exp\left(\frac{-8E_{AB}}{k_BT}\right)\right) \]  \hfill (14)

The interfacial reaction coefficient has units of length per time.