Interfacial Dynamics in Liquid-Solid Mixtures:
A Study of Solidification and Coarsening

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ABSTRACT

Interfacial Dynamics in Liquid-Solid Mixtures:
A Study of Solidification and Coarsening

John W. Gibbs

The microstructural evolution of liquid-solid mixtures is examined using X-ray computed tomography to make in-situ, 4D (three spatial dimensions and time) measurements of the interfaces between the liquid and solid phases. Samples are a variety of hypo-eutectic Al-Cu alloys and the total characterized volume is approximately 1 mm$^3$. The coarsening datasets span solid volume fractions of 30% to 80% and have durations of up to 15 hours, making them some of the largest, most comprehensive coarsening datasets.

This data is used show that the solid fraction does not have a significant effect on the coarsening rate, unlike in a system of spherical particles. The interfacial curvature and velocity data that is made possible by the 4D measurements is used to develop a relationship between interface shape and the average normal velocity for a piece of interface with that shape. This model accounts for both capillarity and shape-related diffusional effects. Neighborhood related diffusional effects lead to a distribution in velocities about the mean; these distributions are examined and shown to follow a Gaussian distribution.
A novel new data collection and processing algorithm for X-ray computed tomography, time-interlaced model-based iterative reconstruction, is used to achieve 4D data with micrometer level spatial resolution and 1.8 second temporal resolution. This is approximately an order of magnitude better than what has been achieved before and yields the first data with sufficient spatial and temporal resolutions to characterize the microstructure during solidification.

The resulting data of dendritic growth in an Al-24wt%Cu alloy that is being cooled at 2°C/minute shows the formation of split tip secondary dendrite arms that have not been seen before in transparent organic analogues. A single free-growing dendrite is isolated from this data and analyzed as a function of distance from the tip, resulting in relationships for the volume of solid, $V_s \propto \hat{Z}^{1.44}$, the liquid solid interfacial area, $V_{l/s} \propto \hat{Z}^{1.32}$, and mean curvature, $H \propto \hat{Z}^{-0.21}$. The overall dendritic morphology is also characterized, proving the first quantitative 3D data that can be compared to phase field simulations.
Acknowledgements

The support of friends, family, and colleagues has been invaluable while I’ve been working on my PhD over the last four years. In particular, my advisor Peter who has spent countless hours guiding me through this research and most of all, I am grateful to my wife Meghan who has sacrificed so much over the past few years so that I could go back to school.

I would like to acknowledge the funding provided by DOE that allowed us to do the experiments in 2008 and 2012 at the Swiss Light Source, from an AFOSR MURI grant that funded the solidification experiments in 2013 as well as much of the development of the TIMBIR algorithm, and finally a DOE NNSA Stewardship Science Graduate Fellowship that funded me for most of my time at Northwestern.
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CHAPTER 1

Introduction

Dendrites commonly form in a variety of materials from snowflakes to geological samples and, as will be discussed here, solidifying metals. The dendrites that form in metals and alloys have complex morphologies and evolution patterns. Their ultimate morphology has a large impact on the chemical and mechanical properties of the overall material. This makes understanding dendritic growth and the subsequent microstructural evolution an important step in being able to predict the properties and performance of metals.

Much of our current understanding of dendrites during solidification and coarsening comes from studying transparent organic analogs that are thought to behave very similarly to metals. These experiments produce time-resolved, 2D information about the dynamics of the system. This approach was later extended to metals by using a X-ray radiography but this was still a fundamentally 2D experiment. Research has also been done using serial sectioning and focused ion beam milling to generate 3D datasets; however, these methods lose the time-resolved capabilities of the previous methods.

The next logical experimental frontier is making time-resolved, 3D measurements of evolving microstructures. This would resolve any issues with quasi-2D samples where important physics of the evolution are changed by the geometric constraints. The 3D spatial information is also necessary for calculating interfacial curvatures that drive coarsening and for characterizing the complex shapes of secondary dendrite arms that have so impossible to fully resolve because of the superimposing that happens with 2D projections of a
3D shape. Equally important is the time-resolved aspect as it allows for understanding the evolution of the microstructure, comparing the experiments to dynamical theories and for validating microstructural evolution simulation methods.

In this work, X-ray computed tomography is used to make these 4D (3 spatial dimensions and time) measurements of various Al-Cu alloys during in-situ solidification and isothermal coarsening experiments. X-ray computed tomography has held the potential to make time-resolved, 3D measurements of dendritic solidification for several years; however, it has fallen short of being able to make these measurements due to insufficient temporal resolution when micrometer scale spatial resolution is required. We have been able to overcome these limitations of spatial and temporal resolution by developing a new algorithm for tomographic reconstruction that has made it possible to make the first 3D, time resolved measurements of dendritic solidification in a metal.

This thesis is organized into two main sections: a background section and a results section. The background information is distributed over three chapters that contain the basic materials science background, then a combination of literature review and a description of methods used in the experiments and finally a similar literature review and description of the computational methods used here. The results and discussion will form the second half of the thesis. An appendix is also included to cover any details that are important but overly long and distracting from the main points.
CHAPTER 2

Background

Dendritic growth is the dominant solidification mode in metals. Not only are dendrites common, with the steel industry forming upwards of $10^{18}$ dendrites per year, they are also incredibly influential: the dendrite growth patterns affect fluid flow during solidification, which can result in porosity formation, hot tearing and macro-segregation. Furthermore, the dendrite arm spacing in the solidified part also has a strong effect on mechanical properties and chemical homogeneity. Coarsening also has a very prominent role in determining the properties of a cast part, as it is the combination solidification conditions and coarsening that determine the final solidification microstructure [1].

Despite the importance of the dendritic growth and coarsening processes and the many studies that have been performed, there are many open questions about these phenomena. For instance, transparent analogues have been used to develop power laws for envelope and 2D perimeter of dendrite sidebranches as a function of distance from the dendrite tip but there are no 3D equivalents for total volume of solid or actual surface area. Furthermore, since there are no 3D observations of free-growing dendrites, it is unclear how dendrites evolve, which makes it impossible to validate solidification models like the phase field model. This chapter will cover what is known in the literature about solidification with a review of the physics involved and then an overview of the relevant literature. A similar treatment is then given to coarsening. While there have been many successful methods for
simulating both solidification and coarsening, particularly with the phase field method, these are outside the scope of this work and will not be reviewed.

The focus of these sections will be on two-component alloys with diffuse or rough, rather than atomically sharp, interfaces. This distinction is important because materials with atomically rough interfaces will exhibit rounded interfaces and classically shaped dendrites whereas the atomically sharp interfaces will result in faceted microstructural features. As a rule of thumb, materials that have a ratio of molar entropy of fusion to the universal gas constant, $\frac{\Delta S_f}{R}$, that is less than 2 will have rough interfaces as is depicted in Figure 2.1 \textsuperscript{2}. Since the relative entropy controls the dendrite morphology, it is an important parameter when determining whether or not a transparent organic material will be a good analogue for metallic materials. Some values for various metals are listed in Table 2.1 to indicate which materials will form with rough or sharp interfaces.

