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Four Dimensional Evolution
of Grains and Interfaces in Materials

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ABSTRACT

Four Dimensional Evolution
of Grains and Interfaces in Materials

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A phase-field model has been developed to study the effect of triple junction (TJ) mobility on 2-D grain growth kinetics. For low TJ mobility the average grain size increases linearly in time, followed by a transition to classical parabolic kinetics as the average grain size increases. The distribution of grain boundary curvature is examined. In the low TJ mobility simulations the distribution has a peak at zero curvature and approaches the grain boundary mobility limited steady-state distribution at larger sizes. Even for extremely low TJ mobility, a small fraction of the grain boundary length has nonzero curvature and thus a lack of self-similarity is observed for all TJ-limited simulations.

Furthermore, a forward projection technique has been developed for 3D reconstruction of x-ray diffraction contrast tomography (DCT) data. A diffraction pattern is simulated for each grain and a Monte Carlo algorithm minimizes the energy cost function, which is related to the difference between the simulated and experimental
diffraction patterns. The result is a grain map that is 17% more space-filling than algebraic reconstruction. A similar algorithm was developed to consider all grains at once, looping through several orientations for each undefined voxel and choosing an optimal orientation. This method, tested on a strontium titanate sample, results in space-filling and smooth junctions.

The single-grain forward projection algorithm was used to reconstruct data from an ex-situ DCT grain growth experiment, in which 7 timesteps during grain growth of a high-purity aluminum wire were collected. Abnormal grain growth occurred on the surface; large cube-texture grains absorbed the small random-texture grains. Higher-angle boundaries have been shown to move more rapidly relative to low-angle boundaries.

Finally, 4D solid-liquid dendritic structures were analyzed. An algorithm was created to automatically find pinching events caused by Rayleigh instabilities. Pinch-off diameters were calculated as a function of time; the average pinching rates match theoretical values within 6% [1,2]. The shape of the pinching events approaches a self-similar shape and scales with $t^{1/3}$. This approach to the self-similar shape occurs regardless of the initial conditions and is theoretically a universal phenomenon for Rayleigh instabilities.
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CHAPTER 1

Introduction

Grain growth and coarsening occur in many polycrystalline materials in order to reduce the free energy of the system. Especially during high temperature processing and operation, the grain growth rate can be significant and will often affect the mechanical, chemical, and electrical properties of metals and ceramics \([6,12]\). For instance, grain growth and particle coarsening contribute to the failure of high-temperature energy generation materials such as turbine blades and discs \([12]\). By fully understanding and controlling grain growth we hope to ultimately be able to optimize and customize properties, accurately predict component failure, and improve efficiencies of various energy technologies.

Grain boundaries, the interfaces between two grains, drive grain growth by moving towards their centers of curvatures. In the process, large grains grow at the expense of smaller grains. Triple junctions, the intersection of three grains, are often assumed to have near-infinite mobility and move with the grain boundaries in order to maintain their equilibrium dihedral angles \([13,14]\). However, research has shown that triple junctions can have low mobilities under certain conditions \([3,15,17]\). In particular, triple junctions can be quite slow relative to grain boundaries in small grains or low temperatures and can significantly affect grain boundary curvatures. Because grain growth is typically driven by curvature, triple junctions can thus change the overall kinetics, both quantitatively and qualitatively. These effects can be drastic and can
potentially cause phenomena such as grain stabilization \(^3\)\(^8\)\(^9\). Grain stabilization is the cessation of grain growth, and its occurrence is not fully understood, especially in nanocrystalline materials \(^3\)\(^18\)\(^20\)\(^25\).

The phase-field model has been shown to be quite effective in simulating granular or multiphase microstructures at the mesoscopic length scale \(^26\)\(^30\). The model is composed of a number of order parameters, where each order parameter represents a single grain orientation or phase. The order parameters and their gradients determine the free energy functional, and evolution is then determined by numerical minimization of this free energy. Importantly, interfaces are diffuse and do not need to be explicitly tracked, thus simplifying complex topological transitions. The phase-field model has the additional advantage of being able to incorporate conserved order parameters such as solute or impurity concentrations, which have been shown to play a large role in nano-scale materials \(^20\)\(^25\)\(^31\)\(^33\).

This work aims to develop a multi-order parameter phase-field model that accounts for triple junction mobility in two dimensions. The ultimate goal is to improve the predictive capabilities of nanocrystalline grain growth simulations in complex materials, which could help reduce design costs by obviating the need for costly experiments.

In order to validate increasingly complex models, it is essential that 4D (3D and time) characterization methods keep up with computational methods, such that the two can be directly compared and provide feedback to each other. Nondestructively characterizing materials in three dimensions requires large penetration power and thus typically uses synchrotron x-rays. For studying two-phase materials, absorption contrast tomography (or x-ray computed tomography, XCT) is ideally suited, and can achieve
spatial and temporal resolution on the order of 1 µm and 1 min, respectively [34–37].

In this work, in-situ 3D XCT has been used to study solid-liquid dendrite coarsening, providing new insight into the self-similarity of Rayleigh instabilities.

For single-phase materials, however, current 4D methods are relatively slow and costly [38–44]. Diffraction contrast tomography (DCT) is a technique that illuminates a sample with an x-ray beam and uses the diffraction information to reconstruct the grains [42–44]. DCT currently has the highest temporal resolution of the 3D x-ray techniques - due to its smaller scan time - and thus has the greatest potential for resolving complex grain boundary motion. The synchrotron experiment, however, is only the first step in the characterization process; the enormous amount of raw data must be processed to segment and index the diffraction spots and ultimately reconstruct the grains. These post-processing steps are quite complex and do not always produce physically realistic reconstructions, i.e. it does not perfectly resolve all of the grain boundaries.

In this work, DCT has been used to study grain growth of high-purity aluminum in three dimensions. A forward modeling technique has been developed to simulate the intensities of the diffraction spots and iteratively improve the quality of the reconstructions. These new reconstructions allow for more accurate calculations of grain boundary curvatures and velocities as a function of grain size and grain orientation. The goal of this project is to open the doors to reliable 4D characterization of more complex and technologically relevant materials such as nanocrystalline materials, nickel-base superalloys, or silicon computer chips.
Simulation and characterization are two sides of the same coin, synergizing and providing feedback to each other. Simulations may provide incite into complex interface kinetics that are currently impossible to characterize experimentally. Characterization provides incite into real materials, whose features can then be incorporated into simulations. Ultimately, this synergy between simulation and characterization is essential for, and fundamental to, the advancement of materials science and technology.
2.1. Grain Growth

Many common materials are composed of crystal domains of a certain orientation called grains. The regions where grains meet are called grain boundaries and often have relatively high energy because they disturb the periodicity of the atomic structure. This additional energy at the boundaries, interfacial free energy, drives the boundaries to move towards their centers of curvatures to reduce the interfacial area and its corresponding free energy. Triple lines, the intersection of three grains, and quadruple junctions, the intersection of four grains, move in unison with grain boundaries. In general, grain growth is the process of large grains getting larger and small grains getting smaller, with the average grain size increasing as small grains disappear.

Grain boundary curvature is thus typically the driving force of grain growth. Curvature-driven boundary motion is due to the difference of capillary forces – or the pressure, \( P \) – on both sides of a curved interface \[13\,14\,45\]:

\[
(2.1a) \quad P = \sigma H \\
(2.1b) \quad V = mP = m\sigma H
\]
The variables $\sigma$, $H$, $V$, and $m$ are the GB energy, mean curvature, velocity, and mobility, respectively. Atoms near the boundary are thus driven to move from the high-pressure side to the low-pressure side, resulting in net motion of the interface towards its center of curvature. Grain boundaries may be subjected to other driving forces, such as during recrystallization of a heavily cold-worked polycrystalline metal or in the presence of a large gradient in concentration, magnetic field, or temperature $^{46,47}$. In general, the shape of a grain boundary can be characterized by the mean curvature, $H$, and Gaussian curvature, $K$, which are given by

\begin{align}
H & = \frac{1}{R_1} + \frac{1}{R_2} \\
K & = \frac{1}{R_1 R_2}
\end{align}

where $R_1$ and $R_2$ are the maximum and minimum radii of curvature, respectively; see Figure 2.1. Non-zero mean curvatures in the grain boundaries arise, in part, from the interfacial force balance at each triple line (or triple junction, in 2D). That is, with every grain boundary is associated an interfacial energy – or surface tension – that varies as a function of the misorientation of the two associated crystal lattices. The dihedral angles of the triple junction can thus be determined by Young’s theorem, or the “sine rule” (Equation 2.3), which is a simple force balance of the three GB surface tensions.

\begin{equation}
\frac{\sigma_1}{\sin \theta_1} = \frac{\sigma_2}{\sin \theta_2} = \frac{\sigma_3}{\sin \theta_3}
\end{equation}
Figure 2.1. The principal – or maximum and minimum – radii of curvature, $R_1$ and $R_2$, and the normal direction, $n$, for a point P on a saddle-shaped surface.

The angle $\theta_i$ is the angle opposite of the grain boundary with energy $\sigma_i$. For a 2D isotropic system, the dihedral angles of the triple junctions are 120°. In such a system, simple geometry can be used to conclude that a grain with more than six sides will have concave grain boundaries (and will grow) and a grain with less than six sides will have convex grain boundaries (and will shrink). This is the 2D von Neumann-Mullins (VNM) theory, shown mathematically in Equation 2.4:

\[
\frac{dA}{dt} = \frac{m\sigma\pi}{3} (n - 6)
\]

where $A$ is the grain area and $n$ is the number of sides of the grain. Note that the rate of area change is independent of grain size and can be determined solely by topology, i.e. the number of sides or triple junctions. On average the von Neumann-Mullins relation has been shown to be quite accurate for 2-D isotropic simulations. In real systems, the angles are dependent on the grain boundary orientations,
and so Herring modified Young’s theorem to take an orientational torque term into account \[52\].

Assuming that the velocity of the boundary is proportional to the mean curvature, a parabolic growth rate (Equation 2.5b) can be derived by solving the differential equation (Equation 2.5a):

\[
\frac{dD}{dt} = \frac{m\sigma}{D} \tag{2.5a}
\]

\[
\langle D \rangle^2 - \langle D_0 \rangle^2 = m\sigma(t - t_0) \tag{2.5b}
\]

where \(\langle D \rangle\) is the average grain diameter and \(\langle D_0 \rangle\) is the initial average grain diameter at time \(t_0\), the onset of steady-state growth \[53\]. Because the GB velocity is not always directly proportional to the curvature, Equation 2.5b is often written more generally to include a grain growth exponent, \(n\), for \(t >> t_0\) and \(D >> D_0\) \[54\].

\[
\langle D \rangle = kt^{1/n} \tag{2.6}
\]

The grain growth exponent and rate constant are determined by many, often competing, forces, such as the diffusion mechanism, the solubility and concentration of impurities, the number and type of phases present, and the triple line and quadruple junction mobilities \[47,55,59\]. Below are listed a few theoretical exponents \[55,59\]:

- \(t^{1/2}\): GB curvature-limited growth (the “ideal” case)
- \(t^{1/3}\): Diffusion-limited coarsening
- \(t^{1/4}\): Growth limited by stochastic jumping across boundaries
• $t^1$: Triple junction dihedral angle-limited growth

Experimental values for the growth exponent vary widely between 1 and 10, with values greater than 2 being the most typical. For example, the growth exponent has been measured to be:

- 8.3 for a 2024-T3 aluminum alloy
- 4.0 for nanocrystalline copper
- 3.6-25 for nanocrystalline aluminum
- 1.0 for nanocrystalline iron
- 2.0 (the “ideal” parabolic value) for high-purity coarse-grained materials such as Cd, Fe, and Sn at high temperature
- 2.0 for 2D phase-field simulations
- 2.08, asymptotically approaching 2.0, for 2D and 3D Monte Carlo simulations

Clearly the wide range of grain growth exponents suggests that there are multiple driving forces for grain growth. Furthermore, reliably measuring the growth exponent is difficult because the average grain size must increase substantially, during which time other driving forces may come into play and change the kinetics.

Macpherson and Srolovitz formulated a three-dimensional equivalent of the von Neumann-Mullins equation. Unlike the VNM, the growth rate of individual grains is not determined uniquely by topology. As seen in Equation $2.7$, the change in grain volume over time, $dV/dt$, is dependent on the mean width, $L(D)$, and triple line lengths, $e_i(D)$.
\[
\frac{dV}{dt} = -2\pi m\sigma \left( L(D) - \frac{1}{6} \sum_{i=1}^{n} e_i(D) \right)
\]

Some simulations have shown that this equation holds true for individual grains \[66-69\], but it has not been fully tested on experimental data. From this equation, however, it is clear that topology - i.e. the connectivity of grain boundaries, triple lines, and quadrajunctions - plays an important role in grain growth kinetics.

In general, topological transitions must occur for grains to shrink or grow \[70-72\]. A shrinking grain, for instance, undergoes multiple topological transitions from 10 to 9 to 8 sides, etc., until it has 4 sides (i.e. a tetrahedron) and shrinks until it disappears. Some grain growth models, such as vertex models \[48\], explicitly include topological transitions, while others, such as phase-field \[26\] or Monte Carlo \[73\], include topology implicitly.

As seen in Young’s equation (Equation 2.3), interface energy anisotropy can significantly affect triple line dihedral angles. In general, anisotropic grain boundary energy and mobility has been shown to play a large and important role in grain growth kinetics and microstructure evolution \[46, 59, 73-82\]. Of particular interest is the dependence of mobility on grain boundary misorientation and normal \[46, 80-82\].

The orientation of an atomic lattice can be described in many ways, such as Rodrigues vectors \(R_1, R_2, R_3\), Euler angles, \((\phi_1, \Phi, \phi_2)\), and quaternions, \((q_1, q_2, q_3, q_4)\). Rodrigues vectors will be used in this work \[83, 85\]. A Rodrigues vector, shown in Equation 2.8 is a 3-component vector, \(\mathbf{R}\), whose direction indicates lattice alignment and whose magnitude indicates lattice rotation about the unit vector, \(\mathbf{r}\). For systems
with cubic symmetry, Rodrigues space is composed of a cube with truncated corners of dimensions $(\sqrt{2} - 1) \times (\sqrt{2} - 1) \times (\sqrt{2} - 1)$ [84,86].

\[ (2.8) \quad \mathbf{R} = (R_1, R_2, R_3) = r \tan(\theta/2) \]

The misorientation between two grains can also be defined as a Rodrigues vector, and the normal of the grain boundary is then defined by another two variables; the domain of grain boundary types is thus five-dimensional [59,87]. A Rodrigues vector can be transformed into a 3 x 3 rotation matrix, \( g \). The misorientation between two grains - or two different \( g \) vectors, \( \Delta g \) - is then defined as the rotation required to transform one lattice into coincidence with another:

\[ (2.9) \quad \Delta g = g_B g_A^{-1} = g_B^{-1} g_A \]

This equation does not consider symmetry, i.e. the fact that a cubic lattice is the same as an identical lattice rotated by 90°, for example. If symmetry of cubic structures is to be included, a symmetry operator, \( O_A \), must multiply the \( g \) matrices in the above equation,

\[ (2.10) \quad \Delta g = O_B g_B (O_A g_A)^{-1} = (O_B g_B)^{-1} O_A g_A \]
<table>
<thead>
<tr>
<th>Symmetry Operator</th>
<th>Rodrigues Vector</th>
</tr>
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<tbody>
<tr>
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<tr>
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<td>3-fold on (111)</td>
<td>±(−1, −1, 1)</td>
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</tbody>
</table>

Table 2.1. Rodrigues vectors for the cubic symmetry operators [88].

where $O_i$ is the symmetry operator for grain $i$. For cubic systems, there are 24 crystallographically equivalent rotations, seen in Table 2.1. In order to calculate the misorientation with symmetry included, each rotation matrix, $g$, must be rotated using the symmetry operators until its associated Rodrigues vector is in the fundamental zone. The fundamental zone for cubic-symmetric Rodrigues space is the region in which $(\sqrt{2} - 1) > R_1 > R_2 > R_3 > 0$.

The misorientation rotation matrix $\Delta g$ can then be transformed back into a Rodrigues vector [85]. The disorientation angle, $\theta$, is the minimum angle needed to rotate one grain to align it with another, considering symmetry. The disorientation angle, calculated from $\Delta g$ using Equation 2.11 with cubic symmetry, has a maximum possible value of 62.8° [84][89].

\[(2.11) \quad \theta = \cos^{-1}\left[\frac{1}{2}Trace(\Delta g) - 1\right]\]
The misorientation of a grain boundary can significantly affect the grain boundary energy and mobility. However, because grain boundary misorientation space is five-dimensional, modeling grain boundaries is no simple task. The Read-Shockley energy was proposed to approximate low angle grain boundaries as an array of dislocations. As the disorientation angle increases, the density of dislocations increases and thus the GB energy increases. For example, a pure tilt boundary will have arrays of edge dislocations. Low-angle boundary mobilities have been shown to increase rapidly and proportionally with increasing disorientation angle, up to approximately 13°. Above this critical angle, the GB can no longer be approximated as an array of dislocations and the boundary mobility may not be correlated with scalar parameters such as disorientation angle. Phase-field simulations have shown that anisotropic GB energy, based on the Read-Shockley energy and extended Read-Shockley energy, results in a broadening of the grain size distribution.

Furthermore, simulations have shown that low-energy boundaries are more frequent than high-energy boundaries, thus the distribution of grain boundary misorientations is often highly anisotropic. Experimentally, it is difficult to de-couple GB mobility from GB energy, so typically the reduced mobility, $A_b = \sigma m$, is used. Note, however, that Monte Carlo simulations showed that GB energy anisotropy strongly affects the misorientation distribution, while GB mobility anisotropy does not.

Other “special” boundaries have been found to have relatively high mobility. For instance, coincident site lattice (CSL) boundaries are those in which the crystal of one lattice periodically aligns with another. In particular, every $1/\Sigma$ atoms will be aligned, and so a $\Sigma 3$ boundary is one in which every third atom is aligned at the
boundary. It is generally observed that CSL boundaries have relatively low GB energy due to their higher periodicity. However, their GB mobilities have been observed to be highly mobile or immobile, depending on the GB character \cite{92,96}. For example, $\Sigma 7$ boundaries are generally found to be highly mobile in Al alloys \cite{97} and MD simulations \cite{92,96,98}. $\Sigma 3$ boundaries, on the other hand, have been shown to be mobile or immobile, depending on the boundary plane normal \cite{92}. In addition, in high-purity aluminum, it has been shown that (111) tilt boundaries and certain low-$\Sigma$ boundaries, such as $\Sigma 7$ and $\Sigma 13$, have low activation energies and thus are relatively more mobile at lower temperatures \cite{47,96}.

These special boundaries have more pronounced behavior during recrystallization of heavily cold-worked materials. Beck et al. discovered that $40^\circ\langle 111 \rangle$ tilt boundaries moved substantially faster than any other boundary, and appeared to dominate recrystallization kinetics \cite{46}. This special boundary may be one of the reasons for recrystallized aluminum often having a cube texture in which many of the grains are oriented with $100\langle 001 \rangle$ \cite{99,102}. During grain growth of such textured structures, there has been observed a strengthening of the cube orientation at the expense of the randomly oriented grains \cite{97}. Experiments \cite{103} and Monte Carlo simulations \cite{104} have shown that during recrystallization and grain growth, the boundaries with misorientation angles greater than $30^\circ$ disappear much more quickly than low-angle boundaries, likely due to their higher energy and mobility. This effect has been shown to affect the grain growth exponent, deviating from parabolic kinetics ($R \sim t^{1/2}$) \cite{91}.
Cold-work and recrystallization may be a principal cause of abnormal grain growth. During typical grain growth, at least in isotropic simulations and controlled experiments, the grain size distribution is relatively Gaussian and the maximum grain size is not much more than 2-3 times larger than the average grain size \([105,106]\). During abnormal grain growth, however, there may be a few grains that are much larger than the rest. The majority of the growth thus happens as the large grains grow into and absorb smaller grains \([106]\). The driving force is thought to be prior plastic deformation, texture, or small particles \([97,106,108]\). That is, the large grains are defect-free and the small grains have high dislocation densities \([106,107]\). In addition, it has been shown that these large “abnormal” grains are surrounded by mostly high-angle boundaries, which partially accounts for their high growth rates \([106,109]\); areas with random or high-angle texture grow more quickly than the areas with low-angle cube texture \([108]\).

Overall, grain boundary misorientations can have a large effect on boundary mobility and overall kinetics of interfaces \([47,84,86,93,110,116]\). Grain boundary motion, in general, affects properties and thus needs to be fully understood in order to design materials with high grain boundary density, i.e. nanocrystalline materials. Triple lines are less understood due to their higher complexity and lower dimensionality. They do, however, significantly affect grain boundary motion and play an even larger role at smaller length scales.
2.2. Triple Junction Mobility

Triple junctions play an important role in grain growth kinetics due to their energy [117], mobility [3], impurity affinity [47], and larger volume fraction for small-grained materials [118]. Triple junctions can thus also significantly affect properties, e.g. creep via enhanced diffusivity [119,121] or electrochemical corrosivity via enhanced electron mobility along triple lines [122]. In small-grained materials, there may be many competing mechanisms and driving forces that affect grain growth. However, it has been shown theoretically that triple junctions are more effective at “dragging” the growth rate of nanocrystalline grains, relative to vacancies, particles, and impurities [123]. Overall, triple junctions are not fully understood and are an area of active research.