![Figure 2.1](image_url)  

Figure 2.1. Schematic difference between (left) atomically rough and (right) atomically smooth interfaces from 2.
Table 2.1. Entropy of fusion \( (\Delta S_f/R) \) and interfacial energy anisotropy \( (E) \) for solid aluminum in a hypo-eutectic Al-Cu alloy and for several pure materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystal structure</th>
<th>( \Delta S_f/R )</th>
<th>( E )</th>
</tr>
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<tr>
<td>Al in Al-Cu</td>
<td>fcc</td>
<td>1.30 ( ^2 )</td>
<td>0.010 ( ^3 )</td>
</tr>
<tr>
<td>SCN</td>
<td>bcc</td>
<td>1.44 ( ^4 )</td>
<td>0.005 ( ^5 )</td>
</tr>
<tr>
<td>PVA</td>
<td>fcc</td>
<td>0.90 ( ^6 )</td>
<td>0.050 ( ^6 )</td>
</tr>
<tr>
<td>Xe</td>
<td>fcc</td>
<td>1.71 ( ^7 )</td>
<td>–</td>
</tr>
<tr>
<td>Water</td>
<td>hexagonal</td>
<td>2.65 ( ^2 )</td>
<td>–</td>
</tr>
</tbody>
</table>

2.1. Dendritic solidification

There are two main causes of dendrite formation in metals: constitutional undercooling and thermal undercooling. There are also several smaller effects that that amplify the dendrite formation.

2.1.1. Constitutional undercooling

To understand why dendrites form, consider a planar interface growing in a binary alloy that has an idealized phase diagram as in Figure 2.2. In this problem, heat is being extracted in one direction with the solidification front moving in the opposite direction, as is depicted in Figure 2.3A. Under typical growth rates, local equilibrium conditions will apply and the compositions of the liquid and solid phases at the interface can be determined from the phase diagram. The composition of the solid will vary slightly with position due to forming at different temperatures; however, these variations will be slight and are relatively unimportant, so it is depicted as a constant value. The spatial variations in the liquid composition will be much more significant, both in magnitude and effect. As the solid forms, it rejects solute; this rejected solute must be transported away from the
interface by diffusion in the liquid. The composition in the liquid will be given by the solution to a moving-front diffusion equation:

\begin{equation}
C_l(x) = C_0 + \frac{C_0(1 - k)}{k} \exp \left( -\frac{x}{D_l/v} \right)
\end{equation}

where \( C_l(x) \) is the composition profile in the liquid, \( C_0 \) is the average alloy composition and \( k \) is the partition coefficient, which is defined as the ratio of solid to liquid composition. The diffusion portion of this equation is a function of position, \( x \), and the ratio of the solute diffusivity in the liquid, \( D_l \) to the interfacial growth velocity, \( \nu \). A possible composition profile is drawn in Figure 2.3B.

---

**Figure 2.2.** A schematic phase diagram that is characteristic of most of the theory and experiments described here.
The composition profile, $C_l(x)$, can be used to determine the liquidus temperature as a function of position, $T_l(x)$, from the phase diagram. This is shown in Figure 2.3C along with a possible temperature profile for the sample. These two temperatures will be identical at the interface because of the assumption of local equilibrium.

The driving force for solidification will be related to the undercooling, which is defined as $\Delta T(x) = T_l(x) - T(x)$. The blue highlighted region in Figure 2.3C shows where there is a positive undercooling that is due to the composition gradient in the liquid. This phenomena, which was first described by Tiller [8], is known as constitutional undercooling and will result in dendrite formation because a small perturbation on the interface will be exposed to an increasing amount of undercooling as it grows.

This argument for constitutional dendrite formation depends on the temperature gradient $G = \frac{dT}{dx}$ being sufficiently small that it can be overcome by the constitutional effect. The necessary temperature gradient can be determined by equating the slope of the liquidus temperature at the interface to the actual temperature gradient in the sample:

$$\frac{dT}{dx} = \left. \frac{dT_l(x)}{dx} \right|_{x=0}$$

Equation 2.1 can be combined with an assumption that the liquidus line on the phase diagram is linear with respect to composition to obtain an analytical expression for $dT_l(x)/dx$. When this is combined with Equation 2.2, the following expression is obtained for the critical temperature gradient:
Figure 2.3. (A) shows an alloy that is solidifying with a planar liquid/solid interface. (B) is the composition profile showing the alloy composition ($C_0$) and the actual composition in the solid ($C_s$) and liquid ($C_l$). (C) shows the resulting liquidus temperature ($T_l(x)$) and the actual temperature ($T(x)$). The area in blue indicates where the alloy is undercooled due to compositional non-uniformities.

\[ G_c = -V \left( \frac{m_l C_0 (1 - k)}{k D_l} \right) \]

where $m_l$ is slope of the liquidus line. Implicit in this derivation is that the transformation does not release heat due to the transformation and that the thermal conductivities of the two phases are equal. It also neglects the effects of capillarity, which relates the curvature and chemical potential of an interface and can be significant as feature sizes are on the
order of tens of micrometers or less. However, this equation does indicate that for most metals, dendritic solidification due to constitutional undercooling will be quite common at reasonable solidification speeds and temperature gradients.

2.1.2. Thermal undercooling

Under the right conditions, a second class of dendrites can form called thermal dendrites. These are distinct from constitutional dendrites in that they form due to the melt being thermally undercooled rather than undercooled due to solute segregation. Since segregation is not required, thermal dendrites can even form in pure elements.

To understand the formation of thermal dendrites, consider a melt that is continuously cooling. As a material is cooled from an initially molten state, it will cross the liquidus line and there will be a driving force for solidification; however, solidification does not commence immediately because there is an energy barrier to forming a nucleus, which must be overcome. This results in thermal undercooling existing throughout the melt. At a sufficient driving force, a nucleus of the solid phase will form and start to grow\(^1\).

For simplicity, it can be assumed that the melt is at a uniform temperature. When the nucleus forms and starts to grow, it will release latent heat, bringing the interface up to the equilibrium melting temperature. The heat is transported away through the liquid, resulting in a negative thermal gradient away from the solidification front. Any perturbation will therefore be exposed to a lower temperature and corresponding greater driving force the farther it grows away from the bulk of the interface. Since thermal dendrites do not depend on composition, they can form in either alloys or pure materials\([9, 10]\).

\(^1\)The nucleation process is critically important to solidification but it is outside the scope of this work. For a good review of the subject, see\([2]\).
2.1.3. Other factors influencing dendrite formation

The analysis so far indicates that any perturbation will grow into a dendrite; however, it does not account for the strong crystallographic trends that show up in dendritic solidification. The crystallographic preferences can be attributed to the anisotropy in two terms: the maximum interface growth rate and the interfacial energy.

In a system with rough interfaces, there will be a value of interface growth rate that is limited by atomic attachment kinetics. This growth rate limit will be proportional to the driving force for attachment and can therefore be described as: \( V_{\text{max}} = C \Delta T \), where \( C \) is a coefficient that depends on both thermodynamic and crystallographic factors \[2\]. In most metals, \( C \) is sufficiently large that if the undercooling that is more than a fraction of a degree Kelvin, then \( V_{\text{max}} \) will not be the limiting factor in interfacial growth rates \[2, 10\]. In these cases of ‘large’ undercooling, the interfacial velocity will instead be limited by diffusion rates; either the rate of solute diffusion in alloys or the rate of heat diffusion in pure substances \[10\].

The interfacial energy term will have much more significant effects. Due to the crystalline nature of metals, there will always be some amount of anisotropy in the interfacial energy, with the lowest index interfaces typically having the lowest energy per unit area. This term is described by the interfacial stiffness \[11\]:

\[
(2.4) \quad \Phi(n) = \frac{1}{\gamma_0} \left( \gamma(n) + \frac{d^2 \gamma(n)}{dn^2} \right)
\]
where $\Phi(\vec{n})$ is the anisotropy in the interfacial energy, $\vec{n}$ is the normal vector of the interface, $\gamma_0$ is the average interfacial energy per unit area and $\gamma(\vec{n})$ is the direction-based deviation from the average interfacial energy per unit area. This equation can be thought of as having two separable components: the interfacial energy and its second derivative; these are shown for an Al-Sn alloy in Figure 2.4. note that the derivative term is much more anisotropic than the energy term.

![Figure 2.4. Comparison of the anisotropy in (A) the interfacial energy, $\gamma(\vec{n})/\gamma_0$, and in (B) the interfacial stiffness, $\Phi(\vec{n})$ for an Al-Sn alloy. Note that the scale bar for (A) is 0.988 to 1.008 while the scale bar for (B) is 0.75 to 1.25. The axes relate to the $\{100\}$ directions. Adapted from [11].](image)

This energy anisotropy will result in the low energy interfaces growing more easily and therefore more quickly than other interfaces. When considering the initial dendrite formation, this will result in the low energy interfaces having slightly larger perturbations, which will encounter the greatest driving force for growth under the constitutional or thermal undercooling scenarios and result in these low energy crystallographic directions being preferred.
2.1.4. Dendritic morphology and dynamics

Constitutional and thermal undercooling describe why dendrites form, but they do not give any information about the morphology of the resulting dendrites. Since the morphology and growth rates will determine the overall solidification behavior and the final properties of the microstructure, a significant amount of work has been done to theoretically describe dendrite formation. To do this, researchers have taken the interface stability considerations like those presented for constitutional undercooling further by solving the diffusion equation around a growing dendrite of various shapes and by explicitly analyzing the perturbations to determine the size scales that are most likely to form.

Ivantosv provided one of the first analytical descriptions of the shape of a dendrite [12]. By approximating the shape of the dendrite tip as a paraboloid of revolution that is advancing with a constant tip radius, $\rho$ and at a constant speed, $V$, and considering the steady-state thermal diffusion, Ivantosv determined that $V$ and $\rho$ could be related to the undercooling using:

\[
\frac{T_m - T_\infty}{\Delta H_m/C_p} = \mathcal{P} \exp(\mathcal{P}) \int_0^\infty \frac{\exp(-y')}{y'} \, dy'
\]

where $T_m$ is the melting temperature, $T_\infty$ is the temperature far from the dendrite tip, $\Delta H_m$ is the latent heat of melting and $C_p$ is the heat capacity. On the right hand side, $\mathcal{P}$ is the Peclet number, which is defined as:

\[
\mathcal{P} = \frac{V \rho}{2 \alpha}
\]
where $\alpha$ is the thermal diffusivity when considering dendrites growing in a pure material and it is the solute diffusivity when considering dendrites growing in an alloy. It is important to note that this solution neglects all interfacial energy terms, namely the capillarity and the anisotropy of the interfacial energy. For a given undercooling ($T_m - T_\infty$), these equations can be numerically solved to determine the product of $V\rho$. This result is shown in Figure 2.5.

![Figure 2.5](image)

Figure 2.5. Growth velocity as a function of dendrite tip radius using three different steady-state diffusion solutions (solid lines) as well as the stability criterion (dashed lines). Either the steady-state solution and the stability criterion solution in isolation gives an envelope of possible velocity and radius values but the intersection of the two provides a unique pair of values. From [13]

Mullins and Sekerka extended this analysis by adding interfacial energy terms and considering the morphological stability of various perturbation on the interface [14]. The addition of perturbation analysis allows for capillarity to be included in the calculations and also can be used to determine which perturbation wavelengths are unstable, stable and
which is the fastest growing perturbation wavelength. This is also shown in Figure 2.5 and is labeled as the ‘modified Ivantsov’ model since it uses the same paraboloid of revolution as the Ivantsov model. A similar model was proposed by Temkin that utilized slightly different shape than the Ivantsov shape due to a different choice of boundary conditions [15, 16]; this is the third curve shown in Figure 2.5. The addition of capillarity in both of these models effectively limits the minimum dendrite tip radius, as seen by the curves in Figure 2.5 abruptly curving downward.

Both the modified-Ivantsov and the Temkin models offered a solution to the problem that the original Ivantsov result does not specify a specific value for $V$ or $\rho$. Instead of an infinite number of equally valid solutions, it was decided that the maximum velocity solution was the correct one, as denoted by the dot on each of the ‘modified Ivantsov’ and ‘Temkin’ curves.

This was the thinking until Langer and Müller-Krumbhaar proposed a more accurate method called the marginal stability theory [13]. This theory is another extension of the basic Ivantsosv solution but is different in that it specifically analyzes which perturbations are stable and which are unstable and claims that dendrites will form at the intersection between these two regions, hence the name marginal stability. This results in an additional equation that relates $V$ and $\rho$ [13]:

\[
\sigma^* = \frac{2\alpha \Gamma}{V \rho^2}
\]

where $\sigma^*$ is the stability constant, $\alpha$ is the diffusivity and $\Gamma$ is the capillary length. This curve is shown on Figure 2.5, where it intersects with the Ivantsov solution indicates
the $V$ and $\rho$ values that will result. The stability constant has a theoretical value of $\sigma^* \approx 0.025$ [13].

Kessler, Koplik and Levine added crystalline anisotropy to the existing solutions for dendrite shape and tip velocity [17, 18, 19]. The resulting microscopic solvability theory that they developed showed that anisotropy of the interfacial energy is necessary for dendritic growth.

A further refinement of the dendrite tip shape is the nonaxisymmetric model of Ben-Amar and Brener [20, 21]. This model takes the interfacial energy anisotropy into account to more accurately describe the cross-like cross section of real dendrites. A rendering of this shape is shown in Figure 2.6.

Figure 2.6. A rendering of the non-axisymmetric dendrite shape that is predicted by theory. From [22]
2.1.5. Secondary dendrite arm formation

Most of the investigations of dendrite growth have focused on the dendrite tip. This is mainly due to the tip being simpler in shape and the interest in the tip growth speed. However, the sidebranch structure is also quite important as it is these secondary dendrite arms that sets the characteristic length scale of the microstructure.

There are two main theories for how the secondary dendrite arms form: 1) there are thermal oscillations along the surface of the dendrite that are selectively amplified, similarly to how dendrites from from an initially planar interface, and 2) oscillations in the growth behavior (either tip radius or speed) lead to morphological oscillations along the dendrite that are amplified [23].

The thermal noise theory was described by Brener and Temkin based on the non-axisymmetric dendrite shape [24]. They predicted that very close to the dendrite tip \((Z \approx \rho)\) the secondary arms arising from thermal fluctuations alone would grow according to:

\[
l_2(Z) \propto Z^{2/5}
\]

where \(l_2\) is the length of the secondary arm and \(Z\) is the distance back from the dendrite tip. It is proposed that this would hold for the region near the dendrite tip. Farther back on the dendrite, there exists a steady state region in the range of \(1 < Z/\rho < 1/\mathcal{P}\), where \(\mathcal{P}\) is the Péclet number [24]. In this region, it is predicated that the secondary arms will behave according to:
where $\lambda_2$ is the secondary dendrite arm spacing (SDAS).

### 2.1.6. Experimental findings

People have been aware of the morphology of dendrites for centuries because of cut-and-polish experiments and liquid decanting but the first documented experiments to reveal dendritic evolution were done by Papapetrou in 1935 using a transparent analogue (NH$_4$Cl), as seen in Figure 2.7.