Triple junction mobility has been studied theoretically [4,5,123-130], computationally [4,16,17,67,129,131,135], and experimentally [3,125,126,136,141]. Triple junctions (TJs) move when their equilibrium angles deviate from equilibrium, which happens when their constituent grain boundaries move towards their centers of curvature. The TJ mobility is a parameter that dictates how fast the TJs move when subjected to such driving forces. In order to understand the basics of TJ mobility, an analytical theory for the simplest triple junction geometry – seen in Figure 2.2(a) and 2.2(b) – was developed by Gottstein and Shvindlerman et al. [3,4]. In this geometry, one can calculate the TJ velocity, mobility, and dihedral angle relatively easily. The shape of the grain boundary $y(x)$ for the $n < 6$ geometry is given by:

$$y(x) = \xi \arccos[e^{-\frac{x^2}{\xi + c_1}}] + c_2$$
where $\xi = \frac{a}{2\theta}$, $c_1 = \ln(\sin \theta)$, $c_2 = -\xi(\frac{\pi}{2} - \theta)$, and $n$ is the number of sides. There are only two degrees of freedom; if the grain size, $a$, and angle, $\theta$, are known then the grain boundary (GB) shape can be uniquely determined. The steady-state velocity is also uniquely determined by $a$ and $\theta_a$:

\begin{equation}
V = \frac{2\theta_a m_{GB} \sigma}{a}
\end{equation}

Figure 2.2. Steady-state triple junction geometries. The TJ moves to the right in both cases. The theoretical angle, $\theta$, and GB shapes have been solved analytically [3, 4].
For grains of less than 6 sides, the TJ angles inside the grain are less than their equilibrium values and the grain shrinks (grain #1 in Figure 2.2(a)). In this system with isotropic grain boundary energies, the triple junction velocity, $V_{TJ}$, is

\begin{equation}
V_{TJ} = m_{TJ} \sigma (2 \cos \theta_a - 1)
\end{equation}

where $m_{TJ}$ is the TJ mobility and $\theta_a$ is half the dihedral angle in the direction of the TJ velocity. By setting Equation 2.14 equal to Equation 2.13, the mobility parameter, $\Lambda$, can be derived \cite{17},

\begin{equation}
\Lambda = \frac{m_{TJ}a}{m_{GB}} = \frac{2\theta_a}{2 \cos \theta_a - 1}
\end{equation}

where $m_{TJ}$ and $m_{GB}$ are the TJ and GB mobilities in units of energy per length and energy per area, respectively. For large $m_{TJ}$, $\Lambda$ is large and the denominator on the right side of Equation 2.15 approaches zero and thus $\theta_a$ approaches the equilibrium isotropic value of 60°. In this case, the TJ velocity is dictated by Equation 2.13 (GB-limited kinetics). For small $m_{TJ}$, $\Lambda$ approaches zero and $\theta_a$ decreases, and the TJ velocity is dictated by Equation 2.14 (TJ-limited kinetics). There are two important conclusions from this theoretical analysis. First, decreasing the grain size, $a$, decreases the mobility parameter, $\Lambda$, as well as the TJ angle, and so TJs play a larger role for small grains. Second, by simply measuring the angle and grain size in such a system, the relative TJ and GB mobilities can be determined. A similar analysis can be done for $n > 6$; see references \cite{4,124}. A similar quadruple junction (QJ) mobility parameter is given by Equation 2.16.
where $m_{QJ}$ is the QJ mobility in units of energy per quadruple junction $[5]$. For 2D polycrystalline systems, $\Lambda'$, described by Equation $2.17$ is used to measure the overall effect of TJs and QJs $[142, 143]$, 

(2.17a) \[ \Lambda'_{TJ} = \frac{m_{TJ}\langle D \rangle}{2m_{GB}} \]  
(2.17b) \[ \Lambda'_{QJ} = \frac{m_{TJ}\langle D \rangle^2}{4m_{GB}} \]  

where \( \langle D \rangle \) is the average grain size, or effective grain diameter. Triple junctions and quadruple junctions can thus act as pinning forces on the grain boundaries, as shown in Equation $2.18$ $[47, 141]$, 

(2.18) \[ \frac{d\langle D \rangle}{dt} = \frac{m_{GB}P}{1 + \frac{1}{\Lambda'_{QJ}} + \frac{1}{\Lambda'_{TJ}}} \]  

Grain growth can then be described by Equation $2.19$, which consists of a GB term, a TJ term, and a QJ term $[47, 141]$, 

(2.19) \[ \frac{1}{m_{GB}\sigma} \left( (\langle D \rangle)^2 - (\langle D_0 \rangle)^2 \right) + \frac{1}{m_{TJ}\sigma} \left( (\langle D \rangle - \langle D_0 \rangle) \right) + \frac{1}{m_{QJ}\sigma} \ln \left( \frac{\langle D \rangle}{\langle D_0 \rangle} \right) = t \]
This equation can be simply conceptualized by taking the limit as $D$ approaches zero:

- **GB Kinetics**: For large grains, the parabolic GB term dominates and $\langle R \rangle \sim \sqrt{t}$, just as with curvature-driven grain growth (the growth exponent is 2).
- **TJ Kinetics**: For small grains, the linear TJ term dominates and $\langle R \rangle \sim t$ (the growth exponent is 1).
- **QJ Kinetics**: For very small grains, the exponential QJ term dominates and $\langle R \rangle \sim e^t$. QJ kinetics are even more dependent on grain size due to the $a^2$ term in Equation 2.16.

Linear growth kinetics, i.e. $\langle R \rangle \sim t$, should thus theoretically occur if TJ dihedral angles are the rate-limiting driving force. Such kinetics have been observed in nanocrystalline iron for grains less than 150 nm and a range of temperatures between 400°C - 600°C \[141, 144\]. 3D Molecular Dynamics simulations also observed linear grain growth kinetics and a grain size dependence of the mobility in nanocrystalline nickel \[19\]. It has also been shown theoretically that grain rotation and TJ mobility both need to be taken into account when dealing with nanocrystalline grain growth, and could be part of the explanation for the so-called inverse Hall-Petch effect \[145\].

During grain growth, the values of $\Lambda_{QP}'$ and then $\Lambda_{TJ}'$ will approach infinity as the grain size reaches certain critical values \[130\]. Gottstein et al. has suggested that the critical radii at which point TJs and QJs take on an important role are 275 nm and 50 nm, respectively, for an impurity-doped aluminum sample at 540°C \[130\]. These critical grain sizes depend largely on the temperature but vary from system to system and thus are mostly unknown.
The temperature dependence of GB, TJ, and QJ mobilities have been shown to exhibit Arrhenius behavior \cite{3}. The activation energy increases as the degrees of freedom at the defect decreases. So as temperature decreases, the limiting mobilities transition from grain boundaries to triple junctions to quadruple junctions. Seen in Figure 2.3 is a schematic of the temperature dependence of the TJ, GB, and QJ mobilities. Due to the relative activation energies, decreasing the temperature increases the critical length scales at which TJs and QJs become dominant factors \cite{47}. At low enough temperature, it is clear that most materials could experience TJ- or QJ-limited growth. This effect has been observed experimentally in the study of Zn and Al tricrystal motion \cite{3,47,136,138}. In particular, in the TJ mobility limited regime, the TJ velocities are slower and the TJ angles deviate significantly from their equilibrium values. Similarly, for a 5-sided grain in an effectively 2D polycrystalline aluminum foil, the steady-state TJ dihedral angle was 49° at 250°C and 79° at 300°C \cite{138}. The large difference in angles is likely due to limited TJ mobility at the lower temperature. However, it is also possible that for many materials the critical TJ or QJ temperatures would be so low as to make all junction mobilities effectively zero.

Gottstein et al. developed equations for the rate of area change of n-sided grains in 2D, comparable to the Von Neumann-Mullins but with TJ mobility taken into account \cite{137}. These were derived by treating the triple junctions as mobile defects that act to partially pin the grain boundaries,

\begin{align}
\frac{dA}{dt}(n) &= \frac{m_{GB}\sigma_\pi}{3(1+1/\Lambda)} \left( n \frac{6 + \sqrt{3}\Lambda}{2 + \sqrt{3}\Lambda} - 6 \right), \quad n < 6 \\
\frac{dA}{dt}(n) &= \frac{m_{GB}\sigma_\pi}{3(1+1/\Lambda)} \left( n\frac{1 - \frac{6}{\pi\Lambda B}}{6} - 6 \right), \quad n > 6
\end{align}
Figure 2.3. Arrhenius behavior of GB, TJ, and QJ mobilities \[\text{[3.5]}\]. As temperature increases, the rate-limiting mobility transitions from QJs to TJs to GBs.

where \( B = -\frac{\sqrt{3}}{\ln(\sin(\pi/3))} \). These are considered mixed kinetics, i.e. the TJ angles do not deviate significantly from their equilibrium angles, such that \( 5 < \Lambda < 25 \). Rather than there being a unique critical number of sides, as with the VNM, the critical number of sides is a function of \( \Lambda \), seen in Equation \[\text{2.21}\] \[\text{3.4.124}\].

\[
(2.21a) \quad n^*_L = \frac{2 + \sqrt{3}\Lambda}{1 + \frac{\sqrt{3}}{6}\Lambda}, \quad n < 6
\]

\[
(2.21b) \quad n^*_H = \frac{6}{1 + \frac{6\ln(\sin(\pi/3))}{\pi\sqrt{3}\Lambda}}, \quad n > 6
\]

There is thus a critical number of sides, \( n^*_L \) and \( n^*_H \), for \( n < 6 \) and for \( n > 6 \), respectively. This difference in critical number of sides suggests that there is a range
between $n^*_L$ and $n^*_H$ in which grains are stable. In the work of Pande et al. \cite{145}, it was pointed out that in this “mixed kinetics” theory \cite{137}, the growth rate, $dA/dt$, is positive for all $n$-sided grains for TJ mobility parameters of $1.43 \leq \Lambda \leq 10.73$. Due to conservation of mass, positive growth rates for every grain is impossible, and thus it is possible that such theoretical rates would lead to stabilization of the grain structure.

Gottstein et al. also proposed a pure TJ-limited theory for $dA/dt$ in which TJs fully pin the boundaries and the grains are approximated to be regular polyhedra \cite{124},

\begin{equation}
\frac{dA}{dt}(n) = m_{TJ}\sigma P \cos(\frac{\pi}{n})(2\sin(\frac{\pi}{n}) - 1)
\end{equation}

where $P$ is the perimeter for $n$-sided polyhedra where $n > 3$. These equations require that $\Lambda << 1$. This theory suggests that a 2D arrangement of regular polygonal-shaped grains of $n > 3$ would be stable, if it could be attained. And thus, Gottstein, et al. \cite{3,4,124}, and others \cite{3,18,19,145}, claim that triple junction mobility may be one of the large contributing factors to grain stabilization in nanocrystalline materials.

Triple junction mobility-limited grain growth has been studied using various models \cite{4,17,67,131,133,135,142}. Molecular dynamics simulations have been used to study tri-crystal motion; results are qualitatively comparable to experiments and theory described above \cite{17,131}. Zöllner et al. has proposed a Monte Carlo Potts model that incorporates both TJ and QJ mobility; simulations showed linear and exponential grain growth kinetics, respectively \cite{133}. Triple junction mobility-limited grain growth has also been modeled using vertex models \cite{142} and network models \cite{67,135}. The vertex models and Potts models have both seen a widening of the grain size distribution.
and a lack of self-similarity during TJ mobility-limited grain growth. The vertex model has also been seen to match the TJ-limited and mixed kinetics theories proposed by Gottstein and Shvindlerman, Equations 2.20 and 2.22. Vertex simulations showed that including GB anisotropy results in a much wider triple junction angle distribution. Grain boundary energy anisotropy is thus somewhat coupled with triple junction mobility, as they both affect TJ angles.

Overall, TJ mobility has been shown to affect the grain size distributions, grain growth rates, and growth exponents in small-grained materials, especially at temperatures much less than the melting temperature. Fully understanding how GB, TJ, and QJ mobilities affect kinetics as a function of grain size and temperature is thus a very complex problem due to the changing relatively mobilities of each as time goes on. Due to this strong dependence on grain size, the ability to reliably model TJ mobility will only become more important as nanocrystalline materials become more ubiquitous. Such reliable models would have many applications in design, including grain growth-resistant nano-materials for high-temperature operation and small feature development in electronic transistors.
2.3. Phase-Field Model

There are numerous computational techniques for modeling grain growth, including Monte Carlo Potts [146], Vertex [147, 148], Front Tracking [149], Molecular Dynamics [150], Phase-Field [49, 151], network [67], and Phase Field Crystal [152]. In this work, a multi-order parameter phase-field model has been developed that accounts for triple junction mobility in two dimensions.

The main advantages of the phase-field model are that interfaces are diffuse and smooth and thus less prone to voxelization errors. Furthermore, boundaries and junctions do not need to be individually tracked, nor do topological transitions need to be explicitly incorporated. Conserved phenomena such as composition gradients and bulk diffusion can also be relatively easily incorporated into the model using a Cahn-Hilliard evolution equation [30, 153, 154]. The main disadvantage is that the model is computationally intensive due to the requirement that the number of points through interfaces must be 6-10 and that the grain size must be substantially larger than the interface (about a factor of 10) [155, 156].

The multi-order parameter phase-field model of grain growth was first developed by Fan and Chen [151, 157] and is based off of the diffuse interface theory for non-conserved motion [153, 158]. In the model, a system is composed of a number of non-conserved order parameters, $\eta$, which represent grain orientations. Inside each grain, one order parameter is equal to 1 and the rest are equal to 0 and thus there is one order parameter for each grain in the system. At a grain boundary, one parameter transitions smoothly from 1 to 0 and another transitions from 0 to 1, and at a triple junction, there exists a mixture of three order parameters.
The driving force for microstructure evolution is the minimization of the free energy functional, which is composed of a bulk free energy term $f_o$ and a gradient term that represents the interfacial energy:

\begin{equation}
F = f_o(\eta_1, \eta_2, ..., \eta_p) + \sum_{i=1}^{p} \frac{\kappa_i}{2} (\nabla \eta_i)^2 \tag{2.23a}
\end{equation}

\begin{equation}
f_o(\eta_1, \eta_2, ..., \eta_p) = \mu \left( \sum_{i=1}^{p} \left( -\frac{\alpha}{2} \eta_i^2 + \frac{\beta}{4} \eta_i^4 \right) + \gamma \sum_{i=1}^{p} \sum_{j \neq i}^{p} \eta_i^2 \eta_j^2 \right) \tag{2.23b}
\end{equation}

where $\kappa_i$ is the gradient energy coefficient, $\eta_1, \eta_2, ..., \eta_p$ are the order parameters, $p$ is the number of grains, and $\mu, \alpha, \beta,$ and $\gamma$ are input phenomenological parameters \[151\]. The bulk free energy functional has degenerate minima at $f_o(1,0,0,...,0)$, $f_o(0,1,0,...,0)$, etc.

The smooth interface forms as a tradeoff between the bulk energy, $f_o$, which drives the order parameters to be 0 or 1 everywhere and thus form sharp interfaces, and the gradient energy term, which drives the interface to be diffuse in order to minimize the laplacian. The ratio $\mu/\kappa$ thus determines the interface thickness. The parameters $\mu, \alpha, \beta,$ and $\gamma$ affect the minimum, maximum, and height of the energy barrier between two grains with order parameters $\eta_1$ and $\eta_2$, plotted in Figure 2.4. The parameters ($\alpha = 1, \beta = 1, \gamma = 1.5, \mu = 1$) were chosen to maintain symmetry at the grain boundary, but the results of this work depend weakly on the exact values of these parameters. Figure 2.5 illustrates a plot of a 1D phase-field boundary.

The evolution of the grain boundaries is curvature-driven and is governed by the Allen-Cahn equation \[158\] or the time-dependent Ginzburg-Landau equation, which model nonconserved phenomena,
Figure 2.4. Plot of the bulk free energy, $f_\alpha$, for the order parameter $\eta$ in a two parameter system. The height of the barrier between $\eta = 0$ and $\eta = 1$ is determined by the variable $\mu$ (courtesy of Ian McKenna).

Figure 2.5. Plot of the order parameters (red and blue) through a one dimensional interface. The black line is sum of the order parameters squared, which has a distinct minimum at the interface (courtesy of Ian McKenna).
\[
\frac{\partial \eta_i(r,t)}{\partial t} = L_i \frac{\delta F}{\delta \eta_i(r,t)}, \quad i = 1, 2, ..., p
\]

where \( L_i \) is the mobility. If the \( \frac{\delta F}{\delta \eta} \) term is solved analytically, this evolution equation becomes:

\[
\frac{\partial \eta_i(r,t)}{\partial t} = L_i \left( \mu (-\alpha \eta_i + \beta \eta_i^3 + 2\gamma \eta_i \sum_{j \neq i} \eta_j^2) - \kappa_i \nabla^2 \eta_i \right), \quad i = 1, 2, ..., p
\]

Theoretically, the velocity of the grain boundaries in the phase-field model is normal to the interface and simply proportional to the gradient energy coefficient, \( \kappa \):

\[
V = m\kappa H
\]

In anisotropic simulations, \( \kappa \) is a function of the misorientation, \( \theta_{ij} \), between the grains. For low misorientations, the Read-Shockley model can be used. Typically, the energy of high-angle grain boundaries is set to a constant, except for the special coincidence site lattice (CSL) boundaries which have much lower energy and much higher mobility.

The curvature, \( H \), of a diffuse interface can be calculated using Equation 2.27 where \( n \) is the interface normal. The curvature is solved numerically for each voxel on the grid, and thus the values far from the interface have no physical meaning.
\[ H = \nabla \cdot n \]

\[ n = \frac{\nabla \eta}{|\nabla \eta|} \]

Level-set methods can be used for most smooth interface calculations [161]. In particular, a delta function as described in [162], [163] can be used to locate the interface as well as calculate the surface or line integral along the interface. This equation was developed to calculate surface integrals along signed distance functions but applies equally well to phase-field interfaces. The delta function, \( \delta \), defined in Equation 2.28, is essentially the derivative of the Heaviside function, which in our case is the values of the order parameter [163].

\[
\delta(\eta) = \begin{cases} 
\frac{1}{2e} (1 + \cos(\frac{\pi \eta}{e})) & -e < \eta < e \\
0 & \text{else}
\end{cases}
\]

The delta function is numerically solved at each point in the array and is only non-zero at the interface. The value of \( e \) thus affects the delta function width and must be chosen such that there is at least 1-2 points across the delta function interface at all points. The line integral of a 2D grain boundary, i.e. its length, is then simply the sum of the delta function values.
The velocity, $V$, of a diffuse interface can be calculated using Equation 2.29:

$$V = -\frac{d\eta}{dt} \frac{1}{|\nabla \eta|}$$

This equation is the numerical velocity, whereas Equation 2.26 is the theoretical velocity. For converged kinetics and a small amount of boundary motion, they produce the same result.

To calculate the curvature or velocity for a set of grain boundaries, the delta function can be used to mask out all values away from the interface. In other words, the values of the curvature or velocity at each point can be weighted by the value of the delta function at that point, and in this way the mean curvature along an interface can be calculated accurately.

2.3.1. Numerical Implementation

2.3.1.1. Boundary Conditions. Three possible types of boundary conditions are considered. The first is the simplest: fixed or pinned boundary conditions. All voxels at the boundary of the system are frozen and not allowed to evolve during the course of the simulation. Thus if the system is defined as $1 : N_x$ by $1 : N_y$, then the evolution equation is only solved for voxels $2 : N_x - 1$ by $2 : N_y - 1$. Grains near the edges behave much differently than the bulk grains; this must be considered when dealing with such boundary conditions.

The second is periodic boundary conditions, which mean that the system is effectively surrounded by exact copies of itself. At the end of the array it immediately
wraps around to the beginning, and in every direction. When solving the phase-field
equations (both the energy and the evolution), conditional statements can be included
to make sure that the boundary voxels are treated differently. Again, assume the sys-
tem is defined as $1 : N_x$ by $1 : N_y$. The point $(0,y)$, the point next to $(1,y)$, must
be defined as equal to the value on the opposite side of the system, $(N_x,y)$. Likewise,
point $(N_x+1,y)$ is equal to $(1,y)$. This type of boundary condition is not physical,
but it has minimal boundary effects as long as the grains are substantially smaller than
the system.

The third type of boundary conditions is no-flux, which mean that a point im-
mEDIATELY outside of the grid is set to be equal to the point on the edge of the grid.
Numerically, it is simple to implement; the point $(0,y)$ is set to be equal to $(1,y)$ and
$(x,0)$ is set to be equal to $(x,1)$, etc. This boundary condition causes grain boundaries
to position themselves perpendicularly to the cell boundary, thus it does not allow for
boundary movement into or out of the boundary.

2.3.1.2. Free Energy and Evolution Equations. The evolution equation is solved
numerically using the explicit forward Euler method,

$$
\eta_i(r,t+1) = \eta_i(r,t) + L_i \Delta t \Delta \eta, i = 1, 2, ..., p
$$

where $\Delta \eta$ is equal to the expression in the large parenthesis in Equation 2.25 and
$\Delta t$ is the discretized timestep for the simulation. The timestep must be chosen such
that the system remains numerically stable, and is a function of the mesh spacing, $\Delta x$. 
The laplacian in the free energy equation is calculated for each voxel, \((x, y, z)\), and each order parameter, \(i\), using a central differencing formula:

\[
\nabla^2 \eta_i = \frac{1}{(\Delta x)^2} (\eta_i^{x+1} + \eta_i^{x-1} - 2\eta_i^x) + \frac{1}{(\Delta y)^2} (\eta_i^{y+1} + \eta_i^{y-1} - 2\eta_i^y) + \frac{1}{(\Delta z)^2} (\eta_i^{z+1} + \eta_i^{z-1} - 2\eta_i^z)
\]

Higher order differencing results in greater accuracy, but at a computational cost. However, these numerical solutions have been shown to be sufficient in obtaining approximately converged kinetics.

The thickness of the interface in the phase-field model, which is the number of points between 0.1 and 0.9 for a given order parameter (by convention), can have an effect on the kinetics of the simulations. In particular, if there are too few points through the interface (less than 6 or 7), or the boundary’s radius of curvature is not a factor of two greater than the interface thickness, then the velocity is no longer proportional to curvature \([26, 27, 156]\). For any interface thickness, the number of mesh points through the interface can be changed simply by changing the mesh spacings: \(\Delta x\), \(\Delta y\), and \(\Delta z\). Smaller interface thicknesses are more accurate and thus more desirable. However, if the interface thickness is decreased, then the mesh spacing, \(\Delta x\), as well as the numerical timestep, \(dt\), must be decreased as well. Moreover, decreasing \(\Delta x\) by a factor of 2 means that \(dt\) must be decreased by a factor of 4, and smaller \(dt\) means longer computation times. There is thus a tradeoff between computation time and accuracy that must be considered.
When employing grain boundary energy and mobility anisotropy in a phase-field model, the interface thickness must be fixed, and the timestep of the simulation must also be chosen such that the interfaces with the highest mobilities are numerically stable [77,164].

Overall, the phase-field model has been shown to accurately simulate curvature-driven motion. Considering that its main disadvantage is computational cost, the phase-field model may become more widely used as computation power increases and increasingly more physical features - e.g. solute diffusion, anisotropy, strain gradients, and triple junction mobility - are incorporated into the model.
CHAPTER 3

Methods - TJ mobility

A multi-order parameter phase-field model has been modified to incorporate triple junction mobility. A sparse \cite{165} and parallelized version of this code - originally developed by Fan and Chen \cite{151, 157} - was written in FORTRAN by Ian M. McKenna and Anthony E. Johnson. The code is generalized to run in 2D or 3D, can be implemented for anisotropic systems, and is parallelized to run on multiple processors \cite{166, 167}. In this work, the isotropic 2D version has been used for the TJ mobility simulations, and the isotropic 3D version has been used for experimental data smoothing and simulation.

For large phase-field systems of many grains, most of the order parameters are zero at a given voxel, thus sparse arrays are well-suited. The sparse data structure uses a linked-list derived datatype to store information in memory \cite{165, 168}. At each voxel, order parameters above a certain threshold, $e$, called the sparse tolerance, are stored in the form of a linked-list. Lower values of the sparse tolerance result in more accurate results, i.e. results that match what you would see in a non-sparse array. The kinetics of topological transitions, in particular, depend on the tolerance. However, lower tolerance values also come with an extra computational cost, both in memory and in speed \cite{167}. It has been shown that a tolerance of 0.01 is sufficient for obtaining approximately correct kinetics, and a tolerance of 0.001 provides even more accuracy. A tolerance of 0.001 has been used in these simulations. The array needs approximately 180 Bytes of RAM per grid point, independent of the number of grains.
in the system \[167\]. This is substantially less than the 80 kB of RAM needed per grid point for a non-sparse system of 10000 grains (10000 grains * 8 Bytes per float).