To further the study of transparent analogues for metals and alloys, Jackson and Hunt identified several candidates with an appropriate crystal structure and entropy of melting [4]. In particular Succinonitrile (SCN) with a chemical composition of C$_2$H$_4$(CN)$_2$
has a bcc crystal structure, a convenient melting point of 55°C, a relative entropy of melting value of $\Delta S/RT = 1.44$ and has nearly isotropic interfacial energy [4, 5].

Shortly after the introduction of the marginal stability model, Glicksman did a set of very carefully controlled experiments with free-growing, pure SCN dendrites that started a wave of analysis in the 1980s [26]. These experiments were done in a relatively large bath, allowing full 3D dendrites to grow, although data was acquired with a camera at a fixed location so only 2D projection information is collected. However, by running multiple experiments with the camera at slightly different orientations (see Figure 2.8), they were able to develop some information on the 3D shape of SCN dendrites. Figure 2.9 shows similar data but at higher magnification and emphasizes that the deviation from being a paraboloid of revolution starts very close to the dendrite tip. This was some of the first evidence that led to more sophisticated dendrite tip shapes than the paraboloid of revolution.

Huang and Glicksman made one of the first experimental determinations of the stability parameter, $\sigma^*$ that was introduced by Langer and Müller-Krumbhaar. For the pure SCN system, they found $\sigma^* \approx 0.0195$ [26], compared to the theoretical value that was determined by Langer and Müller-Krumbhaar of $\sigma^* \approx 0.025$ [13].

The side branch length and spacing was also measured by Huang and Glicksman. As can be seen in Figure 2.10, the length of the active secondary dendrite arms, $l_2$, increases almost linearly while the spacing between these arms increases with the power law: $\lambda_2 \propto Z^{1.3}$ [27]. The term ‘active’ secondary arm is used because once a sidebranch becomes shorter than its neighbors, the undercooling that it sees drops to zero and it no longer grows appreciably.
The next major set of experiments were done by Trivedi on SCN-acetone alloys [28]. In addition to being alloys instead of pure materials, these experiments were new in that they used a Bridgman type furnace that can be used to independently control the temperature gradient and the solidification speed. These experiments were done in thin cells of 150 μm thickness; this was shown to be thick enough to not interfere with the growth process but thin enough to minimize the effects of convection. One of the major
the observation field, branches and only a slight variation in sidebranch growth velocity behind branches P and Q, Fig. 9b. One minute between P and Q are clearly slowing down and dropping in Fig. 9. At the time of Fig 9a, branches between P and Q were still relatively close to the dendrite tip, sequenced photographs of such a dendrite are shown across the observation field of the microscope, Time-adjustment process, a dendrite was allowed to grow.

The adjustments in the sidebranch spacing due to competition, and the sidebranch spacing increases continuously with increasing distance away from the dendrite tip. As a result, slow branches decelerate and fast branches accelerate. The slow branches soon drop out, as shown, rapidly with increasing distance away from the dendrite tip. Figure 2.9. Higher magnification of images similar to those in Figure 2.8 showing the deviation from a paraboloid of revolution (dotted line). From [27]

Figure 2.10. A SCN dendrite and its secondary arm envelope. All the secondary are reaching the envelope in the initial growth regime but farther back, where there is competitive growth between the secondary arms, only a few secondary arms reach the envelope. From [27]

Figure 2.8
findings of this study are that the dendrite tip scaling relations that had been theoretically derived and validated by Glicksman [27] in the isothermal experiments also apply to this very different experimental setup. In particular, the dendrite tip radius and secondary arm spacing are shown to not be functions of the temperature gradient in the furnace (see Figure 2.11), lending further evidence to the diffusion controlled growth theories like the marginal stability.

![Figure 2.11](image)

Figure 2.11. Secondary dendrite arm spacing ($\lambda_2$) and tip radius ($\rho$) as a function of temperature gradient for dendrites grown at a constant velocity in a Bridgman type furnace. Note that both quantities are not functions of the temperature gradient. From [28].

In particular, Trivedi found that the secondary dendrite arm spacing near the dendrite tip, $\lambda_2$ and the tip radius, $\rho$, can be related with $\lambda_2 \approx 2.2\rho$ [28]. This is in very good agreement with the theoretical relationship that was predicted by Langer and Müller-Krumbhaar of $\lambda_2 \approx 2.1\rho$ [13] and also with Glicksman's results of $\lambda_2 \approx 3.0\rho$ [27].
Trivedi also noted that the dendrite tip speed-radius relationship that is based on marginal stability analysis could be simplified for the vast majority of growth conditions in which neither the interfacial energy nor the temperature gradients dominated the growth behavior. These simplifications result in the scaling law [28]:

\[
V \rho^2 = \frac{2 \gamma D \Delta H_m}{\Delta S k \Delta T},
\]

where \(V\) is the growth speed, \(\rho\) is the dendrite tip radius, \(\gamma\) is the interfacial energy, \(D\) is the solute diffusivity, \(\Delta H_m\) is the latent heat of melting, \(\Delta S\) is the entropy of melting, \(k\) is the partition coefficient and \(\Delta T\) is the difference between the liquidus and solidus temperatures. When material parameters are plugged into this equation, a relationship of \(V \rho^2 = 411 \, \mu m^3/s\) is found, compared to an experimentally determined value of \(V \rho^2 = 441 \, \mu m^3/s\) [28].

Similar transparent analogue experiments were performed using Xenon by Hürlimann, Bisang and Bilgram [7, 16, 29, 30]. These experiments were done using high purity Xenon, which solidifies with a fcc crystal structure and has an entropy of melting value of \(\Delta S_m/R = 1.71\), both of which make it a good analogue for metals and alloys [16]. The experimental setup was similar to that of Huang and Glicksman in [26] where a 3D dendrite was grown in a large, undercooled melt.

These experiments were able to confirm several important theoretical predictions. One of the important comparison to theory proved that the non-axisymmetric shape prediction of Brener [21] is quite accurate for describing the shape of the dendrite near the tip [16].
Characterizing the sidebranching behavior that occurs just behind the dendrite tip, Hürlimann et al. were able to confirm the theory by Brener and Timken who had predicted that, in the area near the dendrite tip, the secondary dendrite arm spacing, $\lambda_2$, and the length of the secondary dendrite arms, $l_2$, would be proportional to their distance from the dendrite tip, $Z$, as $\lambda_2(Z) \sim l_2(Z) \sim Z/\rho$, where $\rho$ is the dendrite tip radius \cite{7, 24}.

Bisang and Hürlimann later proposed that simple metrics like the secondary dendrite arm length and spacing are not sufficient to fully describe the dendrite shape far from the tip. Instead, they used contour length and projected area \cite{7} and fractal dimension \cite{31} to characterize Xe dendrites. Unfortunately, only the relationship that contour length and projected area are proportional is given; their actual dependence on distance from the dendrite tip are not specified.

![Figure 2.12. A schematic that defines the sidebranch envelope, secondary dendrite arm spacing ($\lambda$), the projected area ($F$) and the contour length ($U$). From \cite{32}](image)
Terrestrial gravity can have significant effects on the morphology and growth behavior of dendrites because of the convection currents that develop in the liquid phase due to either thermal or constitutional density gradients. This can be seen in Figures 2.13 and 2.14. For this reason, the next major round of transparent analogue experiments were done in microgravity conditions on the space shuttle Columbia in 1994 \[33\]. These experiments, called the Isothermal Dendritic Growth Experiments (IDGE), were performed with pure SCN at undercooling values of \(0.2 \, K < \Delta T < 1.3 \, K\). This range of undercooling values is much larger than what had been done before in terrestrial gravity conditions because of convection effects increase with increasing undercooling \[33\].

The primary measurements from the IDGE experiments were dendrite tip radius and tip velocity and resulted in determining a stability parameter value of \(\sigma^* \approx 0.023\) \[35\]. Note that this is quite close to both the theoretical value of \(\sigma^* \approx 0.025\) \[13\] and the value obtained experimentally in terrestrial gravity conditions of \(\sigma^* \approx 0.019\) \[26\].

The data from the IDGE experiments were further analyzed by Li and Beckermann in \[32, 36\] but with a focus on the sidebranching behavior rather than the tip. This analysis used the ideas that are similar to those used by Bisang and H"urlimann of using integral parameters that describe the overall dendrite morphology. Li and Beckerman classified the dendrite into two regimes based on their sidebranching behavior: an initial linear regime in which all sidebranches grow and later non-linear in which there is competitive growth between the sidebranches. This difference can be seen in Figures 2.10 and 2.12 where all the sidebranch tips are touching the sidebranch envelope in the linear regime but not in the non-linear regime. They found that the division between the two
occurs at $Z \approx 30\rho$, which corresponds well with the theory in \[24\] that predicts this change will occur at $Z/\rho = 1/\rho$. 

Figure 2.13. Examples of the asymmetries that can result from growing dendrites in gravity. From \[34\]
Both regimes are characterized the sidebranch spacing \( \lambda_2 \), total contour length \( U \), and projected area \( F \), as shown in Figure 2.12. In the linear regime, they found the following relationships:

\[
\begin{align*}
\frac{\lambda_2}{\rho} & \propto \left( \frac{Z}{\rho} \right)^{0.20} \\
\frac{F}{\rho^2} & \propto \left( \frac{Z}{\rho} \right)^{1.60} \\
\frac{U}{\rho} & \propto \left( \frac{Z}{\rho} \right)^{1.12}
\end{align*}
\]

In the non-linear region, where there is competition between the dendrite arms and only a few continue to grow, the power laws are:
\[ \frac{\lambda_2}{\rho} \propto \left( \frac{Z}{\rho} \right)^{0.48} \]

\[ \frac{F}{\rho^2} \propto \left( \frac{Z}{\rho} \right)^{1.72} \]

\[ \frac{U}{\rho} \propto \left( \frac{Z}{\rho} \right)^{1.50} \]

The authors of the paper note that in this steady state growth regime, \( Z \) is equivalent to \( V t \) or velocity times time, which makes it straightforward to convert these results into time-dependent expressions. Thus, in this non-linear regime that is dominated by coarsening rather than growth, it is expected that the time exponent for the secondary dendrite arm spacing (which represents the size scale) would be about \( 1/3 \). As it is not close to this, it is indicative that either the evolution of the sidebranches is not purely controlled by coarsening or that \( \lambda_2 \) is not the relevant size scale of the system \[32\].

An estimate for the volume (\( V \)) and surface area (\( A_{l/s} \)) of the dendrites is also given in \[36\] is made using a simple model of cylinders with spherical caps. Measurements are made in the non-linear regime, with the linear regime showing a slightly lower (but not reported) slope in Figure \[2.15\]. This method provides relationships of:

\[ \frac{V^3}{\rho} \propto \left( \frac{Z}{\rho} \right)^{2.10} \]

\[ \frac{A_{l/s}}{\rho^2} \propto \left( \frac{Z}{\rho} \right)^{1.92} \]

\[ \frac{S}{\rho^{-1}} \propto \left( \frac{Z}{\rho} \right)^{-0.18} \]
Another Brener and Timken theoretical scaling law that was confirmed was the location of the first secondary arm branch. This is perhaps the most significant finding of the Hürlimann, Bisang and Bilgram experiments because the theory is based on thermal fluctuations near the tip of the dendrite arm being amplified due to morphological instability (the idea behind this is very similar to the reason the planar interface breaks up into dendrites), thus confirming that thermal fluctuations at the tip of the dendrite cause secondary dendrite arms to form.

Further proof for the theory that thermal fluctuations are responsible for secondary arm formation comes from Bisang and Bilgram who showed that the dendrite tip velocity is essentially constant in time (see Figure 2.16). This rules out the possibility that tip...
growth rate fluctuations and the resulting perturbations are responsible for secondary dendrite arm formation.

![Graph showing dendrite tip velocity](image)

*Figure 2.16. Dendrite tip velocity in Xe dendrite growth over time. The constant growth rate is used to rule out the possibility of growth rate fluctuations causing perturbations that grow into sidebranches. From [16]*

While transparent metal analogues have been the most widely used experimental method, it is not the only one. Liquid decanting with either standard imaging or serial sectioning has been used to get static, 3D data of dendrites. This method has the advantage of using metals and being 3D but it suffers from not containing any information on the dynamics of dendritic growth. This type of data has been used as an initial condition for simulations to reveal the fluid flow behavior in directionally solidified castings, as seen in Figure 2.17 [37, 38].

Serial sectioning was also used by Alkemper, Mendoza and Voorhees to very accurately measure the 3D morphology of a dendrite in an Al-Cu alloy, as shown in Figure 2.18 [39].
Figure 2.17. A liquid decanting process is used to perform a 3D characterization of (a) dendrite morphology and (b) connectedness and fluid flow properties in the liquid phase. From [37]

This was used to calculate the curvatures of the dendrite interfaces but does not contain any dynamic information.

Figure 2.18. 3D morphology of a free-growing dendrite in an Al-Cu alloy that was collected via serial sectioning. From [39]
Another technique that has been used to examine dendritic solidification in metals is X-ray radiography. In these experiments, a thin, quasi-2D sample is placed in an X-ray beam. The X-rays are sensitive to both differences in chemical composition and boundaries between phases of the same composition, so this method can be used with either pure materials or alloys. An interesting study used a synchrotron X-ray source to image and quantify the compositional gradients around a dendrite, making it possible to visualize constitutional undercooling, as in Figure 2.19. Note that these experiments are somewhat more limited than the transparent analogues as the X-ray experiments with metals are typically done with quasi-2D samples whereas the transparent analogs are allowed to grow in 3D but are imaged in 2D.

Figure 2.19. Approximate copper content map for a solidifying Al-30 wt% Cu alloy. Colors range from white (5 wt% Cu) to black (30 wt% Cu). From [40]
X-ray tomography has been used to study the 3D morphology of dendrites as they evolve; however, the poor temporal resolution of these measurements has limited them to late-stage dendritic growth when the interfaces are evolving more slowly. This has been used by Limoden, \textit{et al} to examine the evolution of Al-Cu alloys \cite{41}. Figure 2.20 shows the four earliest interface locations in \cite{41}.

While this is a very interesting result that can be used to examine the phenomena like secondary arm selection and the interplay between growth and coarsening, the 22 seconds that are required to collect a 3D dataset means that the dendrite tip is growing much too quickly to resolve. Because the dendrite tip cannot be resolved, it does not allow for measurement of the shape or speed of the dendrite tip, nor does it allow for measuring the properties of the dendrite arm as a function of distance from the tip.