Visualizing the microstructure in a 2D phase-field model is typically done by summing the square of the order parameters, \( \phi = \sum \eta^2 \), at each spatial location. The sum of the order parameters squared is less than 1.0 at all junctions, seen for a TJ in Figure 3.1(a). Another way of visualizing the structure is to sum the order parameters, \( \Phi = \sum \eta \). In a 2D system, with specific phase-field parameters \( \alpha = 1, \beta = 1, \gamma = 1.5, \mu = 1 \), the sum of the order parameters is equal to 1.0 inside grains and at grain boundaries, and approximately equal to 1.08 at triple junctions. This difference is observed in Figure 3.1(b) which images the sum of the order parameters at a TJ.

Calculating the sum of the order parameters thus allows us to distinguish triple junctions from grain boundaries and ultimately to manipulate the TJs and their properties. To account for TJ mobility, the Allen-Cahn mobility, \( L \), was altered to be a function of the sum of the order parameters at each point \((i, j)\), \( \Phi(i, j) = \sum \eta(i, j) \). The goal is to decrease the mobility at the TJs without changing the grain boundary mobility. This is accomplished by making the function, \( L(\Phi) \), a negative gaussian with a minimum at \( \Phi_{\text{min}} = 1.04 \), described by Equation 3.1 and illustrated graphically in Figure 3.1.

\[
L(i, j) = L_{\text{GB}} - \exp\left[-\Phi_{\text{width}}(\Phi(i, j) - \Phi_{\text{min}})^2\right] [L_{\text{GB}} - L_{\text{TJ}}]
\]

The grain boundary mobility, \( L_{\text{GB}} \), is 1.0. The mobility function was set to be a minimum of \( L_{\text{TJ}} \) at \( \Phi_{\text{min}} = 1.04 \), halfway between the GB value (1.0) and TJ value.
(1.08), in order to maintain the stability of the TJ. Furthermore, $\Phi_{width}$ affects the width of the Gaussian in mobility-sum of the order parameter space. $\Phi_{width}$ was chosen to be 5000, small enough that GB mobility is not effected and large enough that the ring of low mobility is several mesh points wide.

Figure 3.1(c) illustrates the mobility of a TJ with $L_{TJ} = 0.01$. Specifically, it is clear that there is a loop around each TJ in which the mobility is substantially reduced. Thus, as the grain boundaries move towards the center, the TJs are essentially held in place by the loops of low mobility. In this case, the TJ mobility is low enough that the grain boundaries have become nearly completely flat. Because the grain boundary curvature is negligible under such conditions, the TJs have become rate-limiting and thus TJ dihedral angles have become the new driving force for subsequent grain growth (or shrinkage, in the 4-sided grain case).

This new driving force does not simply slow down the grain boundaries; there are greater implications. Because the the grain boundaries are flat and the TJ dihedral angles are time-invariant, the driving force is time-invariant. This means that the TJs move at constant velocity as the grain shrinks, unlike in normal grain boundary-limited grain growth in which the grain shrinks faster as it gets smaller. Ultimately, this means that if TJs have low mobility, smaller grains are relatively more stable.

Additional simulations must be done in order to test if the TJ dihedral angles have actually become the new driving force for grain growth.
Figure 3.1. Triple junction mobility model. (a) Sum of the order parameters squared at a TJ. (b) Sum of the order parameters at a TJ. (c) Colormap of the mobility of the triple junction. The center of the TJ is mobile while the area around it is less mobile. (b) Plot of the mobility as a function of the sum of the order parameters.
3.1. Model Validation

3.1.1. Tri-Crystal Simulation

A standard finite difference forward-Euler representation of the evolution equations for the order parameters is used. The grid space is chosen to resolve the peak in the order parameters near trijunctions. Away from the boundaries and trijunctions a sparse matrix approach is used. The code is parallelized over MPI. Fixed boundary conditions are used.

The model has been validated by simulating tri-crystals with the geometry in Figure 2.12(a). Values of 1.0, 0.1, 0.01, and 0.002 were chosen for \( L_{TJ} \). The initial length of the grain in the direction of motion was set to be 10 times the grain size so that there was enough time and space for the tri-crystal to converge to a steady-state shape. Once this steady-state was reached, the angle, \( \theta_a \), was calculated by fitting the grain boundary shape with the theoretical shape given by Equation 2.12. In particular, a code looped through multiple values of \( \theta_a \) and \( a \) (the grain size) until the sum of the squares of the difference between the simulation shape and the theoretical shape was minimized.

Figure 3.2 illustrates the close match between the theoretical shape and the simulated shape, for both low and high values of \( L_{TJ} \). For simulations with no TJ drag, the value of \( \theta_a \) converged to 60° as the grain size was increased.

The TJ mobility, \( m_{TJ} \), was then calculated from the simulated data using Equation 2.15. Note that the calculated TJ mobility, \( m_{TJ} \), is different from the TJ mobility parameter in the model, \( L_{TJ} \).
Figure 3.2. Grain boundary shape of tri-crystals, both simulation and theory. The fitted angles are approximately 59.9° (a) and 48° (b) for GB-limited and TJ-limited ($L_{TJ} = .01$), respectively.

It is clear from Figure 3.3 that the TJ mobility converges as the grain size to interface width ratio increases. The TJ mobility, $m_{TJ}$, converged to values of approximately 0.228, 0.060, and 0.036 for $L_{TJ}$ values of 0.1, 0.01, and 0.002, respectively. Importantly, the convergence of the TJ mobility means that the velocity is proportional to $(2 \cos \theta - 1)$, suggesting that the TJ dihedral angles deviation from equilibrium is now a driving force for boundary motion. Grain boundary curvature still contributes, but the TJ mobility slows the velocity and decreases the angle. This calculation also allows us to choose interfacial widths sufficiently small to ensure that interfacial thickness has a negligible effect on the results of the calculations.

3.1.2. N-Sided Grain Simulation

The evolution of four-sided and five-sided grains were also determined, both to verify the triple junction mobilities, $m_{TJ}$, calculated in the previous section as well as to validate the TJ kinetics theory, Equation 2.22 proposed by Gottstein and Shvindlerman 4. See Figure 3.4 for the geometry used in these simulations.
Figure 3.3. Plot of dimensionless TJ mobility vs. dimensionless grain size. The TJ mobility was calculated from the tri-crystal simulations and converges at a grain size of approximately 20 times the interface width.

For grain boundary-limited simulations, i.e. $L_{TJ} = 1.0$, the growth rate of the grain area, $dA/dt$, is found to be within 5% of the Von Neuman-Mullins values.

For $L_{TJ} = 0.001$, the simulations matched or approached the TJ-limited theory [124] for 4- and 5-sided grains; see Figure 3.4. The values of $m_{TJ}$ were taken from the converged tri-crystal results to calculate $\Lambda$. At a certain point as the 4- and 5-sided grains shrank, the shrinkage rate began to deviate from the theory. This minimum value of $\Lambda$ for which the kinetics are valid is about 0.2, which corresponds to a TJ spacing of approximately 4.0. The TJ spacing, $a$, was approximated as the distance between TJs for regular polyhedra for a calculated area. This deviation from theory for small grains is likely due to a combination of TJ mobility fields beginning to overlap.
as well as large interface widths relative to grain size. Furthermore, this minimum is smaller than for GB-limited growth, in which the 4- and 5-sided grains must have TJ spacings of approximately 6.1 and 5.1 times larger than the interface, respectively. Thus, in the TJ-limited regime, smaller grains are relatively more numerically stable, likely because the velocity is significantly smaller; larger velocities result in greater numerical errors.

Two- and three-sided grains, due to their smaller TJ spacing and higher velocity, will thus contribute the largest error, or deviation from the TJ kinetics theory, as $\Lambda$ becomes small and they shrink and disappear. As long as the average grain size is 5-10 times greater than the interface width then this error is assumed to be insignificant, especially considering the small fraction of 3-sided grains ($< 5\%$) in a 2D polycrystal [49].
Overall, this triple junction mobility-limited phase-field model has been shown to be consistent with previous results in the literature, at least for 2-, 4-, and 5-sided grains. In particular, it is clear that the triple junction dihedral angles deviate from equilibrium and move at a rate proportional to \((2 \cos \theta - 1)\). Moreover, grain boundary mobility is completely unaffected by the presence of trijunction drag. Thus, it is possible to examine intermediate values of \(L_{TJ}\), where there are two competing driving forces for grain growth whose relative importance is a function of the grain size.

3.1.3. Test of Diffuse Interface Equations

Additional simulations have been done in order to test the diffuse-interface equations for curvature, length, and velocity. These equations will be needed both for experimental and simulated data, thus it is important to understand their limitations.

3.1.3.1. Interface Length. First, the boundary curvature and length equations, Equations 2.28 and 2.27, were tested. The grain boundary length of a circle was calculated using the delta function, Equation 2.28[163]. The simulations show that the GB length is not dependent on the delta function width except for small widths of \(e < 0.15\) where voxelization becomes an issue. Figure 3.5 illustrates the same boundary with different delta function widths: 0.1, 0.2, and 0.3. There must be at least 2-3 voxels through the delta interface \((e = 0.2)\) for accurate results.

3.1.3.2. Interface Curvature. The GB curvature moderately depends on the interface width, as seen in Figure 3.6 and Figure 3.7. Increasing the width does not change the values of the curvature; it just changes which voxels along the interface to include. Points farther from \(\eta = 0.5\) (the center of the interface) deviate from the “actual”
curvature, thus wider delta function widths result in greater error in the curvature values. The “actual” curvature was calculated by measuring the area of the grain and calculating the radius as \( r = \sqrt{A/\pi} \). As the simulated circle shrinks, the error in the curvature and the length increases.

The optimal value of \( e \) is thus approximately 0.15, small enough that curvature data has a normalized standard deviation of 7% and large enough that the GB length is converged. Because the curvature data will be weighted by the length data, the
Figure 3.6. Curvature of a circular grain boundary for different grain boundary widths. Smaller widths result in less deviation.

voxels with the largest deviation from the actual curvature will be weighted the least because the contributed “length” of those voxels is smaller than those at the center of the interface. 7% error is thus an upper limit for grains larger than the interface width.

The curvature calculation is done on a grain-by-grain basis and outputs a list of all of the curvature values. This list can be used to create a curvature distribution for the entire polycrystalline system. The distribution must thus be nearly symmetric since the curvature is calculated twice for each boundary, once with positive curvature
The optimal value of $e$ is thus about 0.15-0.20 such that the GB length is stable and the GB curvature standard deviation is minimized.

and once with negative curvature. To avoid triple junctions, voxels with a sum of the order parameters of $\Phi > 1.01$ are filtered out. The curvature values are normalized, or divided by the average curvature for that timestep, such that comparisons can be made between timesteps.

The effects of not filtering the values near the TJ can be significant, especially for small grains. Figure 3.8 illustrate the effects on the curvature distribution for a single timestep for a polycrystalline system. Without the filter, the high curvature regions near the TJ are included in the distribution.

### 3.1.3.3. Velocity of Boundary.

The velocity of a boundary, calculated using Equation 2.29 must be validated. The test was done by calculating the velocity of a flat 1D boundary relative to another 1D boundary at various known distances away. Two
Figure 3.8. Effects of filtering of TJ curvature values on the distribution of a 2D polycrystalline simulation. Without the filter, the high curvature regions near the TJ are included in the distribution.

phase-field boundaries are plotted in Figure 3.9 as an example. Seen in Figure 3.10 are the results of this test. The velocity was normalized to 1 for comparison, and the delta function with $e = 0.2$ was used. As the number of voxels between the two boundaries increased, the value of the velocity dropped significantly. For a distance of more than 3 voxels, the velocity calculation dropped below 90% of the correct value. These calculations were done with 3D data was well, with identical results.

For simulated data, in which the distance a grain boundary travels between individual timesteps is much less than a voxel, Equation 2.29 works well. However, in experimental data, where boundaries may move many voxels, a different method is needed. For distances greater than 1 or 2 voxels, the velocity can be calculated by converting the phase-field data into signed-distance data [163,169]. This type of level-set
method has been used for studying two-phase materials or fluid flow [163, 170, 171].

Just like the phase-field data, the signed-distance data has implicitly defined interfaces. The signed-distance function is one in which the gradient is 1.0 everywhere, and the values are positive inside one phase and negative in another phase. The value of the signed-distance function at each spatial location is then the distance from the boundary. This signed-distance data was created in our system by treating an individual grain as phase #1, and everything else as phase #2. By calculating the gradient at every point and iteratively evolving the array, the gradients approach values of 1.0. The velocity equation was used on this new signed-distance data, illustrating much improved accuracy, seen in Figure 3.10. The maximum distance to the interface was set to be 4, which explains why the velocity accuracy decreases for distances greater than 4 voxels.
Figure 3.10. A single grain, phase-field data (a) and signed-distance data (b). The velocity calculation of a flat 1-D boundary, phase-field (c) and signed-distance (d), is more accurate for the signed-distance function as the distance from the interface increases (e).
3.1.4. Effects of Fixed Boundary Conditions

Typically in grain growth simulations, periodic boundary conditions are used. However, due to certain limitations in the phase-field code, fixed boundary conditions were used in the large 2D simulations. Theoretically, this only affects the grains near the boundaries. However, with fixed boundary conditions, the average grain size is a function of the size of the box that is selected, and of the number of grains that intersect the bounding box. Thus, in order to calculate the average grain size, or any other measures of average properties, the boundaries and the grains near them must be removed.

Stereological methods are commonly used to account for boundary conditions [172]. The size of each grain or particle can be weighted by a count factor, $F$, relating to its size, due to the fact that larger grains are preferentially removed from the bounding box.

\[
F = \frac{W_x W_y}{(W_x - F_x)(W_y - F_y)}
\]

$W_x$ and $W_y$ are the dimensions of the bounding box, and $F_x$ and $F_y$ are the maximum projected dimensions of each grain [172]. The effects of this factor, seen in Figure 3.11, are larger near the end of the simulations due to the larger grain sizes. This count factor is used for all average grain size calculations in this phase-field work.
Figure 3.11. Effect of weighting each grain’s size by a stereological factor, \( F \), for two polycrystalline simulations of 10000 grains with fixed boundary conditions. Without this factor, the average grain size is underestimated, especially as the grain size increases.
CHAPTER 4

Results - 2D Grain Growth

Polycrystals of $10^4$ grains were simulated with a grid size of 2048 x 2048 and fixed boundary conditions. Simulations were done with $L_{GB} = 1.0$ and $L_{TJ}$ values of $10^0$, $10^{-1}$, $10^{-2}$, corresponding to initial $A'$ values of $\infty$, 1.59, and 0.35, respectively. A smaller simulation of 512 x 512, with $10^3$ grains, was done for $L_{TJ} = 10^{-3}$ and $A' = 0.08$.

In the beginning of each simulation, each grain is a single pixel, and these grains grow outwards until they impinge on each other. During this growth and impingement phase, the kinetics are vastly different from normal grain growth kinetics. Once space-filling, the grain size distribution is quite narrow, and the distribution widens as the first grains begin to disappear. This initial transient ends once the size distribution is approximately at steady state. The initial transient has thus been neglected for all calculations of the kinetics.

Lower values of $L_{TJ}$ resulted in slower growth rates, as expected. The average grain size over time is plotted in Figure 4.2. The grain growth exponents were found using a best-fit calculator ($R(t) = At^n + R_0$) in MATLAB. These fits provided values for $R_0$, the initial average radius and y-intercept, which were used to illustrate the exponent in a plot of $\ln(R - R_0)$ vs. $\ln(t - t_0)$, seen in Figure 4.2(b).

The GB-limited simulations ($L_{TJ} = 1.0$) had a growth exponent of 2.06, which is consistent with the theoretical value of 2.0 for curvature-driven grain growth. The
Figure 4.1. Comparison of small section of simulations with $L_{TJ} = 1.0$ (a-c) and $L_{TJ} = 0.01$ (d-f). TJ-limited simulations were much slower and had noticeably smaller grain boundary curvatures. Simulation times, $t$, are equal to the number of timesteps divided by 100.

$L_{TJ} = 10^{-3}$ simulation had a growth exponent of 0.95, which is consistent with the theoretical value of 1.0 for TJ mobility-limited growth. It is clear that as the TJ mobility is decreased, the exponent transitions from 2.0 to 1.0. This transition is seen in the natural log plot, Figure 4.2(b), where the slope transitions from 0.5 to 1.0 with decreasing TJ mobility. Furthermore, as the average grain size increases, the effect of TJ mobility decreases because the parameter of importance, $\Lambda'$, couples the TJ
Figure 4.2. Plot of average grain radius vs. time (a) and plot of the log of grain radius vs. log of time, illustrating $t^{1/2}$ kinetics for GB-limited grain growth and $t^1$ kinetics for TJ-limited grain growth. For mixed kinetics, the temporal exponent lies between 0.5 and 1.

mobility with the grain size. Theoretically, the exponent of all four simulations should converge to 2.0 at infinite time.
As $L_{TJ}$ was decreased, the grain boundary curvatures approach zero, as can be seen qualitatively in Figure 4.3. This suggests that for low TJ mobility, grain boundary curvature plays a small role; TJ dihedral angles become the driving force for grain growth. To quantify the effect on boundary curvature, the boundary curvatures were calculated for each run at several timesteps.

The grain boundary-limited simulation was observed to have a steady state curvature distribution, seen in Figure 4.4(a). As the TJ mobility is decreased, the curvature distribution shifts towards zero curvature, but approaches the GB-limited steady-state curve as simulation time increases. In the smallest TJ mobility employed, the distribution of curvature is initially quite narrow. However, some grains clearly have nonzero...
curvature. This is because although a small average value of $\Lambda'$ was employed, there are grains in the system for which $\Lambda$ is not small, and thus some boundaries are partially limited by boundary curvature. As time progresses, more grains move into this limit and thus the curvature distribution is never time independent. As expected, since
$\Lambda'$ increases with time all of the simulations will reach a steady state distribution of curvature that matches the GB-limited curve.

The area rate of change, $dA/dt$, was calculated for individual grains at each timestep. $\Lambda$ was calculated using Equation 2.15, where $a$ is the approximate TJ spacing for a regular polyhedra in that grain class. Topological transitions were explicitly avoided in this calculation by requiring that the number of sides of a grain do not change when $dA/dt$ was determined.

As a check of the method, we examine the case of GB-limited simulation and compare to the predictions of Von Neumann-Mullins (VNM). As shown in Figure 4.5(a) the values for the average rate of area change, $\langle dA/dt \rangle$, obtained in the simulation are very close to the predicted values.

The $\langle dA/dt \rangle$ values in the TJ-limited simulations are plotted in Figure 4.5. Each point represents an average of multiple grains with similar values of $\Lambda$; the $\Lambda$ bin size was chosen to be roughly constant on a log scale. The $L_{TJ}=10^{-3}$ results were seen to match the TJ kinetics theory, Equation 2.22, especially for grains with less than 6 sides. As $\Lambda$ increases, which is due to the grain size increasing or the TJ mobility increasing, the growth rates transition from the TJ kinetics theory to the mixed kinetics theory, Equation 2.20. The $L_{TJ}=10^{-1}$ results mostly match the mixed kinetics theory, especially for large grains with more than 6 sides. The grain classes with less than 6 sides were thus skewed towards the TJ kinetic-limited growth theory, while the grains with more than 6 sides were skewed towards the mixed kinetics theory. This is consistent with the theory that grains with smaller $\Lambda$ are more affected by TJ mobility.
Figure 4.5. (a) Plot of $\langle dA/dt \rangle$ as a function of the number of sides for GB-limited growth; values match the VNM. The growth rate vs. $\Lambda$ for 4 (b), 8 (c), and 9 (d) sides. The values transition smoothly from the TJ kinetics theory to the mixed kinetics theory to the VNM.

Grain size distributions were calculated at various times. The GB limited simulations achieved a steady state distribution, as expected. Seen in Figure 4.6(a), lower TJ mobility results in a slightly wider grain size distribution relative to the steady state GB limited distribution. Near the beginning of the simulations, the distribution
is narrow, reaches the GB limited distribution, and then broadens further. From there, the distribution remains broader than the GB limited simulation.

![Graph](image)

Figure 4.6. (a) Steady state GB limited distribution with TJ limited distribution at various times. Lower TJ mobility results in a wider distribution. (b) Distribution of the number of sides, at steady state, illustrating that the topology is mostly independent of TJ mobility.

Seen in Figure 4.6(b), the distribution of $n$-sided grains for TJ-limited grain growth is quite similar to that for GB-limited growth.

### 4.1. Discussion and Conclusions

The growth rate of grains has been shown to transition between two TJ kinetics theories and approach the Von Neumann-Mullins values. This transition between multiple theories for TJ-limited growth has not been seen before. Currently, it is clear that no single theory accurately predicts the growth rate and that the relative effects of grain boundaries and triple junctions are still partially unknown. This uncertainty, i.e. lack of a single unifying theory for TJ kinetics, may be partially explained by the
size-dependence of TJ mobility. In other words, triple junction-limited growth is inherently more complex than grain boundary-limited growth because it lacks self-similarity and thus has different kinetics for smaller grains compared to larger grains.

The slight deviations from the \( n = 8 \) and \( n = 9 \) mixed kinetics theory for the \( L_{TJ} = 10^{-1} \) simulations are likely due to grain size effects, i.e. when one side of a grain is roughly the size of the interface width. Deviations from theory may also have been introduced due to assumptions in the \( dA/dt \) calculations, such as the approximation as regular polyhedra in the TJ spacing calculation.

The self-similarity in grain boundary-limited growth is most clearly seen in the curvature distribution. For decreasing TJ mobilities, the deviation from the self-similar curve increases. For extremely low TJ mobility, the curvature distribution approaches a delta function at \( H = 0 \), and yet the kinetics are still not self-similar because the distribution still changes as the average grain size increases. This suggests that models must always incorporate grain boundary curvature, even when dealing with low TJ mobility.

The grain size distribution roughly matches that seen in Weygand et al.’s TJ-limited Potts model [134,142] for intermediate values of \( \Lambda' \). It is expected that if \( L_{TJ} \) were to decrease further, the distributions would widen further. Note, however, that the TJ limited distributions are likely time-dependent. Similar to the curvature distributions, the distributions would likely approach the GB-limited distribution at longer simulation times and thus there is no steady state regime. It is conceivable that if the TJ mobility was low enough, a steady state distribution would be achieved. Interestingly, though, the distribution of the number of grain sides is similar for all of
the simulations. The topology thus appears to be independent of the TJ mobility, at least for the values used in these simulations.

Triple junctions may help explain some of the unusual results seen in nanocrystalline materials, including grain stabilization and linear kinetics. However, linear kinetics are not always observed in nanocrystalline grain growth, and thus there may be many other competing factors that drive grain growth at such small scales. For instance, impurity segregation may play a large role in determining relative mobilities of junctions. As such, it is conceivable that the impurity levels in materials could be explicitly set in order to set the driving force for grain growth. Second phase particles may also result in pinning effects that are qualitatively similar to TJ drag but differ in the way they affect grain boundary curvatures and mobilities.

Extrapolating this work into three dimensions, triple lines and quadruple junctions play an important role in nanocrystalline grain growth. In the same way that low TJ mobility results in low GB curvature, low QJ mobility results in low triple line curvature. The relative effect of each type of junction is a function of the temperature, the grain size, the impurity concentration, and possible other forces. Because the activation energy for QJ mobility is relatively high, QJs may practically be considered infinitely mobile in many systems, just as TJs are often assumed to have infinite mobility. However, any system of grains undergoing growth must contain a certain fraction of very small grains. The smaller the grain, the more it is affected by TJ and QJ mobility. Any evolving system of grains or interfaces will thus be affected by TJ or QJ mobility in some way.
We have developed a phase-field model that includes triple junction mobility. The approach is consistent with theories for the motion of grain boundaries in systems with simple grain configurations. Using this approach we find:

- Linear grain growth is observed for small TJ mobility.
- As TJ mobility or grain size increases, the growth exponent transitions from 1.0 to 0.5 as the driving force transitions from TJ angles to GB curvature.
- The model captures the VNM and TJ limited grain growth theories, as well as the intermediate regimes where neither grain boundaries nor triple junctions dominate the kinetics.
- A steady-state grain boundary curvature distribution was observed for the GB-limited simulations.
- However, for low TJ mobility, the grain boundaries are flat and the curvature distributions are closer to delta functions. These distributions approach the steady state GB limited distribution over time.
- Steady state curvature was not observed for low or intermediate TJ mobility.
- Even without a steady state curvature, the growth exponents for the TJ limited simulations were close to 1.
- Lower TJ mobility results in broader grain size distributions.
- The topology is mostly independent of the TJ mobility.

Overall, these results help establish the importance of TJ mobility. Understanding triple junctions will only become more important as feature sizes in many technologies decrease. Characterization of small features, and their evolution, is expensive and difficult, and so the capability to model and simulate such important features is
essential for the advancement of nanomaterials. The next section will explore the capabilities of experimental characterization of grain growth in three dimensions and in time. Such 4D characterization methods can potentially be used to observe TJ and QJ mobility-limited grain growth, providing unique information that simulations alone cannot discover.
CHAPTER 5

X-Ray Tomography Background

Materials characterization of is one of the oldest and most important ways to assist in the research and development of materials, and has been increasing in complexity at a phenomenal rate. The most common materials characterization methods are scanning electron microscopy (SEM) and transmission electron microscopy (TEM), which can capture high-quality 2D images with spatial resolutions of 1-50 nm and 1-50 Å, respectively \[173\]. Electron back-scatter diffraction (EBSD) has been used extensively in combination with SEM to collect diffraction information from grains and thus calculate grain orientation information, typically with angular resolution on the order of 0.5° \[174,175\].

The main advantage of these 2D methods is that they are relatively inexpensive, fast, and easy compared to 3D or 4D methods. To make inferences about 3D phenomena – such as topological transitions in grain growth and coarsening – using 2D characterization, stereological calculations \[176\] or destructive serial sectioning must be done. Serial sectioning uses a diamond miller or focused ion beam to mill a material one slice at a time, providing a stack of 2D images that can be reconstructed in 3D. Such 2D or destructive 3D techniques are useful for characterizing a single snapshot in time, but provide no information about the evolution of the material.

In order to fully understand the grain growth process, it is necessary to study it in 4D: three dimensions and time. To do this, experimental characterization must
obviously be non-destructive and is thus limited to electron, neutron, or x-ray techniques \[177\]. Electrons can achieve high spatial resolution, but the penetration depth into materials is low. Neutrons have the opposite problem of high penetration depth due to their larger mass, but worse spatial resolution due to their lower beam intensities \[177\]. X-rays are thus currently the best tool for imaging many materials in three dimensions \[178\].

Low energy x-ray diffraction methods have been used for decades for general material characterization, e.g. for estimation of grain sizes \[179\]. The degree of x-ray absorption, $\mu$, is a function of the type of material and the beam intensity, as given by Equation \(5.1\).

\[
\mu \propto \sum_i \left( Z_i^4 \rho_i / E^3 \right)
\]

where $Z_i$ and $\rho_i$ are the atomic number and material density, respectively, for atomic species $i$, and $E$ is the photon energy \[180\]. Low-Z materials such as aluminum or silicon are thus much better candidate materials for x-ray imaging because of their larger penetration depth. Laboratory x-ray sources are typically equipped with copper, molybdenum, or silver targets, producing x-rays of relatively low energy, 8-17 keV, and providing only a few micrometers of penetration \[39\]. Laboratory sources can, however, be equipped with tungsten targets, which produce higher-energy x-rays. Synchrotron sources typically have higher energy x-rays and thus have a penetration
depth of up to millimeters or even centimeters \[39\]. Synchrotron sources have the additional advantage of higher beam intensity and thus better contrast in the diffraction spot images.

X-ray computed tomography (XCT) uses the absorption information to reconstruct multi-phase materials in 3D \[34 \ 37\]. Specifically, the sample is rotated in the x-ray beam and a series of images are taken on a high-resolution detector. Regions within the sample with higher atomic numbers absorb more x-rays, and these fluctuations in the absorption spectrum are measured in the detector images. Algebraic reconstruction or filtered back projection techniques then reconstruct the phases within the sample \[35\ \ 180\]. XCT has been used in-situ to observe evolution of two-phase materials \[36 \ 181 \ 183\].

Grain structures cannot be reconstructed using XCT if each grain is the same phase. One way around this is to precipitate a second phase at the grain boundaries and use XCT to infer the location of the grain boundaries \(167 \ 183 \ 185\). In order to x-ray image a pure material with only a single phase, however, diffraction techniques must be used.

5.1. X-Ray Diffraction Tomography

Bragg diffraction occurs when the wavelength of the light correlates with the spacing of the planes at which the light diffracts, constructively interfering \[186\]. For a given set of atomic planes, x-rays will diffract and constructively interfere only at specific angles, \(\theta\), illustrated in Figure 5.1. The conditions for Bragg diffraction are described by Equation \[5.2\].
(5.2a) \[ n\lambda = 2d\sin(\theta) \]

(5.2b) \[ d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]

where \( d \) is the \((h, k, l)\) plane spacing, \( \lambda \) is the x-ray wavelength, \( n \) is an integer, and \( \theta \) is the angle of reflection.

The diffraction of x-rays depends on the symmetry of the crystals in the material. For aluminum, which has a face centered cubic crystal structure, the diffraction plane indices \((h, k, l)\) must be all even or all odd. The first diffraction planes, in order of increasing diffraction angle, \(2\theta\), are thus (111), (113), (222), (133), (224), etc. [186].

The structure factor, \( F \), is a function of the material symmetry and form factor, \( f \),
which decreases with increasing $\theta$. Equation 5.3 illustrates the structure factor for a FCC material.

\begin{align}
(5.3a) \quad F_{hkl} &= f[1 + (-1)^{h+k} + (-1)^{k+l} + (-1)^{h+l}] \\
(5.3b) \quad F_{hkl} &= 4f \quad \text{hkl all even or all odd} \\
(5.3c) \quad F_{hkl} &= 0 \quad \text{hkl mixed parity}
\end{align}

X-ray diffraction can be used to reconstruct materials in 3D. Three-dimensional x-ray diffraction (3DXRD) uses planar 2D synchrotron x-ray beams of energy 45-100 keV to illuminate 2D cross-sections of a sample \[38, 39, 177, 187\]. Like XCT, the x-rays leaving the sample are collected with a high-resolution detector as the sample is rotated. If the rotation is at a small enough increment, individual grains come and in and out of diffraction at the Bragg angle for various planes. The series of diffraction patterns can be used to reconstruct the slice of the sample with a mapping precision of 5 $\mu$m x 5 $\mu$m x 1 $\mu$m; the process is then repeated for consecutive slices \[188\]. This method measures crystallographic information, elastic strain, and the ultimately the 3D shape of individual grains. The 3DXRD technique has thus been used to study grain growth \[82\], recrystallization, plastic and elastic strain (up to 30%) \[189\], and phase transformations \[177\]. Because of the long data-collection time, however, the number of timesteps is limited.

Similar techniques use a 1-D beam that illuminates a single line through the sample, around 5 $\mu$m thick \[177\]. Decreasing the dimensionality of the x-ray beam increases
the spatial resolution and improves the reliability of the reconstructions, but increases the scan time and thus decreases the potential temporal resolution (i.e. time between scans).

Three dimensional x-ray diffraction imaging is a very active field of research, both experimentally and computationally \[38, 42, 177, 188, 190, 195\]. That is, the synchrotron experiment is only the first step; post-processing of diffraction spots, including segmentation and indexing, significantly affects grain map reconstructions \[38, 188, 191, 195\]. There are various algorithms for reconstructing grain maps from diffraction spots, including variations of filtered back-projection and algebraic reconstruction.

The x-ray technique with the greatest temporal resolution is currently x-ray diffraction contrast tomography (DCT) because the scan time is as low as 2-3 hours \[42, 44, 75\]. Similar to 3DXRD, synchrotron x-rays illuminate the sample, and an area CCD detector is placed within millimeters of the sample and takes images every 0.1° as the sample rotates. The main difference is that the beam illuminates the entire sample at once rather than a single slice. A schematic of this process is given in Figure 5.2. DCT has been used, in combination with absorption contrast tomography, to study strontium titanate \[196\] and propagation of short fatigue cracks in magnesium \[197\] and beta titanium \[198\].

The spatial resolution of 3DXRD and DCT is currently limited by the detector resolution, approximately 1 µm \[188\]. However, the accuracy of grain boundary locations is considerably larger than 1 µm due to limits in the reconstruction algorithms. That is, the segmentation and indexing of diffraction spots is not perfect; overlapping spots
X-rays penetrate sample and diffract at Bragg angle

Figure 5.2. Schematic of the DCT setup, illustrating $\omega$, $\eta$, and $2\theta$. The angle $\eta$ is in the plane of the detector, and the angle $2\theta$ is the diffraction angle, not necessarily in the plane of the figure.

or noise, for instance, can introduce errors in the reconstructions. Furthermore, diffraction spots are assumed to be parallel projections of the grains from which the x-rays are diffracted. As such, the orientation gradients within grains must be limited to about 1%, otherwise the reconstructions are somewhat unreliable near the boundaries [188]. Furthermore, the sample-detector distance affects the quality of the resulting reconstructions. Shorter distances result in greater spatial resolution while larger distances result in greater strain or orientation resolution.

The post-processing is thus a very essential part of the DCT grain reconstruction process, and is where we must focus in order to improve the 4D capabilities of DCT.
5.1.1. Diffraction Spot Analysis

At any given step during rotation of the sample, potentially hundreds of grains fulfill the Bragg condition and create diffraction spots on the detector. These diffraction spots must be thoroughly found, segmented, indexed, and ultimately matched to a specific grain [42–44]. These algorithms assume kinematic scattering (no absorption nor extinction), that the energy bandwidth and divergence of the incoming x-ray beam are negligible, and that the crystallographic space groups are known a priori [39–44].

Segmentation is the first important step in the reconstruction process. Every spot is separated from the others by first segmenting with a lower threshold value. The integrated intensity – i.e. the sum of the detector intensity values – of every spot is then calculated. Spots with integrated intensities below a certain size are discarded.

A second segmentation step takes into account the large point-spread-function of larger spots. That is, larger spots need a larger segmentation threshold value [39].

A single diffraction spot can be spread out over several values of \( \omega \), due to mosaicity or the Lorentz factor, \( L \), given by Equation 5.4

\[
L = \frac{1}{\sin(2\theta)\sin(\eta)}
\]  

(5.4)

where \( 2\theta \) is the diffraction angle and \( \eta \) is the offset angle from the vertical direction on the detector relative to the extinction spot, illustrated in Figure 5.2. If a grain is oriented in a specific way, it is possible for it to fulfill the Bragg condition for a large range of \( \omega \) and thus produce a diffraction spot that is spread out over consecutive
images. Diffraction spots are thus segmented in three dimensions, i.e. on the plane of the detector and in consecutive images (consecutive \( \omega \) values). The algorithm calculates the center of mass of each spot and merges the 3D diffraction “blob” into a 2D spot with an average \( \omega \).

Once the spots are segmented, the code pairs spots with their so-called Friedel pairs \[42\]. Friedel pairs are diffraction spots from the same grain and with the same scatter vector, but separated by 180° in \( \omega \) and \( \eta \). To match pairs, the geometry of the system must be considered. The intersection between the diffracted x-ray and the detector plane, i.e. where the x-ray hits the detector, \((y_{det}, z_{det})\), is

\[
\begin{align*}
y_{det} &= -(L - x_l) \tan(2\theta) \sin(\eta) + y_l \\
     z_{det} &= (L - x_l) \tan(2\theta) \cos(\eta) + z
\end{align*}
\]

where \( L \) is the distance between the center of the sample and the detector, and \((x_l, y_l, z)\) is the location of the diffraction event \[39\].

Friedel pair matching allows us to locate the scattering event, as well as to index the spots to provide the scattering vector, \( G_l \). The algorithm creates a best fit line between the center of mass of each spot within a Friedel pair. This line is used to infer the plane normal and \( \theta \) and \( \eta \), which, in combination with geometry considerations, provides enough information to calculate the scattering vector \[39, 188\]. Friedel pair matching helps improve the accuracy of the orientation and location calculations.

An indexing step then works iteratively to match spots to each other and to grains. It groups pairs to build grains, merges grains together that have the same orientation
and location, adds to existing grains, and then repeats these three steps. The output is a list of all of the grains, including their respective diffraction spots, the grain’s center of mass, and the grain’s mean orientation.

5.1.2. Reconstruction

Once all of the spots have been grouped together into their respective grains, and each grain’s orientation and center of mass is determined, each grain is reconstructed one at a time using an algebraic reconstruction technique (ART) \[42, 180\].

ART is an iterative process that attempts to solve a linear system of equations, \(Ax = b\), where \(A\) encapsulates the experimental geometry, \(x\) represents the grain map, and \(b\) is the detector pixels which contain the diffraction spot information \[192\]. Reconstructing the grain map, \(x\), is thus an inverse problem. The diffraction spots are treated as parallel projections of the grain, i.e. there are no orientation gradients within a grain \[42\]. See \[188\] for more details on this reconstruction method.

Once individually reconstructed, all of the grains are assembled into a single volume. Because each grain is done one at a time, and thus each grain knows nothing about any of the others, the resulting grain map is not necessarily space-filling. Any voxels that have conflicting assignments, i.e. they belong to two different grains at the same time, are set to zero. In the ART reconstructions in this work, there is a significant number of undefined voxels, as seen in a slice of the reconstruction in Figure 5.3.

Typically, the grains are dilated in order to space-fill the reconstructions \[42, 44\], \[193, 196\]. It has been shown that the dilated volumes resolve the boundaries within 3 \(\mu\)m on average, although some boundaries are much less accurate \[44\].
Figure 5.3. Slice of the grain map reconstruction using the ART method. Undefined voxels, i.e. empty and overlapping space, are dark blue.

Some algorithms fill in the empty space in 3DXRD data by applying the knowledge that certain grain boundary configurations are more likely \cite{192,199,200}. For instance, in \cite{192} a Gibbs potential is associated with every possible 2D configuration of a grain boundary, and thus a voxel’s orientation is determined by both the diffraction pattern as well as the shape of the boundary.

The direct beam images are used to reconstruct the absorption tomogram of the sample. The two “phases” in this tomogram are the material and the air around it. Because the absorption of air is negligible, the contrast in the tomogram at the surface is extremely high and thus is trivial to segment. This step simply creates the outline of the sample and can be superimposed onto the DCT reconstructions \cite{188}. 

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5.3.png}
\caption{Slice of the grain map reconstruction using the ART method. Undefined voxels, i.e. empty and overlapping space, are dark blue.}
\end{figure}
5.1.3. Errors in Reconstruction

Reconstruction errors (i.e. empty and overlapping space) are important to consider when analyzing the reconstructed data. Typically, errors are due to \[43,44\]:

- **Mosaicty**: orientation gradients in the grain that are not taken into account during reconstruction. That is, the diffraction spots are assumed to be parallel projections of the grains. Heavily deformed grains cannot be reconstructed using this method.

- **Point spread of the detector intensities** may add to the difficulty in resolving boundaries.

- **Phenomena** such as dynamic diffraction and uneven absorption will affect the detector images.

- **Overlapping diffraction spots** adds complications to segmentation and reconstruction. The obviously overlapping spots are removed from the reconstruction, but not all overlaps are obvious. The greater the number of grains, the larger the fraction of spots that are overlapping.

- **Grains smaller than 5 \(\mu\text{m}\)** may not be found because their diffraction spots have low intensity and may be hard to distinguish from noise.

The current reconstruction codes are excellent at providing the average orientation and location of each grain in the sample, but the grain boundaries, and especially the triple junctions, are not always fully resolved. Volume dilation, which fills the space in the reconstruction, can be used subsequent to reconstruction if one is interested in volume information at one timestep. However, in order to study the grain boundaries and measure how they evolve in time, the boundaries must be more reliably reconstructed.
5.1.4. Forward Projection

Grain reconstructions can be improved using alternative methods in addition to the existing ART methods. Forward projection is a method that simulates the diffraction spots for each grain and matches them to the experimental diffraction spots, iteratively improving the grain shape until the match is converged. Forward projection has been used for x-ray computed tomography (XCT) \cite{35,201,202} and 3DXRD \cite{203,206} as an alternative to filtered back-projection or ART.

In \cite{203,206}, diffraction spots for 2D slices are forward projected; the 2D reconstructions are later compiled into a 3D volume. A Monte Carlo algorithm iteratively selects a voxel, and then updates changes in the diffraction pattern and calculates the cost function. It does this for many different orientations and choses the orientation that minimizes the cost function. It then iteratively selects optimal orientations at random voxels until the cost function converges. Grain boundaries are resolved to within 10 $\mu$m and orientation resolution is approximately 0.1% \cite{205}. The diffraction spots are thresholded and thus intensity variations within a diffraction spot are not considered. Because the orientation of individual voxels can be determined using this method, mosaicity can be measured and sub-grains can be found \cite{204}. This method is useful for reconstructing heavily deformed grains and measuring the recovery process.

In DCT, because the entire sample is illuminated at once, the diffraction spots represent 3D data. Thus, the forward projection is an inherently 3D problem that, until now, has not been used for DCT grain reconstruction.
CHAPTER 6

Forward Projection Method

A forward projection technique has been developed for three-dimensional reconstruction of x-ray diffraction contrast tomography data. This code creates a simulated diffraction pattern for each grain and uses a Monte Carlo algorithm to minimize the cost function, which is related to the difference between the simulated and experimental diffraction patterns. Overall, the algorithm has a few similarities to Suter et al.’s work \cite{Suter203}, in that the diffraction spots are simulated and iteratively improved. However, this algorithm runs for one grain at a time and actually simulates the intensities of the diffraction spots, whereas Suter et al.’s work considers multiple grains at once and simulates segmented diffraction spots.

6.1. Algorithm

6.1.1. Setup

Before running the code, a small lookup table is compiled which contains the values of $\omega$, $\eta$, and $\theta$ and the Lorentz factor and Structure factor for each diffraction spot for that grain. The table also contains the location of the algebraically reconstructed grain’s center of mass (COM) on the detector for each of the diffraction spots. This is done using a code that predicts the location on the detector based on the geometry of the x-ray experiment, Equation \ref{detector_location}. It is done for the center of mass only; for other voxels, the detector location can be calculated relative to the COM’s location.
6.1.2. Initial Condition

The initial condition, i.e. the initial grain shape, is the algebraically reconstructed
grain. The list of diffraction spots - *difstack* - for that grain is extracted from the
database. This list is simply an array of cropped diffraction spots of size $U \times V \times N_s$
for that specific grain, where $N_s$ is the number of spots and $U$ and $V$ are large enough
to encapsulate a single spot at a specific $\omega$. The whole detector, whose size is 2048
x 2048 x 3600, is thus not considered. A list of simulated diffraction spots - *simstack*
- is created from the initial grain shape. For each voxel in the grain, and for each
diffraction spot for that voxel:

- The location on the detector, $(x, y, \omega)$, is calculated using the COM’s detector
  location and the known geometric relation between the voxel and the COM.

- The detector location, $(x, y, \omega)$, is converted into the location, $(u, v, N)$, in
  *simstack*, where $N$ is the diffraction spot identification number for that grain.

- The intensity addition, $I_{wn}$, a function of the Lorentz and structure factors, is
  retrieved from the lookup table and added to *simstack* at the location $(u, v, N)$.

These steps are done for each voxel in the grain for each of its known diffraction
spots, resulting in an array of diffraction spots (*simstack*) that closely resembles the
experimental diffraction spots (*difstack*). Figure 6.1 illustrates an ART grain (a) and
its simulated diffraction spots (c) compared with the experimental diffraction spots (b).
Qualitatively, the simulated spots look similar to the experimental spots but are much
smoother and rounded out, which is expected because the ART grains are mostly round
and do not have many sharp space-filling features such as triple lines and quadruple
points.
6.1.3. Iteration

To improve upon the initial condition, an iterative Monte Carlo code is used. One Monte Carlo step (MCS) is considered to contain all of the voxels within 1 voxel of the surface. These voxels are found by subtracting the dilated grain from the eroded grain, using MATLAB functions `imerode` and `imdilate`. For each of these voxels, which are either a 1 or a 0, the value is flipped and intensity is added or subtracted from the diffraction spots at specific pixels in `simstack`. The change in difference between `simstack` and `difstack` is calculated. If this change is negative (or sometimes if it is positive, based on the voxel’s Monte Carlo temperature, $T_V$), then the change is accepted and the code loops to the next voxel. After looping through each voxel in that Monte Carlo step (in a random order), a new batch of voxels is obtained based on the new configuration.

The final forward projected spots are seen for a grain in Figure 6.1(e); they match the experimental spots much more closely and appear to have sharper features. This closer match suggests, though does not guarantee, that the grain reconstruction is improved. In Figure 6.1, the final forward projected grain is considerably larger and has more outward curvature, but the surface is relatively rough.