2.2. Coarsening

The interfaces in a system will have a higher energy per unit volume than the uniform portions of the system. This applies to single-phase crystalline systems where the interface are grain boundaries and it also applies to multi-phase systems where the interfaces are the boundaries between the different phases. In any of these systems, it is possible to decrease the total energy of the system by reducing the total interfacial area; this process of interfacial energy driven evolution is called coarsening\textsuperscript{2}.

Coarsening commonly refers to the case in which the phases fractions remain constant; however, coarsening that occurs during a transformation is an equally interesting and relevant, although less well studied, problem.

\textsuperscript{2}Coarsening commonly refers to the case in which the phases fractions remain constant; however, coarsening that occurs during a transformation is an equally interesting and relevant, although less well studied, problem.
interfacial curvatures causes gradients in composition and results in mass flow down the composition gradient. This will leave the interfaces at an out-of-equilibrium composition and equilibrium will try to be restored by a phase transformation at the interface either releasing or absorbing solute. This phase transformation results in interfacial motion and is the mechanism by which microstructural evolution occurs during coarsening. These
effects will be discussed in this section, followed by an overview of the existing literature on coarsening.

2.2.1. Capillarity

Capillarity is the link between the curvature of an interface and its chemical potential. When considering pure materials, capillarity affects the equilibrium transformation temperature between the two phases while in a multi-component alloy, it affects the chemical composition at the interface between the phases. The analysis using temperature and composition effects are roughly analogous. Considering the multi-component case the capillarity can be described by the Gibbs-Thomson equation \[42, 43\]:

\[
(2.20) \quad C^\alpha_c = C^\alpha_{e} + \Gamma^\alpha_c H
\]

where \( C^\alpha \) and \( C^\alpha_{e} \) are the interfacial and equilibrium molar fractions of component \( B \) in phase \( \alpha \), respectively. The capillary length of phase \( \alpha \) is represented by \( \Gamma^\alpha_c \) and \( H \) is the mean curvature. The interfacial mean curvature is the average of the two principal curvatures, \( \kappa_1 \) and \( \kappa_2 \), which are the smallest and largest curvatures on an interface. These principal curvatures can be determined from the principal radii of curvature using:

\[
\kappa_1 = 1/R_1 \quad \text{and} \quad \kappa_2 = 1/R_2.
\]

For a sphere, the two principal curvatures are the same and \( H = 1/R \); for a cylinder, one of the principal curvatures is zero and the other is the reciprocal of the radius of the cylinder, \( 1/R \), the mean curvature is given by \( H = 1/(2R) \). The sign of a principal curvature is typically negative if it is concave towards the solid phase (e.g. a solid sphere) and
positive if the interface is concave towards the liquid phase. Some examples of various interface shapes and their principal radii of curvature are shown in Figure 2.21.

![Figure 2.21. Three different types of interfaces: a sphere with $R_1 = R_2$, a cylinder with $R_2 = \infty$ and a saddle shape in which $R_1$ and $R_2$ have different signs. From [2]](image)

The capillary length is defined as:

\[
\Gamma_c^\alpha = \frac{V_m^\beta \gamma}{(C_e^\beta - C_e^\alpha) G_m^{\alpha''}}
\]

where $V_m^\beta$ is the molar volume of the $\beta$ phase, $\gamma$ is the interfacial energy per unit area and $G_m^{\alpha''}$ is the second derivative with respect to composition of the molar Gibbs free energy. Because of the complexity in the $G_m^{\alpha''}$ term for real materials, the capillary length is determined experimentally more often than from Equation 2.21. Typical values of the capillary length are on the order of nanometers.

### 2.2.2. Theoretical coarsening rates

While there has been a significant amount theoretical work done on describing the evolution of microstructures during coarsening, the vast majority of it is done on systems of
spherical particles. This assumption of a system of spherical does not fit with the morphologically complex systems that are being considered in this work; however, it has been found that these theoretical models can be applied to morphologically complex systems with surprisingly good results [44]. For this reason, and also because there are relatively few theories for the coarsening of morphologically complex systems, the spherical particle coarsening theories will be briefly reviewed, followed by a review of the existing theories for the coarsening of morphologically complex systems.

In order to form a theory for the rate of coarsening, it is necessary to develop a kinetic equation that determines the interfacial velocity as a function of its curvature. This is done by assuming that the system is composed of infinitely separated particles, such that each particle is only interacting diffusively with a surrounding mean field. The solution to the diffusion equation for this case is:

\[ C(r) = a_1 + \frac{a_2}{r} \]

where \( a_1 \) and \( a_2 \) are constants and \( r \) is the radial distance from the interface of the particle. The constants can be determined by using the Gibbs-Thomson equation as one boundary condition and the mean field at \( r = \infty \) as the second boundary condition.

To get an interfacial growth rate equation, the solute flux at the interface is determined from Equation 2.22 and this is equated to the particle growth rate for a given solute flux, resulting in:
\[
\frac{dR}{dt} = \frac{D \Gamma_c}{C_B^{\beta,e}} - \frac{1}{C_B^{\alpha,e}} \frac{1}{R} \left( \frac{1}{R_c} - \frac{1}{R} \right)
\]

where \( R_c \) is the critical radius at which a particle will neither grow nor shrink. In practice, this is often close to the average particle radius in the system.

Equation (2.23) can be integrated with respect to time to obtain the well-known relationship between particle size and time:

\[
R^3 - R_0^3 = Kt
\]

Further analysis of the growth rate equation can be done to determine the steady state distribution of particle sizes, as was originally done by Lifschitz and Slyozov \[^{45}\] and Wagner \[^{46}\]. While these distributions are outside the scope of this work since they have little bearing on the evolution of morphologically complex systems, one interesting and relevant phenomena is the concept of self-similarity that results from this analysis. In this case, self-similarity means that when the particle size distribution is scaled by the average particle size, \( \langle R \rangle \), it is independent of time.

There have been many studies to extend this infinitely-dispersed-particle analysis to more practical finite amounts of the coarsening phase \[^{47, 48, 49, 50, 51, 52}\]. What is notable about these works is that they all predict differing shapes for the particle size distributions but the same temporal exponent of \( R^3 \propto t \) and the existence of a self-similar distribution \[^{53}\].
The rate constant, $K$, in Equation 2.24 has been determined either experimentally or analytically for a variety of different conditions. In Lifshitz and Slyozov’s work on infinitely dilute systems, $K = \frac{4}{9} \frac{D_{cc} V_m}{T^2}$ [54]. Later work on finite volume fraction systems showed that this rate constant is a function of volume fraction of the coarsening phase, as shown in Figure 2.22. It is assumed that morphologically complex systems follow a similar trend of more dense systems exhibiting faster coarsening rates [44].

Figure 2.22. Experimental data for the rate constant $K$ in the equation $\langle R \rangle^3 - R_0^3 = Kt$ from a variety of systems (points) along with a mean field approximation (solid line). From [53].

Drew determined equations that govern the curvature evolution of an arbitrarily shaped interface as a function of the velocity field of that interface [55]. When these equations are coupled with a model of the system that provides the interfacial velocity field, they can be used to determine the complete location and shape evolution of the interface. Drew presents several examples of simple systems in which these interfacial...
speed models are known. In these examples, it is possible to determine the evolution of particular interfacial shapes and ultimately the evolution of the statistics of a full system. Unfortunately, models of the interfacial velocity are not available for complex systems such as coarsening or solidification.

Theories for dendritic coarsening have been developed in which the dendrite shape is assumed to be a series of cylinders and spherical caps, as shown in Figure 2.23 [56]. These assumptions typically do not hold up well as the dendritic structure rapidly devolves from well defined shapes to complex shapes that are difficult to describe analytically, as seen in Figure 2.24.

Figure 2.23. A geometric description of a dendrite that is used to formulate a model for how the dendrite will coarsen. This simple description typically does not describe the dendrite shape very well as coarsening progresses. From [56]

An interesting observation of Marsh and Glicksman is that the diffusional flux lines matter much more in complex morphology systems than in a system of spheres [44]. Since the flux lines largely radiate in normal directions from the interface, a sphere will
Fig. 1--Quenched microstructures of a Sn-40 pct Bi alloy held isothermally just above the eutectic temperature: (a) as-cast, (b) after 10 min, (c) after 2.5 h, and (d) after 10 days.

Scales, this capillary shift is well represented by the line-arized Gibbs-Thomson equation, which can be written in dimensionless form as

\[ \frac{O(i)}{R_1 R_2} = \frac{1}{2H} \]

where \( O(i) \) represents the equilibrium value of the dimensionless concentration (supersaturation) at a point \( i \) on the interface, \( R_1 \) and \( R_2 \) are the two principal radii of curvature of the interface, each being scaled in Eq. [1] by the appropriate capillary length of the alloy, \( L_e \), and \( H \) is the dimensionless mean curvature, defined here as the average of the principal curvatures. Note that \( 2H \) is the geometric coefficient \( \frac{dA}{dV} \) that relates the differential area and volume changes associated with the local normal displacement of an interface.

The magnitude of the equilibrium solute supersaturation at an interface is thus proportional to the local mean curvature of the interface. Spatial variations in the equilibrium supersaturation over an interface having a nonuniform curvature lead to concentration gradients, which in turn excite fluxes of solute and enthalpy through the embedding matrix phase. These diffusional interactions stimulate the growth of flatter interfacial regions and lead to remelting of more highly curved regions. The net effect of this process is an increase in the average lengthscale (e.g., mean particle radius) of the microstructure and a corresponding decrease in the average interfacial curvature.

The bulk phases in mushy zones are in local thermodynamic equilibrium during late-stage coarsening. This occurs because the excess interfacial free energies, on a unit volume basis, are much smaller than are the volumetric energies in solid-liquid alloy systems at typical microstructural lengthscales (1 to 100/xm). Thus, the variations in concentrations that develop along a solid-liquid interface having nonuniform curvatures are much smaller than the concentration differences between the bulk phases. The enthalpy and solutal fluxes that lead to coarsening occur at essentially constant phase volumes and cause only insignificant changes in the phase fractions present. Recent analyses \(^{41}\) have shown that coarsening models based on a constant solid fraction can be used to describe the general behavior of solidifying mushy zones in numerical analyses. The progress of coarsening in such analyses is calculated using a rate constant that is updated over each computational time-step to reflect the local temperature and solid fraction.

The small magnitude of concentration shifts induced by the Gibbs-Thomson effect suggests further that solute diffusion occurs quasi-statically during Ostwald ripening. The dimensionless concentration field, \( O(r) \), in the matrix is,

have flux lines radiating in all directions evenly, whereas a saddle shaped interface will have converging flux lines in one principal curvature direction and diverging flux lines in the other direction. The converging flux lines will result in a build-up of solute and significantly slow diffusion away from the interface. Although this is a purely qualitative argument, it demonstrates that there are shape-based parameters that will affect the motion of an interface.

An attempt to develop a quantitative theory involving these flux lines was presented by DeHoff in \(^{57}\). This “connected neighbor” theory explicitly models the diffusional interactions of particles instead of using a mean field approximation in which the particles
are treated as being infinitely separated and only interacting with the average properties of the system; this distinction is shown graphically in Figure 2.25. This idea can be used to develop a new interfacial velocity equation to replace Equation 2.23 [57]:

\[
\nu = \frac{D \Gamma_c}{C_B^{\beta,e} - C_B^{\alpha,e}} \frac{1}{\lambda} (H_n - H)
\]

where \( \lambda \) is the characteristic diffusion length scale between the interface of interest and its relevant neighboring interface and \( H_n \) and \( H \) are the mean curvatures of the neighbor interface and the interface of interest. This equation can be used to develop a steady-state particle size distribution and equations that describe the evolution of the average size scale of the system. The trouble with this formulation is in determining \( \lambda \) and which interfaces are connected pairs. This would require full knowledge of the microstructure and solving the diffusion equation for the entire domain. Since the results of this analysis are dependent on the input microstructural morphology, it is difficult to generalize these results.

Figure 2.25. Comparison of (left) DeHoff’s connected neighbor description of compositions and composition gradients and (right) a classical mean field theory as is used in LSW and many other theories. From [57].
2.2.3. Experimental findings

For systems of spherical particles, it has been shown that the temporal exponent for average particle size of $\langle R \rangle^3 \propto t$ is correct and that the particle size distribution becomes self-similar at long times [58, 59].

The growth/dissolution rate of spherical particles ($\dot{R}$) was examined by Voorhees using a finite-volume-fraction, interacting-particle simulation [54]. The results of this are plotted in Figure 2.26 as the source/sink rate ($B = R^2 \dot{R}$) which is proportional to the rate of change of a particles volume. Note that the change between particles shrinking and growing occurs around $R = \langle R \rangle$ and also that dispersion in velocities for a given particle radius increases with increasing radius.

Early work on the coarsening of systems of non-spherical particles was done by Flemings et al who used post-mortem sectioning to consider the secondary dendrite arm spacing of dendrites as a function of coarsening time [1]. This is a very important work in that it showed the dendritic morphology in a casting is controlled by coarsening, contradicting earlier theories that secondary dendrite arms are indefinitely stable after forming.

While secondary arm spacing works well for characterizing microstructures with strongly dendritic character; however, as the dendritic structure coarsens, it becomes increasingly difficult to define the dendrite arms and therefore the dendrite arms spacing as can be seen in the series of images in Figure 2.24. In these cases, the surface area per unit volume, $S_v$ is a better characteristic size scale as it is independent of the morphology of the microstructure [60, 61].

One of the remarkable things about coarsening in morphologically complex systems is that the rate of change of $S_v$ can be very well described using theories that were
The Theory of Ostwald Ripening

Figure 4. Discrete $B(p)$ data at $\omega = 0.1$ derived from the simulations of VG. The scatter in the value of $B_i$ for a given particle size is a result of diffusional interactions or "soft collisions" between particles which occur at finite $\omega$.

All of the theories are in general agreement on the following points:

1. The temporal power laws originally reported by LS are not a function of $\omega$; however, the amplitude of the power laws is $\omega$ dependent;
2. Scaled time invariant distribution functions exist at finite $\omega$ in the long-time limit;
3. As $r$ increases, the time invariant distributions become broader and more symmetric than the LSW distribution;
4. The rate constant rises rapidly at low $\omega$ and is followed by a slower increase with $\omega$;
5. The predictions for $K(r)$ of GV and MR are almost identical up to $r \approx 0.1$, as shown in Fig. 2;
6. The $B(p)$ functions of MR and GV are quite similar and in agreement with the VG simulation data, all three descriptions showing increased diffusional interactions with increasing $\omega$ which result in an increase in the absolute value of the statistically averaged coarsening rate of a particle in a given size class. Note that the mathematical similarity between the $B(p)$ functions predicted by BW and MR is deceiving, since the values of the numerically determined parameters in each theory will be different.