6.1.4. Scale Factor

Several features have been included in the code to improve the overall shape of the grains. The intensity of the diffraction spots is determined by the Lorentz factor, the structure factor, and initial intensity of the x-ray beam. This initial intensity, $I_0$, rather
Figure 6.1. One grain, before (a) and after (b) forward projection. Comparison of experimental diffraction (c) spots with initial (d) and final (e) forward projections. Monte Carlo iteration results in a closer match between experiment and simulation.
than being input \textit{a priori}, is varied during the forward simulation until a value is converged upon. Specifically, after each Monte Carlo step, the scale factor that multiplies each of the diffraction spots is changed slightly (about 1\%) in a random direction. If this change improves the match between \textit{simstack} and \textit{difstack} (or sometimes if it does not, based on the temperature, $T_{SF}$), then the change is accepted. In all simulations, this scale factor converged along with the cost function.

In theory, the value of this scale factor, $I_0$, should be the same for every single grain. In practice, the scale factors did not all converge to the same value; see Figure 6.2. The reason for this discrepancy is unknown, though there is a slight dependence on grain size. The difference could be due to the number of spots for each grain, which decreases slightly for decreasing grain size.
6.1.5. Surface Area Parameter

To avoid a microstructure in which the grain boundaries are noisy and have regions of extremely high (and unrealistic) curvature, a surface area penalty term was included in the algorithm. For every perturbation, the change in surface area of the grain is calculated, weighted, and added to the cost function. This causes the system to preferentially avoid “holes” in the grain, i.e. undefined voxels surrounded by defined voxels or vice versa. It ultimately results in smoother and more physical grain boundaries.

For a candidate voxel, the surface area penalty is equal to 3 minus the number of nearest neighbors that belong to the grain. Thus if a candidate voxel is surrounded by 1’s, the area cost is -3 and the voxel’s chances of being accepted will be weighted in its favor. Alternatively, if a candidate voxel is surrounded by all 0’s, then the area cost is 3, and the voxel’s acceptance is undesirable. This concept is illustrated in a 2D schematic in Figure 6.3. The area cost is multiplied by an area weight term, $A$, which is a parameter that is tuned to control how significantly the surface penalty affects the grain shape. If $A$ is small, the grain does not change, and if $A$ is large, the grain approaches the shape of a sphere. There is thus an optimal value which smooths the surface but doesn’t significantly affect the shape.

Furthermore, voxels that are completely isolated, i.e. 1’s surrounded by 0’s or 0’s surrounded by 1’s, are explicitly removed from the grain map (and simstack is updated with these changes) after each Monte Carlo step. These geometries are assumed to be unphysical.
6.1.6. Removal of Voxelized spots

A certain fraction of the simulated spots have numerical errors in the simstack intensity due to the voxelization of the grains. These errors appear at certain values of $\omega$ due to stacks of voxels lining up in a periodic way. See Figure 6.4 for an example of a voxelized spot and the intensity across the spot. Including these spots in the forward simulation significantly increases the noise in the reconstructions. Decreasing the mesh spacing of the grain and the detector decreases the magnitude of these errors but with a computational cost. Instead, these spots, consisting of about $5 - 10\%$ of the total, are removed entirely from the algorithm.

6.1.7. Removal of Overlapping Spots

Some diffraction spots overlap with others, and it is especially likely to occur if the grain of interest is large. If two spots are overlapping and yet are still included in the forward projection for both of those spots’ respective grains, then error is introduced. This error is due to:

- Increase in the intensity at certain pixels.
Figure 6.4. Image of a voxelized spot due to the voxelization of the grain (a), with a plot of the intensity across the spot (b). Spots such as this have been removed from the forward projection data.

- Increase in the integrated intensity, resulting in incorrect converged scale factors.
- Changes in the shape of the spots, i.e. making the spot larger.
- Incorrect center of mass calculations, resulting in a spot being shifted from its correct location in \textit{difstack}.

Figure 6.5 illustrates a montage of diffraction spots for a grain, with a few overlapping spots, highlighted. Any spots that obviously overlap with other spots have been removed entirely from the simulations. Again, these spots account for 5 – 10% of the total.
6.1.8. Convergence

Once the value of the cost function and the scale factor both converge to within 0.5%, the simulation is stopped. To do this, the two convergence factors are calculated to be the standard deviation of the cost function and the scale factor of the previous 10 Monte Carlo steps. When both of these standard deviations becomes less than 0.5% of the cost function, the simulation stops and outputs the solution. Typically
the simulations converge somewhere between 20-100 MCS, with larger grains requiring more MCS.

6.2. Algorithm Validation

Simulated data was used to test the forward projection algorithm’s robustness in arriving at the correct solution of the grain shape. The “simulated” difstack was produced using the forward projection code for a fully space-filling grain in the high-purity aluminum reconstruction (discussed in later chapters). This test grain, i.e. known solution, is shown in Figure 6.6.

The forward code was then run with no initial guess to test how quickly the grain shape and diffraction spots reach the known solution. For each plot in this section, each line represents an average of 5 runs. Specific parameters in the code were altered to test their effect on the convergence of the cost function.
6.2.1. Surface Area Test

The first test was the surface area penalty term, varying the surface weight \( A \) from 0 to 30. Figure 6.7 illustrates the result. The maximum rates of convergence occurred for \( A = 5-15 \). Zero or large values of \( A \) (20+) resulted in slower convergence. This test suggests that the surface area penalty speeds up convergence because it keeps the grain boundary shape smoother and more physical. For large values of \( A \), however, the shape is forced to be too smooth and spherical and often never finds the exact solution. It is thus desirable to have an intermediate value of \( A \) (5-15). Note that as the scale factor changes, \( A \) is changed proportionally.
6.2.2. Scale Factor Test

The next test is the effect of having an incorrect scale factor, or beam intensity, $I_0$. Simulations were done with scale factors of 2.0 and 0.5, with 1.0 being the correct factor. No surface area penalty term was included. Figure 6.8 illustrates the effect on the grain shape. Neither simulation converged to the correct solution, and both shapes are quite different than the actual shape. As expected, a scale factor that is too large results in too small of a grain, and a scale factor that is too small results in too large of a grain. It is thus very important that the scale factor be accurate when forward projecting the grain.

The next test was to allow the scale factor to change during the simulation, via a Monte Carlo algorithm, to see if the scale factor converges onto the correct value. Figure 6.9 illustrates the rate of convergence of the scale factor; in all runs the factor converged upon the correct value. For $A = 0$, the scale factor converged within about 50 MCS, on average, whereas with higher surface weights it converged at about 30 MCS, on average. The cost function converged in a way that was qualitatively similar.
Figure 6.9. Comparison of convergence of the scale factor for different values of $A$. The scale factor converges more quickly for $A = 20-30$, in about 30 Monte Carlo steps versus about 50 for $A = 0$.

to the previous test with no variable scale factor, but the simulations with $A = 5-15$ required about 50% less MCS to converge.

Overall, the correct solution was found even when the initial scale factor was significantly larger or smaller than 1.0, and convergence happened faster when a surface penalty of $A = 5-15$ was included.

6.2.3. Integrated Intensity Test

Noise was included in the diffraction spots by changing the integrated intensities of spots. In the previous simulations, the integrated intensity of each spot was set to unity. In the following runs, the integrated intensity of each spot is changed by multiplying it by a number within a gaussian distribution about 1.0, using the $\text{randn}$ function in MATLAB. The magnitude of the error, or the gaussian width, was varied.

\begin{equation}
\text{noise}(k) = 1 + \text{weight} \cdot \text{randn}(1)
\end{equation}
Figure 6.10. Cost function convergence for a noise weight of 0.1. The runs for noises of 0.2 and 0.3 were qualitatively similar. The $A = 10-20$ runs produced better results than the $A = 0$ or $A = 30$ runs.

\begin{equation}
    \text{dif stack}(k) = \text{dif stack}(k) \ast \text{noise}(k)
\end{equation}

Forward projections were done for error weights of 0, 0.1, 0.2, and 0.3, with surface weights of 0, 10, 20, and 30. Figure 6.10 illustrates the convergence of the cost function for a error magnitude of 0.1. The code did not always find the correct solution, especially as the noise weight increased. Overall, the surface area term seemed to balance out some of the integrated intensity errors and produced better and more physical solutions. While the simulations did not always find the exact solution, the surface area term helped steer it in the right direction.

6.3. Multiple Grain Method

Alternate forward projection methods were developed to consider all grains at once in order to space-fill the grain reconstructions.
(a) $A = 0$  
(b) $A = 15$

Figure 6.11. Comparison of grain shape for $A = 0$ (a) and $A = 15$ (b). Both runs have noise weights of 0.1. The surface area penalty helps keep the boundaries smooth and less affected by “incorrect” data.

6.3.1. Method # 1

In the first multiple-grain method, the complete grain map and every single diffraction spot was simulated at once. The detector images alone require a 2048 x 2048 x 3600 array; each image is 2048 x 2048 and there are 3600 images, totaling approximately 15 gigapixels. In order to store this in memory, for both the actual images as well as the simulated images, sparse arrays must be used. Sparse arrays are very useful for datasets in which most of the points are zero. Indexing and manipulating sparse arrays is slightly slower and a bit more involved, so there is a computational cost involved.

The algorithm has been developed in MATLAB to facilitate incorporation with existing reconstruction codes. MATLAB does not allow for 3D sparse arrays, at least with any built-in functions. To get around this, a structure of 2D arrays was used,
i.e. a structure of size 1 x 3600 where each element in the structure represents the 2D sparse detector image for that value of ω.

First, experimental detector images had to be converted to this type of sparse array. This was not done by converting the original detector images, which contain a fair amount of noise which we do not wish to include. Instead, a blank sparse array was created, and then an algorithm looped through each grain and each of its diffraction spots and added it to the new sparse array. The final size of the 3D array was approximately 1GB, a huge memory savings.

Next, the simulated detector images were created using the results from the single-grain forward projection, using the same method as for the experimental data. The scale factors used are thus the converged scale factors from the forward projection.

In the multiple-grain forward projection algorithm, the initial condition is thus the final grain map of the single-grain forward projection. The code finds all of the empty voxels that are tangent to defined voxels (i.e. voxels that have been assigned to a grain), and simulates the change in diffraction spots that would happen if it flipped to one of its neighboring orientations. It does this calculation for each neighboring orientation (voxels within a 3x3x3 cube of the voxel) and chooses the orientation that most minimizes the cost function, i.e. the difference between the experimental and simulated detector images. Note that because it must chose an orientation, it is now possible for the cost function energy to rise as the voxels are filled in, even with a Monte Carlo temperature of 0.

This code essentially dilates the boundaries until they meet, at which point all voxels which neighbor voxels with differing grain IDs are reiterated to calculate the
optimal orientation. This allows for pixel-by-pixel movement of the interface, until the energy converges to a minimum.

6.3.2. Method # 2

An alternative multiple-grain method has been developed. This method is simpler and faster, and has more similarities to \[ \text{203} \] due to the use of segmented diffraction spots. This method, similar to the previous multiple-grain method, loops through each of the undefined voxels and considers several candidate orientations. However, the diffraction pattern is not simulated. Rather, for each orientation, the number of diffraction spots to which the voxel contributes is counted. At a given voxel, the orientation that is selected is the one that maximizes the fraction of contributed diffraction spots. In this way, all of the undefined voxels are assigned to a particular grain, relatively quickly.

Figure 6.12 illustrates a cross-section of a strontium titanate microstructure, courtesy of Barbara Lödermann and Melanie Syha, Karlsruhe Institute of Technology \[ \text{196} \]. A particular voxel is selected, and the orientation of the large highlighted grain is tested. Seen in Figure 6.12(b) is a montage of segmented diffraction spots for this particular grain, highlighting the voxel’s forward projected location on those spots.

For each potential orientation, the number of diffraction spot “hits” and “misses” is counted, and the optimal orientation is selected based on the largest fraction of hits. These two multiple-grain methods are tested with experimental data in the next chapters.
Figure 6.12. (a) Slice of ART reconstruction, with the current test grain highlighted in blue. (b) Montage of several segmented diffraction spots for an individual grain, highlighting a voxel’s forward projected location.

6.4. Discussion and Conclusions

This chapter has demonstrated that the developed single-grain forward projection algorithm is relatively robust and can successfully reconstruct simulated noisy data. Ultimately the algorithm is not perfect; there are still several potential sources of error for which this algorithm cannot completely compensate.

- Voxelization errors: at certain values of $\omega$, the discretization of the grain results in diffraction spots with periodic stripes of high intensity. The spots where these errors are large are removed, but some of these errors, though small in magnitude, still remain.
- Mosaicity: each voxel in the grain is assumed to have the same orientation.
- Errors in the integrated intensity due to inexact scale factors (beam intensity).
• Overlapping spots still occur. The least obvious occurrences are when a small spot is entirely within a larger spot.
• The surface penalty term may cause a slight “rounding out” of the grain reconstructions.

The convergence of the scale factors for each grain suggests that the integrated intensity of the diffraction spots does not need to be known a priori. Rather, the simulation will find the correct value, even when subjected to noise. This suggests that even noisy data sets, or datasets in which the overall beam intensities are unknown, can still be reconstructed using this method.

The incorporation of the surface area penalty term has certain implications for the reconstructions, namely that triple lines and especially quadrajunctions will inevitably be slightly rounded out. The shape of these grains will thus be more realistic in that the boundaries will be smoother, but less realistic in that sharp features may not be as well resolved. Not even considering the speedup in convergence due to including the surface term, there is a tradeoff to consider between smooth boundaries and sharper feature resolution. Overall, though, if the surface weight, $A$, is small, the effects on grain topology are assumed to be negligible compared to the improvements in boundary smoothness.

It is conceivable that, instead of a surface area penalty, a configurational term could be included to penalize certain unrealistic shapes relative to others. This method was used in [192] in two dimensions for 3DXRD data in which multiple grains were reconstructed concurrently, producing reconstructions with smooth boundaries.
The noise test results are particularly significant because it shows that individual diffraction spots can have errors in their integrated intensities. These errors may be due to phenomena such as spot overlap, mosaicity, or even errors in the calculation of the Lorentz and structure factors. Even with error weights of 0.3, the grain reconstructions closely match the known shape. Importantly, the surface penalty term helped balance out some of this noise and resulted in faster convergence, keeping the shape more physical and thus limiting the number of potential solutions.

The multiple-grain forward projection algorithms have not been fully validated, but they have the greatest potential for improving the DCT reconstructions because they enforce a space-filling requirement.

We can make the following conclusions about the single-grain forward projection algorithm:

- The iterative forward projection results in diffraction spots that better match the experimental spots.
- Including a surface term to minimize noise along the grain boundaries increases the speed of convergence and results in more physical grain shapes.
- The beam intensity (scale factor) must be correct. That said, if it is allowed to vary, it will converge to very close to the correct value.
- Even with varying amount of error in the integrated intensity, as is what is seen in the experimental data, the grain can be reliably reconstructed if the scale factor is allowed to vary, especially if a surface area penalty is included.

The fact that the final forward projected diffraction spots better match the experimental spots, relative to the initial forward projection, suggests that the forward
projection produces improved reconstructions. This is not guaranteed, however, based on the errors and assumptions in the model, and thus a more rigorous test is necessary in order to completely validate the model.

In the next sections, this algorithm has been used to fully reconstruct a high-purity aluminum sample. The multiple-grain algorithms are also attempted in order to space-fill the final reconstructions.
CHAPTER 7

Experiment

The grain growth kinetics of a 99.999% pure aluminum wire have been studied using diffraction contrast tomography (DCT). In preparation for beam time, the sample was processed by David Rule and Pat Patterson (University of Florida). The sample was quenched in liquid nitrogen, rolled, and then recrystallized to an average grain diameter of approximately 100 µm. The sample was then cut into a cylindrical shape with a diameter of approximately 1 mm.

The experimental setup was built at beam line id11 at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The experiment was conducted by Wolfgang Ludwig (ESRF), Andrew King (ESRF), Erik Lauridsen (Riso), Stefan Poulsen (Riso), Burton Patterson (University of Florida), David Rule (University of Florida), and Anthony Johnson (Northwestern University).

The sample was mounted on a motorized stage. The furnace, also attached to a motorized stage, could be lowered onto the sample. The furnace consisted of three heating elements, with respective thermocouples, that ensure that a large region inside the furnace is isothermal at 413°C. This temperature corresponds to 62.5% of the melting temperature. All annealing steps were done in open air.

Before annealing, the sample was imaged using DCT. Again, see Figure 5.2 for a schematic of the experimental setup. A CCD detector was placed about 1 mm from the sample, and 3600 images were taken as the sample rotated 360° at intervals of 0.1°.
Table 7.1. Length of anneal for each timestep in the experiment.

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<tr>
<th>Timestep</th>
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Every 100 intervals, the sample was moved out of the beam to collect a control image for measuring noise. Each DCT scan took approximately 3 hours.

Once the first dataset was collected, the sample was annealed by lowering the furnace onto the sample. The heating time was 1-3 minutes, excluding the approximately 20 seconds that the furnace was moving onto or off of the sample. After annealing, the shutter was re-opened and the x-ray scan begun. The heating and scanning steps were repeated 9 times. The heating times and temperatures were chosen such that a small but finite amount of grain growth was observed during the anneal. To tune the anneal time, analysis of the detector images was done in MATLAB at the ESRF during the course of the experiment. Integrated intensities and shapes of individual diffraction spots before and after annealing were compared in order to determine the extent of grain boundary motion. Initially, anneal times of 1-2 minutes were chosen, but 3-minute anneals were chosen for the later timesteps in order to increase the extent of grain growth. The timesteps chosen are shown in Table 7.1.

Each time the annealing began, the sample’s temperature increased until its temperature matched that of the furnace. The ideal situation is if this initial transient is
negligibly short and thus the process can be approximated as isothermal. The thermal diffusivity, $\alpha$, describes the rate at which heat travels through the sample,

\begin{equation}
\alpha = \frac{\kappa}{\rho C_p}
\end{equation}

where $\kappa$ is the thermal conductivity, $\rho$ is the density, and $C_p$ is the specific heat. For aluminum, the thermal diffusivity is thus 84.2 mm$^2$/s. This value is high enough to assume that the sample reached temperature quite quickly and that the anneal was thus isothermal.

As soon as detector images were collected, the segmentation process was begun, followed by indexing and algebraic reconstruction. Overall, these steps took several weeks to complete because certain parameters, such as those for segmentation, grain merging, etc., needed to be fine-tuned. Figure 7.1 illustrates the final ART 3D reconstructions at four different timesteps during the anneal. The reconstruction algorithms appear to have successfully found most of the large grains, but also many of the small surface grains. Unfortunately the reconstructions are only about 70% space-filling, but overall they are quality datasets and they have provided an excellent initial condition for further post-processing steps.

Furthermore, the annealing has clearly resulted in grain growth. The extent of grain growth is small, as desired, thus it may be possible to observe individual grain boundary motion. This dataset is the first to capture small amounts of grain boundary motion over multiple timesteps during grain growth.
Figure 7.1. 3D ART reconstruction at multiple timesteps. It is clear that grain growth has occurred. Most of the grains are reconstructed, though the sample is not space-filling. The grain colors represent the orientations from the standard stereographic triangle relative to the z-axis of the sample.
CHAPTER 8

Forward Projection Results

After reconstructing and assembling the aluminum dataset using the existing techniques (ART), it is clear that we found most, if not all, of the grains and their respective orientations. However, there are still undefined voxels, approximately 30% of the reconstructions. Thus, grain boundaries, triple lines, and quadrajunctions are not fully resolved.

The developed forward projection codes have been used as an attempt to improve the degree of space-filling of the reconstructions and thus increase the reliability of the boundary locations.

8.1. Single Grain Method

The single-grain forward projection technique described in Chapter 6 has been used to 3D reconstruct the DCT aluminum grain growth data.

The Monte Carlo voxel temperature, \( T_V \), relates to the likelihood that a change with positive energy will be accepted. \( T_V \) was chosen to be 7, with a simulated anneal that decreases the temperature by 1% after each Monte Carlo step.

The scale factors were allowed to vary, and in all cases they converged. The temperature for the scale factor variation, \( T_{SF} \), was set to be 100 times larger than \( T_V \). It needs to be so much larger because the differences in the cost function associated
Figure 8.1. A single grain during forward projection, at different numbers of Monte Carlo steps, with a surface area weight of 5. Convergence occurs within approximately 20 MCS.

with changes in the scale factor are much larger than differences from individual voxel changes. $T_{SF}$ also decreased after each MCS, simulating anneal.

Furthermore, bad spots (spots with grain voxelization errors), and overlapping spots, were entirely removed and disregarded.

The evolution during the forward projection (with $A = 5$) of a grain is shown in Figure 8.1. Roughly 20 MCS were required for the grain shape to reach its approximate converged shape. This converged shape, though still having a rough boundary, has sharper features and outward curvature that suggests the grain now has a more physical shape. Figure 8.2 illustrates the convergence of both the cost function and the scale factor for a particular grain. Such plots for almost all of the other grains are qualitatively identical.

The effect of the surface area term, $A$, which penalizes noisy or pixelated boundaries and favors smooth boundaries, is shown in Figure 8.3 for a single grain. The forward projection was run to convergence at different values of $A$ between 0 and 50. The
optimum value of $A$ maximizes smoothness without forcing the grain to be spherical, as is seen for large $A$. This optimal value was chosen to be approximately 10.

Because of the empty space in the ART reconstructions, one would expect that a reliable forward simulation would effectively dilate the grains and fill in that space. In most cases, the forward projected (FP) grains are larger than their ART predecessors, as seen in an example of an ART grain overlaid with a FP grain in Figure 8.4.

The code was parallelized simply by running each simulation one grain at a time. On only 8 processors on a desktop computer, the simulations could be done in MATLAB for the entire 4D dataset in about 3-5 days. The forward projected grains are then assembled into a single volume in a matter of minutes.

The effect of the surface area penalty term is seen very clearly in Figure 8.5, in which two reconstructions were done, one without a surface penalty and one with a surface weight of 10. The surface penalty considerably increases the smoothness of the
Figure 8.3. A single grain at convergence for varying values of $A$ after 20 MCS. The overall boundary shifts slightly inward for finite values of $A$. Even higher values shift the grain into a rounded and faceted shape.

boundaries without significantly affecting the shapes of the grains. The boundaries are still not completely smooth but are generally much more physical.

The effects of removing the overlapping spots are illustrated in Figure 8.6. The amount of overlapping space is substantially reduced if the overlapping spots are removed.

Figure 8.7 illustrates the final FP reconstructions compared with the ART reconstruction, both in 2D (a,b) and in 3D (c,d). Overall, the boundaries are still relatively
Figure 8.4. ART grain (green) and forward projection (orange) grain overlaid at two different viewing angles. The FP grains were generally larger than the ART grains.

Figure 8.5. Slices of the grain map reconstruction for a surface weight of 0 (a) and a surface weight of 10 (b). The surface term results in much smoother boundaries, and roughly the same degree of space-filling. The wire diameter is approximately 1 mm.
noisy, but the amount of empty and overlapping space is reduced. The average amount of filled space in the reconstructions is 70% for the ART reconstructions and 75% for the forward projected reconstructions. This may not seem substantial, but it nonetheless suggests an improvement. Unlike in the ART data, many of the triple junctions are resolved. However, not all regions show improved boundary resolution.

Overall, the forward projection results in reconstructions that are more space-filling, though clearly not perfect. The precision of the location of the grain boundaries and triple junctions is slightly greater than the ART reconstructions. Many boundaries appear to only have a couple voxels of overlapping or empty space, but there are still errors and uncertainties as large as 5-10 voxels.
Figure 8.7. 3D reconstruction using ART (a, c) and forward projection (b, d). The forward projected volume has substantially less empty space.
8.2. Multiple Grain Method

In order to space-fill the grain maps via forward projection, the developed multiple-grain forward projection algorithms were used. These codes have not been fully validated, and are thus preliminary, but their results are significant because they space-fill the DCT reconstructions.

8.2.1. Method #1

Multiple-grain method #1 simulates the entire detector and iterates through each voxel to pick an optimal orientation. Figure 8.8 shows iterations of this code for a slice of a small region. The code does not loop through every single voxel during each MCS, which is why there are some undefined voxels in the middle of the grain. Given enough iterations, all of the empty space would be assigned an orientation, or a grain ID. The code results in relatively smooth, and space-filling, grain boundaries, at least for this small region.

Unfortunately, there are currently problems in the code that cause particular grains to be weighted more heavily than others and thus cause them to grow into the grain boundaries of neighboring regions. There could be a problem with the scale factors for each grain, or possibly even the number of diffraction spots for each grain. That is, grains with more spots, or more intense spots, may be preferentially weighted.

Overall, as seen in Figure 8.8, this multiple-grain method shows great promise for creating reliable space-filling reconstructions.
Figure 8.8. Multiple-grain forward projection, showing one slice. Near the end of the simulation, the boundaries have met and the reconstruction is mostly space-filling.

8.2.2. Method #2

Multiple-grain method #2 does not simulate the diffraction spots. Instead, it simply picks the optimal orientation for each voxel, based on the fraction of diffraction spots to which the voxel contributes for each orientation.

The method has been tested on the aluminum sample, but results are inconsistent and quite unphysical. Similar to the results of multiple-grain method #1, certain grains
are heavily favored in terms of selection, such that a grain will grow well beyond its original shape into the grain boundaries of other grains.

This multiple-grain method has also been tested on a strontium titanate sample investigated in [196], courtesy of Barbara Lödermann, Melanie Syha, and Peter Gumbsch, Karlsruhe Institute of Technology. Shown in Figure 8.9 are slices of the reconstruction, before and after applying the multiple-grain forward projection. The forward projected reconstruction (Figure 8.9(b)) looks very similar to the dilated reconstruction (Figure 8.9(c)). The confidence - the total fraction of diffraction spots to which the voxel’s orientation contributed - at each voxel was also imaged (Figure 8.9(d)). An EBSD “flood filled” image was included in Figure 8.9 for comparison. The EBSD image does not perfectly match either reconstruction, possibly because of sample tilt and uncertainty as to the exact slice in the sample.

Overall, the results look physical; that is, grains do not appear to dilate into regions where they do not belong. Furthermore, considering no smoothing was done, the resulting boundaries are quite smooth. The confidence at all of the undefined voxels is relatively high; almost entirely greater than 70%.

The algorithm was also run “from scratch,” meaning that no initial grain shapes were considered and all voxels were initially undefined. Figure 8.10 illustrates the results of this method. The reconstructions look quite similar to the previous reconstructions, which suggests that this forward projection model is working quite well compared to the ART method. The confidence, seen in Figure 8.10(c), is 1.0 inside most grains. Furthermore, the lower-confidence regions are near the triple junctions, which are the regions that show the greatest deviation from the EBSD image.
Figure 8.9. A slice of the strontium titanate reconstruction, showing the original (a), dilated (b), and the multiple-grain forward projection (c) with its confidence (d). An EBSD “flood filled” image is also compared (e) (courtesy of Barbara Lüdermann, Melanie Syha, and Peter Gumbsch, Karlsruhe Institute of Technology). The confidence is greater than 70% for most of the undefined voxels, and considering no smoothing was done, the resulting boundaries are quite smooth. Overall the dilated and forward projected reconstructions are quite similar, but don’t perfectly match the EBSD image.
Figure 8.10. A slice of the strontium titanate reconstruction, showing the forward projected reconstruction (a) and “from scratch” forward projection (b) with its confidence (c). The confidence is 1.0 inside most grains, and the regions of relatively low confidence are often the regions that deviate the most from the EBSD images.

This algorithm could be improved by changing parameters in the algorithm until the reconstructions match the EBSD images. This algorithm, though much simpler than Method #1 for multiple-grain forward projection, seems to work more reliably and much faster, at least for the ceramic dataset.

8.3. Additional Reconstruction Processing Steps

For 4D analysis, the single-grain forward projected reconstructions were dilated and smoothed. This was done in a single step by inputting the reconstructions into the phase-field model, similar to the method in [185]. During the phase-field smoothing of these datasets, there is a large driving force for grain boundaries to “fill in” the undefined voxels. This large driving force exists because the free energy is a minimum when the sum of the order parameters is 1.0, yet the undefined voxels have all zero
order parameters. Fully-space-filling grain boundary motion, on the other hand, is only
driven by curvature, a relatively smaller driving force. Thus, the phase-field code is
run for 400 timesteps, enough time for all of the empty space to fill in but not enough
time for most boundaries to move substantially.

The phase-field code was run with parameters \( \alpha = 1, \beta = 1, \gamma = 1.5, \mu = 1 \), and
with a mesh spacing of \( dx = 0.4 \) and timestep of \( dt = 0.01 \). With this mesh spacing,
the initial average grain diameter is about 3.5 times larger than the interface. For
dilation purposes, this is satisfactory.

Figure 8.11 illustrates the sum of the order parameters at each voxel for a slice
of a 3D volume during phase-field dilation. Blue space is initially empty, and after
400 timesteps the empty space is gone. Figure 8.12 illustrates the grain IDs for the
same simulation, showing that 400 phase-field iterations does not substantially move
most boundaries. The majority of the movement is that into the empty space as well
as the smoothening of noisy boundaries. However, any small high-curvature grain
boundaries are assumed to be inaccurate, because 400 timesteps does result in some
motion. There is thus a trade-off between having a physically realistic structure and
a reliable characterization. Any analysis in this section must be done for the larger
grain boundaries only. Overall, it is assumed that the resulting structure is much more
physical, both because it is space-filling and also because the boundaries are smooth.

The phase-field dilation ultimately dilated some grains more than others, but this
is difficult to avoid. Figure 8.13 shows a fully dilated grain overlaid with the FP grain,
at two different viewing angles. The shape changes substantially in some areas and
minimally in others. This suggests that the FP grains were not entirely accurate and that the grain boundary locations may have some degree of error.

The multiple-grain forward projection method can theoretically be used as an alternative to running the phase-field. However, even after the space-filling forward
Figure 8.12. Phase-field dilation, showing grain IDs. The location of the boundaries does not change significantly.

projection is run, the boundaries are not completely smooth. So the phase-field can be used for a shorter number of timesteps to create diffuse boundaries and remove some small amount of noise in the boundaries. Irregardless, the multiple-grain forward projection has not yet been successfully implemented on the aluminum dataset.

In order to define the sample surface, the absorption tomogram was created. The direct beam on the detector images provides the absorption information for the sample, assuming that the intensity of diffracted grains is negligible compared to the intensity of
Figure 8.13. Forward-projected (green) and fully dilated (orange) grain overlaid at two different viewing angles. The dilation causes some large movement in the location of the interface.

the direct beam. The absorption tomogram was created using a filtered back-projection technique by Erik Lauridsen (Risoe) and Wolfgang Ludwig (ESRF). The tomogram has very good contrast between the absorbing species (aluminum) and the non-absorbing species (air). Seen in Figure 8.14 is a slice of the tomogram, the intensity profile, and the final 3D reconstruction. The average upper and lower intensities were calculated based on the intensity profiles; the tomograms were then segmented by the average of these two values. Once constructed, the segmented tomogram was used as a mask to remove any voxels outside of the boundary of the sample.

Once fully space-filling and confined within the bounds of the sample, datasets at different times were aligned such that the surface at timestep 2 is in the same place as in timestep 3 and 4, etc. The absorption tomogram reconstructions at each timestep were aligned using a 3D mutual information registration code in IDL (courtesy
of John Gibbs and Begum Gulsoy, Northwestern University), similar to what was done in [167]. Each timestep was aligned with the first timestep. The amount of
registration between timesteps is on the order of 1-5 voxels in each dimension. For the voxelized (segmented) data where each voxel is attributed a grain ID, the registration was rounded to the nearest voxel. Thus there is still misalignment, as much as half a voxel in each direction. However, the phase-field data has diffuse interfaces and thus the registration was interpolated to achieve sub-voxel registration. The phase-field data was thus used for all 4D calculations, i.e. boundary velocity.
8.4. Discussion and Conclusions

We have established that the single-grain forward-projection method is better able to resolve the grain boundaries in the diffraction contrast tomography data, when compared with the ART technique.

However, it is important to note that the reconstructions are still not perfect, and thus completely reliable boundary calculations are not possible. In some cases, the grain boundaries are resolved within 1-2 voxels, while in others the uncertainty is 5-10 voxels. Particularly for small grains, this error could be on the order of the size of the grain, which suggests that small grains should not be considered reliable reconstructions.

Furthermore, the uncertainty in the triple line locations is even greater than for grain boundary locations. This means that calculating grain boundary curvature, which is a function of the triple line locations, may not be possible, at least for small boundaries. This also means that calculations such as triple line dihedral angles or triple line curvatures are also not possible with the existing reconstruction method.

The multiple-grain methods are ultimately the best way to space-fill the reconstructions, because it essentially forces each grain to consider its neighbors. For the strontium titanate sample, the forward projected reconstructions closely matched the ART and dilated reconstructions. This suggests that the new algorithm is accurately reconstructing the grains in a space-filling manner. These multiple-grain methods are in the process of being more rigorously tested using direct comparison with EBSD measurements of slices of the strontium titanate sample. Because of sample tilt in the
DCT or EBSD measurements, 2D comparison is difficult. In order to truly test these simulations, 3D registration of forward projection results to 3D EBSD must be done.

All of these forward projection methods have the potential to resolve orientation gradients within grains, by iteratively looping through regions of orientation space, similar to [203]. For pure materials with low dislocation density, using the mean orientation is likely sufficient. However, it is possible that the aluminum reconstructions would be substantially improved if orientation gradients were considered. This would come at a high computational cost relative to the current algorithm, because each voxel would need to loop through orders of magnitude more orientations.

Furthermore, the phase-field method has been used to dilate and smooth the structure. The result is a space-filling dataset in which calculations of boundary curvature and velocity are trivial. A small amount of boundary motion is unavoidable with this method, but these errors are assumed to be relatively small. However, any 4D analysis must consider all potential errors in these reconstructions, which can be summarized as follows:

- Experimental errors: isothermal approximation, duration of anneal approximation, movement of sample between timesteps, noise.
- Forward projection errors: orientation gradients, voxelization, overlapping spots, surface area penalty, noise.
- Phase-field smoothing errors: dilation, evolution.
- Registration errors: rounding, sample rotation.
Overall, 3D analysis - such as texture, grain size, etc - will be reliable, but 4D analysis may only be reliable for large grain boundaries. We can make the following conclusions regarding the forward projection of DCT data:

- Including a surface term to minimize noise along the grain boundaries results in more physical grain shapes.
- The beam intensity (scale factor) of simulated data, if allowed to vary, will converge to a constant value.
- The forward projection algorithm results in reconstructions that increase the space filling from 70% to 75%, decreasing the amount of empty space by 17%.
- The datasets have been input into a phase-field code, which simultaneously dilates and smoothes the structure. The interfaces become diffuse, allowing for simplified boundary calculations and analysis.
- A multiple-grain forward projection method has been developed that segments the diffraction spots. This method space-fills the reconstructions and appears to work extremely well for a strontium titanate dataset.

Overall, the forward projection method has great potential for improving the reconstructions of DCT data and thus improving the reliability of any 3D or 4D calculations of interfaces. The multiple-grain forward projection, in particular, has the greatest potential because it results in a space-filing grain map.

The next section will discuss the 4D grain growth kinetics of the high-purity aluminum sample. Error in the analysis due to reconstruction errors will be discussed further.
CHAPTER 9

4D Grain Growth

Three-dimensional grain growth has been studied experimentally, but typically with serial sectioning and stereological methods. Here we present the first analysis of grain growth in three dimensions with multiple timesteps, although similar methods have been used to study recrystallization \cite{177,207}. In this work we show novel 3D visualizations of grains and include 3D calculations of grain boundary motion. Despite a certain amount of uncertainty in the reconstructions, the results illustrate and suggest that much can be learned from non-destructive 3D x-ray techniques such as diffraction contrast tomography.

9.1. Results

Once the grain maps are space-filling, smoothed, and aligned, 3D and 4D visualization and analysis is possible. Each grain is output from the phase-field smoothing code and then meshed at a threshold value of 0.5, exactly at the center of the grain boundary. This converts the interfaces into an array of polygons which are then visualized in IDL or MATLAB. Several of the 3D visualization codes were written by I. M. McKenna and D. J. Rowenhurst (Northwestern University alumni).

For visualization, each grain is colored by an identification number or its orientation. The MATLAB toolbox MTEX has been used for orientation analysis. This toolbox is typically used for EBSD data, but supports 3D EBSD data, which is essentially
equivalent to the DCT data. In order to input the DCT data into MTEX, the 3D reconstructions are saved as a series of 2D ANG files which store each voxel’s location, phase, and orientation.

Figure 9.1 illustrates the reconstructions at different timesteps, colored by the \( \langle hkl \rangle \) values determined using MTEX. In particular, the \textit{orientation2color} function was used to convert Rodrigues vectors into colors that are associated with the orientation relative to the \( z \)-axis of the cylindrical sample. The standard stereographic triangle for coloring grains by orientation in seen in Figure 9.1.

9.1.1. Grain Size Analysis

It is apparent from Figure 9.1 that there is a wide distribution of grain sizes, at least on the surface, and that many of the smaller grains disappear during evolution. The grain radii were calculated by summing the number of voxels in each grain and approximating the grains as spheres. As seen in Figure 9.2, the average grain radius increases from about 60 \( \mu \text{m} \) to 105 \( \mu \text{m} \). This plot was fitted to an exponential curve, \( y = ax^b + c \), with values of \( a \), \( b \), and \( c \) are 0.94, 58, and 0.59, respectively. The temporal exponent, 0.59, is close to the “ideal” value of 0.5. However, the change in the average grain size is not very large, so the growth exponent calculation is not necessarily accurate, despite the excellent fit to an exponential curve.

Figure 9.3 shows the histogram, both for grain radius and for number of faces, for the 3D data set over time. The grain size distribution is extremely skew right, i.e. there are a large number of small grains and several large grains that are 5-10 times larger. The peak is at approximately 1/3 of the mean radius. Furthermore, the peak
Figure 9.1. Evolution of a cross-section of the fully reconstructed sample. The color of each grain is the $\langle hkl \rangle$ poles relative to the z-axis of the cylinder.
Figure 9.2. Change in average grain radius over time. Much of this increase is due to the disappearance of small surface grains. The data exhibit a smooth fit to an exponential curve with exponent 0.59.

in the number of faces distribution is around 6-7, which is much less than has been observed for 3D systems, typically 10-14 [64,185].

This wide distribution of grain sizes may be an indication of abnormal grain growth, at least on the surface. Figure 9.4 illustrates qualitatively the grain size as a function of the position in the sample. Comparing Figure 9.4(a) with Figure 9.4(b), it is quite clear that the grain size inside the sample is substantially larger, and that almost all of the small grains are on the surface. These small surface grains are likely a result of room temperature recrystallization on the surface, which has been observed for heavily deformed high-purity aluminum [208]. In this case, the surface grains likely recrystallized when the sample was lathed into a cylindrical shape.

To distinguish between grain “interior” kinetics and grain “surface” kinetics, grain size distributions were created separately for each distinct region, seen in Figure 9.5.
Any grain that is touching the surface in the first timestep is considered a surface grain, even if it evolves and leaves the surface in later timesteps. The interior grains have an initial average grain radius of approximately 76 µm, while the exterior grains have an initial average grain radius of approximately 35 µm. Furthermore, the interior grains have a distribution of the number of faces that much more closely match that seen in the literature, with an average number of faces of 14.94 initially and 11.39 finally [64, 185, 209]. This decrease in average number of faces is likely due to the large grains reaching the surface as small grains disappear.

From these grain size distributions, it appears that grain growth inside the sample is relatively “normal,” while grain growth on the surface is abnormal. Figure 9.6 illustrates the evolution of two large surface grains. Their movement along the surface
Figure 9.4. Reconstructed sample, illustrating interior (a) and surface (b) of sample. The color of many of the large interior grains is red or red-brown, meaning they are mostly aligned with the \(\langle 001\rangle\) direction. On the surface, however, there are small grains with no obvious texture. In (c), an image looking down the wire at the first timestep, showing the ring of small grains at the surface.

of the sample is much faster than their movement inside the sample because the surface grains are smaller and thus there is a higher driving force for motion.
Figure 9.5. Histograms for the radius (a) and the number of sides (b) for surface and interior grains, at timestep 2. The histograms for the surface and the interior are vastly different.

9.1.2. Orientation Analysis

Orientation texture in the sample may provide information about the sample’s processing history and may explain why grain growth occurs as it does. It is clear from Figure 9.4 that in the sample interior, there are regions of large grains with similar
Figure 9.6. Evolution of the two large abnormal grains, looking down the z-axis of the cylindrical wire. All other grains have been removed from view, and the surface is highlighted. It is clear that the larger surface grains are essentially moving through the smaller surface grains and wrapping around the surface.

orientations, almost entirely shades of red, brown, and purple. These colors correspond to orientations aligning with the \(\langle 100 \rangle\) direction. The surface, on the other hand, is composed of mostly small grains that appear to have relatively random orientations.
That is, red, green, and blue (corresponding to the \(\langle 100\rangle\), \(\langle 110\rangle\), and \(\langle 111\rangle\) directions, respectively) are relatively equally represented.

Pole figures were created in MTEX. Pole figures, which are essentially stereographic projections of the spherical orientation distribution, do not normalize by grain size. Larger grains thus have a larger contribution in each pole figure. Figure 9.7 shows the evolution of the texture of the entire sample. The peaks in the distribution, which are close to the \(\langle 100\rangle\) direction, sharpen over time. If these orientations are rotated by an Euler angle of \((18.3, 12.6, 0)^\circ\) then the peaks perfectly align with the \(\langle 100\rangle\) direction. This alignment means that there is a clear cube texture in the sample, but that the \(\langle 100\rangle\) peak in the crystal frame does not align with the z-axis of the cylinder. These pole figures match those seen in the literature for recrystallized aluminum

Figure 9.7. \(\{100\}\) pole figure, calculated in MTEX, for several timesteps. There is clearly a cube texture whose peaks sharpen a bit over time.
The orientations were thus rotated by an Euler angle of \((18.3, 12.6, 0)\)° and then filtered based on grain size. Figure 9.8 shows pole figures for large grains (greater than the mean) and small grains (less than the mean). This is roughly equivalent to isolating interior grains from surface grains, though not exactly. In Figure 9.8, unlike in Figure 9.7, each point is a single grain. The large grains have distinct \((100)\) cube texture, and are small in number. The numerous small grains, however, have a more random texture, with a few “empty” regions that are likely due to the sample processing prior to recrystallization and grain growth.

![Figure 9.8](image)

Figure 9.8. Pole figure for large (a) and small (b) grains, illustrating cube texture for large grains and more random texture for small grains.

Furthermore, the sharpening of the cube texture peaks over time has been seen in previous studies of recrystallization and grain growth [97]. This increase in cube texture was also found to be correlated with a decrease in number of randomly oriented...
grains during anneal [97]. The recrystallization texture may explain why abnormal
grain growth is observed on the surface; interior cube-texture grains grow at the expense
of random-orientation surface grains.

9.1.3. Misorientation Analysis

To get a more complete story, grain boundary misorientation analysis has also been
done. The disorientation of each grain boundary was calculated using Equation [2.10]
In particular, a code looped through every symmetry rotation, \( O_i \), of which there
are 24 for a cubic system, and found the misorientation with the lowest angle, \( \theta \),
within the Frank-Rodrigues fundamental zone. The results of this code are a particular
misorientation Rodrigues vector and an associated disorientation angle for each pair
of grain boundaries. These calculations were verified using MTEX, which can also
output the misorientation in axis-angle form. The angle is the minimum angle needed
to rotate one grain into coincidence with another, and the axis is the direction about
which this rotation is done. The disorientation distribution was calculated for each
timestep for interior and exterior grains, seen in Figure [9.9]

The surface has very little texture and thus has random-angle grain boundaries,
roughly matching the Mackenzie distribution of randomly oriented boundaries [89].
However, the interior of the sample is cube textured and has relatively more low-angle
grain boundaries. This difference between large and small grains is consistent with the
literature for abnormal grain growth of recrystallized structures [106,108,109].

The number of grain boundaries of certain types, and how that number changes
over time, can provide information about the relative mobility and/or energy of each
Figure 9.9. Disorientation angle distribution at the first timestep, showing the difference in distribution between inner grain boundaries and surface grain boundaries (a). The surface grain boundaries have roughly random texture (matches the dotted line). Evolution of the total distribution (b), showing a slight increase in low-angle boundaries during grain growth.
type of boundary. Figure 9.10 illustrates the total number of grain boundaries that fall into a certain disorientation angle “bin” of size $10^\circ$. The bin with the largest number of boundaries is $40^\circ - 50^\circ$ with approximately 3000 boundaries, and the bin with the smallest number is $< 10^\circ$ with 400 boundaries. This is simply changing the bin size of the disorientation angle distribution. From the evolution of the fraction of remaining boundaries in each bin, however, it is clear that there is a correlation with misorientation angle. In particular, the higher the misorientation angle, the less remaining boundaries (by fraction) at the end of grain growth. This suggests that such higher-angle boundaries may have higher mobility and thus evolve faster and more quickly remove themselves from the structure.

![Figure 9.10](image)

Figure 9.10. Number (a), and fraction (b), of boundaries over time. The low-angle boundaries are less common, and also show a relatively smaller decrease in number.

Special boundaries were also found in order to attempt to compare their mobility to other boundaries. Of particular interest are misorientations whose axes align with
the ⟨111⟩ direction. The ⟨111⟩ tilt boundaries have been shown to be particularly mobile during recrystallization \[46\textbf{100}\]. To get an idea of how these boundaries are evolving, the number of certain types of special boundaries were simply counted at each time, completely independent of grain boundary normals. Because the normals are somewhat unreliable in the reconstructions, especially in the small grains, it is not possible to determine if these boundaries are pure tilt or pure twist or something in between.

There were about 500 ⟨111⟩ boundaries, initially, and the number decreased substantially over the course of the experiment. However, if low-angle and high-angle ⟨111⟩ boundaries are isolated, it becomes clear that low-angle ⟨111⟩ boundaries are less common but also show a relatively smaller decrease in fraction. This suggests a lower mobility for low-angle ⟨111⟩ boundaries, which would be consistent with the literature \[47\].

Combining all of the boundary counts into one plot illustrates relative mobilities of each boundary. The frequency of Σ7 boundaries was also included. Overall, the low-angle ⟨111⟩ boundaries show the smallest decrease in number, while the high-angle ⟨111⟩ and Σ7 boundaries showed the greatest decrease in number, significantly more than even the regular high-angle boundaries, \(\theta > 40^\circ\). It is possible that these special boundaries are not frequent enough for these statistics to be completely reliable. Furthermore, there are multiple reasons why these correlations could exist:

- The mobility is higher for these high-angle boundaries, which causes them to move more quickly and remove themselves from the system.
- The energy is higher, resulting in a preferential removal from the system.
• The boundaries at the end of grain growth may be entirely different from the ones at the beginning, i.e. perhaps all boundaries decrease in number equally but low-energy or low-mobility boundaries are preferentially created during topological transitions.

Figure 9.11. Fraction of different boundaries over time. The low-angle \langle 111 \rangle boundaries show the smallest relative decrease in number.

9.1.4. Individual Grain Analysis

Individual grains have been extracted from the 3D phase-field dataset. First, the surface is meshed at a threshold of 0.5 using the *isosurface* function in MATLAB or IDL. The curvature of the grain boundaries can be easily calculated using Equation 2.27 because the interfaces are diffuse. The curvature is calculated at each voxel for a particular grain, interpolated onto the meshed surface, and then visualized in MATLAB; see Figure 9.12. The curvature is not completely smooth across some of the boundaries. Errors in the curvatures may be due to a combination of reconstruction artifacts and phase-field smoothing.
Figure 9.12. Evolution of a single grain, with the curvature interpolated onto the surface. The curvature at the triple lines (in red) have no physical meaning.

Furthermore, the velocity of the boundaries was calculated by converting the phase-field data into signed-distance data and then using Equation 2.29. The mobility at each voxel is simply the velocity divided by the curvature. In reality, lower-curvature regions should also have lower velocity. However, in noisy experimental data, it is possible to have close to zero curvature and yet finite velocity, making the mobility extremely large and unrealistic. Figure 9.13 illustrates the curvature, velocity, and mobility along the boundaries for a grain. The curvature values are relatively smooth. The velocity is more prone to error, however, because it relies on later timesteps which, for the experimental data, may not put the interface in the correct location. The mobility values, therefore, approach positive or negative infinity whenever the curvature or velocity flips sign.
Figure 9.13. An individual grain, showing curvature (a), velocity (b), and mobility (c) interpolated onto the surface. The mobility values are extremely noisy.

There are thus boundaries, or regions within a boundary, in the data that have a negative mobility. This is most likely due to errors in the velocity due to 4D reconstruction errors. Curvature calculations are more likely to be reliable because they are
done in 3D (not 4D), though in some cases grain boundaries may move away from their centers of curvature in order to absorb highly deformed grains.

The disorientation at each grain boundary has been used to color the surface of individual grains in 3D, seen in Figure 9.14. Qualitatively, it is observed that the higher-angle grain boundaries move relatively faster. Not all of the high-angle boundaries move quickly in every timestep, but the orange- and red-colored grain boundaries appear to be where most of the motion is occurring. There is clearly some amount of mobility anisotropy during grain growth of aluminum, observed in 3D for individual grains for the first time.

9.1.5. Individual Grain Boundary Analysis

Because of the noise in the velocity and thus also the mobility, individual boundaries need to be extracted. Then, in order to get a more accurate measure of the mobility, the mobility is calculated as the average velocity divided by the average mean curvature for an individual boundary.

To isolate an individual boundary from a grain, the neighboring grain information is needed. If grain #1 and #2 are neighbors, for instance, then the grain boundary between them can be extracted by only considering the region where $\eta_1 > 0.4$ and $\eta_2 > 0.4$. These bounds only occur within the boundary, and both $\eta_1$ and $\eta_2$ decrease below 0.4 as the triple line is approached. Figure 9.15 shows the curvature, velocity, and mobility plotted on an individual boundary. Note that there are regions where the curvature flips sign; at these specific locations the mobility approaches negative and positive infinity.
Figure 9.14. Evolution of individual grains, with the disorientation angle colored onto the surface. The color bar ranges from $0^\circ$ to $63^\circ$, which is just over the maximum possible disorientation angle of $62.8^\circ$. Most of the grain growth appears to be due to the high-angle boundaries.
Figure 9.15. An individual grain boundary, showing curvature (a), velocity (b), and mobility (c). The mobility values approach positive or negative infinity when the curvature switches sign.

The average mobility was calculated for all boundaries. However, due to the uncertainty with respect to some aspects of the reconstruction, certain filters had to be applied in order to remove boundaries from the statistics that are expected to have
large error. These filters are described below, and the thresholds for each filter are somewhat arbitrary:

- In cases where the average mean curvature is close to zero, the mobility calculation is still quite unreliable. Any boundary with average curvature less than $0.02 \, \mu m^{-1}$ is disregarded.
- Velocities corresponding with motion of less than 2 voxels were disregarded, because anything less could be motion due to noise/error.
- Small grains have more unreliable reconstructions, and have also evolved more significantly during the phase-field smoothing. Thus, any grains of radius less than $30 \, \mu m$ are disregarded.
- Small grain boundaries are also discarded (boundaries with number of voxels less than 1000).

Applying this filter, 239 grain boundaries were found. The median mobility for these boundaries is $20.3 \, \mu m^2/s$, whereas the median mobility for all boundaries was $4.3 \, \mu m^2/s$. The larger mobility for the filtered grains is expected because low-mobility grain boundaries were preferentially filtered out due to the velocity filter.

Figure 9.16 shows the movement of an individual grain boundary, with a plot of its mobility over time. The curvature is overlaid on the surface of the grain boundary. This particular boundary has a relatively constant mobility of 20-40 $\mu m^2/s$, though this is not the case for all boundaries. This boundary’s misorientation is 43.4°. This type of visualization and analysis of individual grain boundaries in three dimensions and time is unique to this work.
Figure 9.16. Evolution of a single grain boundary (a), along with the mobility vs. time (b).
9.2. Discussions and Conclusion

Overall, it is quite clear that abnormal grain growth is occurring on the surface. In particular, it appears that there are many small grains with high-angle grain boundaries on the surface, and few larger cube-texture grains are moving quickly across these grains as they disappear. These smaller grains are likely due to recrystallization after the sample was lathed into a cylindrical shape.

Inside the sample, there appears to be a more normal growth process occurring with a more normal grain size distribution. There are a large fraction of low-angle grain boundaries inside the sample, which could partially explain the small amount of movement seen inside the sample compared to on the surface.

The rate at which certain types of boundaries disappear cannot necessarily be correlated to the respective mobilities of these boundaries. However, it has been observed in the literature that low-energy boundaries increase in number relative to high-energy boundaries over the course of grain growth \[59,112\].

Qualitatively, it has been observed that higher-angle boundaries have higher velocities. For many grains, the majority of growth occurs as the high-angle boundaries move, while the low-angle boundaries experience minimal movement. This type of boundary anisotropy has not been observed in three dimensions.

Quantitative calculation of grain boundary velocity and mobility in three dimensions for several timesteps has also not been done until now. Even with an unknown degree of error, these results illustrate the huge potential that DCT has for 4D characterization. If the multiple-grain code were shown to more accurately reconstruct the grain boundaries, then grain boundary mobility could be more reliably calculated and
correlated with misorientation. Then, if orientation gradients could be resolved, the grain boundary velocity could be correlated with approximate mosaicity or dislocation density.

The main conclusions of this 4D analysis can be summarized as follows.

- The interior of the sample is composed of large recrystallized grains with cube texture and low-angle boundaries, while the surface grains are smaller and have more random texture and high-angle boundaries. The cube texture increases during grain growth as the larger cube grains dissolve many of the smaller surface grains.
- Special \(\langle 111 \rangle\) boundaries show more extreme behavior, with low-angle boundaries changing little in number and high-angle boundaries mostly disappearing during grain growth.
- Higher-angle boundaries are observed to account for the majority of growth for many grains.

As the quality of the reconstructions improves, grain boundary mobility calculations will become increasingly reliable, and at increasingly smaller scales. Four-dimensional nanocrystalline characterization will likely be possible within the next decade or two. With the help of the exponential growth in computational power, 3D reconstruction could one day be a trivial problem. If DCT could ever become as ubiquitous as the TEM or SEM, it would revolutionize the way in which metals and ceramics are studied, designed, and built.
In order to learn even more from this dataset, it can be input into a phase-field model. The experimental and simulated data can then be directly compared, providing additional incites into potential errors in both the phase-field model and the reconstructions.
CHAPTER 10

Experiment vs. Simulation

In this chapter, a direct comparison between experimental and simulated data is conducted. To do this, the final reconstruction of the single-grain forward projection from the first experimental timestep was input into the 3D phase-field model, and grain growth was simulated for longer times. This analysis is similar to what was done in [167], except in this work there are 8 (not 2) experimental timesteps with which we can compare simulated data. Simulations were run for approximately 5000 timesteps, until the microstructure matches the last experimental timestep.

In these phase-field simulations, no-flux boundary conditions were employed. However, the order parameters were allowed to grow and evolve outside of the sample. Then, for analysis, everything outside the boundaries of the sample was removed. As far as the sample is concerned, there are essentially no boundary conditions.

Figure 10.1 illustrates the phase-field simulations reconstructed in 3D, at several timesteps, colored by grain ID. Unlike the experiment, all of the small grains disappear relatively quickly. Thus, the largest discrepancies between experiment and simulation are near the surface of the sample. Grains near the core of the sample are where the 4D analysis should be focused.

Before the experiment can be compared to simulations, the timesteps in the simulation must be matched to the experimental timesteps. Because the phase-field method
Figure 10.1. Evolution of simulated structure, colored by grain ID. The small surface grains disappear relatively quickly.
is phenomenological, the mobility of the boundaries and timesteps are somewhat arbitrary. The datasets are matched by creating an array where each voxel is 1 if the simulation and experiment are different, and 0 if they are the same. The cost function is simply the sum of that boolean array, and the mismatch is the percentage of voxels that are different.

![Graph showing matching simulation to experiment for each experimental timestep. Later experimental timesteps correspond with later simulation timesteps. However, the time intervals for experiment and simulation do not match up precisely.](image)

Figure 10.2. Matching simulation to experiment for each experimental timestep. Later experimental timesteps correspond with later simulation timesteps. However, the time intervals for experiment and simulation do not match up precisely.

Furthermore, it is worthwhile to test how much the matched timesteps are a function of the volumes with which we are matching. For instance, if the bottom and tops of the cylinder are removed from the simulated data, the matched timesteps change. Ideally
we would like to remove all of the surface grains from the matching algorithm because that is where we know there is substantial error. Matching was thus done for the whole sample as well as a slimmed down version of the sample that erodes everything within 20 voxels of the sample surface. This erosion was done using the `imerode` function in MATLAB for the segmented absorption tomogram.

The matched timesteps are shown in Table 10.1. Including erosion (and thus excluding surface grains) improved the match significantly, decreasing the mismatch fraction from 7.3% to 4.6% at the second timestep and 18.9% to 13.3% at the final timestep. The mismatch increases for later timesteps, suggesting that the simulation is not perfect and is diverging from the experimental data.

Once matching is completed, individual grains are compared, experiment vs. simulation, for the 7 timesteps of the experiment. An example of a particularly good match is seen in Figure 10.3. For this grain, the size difference between simulation and experiment is negligible, though there are obvious topological differences. Overall, many of the matches were not so good, particularly near the surface.

<table>
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<tr>
<th>Timestep</th>
<th>(t_{\text{EXP}}) (min)</th>
<th>(t_{\text{SIM}})</th>
<th>% Mismatch</th>
<th>(t_{\text{SIM}}) with erosion</th>
<th>% Mismatch</th>
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<td>NA</td>
<td>NA</td>
<td>NA</td>
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<td>1</td>
<td>7</td>
<td>7.3</td>
<td>11</td>
<td>4.6</td>
</tr>
<tr>
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<td>3</td>
<td>28</td>
<td>13.6</td>
<td>36</td>
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</tr>
<tr>
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<td>29</td>
<td>14.1</td>
<td>39</td>
<td>9.3</td>
</tr>
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<td>53</td>
<td>12.8</td>
</tr>
<tr>
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<td>9</td>
<td>71</td>
<td>17.3</td>
<td>71</td>
<td>11.7</td>
</tr>
<tr>
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<td>12</td>
<td>102</td>
<td>18.9</td>
<td>103</td>
<td>13.3</td>
</tr>
</tbody>
</table>

Table 10.1. Matched timesteps, simulation to experiment, with % matching. Excluding the surface voxels (15 voxels) results in approximately 50% better matching Simulated times \(t_{\text{SIM}}\) are the number of timesteps divided by 50.
Figure 10.3. Evolution of a single interior grain, experiment (red) vs. simulation (blue), illustrating relatively close match.

Even though individual grains did not all match well, some “global” measures suggested that the experiment and simulation were not so different. For instance, the average grain size inside the simulated sample was within 5-10% of the experimental grain size at all timesteps.

10.1. Discussion and Conclusions

Overall, the simulation of the experimental data did not wholly match what was seen in the experiments, likely due to the abnormal nature of the actual grain growth process, inaccuracies in the reconstructions, and approximations in the simulations. However, certain grains or features did match well, suggesting that grain growth in the
experiment is at least somewhat driven by boundary curvature and that some regions may be considered relatively isotropic in terms of boundary mobility.

There are several errors that make direct comparison difficult, both experimentally and computationally. First, the experimental reconstructions are not complete, and thus many of the grain boundaries are not fully resolved. This results in discrepancies between experimental timesteps as to the location of the boundaries. This causes errors in the grain boundary curvatures as well. Furthermore, discrepancies may be explained by the topological errors in the reconstruction. Changing one grain’s topology can have a large effect on its growth. Thus, if many grains have topology errors, then it could significantly affect the match to simulation.

Computationally, the boundary conditions are difficult to simulate. Many of the small surface grains disappear during the experimental anneal, but many of them do not. This suggests that the boundary conditions are partially frozen and partially something else, such as no-flux. This could be due to a small surface oxide that pins some boundaries but allows other boundaries to move if their driving forces for movement are larger, for instance. The simulations do nothing to account for anisotropy in the grain boundary mobility, as is observed near the surface as some grain boundaries belonging to small grains move very quickly while others do not move at all. This apparent anisotropy may be a result of energy or mobility anisotropy, but may also be a function of the dislocation density in the smaller grains or the pinning effect of the surface oxide.

In order to improve the match of the simulations to experiment, the simulation must include more of the real physics of the experiment. This includes more complex
boundary conditions and anisotropy in grain boundary mobility. If one were to include
these other features in the simulation, and the match improved, that would be a direct
illustration that aluminum has boundary mobility anisotropy, for example. Such calcu-
lations were done in 167 in the analysis of two 3D timesteps during grain growth. In
particular, boundary mobility was tuned for individual boundaries in the simulation,
showing by comparing with experiment that particular boundaries were substantially
more mobile.

Furthermore, if boundaries in the experiment and simulation aligned at multiple
timesteps, the velocity could be calculated more accurately using the phase-field data
because of the many additional timesteps that occur in between experimental timesteps.

Even though this work is preliminary, it shows how experiment and simulation have
the potential to work together to study grain growth in three dimensions. In the next
Chapter is a perfect example of how simulation and experiment have been used to
study the coarsening of solid-liquid dendrite coarsening.
Solid-liquid dendrite coarsening has been studied using 4D in-situ x-ray absorption contrast tomography (XCT). Dendrites are tree-like structures that form during solidification of a metal and can significantly affect properties such as ductility and tensile strength \[213\]. In this work, solid-liquid dendrites have been used to study Rayleigh instabilities, in which a rod of one phase separates into spheres. Rayleigh instabilities are ubiquitous in multi-phase materials and can have profound effects on properties \[214,215\].

11.1. Background

When a rod-shaped phase is embedded in another, a Rayleigh instability, which is a perturbation of wavelength greater than \(2\pi R\), may occur and cause the rod to break down and separate into spheres. This instability is driven by the reduction of interfacial energy, and can have a large effect on the behavior of multiphase materials. For example, cylindrical eutectic phases can break up into spheres and affect mechanical properties \[216,219\]. Metal nanowires have also been observed to separate into spheres, which could detrimentally affect the properties of proposed device applications \[215,220\]. Rayleigh instabilities also cause the breakup of dendrite arms during dendrite coarsening \[1,2,221,222\]. An example of a pinching event in solid-liquid dendritic structure is shown in Figure 11.1.
Nichols and Mullins demonstrated that as a pinching event occurs, there is a singularity in which the curvature becomes infinite, right at the pinching point in space and time \[223\]. This singularity introduces nonlinearities in the governing equations, yet the initial conditions becoming decreasingly important as the singularity is approached. That is, the shape of the pinching event becomes locally determined.
11.1.1. Theory and Simulations

Larry Aagesen et al. showed that the shape near the singularity becomes independent of the initial conditions and invariant in time, i.e. self-similar \([1,2]\). That is, the pinching event approaches a shape such that when scaled by the diameter of the cylinder it doesn’t change in time. The analysis was done for a cylindrical rod surrounded by a different phase, where in one case the high diffusivity phase, \(\alpha\), was the rod and in the other case the high diffusivity phase was the surrounding region. The low diffusivity phase, \(\beta\) was assumed to have zero diffusivity. Pinching is then caused by the diffusional motion of solute atoms through the high-diffusivity \(\alpha\)-phase driven by the interfacial energy between the two-phases. The diffusion field in the \(\alpha\) phase is given by the classic diffusion equation,

\[
\frac{\partial C_\alpha}{\partial t} = D_\alpha \nabla^2 C_\alpha
\]

(11.1)

where \(C_\alpha\) is the concentration of solute and \(D_\alpha\) is the diffusion coefficient of solute in the noted phase. Assuming the diffusion field relaxes much faster than the interface moves, the diffusion field is quasi-stationary, and the diffusion equation can be approximated by Laplace’s equation:

\[
\nabla^2 C_\alpha = 0
\]

(11.2)

The first boundary condition at the interface is the Gibbs-Thomson equation,

\[
C_\alpha = C_\alpha^0 + (C_\alpha^0 - C_\beta^0) d_0 H
\]

(11.3)
where $C_{\alpha}$ is the solute concentration on the $\alpha$ side of the interface, $C_{\alpha}^0$ and $C_{\beta}^0$ are the equilibrium solute concentrations in the noted phases at a flat interface, $d_0$ is the capillary length, and $H$ is the mean interfacial curvature. The other boundary condition is the interfacial mass balance,

\begin{equation}
(C_{\alpha}^0 - C_{\beta}^0) v = -D_\alpha \frac{\partial C_{\alpha}}{\partial n}
\end{equation}

where $v$ is the interfacial velocity in the normal direction, and $\partial C_{\alpha}/\partial n$ is the derivative of the concentration field in the normal direction, where a positive normal is pointing from the $\alpha$ phase to the $\beta$ phase.

It was assumed that the interface is axially symmetric about the $z$-axis, and thus the position of the two-phase interface as a function of time can be given in cylindrical coordinates $(r, z)$, see Figure 11.2. Near the point of pinching, the interface asymptotically approaches two opposing cones, each with cone angle $2\theta_c$.

The interface coordinates were written in terms of self-similar variables as:

\begin{equation}
\eta = \frac{rB}{(t_s - t)^\delta}, \xi = \frac{zB}{(t_s - t)^\delta}
\end{equation}

where $\eta$ and $\xi$ are the radial and axial coordinates in the time-independent similarity variables, $t_s$ is the time the singularity occurs, and $B$ is a scaling constant dependent on material properties. In the similarity variables, the position of the interface is given by the function $\eta = f(\xi)$, or defined parametrically, $F = \eta - f(\xi) = 0$.

It was determined if a valid similarity coordinate system exists by finding the exponent $\delta$ of the similarity variables required to eliminate the time dependence in the boundary conditions. The difference between the solute concentration in the liquid and
the equilibrium concentration in terms of a scaled concentration in similarity variables, $\tilde{C}(\xi, \eta)$ is

$$C_\alpha (r, z, t) - C_\alpha^0 = t^\delta A \tilde{C}(\xi, \eta)$$

where $\delta$ is a constant and $A$ is a scaling constant dependent on material properties. Substituting this into (11.3) and using the fact that real-space derivatives give $B/(t_s - t)^\delta$ times derivatives in the similarity variables, we obtain

$$(t_s - t)^\delta A \tilde{C}(\xi, \eta) = (C_\alpha^0 - C_\beta^0) d_0 \frac{B}{(t_s - t)^\gamma} (\nabla_{\xi, \eta} \cdot \hat{n})$$
In order for a valid similarity solution for the concentration and interface shape to exist, the time-dependence on the left and right hand sides of the equation must cancel, meaning that $\gamma = -\delta$ is required.

The solute conservation boundary condition (11.4) is also transformed into similarity variables. To find the normal velocity of the interface in similarity variables, the material derivative at the interface was used. Dividing by $|\nabla F|$ and using the chain rule for $\partial F/\partial t$, the equation becomes

$$\frac{(C^0_\alpha - C^0_\beta)}{B} \frac{(t_s - t)^{\gamma-1}}{(\sqrt{F_x^2 + F_y^2})^{\gamma}} = D_\alpha \frac{(t_s - t)^\delta}{(t_s - t)^{\alpha}} AB \left( \hat{n} \cdot \nabla_{\xi,\eta} \tilde{C} \right)$$

Comparing the time dependence on the left and right sides yields $\gamma - 1 = \delta - \gamma$. Substituting $\gamma = -\delta$ from (11.7), the required exponents for a similarity solution consistent with the boundary conditions are

$$\gamma = \frac{1}{3}, \delta = -\frac{1}{3}$$

Thus the problem is reduced to solving Laplace’s equation in similarity variables on the boundary. A similarity solution also requires using $B = (D_\alpha d_0)^{-1/3}$ and $A = (C^0_\alpha - C^0_\beta) (d_0^2 / D_\alpha)^{1/3}$.

After transforming to the self-similar coordinate system of Equations (11.5), the shape of the interface was determined by solving Laplace’s equation $\nabla_{\xi,\eta}^2 \tilde{C} = 0$ numerically using a boundary-integral method. Green’s Third Identity can be used along with the free-space Green’s function for Laplace’s equation to yield an integrodifferential equation for the scaled concentration $\tilde{C}(\xi, \eta)$ on the interface, see [1][2].
Depending on whether the high diffusivity phase is the matrix or rod, there are two different formulations for the kernels of the integrodifferential equation. For the case of a rod with zero diffusivity embedded in a matrix with nonzero diffusivity the integration is performed along the $\xi$-axis, and the angular integral is rewritten as a complete elliptic integral of the first kind and approximated using the polynomial approximation of \[224\]. See \[1\] and \[2\] for the complete details of the theoretical work.

First, solutions were found describing the shape of a rod undergoing pinching where diffusion is solely in the matrix. An iterative process was used to search for the solutions. A coarse grid spacing along $\xi$ was used to search for solutions as $\theta_c$ was varied through the range where a solution is expected based on the experimental data. Solutions were obtained for some values of $\theta_c$ in this range, and these solutions were used as an initial guess for the solution with a finer grid spacing. As the grid spacing was made finer, the boundary condition at $\xi = 0$ was changed, fixing $f(0)$ rather than $f'(\xi) = 0$. The angle and $f(0)$ were iteratively refined until a smooth solution with $f'(0) = 0$ was found. The angle was converged to $\theta_c = 40^\circ \pm 1^\circ$ and $\theta_c = 38^\circ \pm 1^\circ$ for solid and liquid pinching events, respectively. The interface shape is shown in Figure 11.2. Other solutions may exist as well, but based on experimental observations, only the solution with the largest cone angle will be observed experimentally \[1\] \[225\].

The dynamics of the pinching process can be determined using the self-similar variables. A quantity of experimental interest is the diameter at the center of a pinching solid rod, $D(t)$, which is given by $\eta(\xi = 0) = f(0)$. Using the definitions of the self-similar variables, the diameter decreases in time as
\[ D(t) = K (t - t_s)^{1/3} \]

where \( K \) is the rate constant for the pinching process,

\[ K = 2 f(0) (D \alpha d_0)^{1/3} \]

and the similarity solution for the interface shape at \( \xi = 0 \) gives \( f(0) \). Thus materials parameters and \( f(0) \), the interface location at the pinching point in similarity variables at \( \xi = 0 \), fix the dynamics of the pinching process. If the \( \alpha \) phase is the matrix, as in the case considered above, \( f(0) = 0.88 \). If the high diffusivity phase \( \alpha \) is the rod, then the expression for the rate constant is identical except for the location of the interface at the pinching point in similarity variables, which gives \( f(0) = 0.6 \) in this case. It is also clear that the kinetics of pinching are independent of the difference in concentration between the two phases at the interface. After pinching the rate constant changes, again, only by \( f(0) \). If we take the interface shape to be that which is fixed by the shape with the largest cone angle prior to pinching, then \( f(0) = 1.3 \) for \( \alpha \)-phase rods.

11.2. Experiment

11.2.1. Experimental Procedure

Al-Cu samples of various Cu compositions were directionally solidified to form Al-rich dendrites, after which 1 mm diameter samples were cut out of the ingot and mounted in a custom-made furnace. The samples were then brought to the TOMCAT beamline
located at the X02DA port of the Swiss Light Source (SLS) at the Paul Scherrer Institut. The samples were heated and coarsened in-situ at 565°C, which is 17°C above the eutectic temperature. Data were analyzed for a Al-26 wt.% Cu sample and a Al-15 wt.% Cu sample. These compositions correspond to solid volume fractions of approximately 42% and 74%, respectively, based on the Al-Cu binary phase diagram. These two samples were chosen for analysis because the Al-15 wt% Cu sample contains multiple liquid pinch-offs, and the Al-26 wt% Cu sample contains multiple solid pinch-offs. Relating to the theoretical analysis, the high diffusivity phase $\alpha$ is the liquid and the low diffusivity phase $\beta$ is the solid.

The X-ray photon energy at the SLS was 20 keV. 721 projections, with 80 ms exposure times, were captured over the 180° of sample rotation. The 2048 x 2048 pixel CCD camera was a Ce-doped YAG scintillator with a thickness of 20 $\mu$m, a 280° digital/analog converter, and a 10MHz read-out speed. A total of 1024 slices, with a spatial resolution of 1.48 $\mu$m$^3$/voxel, were collected every 2 min 30 sec and 3 min 52 sec for the Al-15 wt% Cu and Al-26 wt% Cu samples, respectively. Further information about the TOMCAT beamline and the details of the experiment can be found in [181] and [226], respectively.

11.2.2. Experimental Analysis

The reconstructions were created directly at the SLS using a filtered back projection technique. The resulting three-dimensional gray-scale tomograms were then input into Interactive Data Language (IDL) and segmented to black and white. An IDL program was developed to automatically find pinching events. The program loops through each
two-dimensional x-y slice and searches for small circular cross-sections, which are then fed into a second program that determines if it is a pinch-off by measuring the diameter of the cross-section as well as the diameters of the circular cross-sections in the slices above and below it. If there is a clear minimum in the diameter in the z-direction (as opposed to a maximum, as would be seen in a spherical particle), then it is a pinch-off whose principal axis is aligned with the z-axis. The location of each pinch-off in space and time is then fed into a program that measures the diameter as a function of time. At a given time and slice, the program counts the number of pixels across the cross-section at different lines in both the x and y directions. The diameters in the x- and y-plane for that slice are then chosen to be the maximum number of pixels. Then, the diameter of the pinch-off at that timestep is chosen to be at the slice with the minimum diameter. The smaller of the x and y diameters is chosen because if the pinch-off is slightly misaligned with the z-axis then the cross-section is elliptical and thus the smaller cross-section diameter is more representative of the actual diameter.

The rate constant is then calculated to be the cube root of the linear slope of the diameter cubed versus time plot. This program loops through different times and for many pinch-offs and automatically calculates the rate constant for each, using at least 4 timesteps prior to $t_s$. Images are produced for each pinch-off in order to verify that they are in fact pinching events.

The distance between the receding cones was also calculated automatically in IDL using the known locations and $t_s$ values of the pinch-offs from the pinch-off finder code. Because these pinch-offs are all roughly aligned with the z axis, the code loops through each z slice until it finds the ends of the top and bottom cones and then records the
locations. It then calculates the difference between the two points and repeats for later timesteps, for a total of 5-10 timesteps. The post-pinch-off rate constant is then taken as the cube root of the slope of the distance cubed versus time plot.

Next, the interface shapes were box-car smoothed to remove noise from the interface. A 3D representation of the theoretically predicted interface shape was then created for the solid and liquid solutions with 80° and 76° cone angles, respectively. A comparison between the predicted and measured liquid morphologies is given in [1]. The arrays of both the experimental data and the theoretically-determined shape were then imported into the visualization program Amira and cropped to the location of individual pinching events.

The pre-pinch-off experimental surfaces were then aligned to the theoretically predicted surface by first scaling the experiment to match the diameter of the theory. The surfaces were then aligned using the rigid surface alignment function in Amira. This function changes only the position (not the size) of the experimental shape to align the surfaces. This alignment process was repeated for a series of times leading to the singularity. The distance from the theoretically predicted shape to the closest point on the experimental shape was then calculated and illustrated on the theoretical shape as a color contour plot as a way to demonstrate the interface agreement between the two surfaces.

11.3. Results

First, the self-similar shape predicted theoretically for a solid rod pinching in a high diffusivity liquid is compared with experiment. Here the distances between experiment
and theory are recorded in similarity variables, which have a fixed scale as the real variable scale bar grows in time, as seen in Figure 11.3. The images are shown in similarity variables to illustrate that the improved agreement as \( t_s \) is approached is not just a result of the changing length scale. The agreement is quite good at the final timestep before pinching, this pinch-off exhibits an excellent fit to theory. Figure 11.3 illustrates this approach to the theoretical shape; at the latest time there is a large region where the difference between experimental and theoretical surfaces is approximately 0.3 or less, which is approximately half of the experimental spatial resolution of 1.48 \( \mu m/pixel \). It is difficult to determine whether the theoretically calculated cone angle has the correct value due to spatial and temporal resolution limits. This also means that we cannot differentiate between the solid and liquid shapes by their cone angles alone. However, in almost all of the solid and liquid pinching events found, the angle approaches the theoretical angles of 80° and 76°, respectively, and the overall fit to the theoretical shape improves as the singularity is approached.

The kinetics predicted by the similarity solutions are also compared to the experimental data. Figure 11.2 shows a plot of one solid pinch-off diameter as a function of \( (t - t_s)^{1/3} \), showing images corresponding to a few data points. The excellent fit to a straight line indicates that the temporal exponent of 1/3 holds for a surprisingly long time. Thus the kinetics seem to be described by the similarity solution well before the interface shape is well described by the similarity solution. The ability of the similarity solution to describe the kinetics of the pinching process is further examined by determining the rate constant, \( K \) as given in Eq.11.11, from the slope of the line shown in Figure 11.2. To compare with the theoretical predictions we use the liquid
diffusion coefficient \( D_\alpha = 8.3 \times 10^{10} \text{ m}^2/\text{s} \), [1] and capillary length \( d_0 = 2.27 \text{ nm} \) [227] along with \( f(0) \) appropriate for a rod of solid (\( \beta \)) pinching by diffusion in a liquid (\( \alpha \)) matrix. This gives \( K = 2.15 \mu\text{m/s}^{1/3} \), which is only 6% smaller than that measured experimentally.

It is possible to predict the dependence of the rate constant on the materials parameters \( D_\alpha \) and \( d_0 \) simply using the fact that the process occurs by interfacial energy driven bulk diffusion. The key prediction of the theory is that the kinetics depend on \( 2f(0) \), which appears in the rate constant in Equation [11.11]. As mentioned above, \( f(0) \) is different depending on whether diffusion occurs inside or outside the rod. Thus, a particularly stringent test of theory is to determine if the rate constants for pinching are different for solid rods pinching in a liquid, or liquid rods pinching in a solid.
40 liquid rods and 19 solid rods undergoing pinching were found. The average solid-rod rate constant was 2.28 \( \mu m/s^{1/3} \) with a standard deviation of 0.290 \( \mu m/s^{1/3} \), and the average liquid-rod rate constant was 1.40 \( \mu m/s^{1/3} \) with a standard deviation of 0.236 \( \mu m/s^{1/3} \). Using the predicted values for \( f(0) \) gives a solid-rod rate constant of 2.15 \( \mu m/s^{1/3} \) and a liquid-rod rate constant of 1.47 \( \mu m/s^{1/3} \). Note that the materials parameters appearing in both rate constants are identical and thus the reason why the rate constants are different are the values of the similarity solution at the pinching point.
Figure 11.5. Solid pinch-off diameter over time, exhibiting a clear $t^{1/3}$ dependence and an approach to the self-similar shape as $t$ approaches $t_s$.

The solid-rod and liquid-rod rate constants are 6% greater and 5% less than the theoretically predicted rate constants, respectively. This indicates an excellent agreement between theory and experiment, given the uncertainties in the materials parameters and error in the experiment. To determine if these two rate constants are different due to the differences in $f(0)$, we examine a histogram of the rate constants shown in Figure 11.6. It is clear that the distributions are distinct and that the theoretically predicted rate constant falls in the center of both distributions. Additionally, a one-tailed t-test of the experimental solid and liquid rate constants results in a p-value of $6.3 \times 10^{-13}$. The p-value essentially represents the probability that the two groups of
Figure 11.6. Histogram of rate constants from experimental data. The solid and liquid pinching events exhibit different velocities of pinching, values which match quite closely (about 5%) with theory.

data (the liquid and the solid pinch-off rate constants) are from the same group, and so this low p-value indicates that the difference between the average solid and liquid pinch-off rate constants is quite statistically significant.

We thus show that the rods are pinching in a self similar fashion and that the kinetics is well described by theory and the known materials parameters and that the path through which diffusion occurs affects the dynamics of the pinching process, but not the temporal power law.
Seen in both Figure 11.2 and Figure 11.3, the agreement between theory and experiment improves as the singularity is approached, since initial conditions have less influence and the shape becomes locally determined. In some cases, the mean deviation between shapes just before pinch-off is less than the 1.48 µm resolution of the X-ray tomography scan. In other cases, the initial shapes of the rods were asymmetric about the pinching axis and thus the singularity did not achieve high degrees of self-similarity under the temporal and spatial resolution constraints of the experiment. However, in all 69 cases examined the agreement between theory and experiment improved as the singularity was approached. Interestingly, despite the apparent disagreement in the shape of the interface, the kinetics are still well described by the similarity solution, as shown above. Thus, to the resolution of the tomography, the experiments confirm that some distance from the pinching point, the shape approaches a cone with the predicted cone angle of 76° for liquid pinching and 80° for solid pinching. Unfortunately, due to spatial resolution constraints, it is difficult to differentiate the solid and liquid pinch-offs by their cone angles alone. However, the kinetics of the pinching process measured experimentally agree with the predictions of theory. We therefore conclude that the pinching process under interfacial-energy-driven bulk diffusion is governed by a unique self-similar solution dependent only on whether diffusion occurs inside or outside the rod.

11.3.1. Interfacial Evolution Post Pinching

The distance between receding cones were calculated in IDL for all 40 liquid pinchoffs and the results show that the cones recede with a temporal exponent of 1/3. The
average rate at which they separate is 3.46 \( \mu m/s^{1/3} \), with a standard deviation of 1.34 \( \mu m/s^{1/3} \). The average \( R^2 \) value for the linear fit is 0.961, with a standard deviation of 0.0382. The theoretically calculated rate constant for receding liquid cones is 3.31 \( \mu m/s^{1/3} \), which is only 4-5% less than the experimental value. Due to the smaller temporal resolution of the sample that contained solid pinching events, as well as the larger rate constant, the solid tube post-pinching rate constants were not calculated.

Seen in Figure 11.7 is a plot of the distance between receding liquid cones versus \((t-t_s)^{1/3}\), illustrating that a temporal exponent of 1/3 accurately describes the kinetics.

The shape after pinching is set by the universal shape prior to pinching, even though we cannot describe the evolution very close to the pinching event. Even though the kinetics match the theory quite well, the post-pinching shape deviates from the theoretical shape relatively quickly and thus we did not do a shape comparison as with the pre-pinching shape.

**11.4. Conclusions**

The dynamics of rods pinching by diffusion either inside the rod or in the matrix was examined. Self similar shapes and the dynamics of the pinching process, prior to and after pinching were determined theoretically and compared to experiment. From the excellent agreement between theory and experiment we conclude that:

- Sufficiently close to the pinching point, the pinching process, both prior to and after pinching, is universal. The shape of the interface is independent of the materials system and initial conditions. The dynamics is described by unique temporal power laws.
Figure 11.7. Distance between receding sections after pinching, exhibiting a clear $t^{1/3}$ dependence

- The shape of the interface after pinching is fixed by the universal shape prior to pinching, despite the inapplicability of the similarity solution very close to the pinching point.
- The dynamics of the pinching process are well described by the theoretically predicted power laws surprisingly far from the pinching point.

Thus, it is possible to estimate the time required for a wide range of microstructures to break up by capillary driven bulk diffusion. Such two-phase mixtures include dendritic solid-liquid mixtures, rod-like eutectics, and bicontinuous two-phase mixtures such as those found following spinodal decomposition in polymer blends.
CHAPTER 12

Future Work

Phase-field simulation and x-ray diffraction tomography are very active fields with many unanswered questions. There are thus many directions one could take this research, both computationally and experimentally.

12.1. Phase-Field Simulations

The phase-field model in particular has been shown to simulate grain boundary curvature-driven kinetics combined with triple junction angle-driven kinetics. Longer, larger simulations can be run with increasingly small TJ mobilities. The next obvious step is to take the model into three dimensions and include quadruple point mobility. In order to be able to tune the triple line and quadruple junction (QJ) mobilities entirely independently, a slightly different approach must be taken. If the exact same model were extended in 3D, the triple lines and quadruple points would have similar mobilities and thus it would be difficult to tease out the effects of each. In other words, there needs to be a way to decrease the QJ mobility without decreasing the TJ mobility, and vice versa. The TJs are tracked using the sum of the order parameters, so perhaps the QJs can also be tracked in this way. TJs have a sum of the order parameters of 1.08 at the center of the TJ, whereas QJs have a sum of the order parameters of 1.2 at the center of the QJ. A Potts model has incorporated TJ and QJ mobilities \[133\] and has shown that they each affect the kinetics in very unique ways.
Furthermore, the triple junction mobility can be included in combination with grain boundary mobility anisotropy. MD simulations \cite{17} have shown larger TJ effects at special highly-mobile boundaries such as coincident site lattice boundaries. It is thus conceivable that the effects of TJ mobility would be considerably altered if GB anisotropy were to be included in the TJ mobility-limited simulations.

Finally, because triple junctions play a large roll for small-grain materials where substantial impurity segregation has been measured, one could include an impurity concentration as a conserved order parameter in the model. The triple junctions could, for instance, be set as energetically favorable locations for the impurities to segregate. Then, the triple junction and grain boundary mobilities could be set to be a function of this solute concentration. By correlating impurity segregation in the model and comparing with experiments of nanocrystalline grain growth, a dependence of triple junction mobility on impurities may be determined.

\subsection{4D Grain Growth Characterization}

The multiple-grain forward projection code has great potential for improving 4D characterization. Once this code is fully operational, back-projection or algebraic reconstruction will become completely unnecessary. All that is needed is the grain centers of mass and the orientations, which is provided from the indexing code. The code can be re-written in a faster language such as C/C++ or FORTRAN, at which point it is possible that orientation gradients could begin to be resolved. That is, instead of simply testing all of the known mean orientations in the sample, the algorithm could
vary the orientation on a voxel-by-voxel basis, similar to what was done in [203, 204].

This vastly increases computation time because orientation space is quite large.

Furthermore, the multiple-grain codes have potential to reliably complete the DCT reconstructions. These codes must be tested and validated by comparing the reconstructions with 3D EBSD data. In this way, the parameters in the forward projection may be tuned such that the two different reconstruction methods match. Once validated, these codes will facilitate novel and reliable interface calculations.

It would also be desirable to parallelize the codes. The specifics of how to do this, however, are challenging because the sample cannot be reconstructed one slice at a time. It is possible the code could be separated into regions, not slices, but there would still need to be a fair amount of communication between regions in order for the simulated detector images to keep up with any changes in the grain map.

12.3. Experiment vs. Simulation

In order to better directly compare experiment to simulation, the model can be improved in a number of ways. One of the most important things to consider is the boundary conditions at the surface of the sample. One could try using no-flux or fixed boundary conditions at the sample surface, or perhaps a combination of the two. This would result in a more physical simulation.

The mesh spacing could also be decreased in order to increase the accuracy of velocity of the high-curvature regions. This would come at a computational cost.

One could include anisotropy by making the mobility a function of the known misorientations between grains. In particular, one could assign high mobilities to the
high-angle grain boundaries seen at the surface of the experimental reconstructions. If this resulted in a better match between experiment and theory, it would suggest that the sample experiences mobility anisotropy during grain growth.

Overall, directly comparing experiment and simulation is the best way to advance the capabilities of each. As these two different approaches improve, the synergy increases and thus there is still much to be learned from studying models and characterization of grain growth.
CHAPTER 13

Conclusions

This work has strived to expand the computational capabilities of phase-field simulations and 4D characterization techniques, in order to ultimately provide new incites into the kinetics of grain boundary and interface motion.

First, the phase-field model was altered to incorporate triple junction mobility. TJ-limited kinetics differ significantly from grain boundary-limited kinetics. In particular, low TJ mobility slows grain growth and results in near-zero boundary curvature and a lack of self-similarity. As either the grain size or the TJ mobility increases, there is a decreasing effect of TJs and a transition from linear to parabolic growth kinetics. The lack of self-similarity is seen most obviously in the evolution of the curvature distribution. For normal kinetics, this distribution is time-invariant. However, low TJ mobility sharpens the peak, which results in an evolution of the distribution as the grain size increases. The growth rate of individual grains has also been shown to smoothly transition between two TJ mobility theories and ultimately approach the von Neuman-Mullins for larger grain sizes. Overall, results show that the TJ mobility and grain size are intimately linked. These simulations have been shown to successfully implement triple junction mobility, improving the phase-field model’s ability to simulate nanocrystalline grain growth.

A forward projection algorithm for the simulation of diffraction spots in Diffraction Contrast Tomography has also been developed, in collaboration with Erik Lauridsen.
Unlike previous forward projection methods, the intensities of the diffraction spots are simulated. Analysis of simulated data show that including a surface area penalty to minimize noise along the grain boundaries increases the speed of convergence and results in more physical grain shapes. In addition, the beam intensity (scale factor) of simulated data, if allowed to vary, will converge to very close to the correct value. This convergence occurs even if noise is included in the integrated intensity values, and especially if a surface area penalty term is included. The forward projection algorithm results in reconstructions that increase the space filling from 70% to 75%. Many, though not all, of the large grain boundaries can be considered reliably reconstructed, especially compared to the previous ART method.

A simpler, multiple-grain, forward projection method has been developed that segments the diffraction spots and enforces space-filling. This method works well for a strontium titanate dataset, filling in the undefined space in the ART reconstructions in a physical way that is consistent with the synchrotron measurements. This method has not yet been successful for the aluminum dataset. This discrepancy in quality of the results may be due to smaller orientation gradients in the ceramic sample.

The single-grain forward projection algorithm, along with phase-field smoothing, has been used to reconstruct a high-purity aluminum sample at several timesteps during grain growth. Orientation analysis in MTEX shows that the interior of the sample is composed of large recrystallized grains with cube texture and low-angle boundaries, while the surface grains are smaller and have more random texture and high-angle boundaries. The cube texture increases during grain growth as the larger cube grains dissolve many of the smaller surface grains. The smaller the misorientation angle of a
grain boundary, the smaller the percent decrease during grain growth. Special (111) boundaries show more extreme behavior, with low-angle boundaries changing little in number and high-angle boundaries mostly disappearing during grain growth. It has been observed for individual grains that the growth process is mostly dominated by high-angle boundaries. Individual mobility values are difficult to measure based on the resolution of the data, but by applying certain filters, some reliably-reconstructed boundaries have been found and analyzed.

Finally, the dynamics of rods pinching by diffusion was examined. Theoretically-determined kinetics and self similar shapes were compared to experiment. From the excellent agreement between theory and experiment we conclude that sufficiently close to the pinching point, the pinching process, both prior to and after pinching, is universal. That is, the shape of the interface is independent of the materials system and initial conditions. The dynamics are described by unique temporal power laws whose rate constants match the experimental values within 6%.

Overall, characterization of increasingly complex materials will lead to validation of increasingly complex models. Specifically, 4D characterization of materials during grain growth can allow for the testing of more complex phase-field models that incorporate increasingly more physics such as triple junction mobility, grain boundary energy and mobility anisotropy, diffusion, etc. Ultimately, we would like to be able to characterize grain growth in 4D with fully resolved boundaries and junctions, quickly and reliably. Once this is possible, the feedback loop between experiment and simulation will shorten in time, and the 3D models will be more easily validated. Once models have been shown to be reliable in predicting experimental outcomes, experiments will become
decreasingly necessary. This is especially true as computational power increases. This work has aimed to shorten this distance between simulation and experiment from both sides, improving 4D characterization while at the same time improving the predictive power of phase-field models.
References


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