Figure 2.26. Interfacial source/sink rate ($B = R^2 \dot{R}$) as a function of particle size. Note that the particles shrink for $R < R_{av}$ and grow for $R > R_{av}$ and also that the spread of $B$ for a given $R$ value increases with increasing $R$. From [54]

derived for systems of infinitely separated spheres. This was first shown by Marsh and Glicksman [44], as shown in Figure 2.27 using 2D sections and confirmed by others using 3D methods [62, 63].

The first in-situ, 4D measurements of coarsening metals was made by Limodin et al [62]. This work was done using an Al-16 wt% Cu alloy which resulted in a relatively high solid fraction of $f_s = 0.68$ vol% solid and showed a temporal evolution of $S_v \propto t^{-1/7}$ rather than the $S_v \propto t^{-1/3}$ that is predicted by LSW analysis and has been seen in earlier studies. This is attributed to the coarsening mechanism being primarily coalescence of
Figure 2.27. Surface area per unit volume \((S_v)\) as a function of time for an initially dendritic microstructure showing that the time evolution of the microstructure can be described with \(S_v \propto t^{-1/3}\). From \([44]\).

touching particles. Another in-situ study of Al-Cu alloys resulted in a similarly high temporal exponent of \(S_v \propto t^{-1/4.2}\) \([64]\).

These anomalously high temporal exponents could simply be due to the system still being in a transient state. Alkemper studied Pb-Sn samples that were coarsened in microgravity and characterized using serial sectioning and found that the initial transient period in the system was quite strong over the first hour of coarsening and didn’t fully go away after 10 hours of coarsening \([59]\), as seen in Figure 2.28. Since the in-situ studies were only carried out for slightly over an hour, it is likely that they were still in a transient regime.

One difference that appears to be confirmed between systems of spherical particles and complex morphology systems is the presence of a self similar distribution. In studies
Figure 2.28. The time evolution in the coefficient $K$ in the expression $S_v^{-1} = K t^{1/3}$. The early-time evolution of this coefficient indicates that the system doesn’t reach steady-state until at least $t^{1/3} = 20$ s$^{1/3}$ or about 2 hours. From [59]

of directionally solidified Al-Cu alloys, it is found that the interfacial shape distribution$^3$ does not reach a steady state distribution even after 16 hours of coarsening [63, 65].

In high volume fraction samples, this is thought to occur because the microstructure decomposes into a series of liquid tubes and liquid walls, as seen in Figure 2.29, which significantly alters the possible diffusion pathways.

In-situ coarsening experiments have recently made it possible to validate the accuracy of the phase field model that is commonly used to study solidification and coarsening. Aagesen performed phase field simulations using experimentally collected microstructure information as an initial condition and compared the resulting interfacial velocity to that of the experiments [66]. After correcting for materials parameters, the two methods

$^3$The interfacial shape distribution is similar to the particle size distribution but uses interfacial curvatures instead of particle radii. It will be described further in the Computational Methods chapter.
produced interfacial velocities that were very similar, as shown in Figure 2.30. This indicates that the phase field method works quite well for studying coarsening.
Another use of in-situ characterization has been to examine the coarsening mechanisms in dendritic liquid-solid Al-Cu alloys. Terzi et al observed at least three simultaneous coarsening mechanisms that had been proposed in the literature: small dendrite arm melting; interdendritic groove advancement; and coalescence and groove advancement (shown in Figure 2.31). This wide variety of simultaneous coarsening mechanisms highlights how difficult it is to develop a model that can accurately describe the coarsening process in morphologically complex microstructures.

Figure 2.31. Interfacial locations in a dendritic liquid/solid mixture showing the liquid phase over time. As the arms of liquid pinch off, they create liquid droplets that will be isolated from the rest of the system due to the low diffusivity in the surrounding solid. From [64]
CHAPTER 3

Experimental methods

A variety of binary Al-Cu alloys are used to study the solidification and coarsening processes. These alloys are used for several reasons: 1) because their properties make them excellent candidates for studying solidification and coarsening; 2) their properties are well known and documented; 3) these alloys work very well with X-ray computed tomography (CT) that is used to collect data. X-ray CT is used to characterize the microstructural evolution because it is the only technique that can produce time-resolved, 3D measurements that have micrometer scale resolution. Many of these 3D characterizations are performed in order to get the time-resolved, 3D data that is required for this project. Experiments are done at a synchrotron since the high photon flux that is available at a synchrotron makes it possible to have a temporal resolution of seconds to minutes. This chapter will cover the Al-Cu material system, sample preparation and experimental setup. The materials and experiments are quite similar between the solidification and coarsening experiments; the differences between the two will be discussed at the end of the chapter.

3.1. Properties of the Al-Cu system

The Al-Cu system is well suited to studying both solidification and coarsening because the solid/liquid interfacial energy has very little crystallographic anisotropy and has well known values of its Gibbs-Thomson coefficient and diffusion coefficient. To work well with X-ray CT, the liquid and solid phases must have a significant difference in atomic number,
which the hypo-eutectic Al-Cu system provides by having a relatively large difference in atomic number between the two elements present and also a large difference in composition between the two phases as can be seen in the phase diagram in Figure 3.1.

![Phase diagram for the Al-Cu system. Adapted from 67](image)

**Figure 3.1.** Phase diagram for the Al-Cu system. Adapted from [67]

### 3.1.1. Interfacial energy

The anisotropy of the interfacial energy is a very important part of any solidification or coarsening experiment. The microscopic solvability theory showed that some finite amount of interfacial energy anisotropy is necessary for dendrite formation and it will be inherent in any material that has crystallographic features; however, minimal anisotropy is preferred since the majority of the theories that describe solidification and coarsening are based on idealized, perfectly isotopic interfacial energies and also because it is not possible to measure the crystallographic directions in these experiments so any effects due to crystallographic anisotropy are difficult to quantify.

The Al-Cu system is an ideal candidate for these experiments because it is one of the few metallic systems for which the interfacial energy is known. To determine the
anisotropy, Liu, Napolitano and Trivedi \[3\] heated single crystal samples of Al-4 wt% Cu to form liquid droplets trapped in the solid. The samples were held at temperature to allow the shape of the liquid droplets to equilibrate. The samples are then quenched and sectioned along a \(\langle 1 \ 0 \ 0 \rangle\) direction of the single crystal solid and the shape of the droplets are measured from images like the one in Figure 3.2. The anisotropy can then be determined from the shape measurement. This results in an anisotropy factor of \(\mathcal{E}_4 = 0.0098\) when using the common anisotropy description of:

\[
\gamma(\theta) = \gamma_0 (1 + \mathcal{E}_4 \cos(\theta))
\]

where \(\gamma_0\) is the average interfacial energy, \(\mathcal{E}_4\) is the anisotropy factor in one of the 4-fold symmetric planes (i.e. normal to a \(\langle 1 \ 0 \ 0 \rangle\) direction) and \(\theta\) is the angle from one of the 4-fold symmetric directions. This relatively small amount of anisotropy will be enough to result in dendritic solidification with branches along the \(\langle 1 \ 0 \ 0 \rangle\) directions, but it is also small enough that it will not significantly affect the coarsening experiments.

3.1.2. Gibbs-Thomson coefficient

The Gibbs-Thomson coefficient for the solid \(\alpha\)-Al phase in a near-eutectic composition liquid can be found in \[68\]. The value is determined by using a sample that contains two grains and placing the sample in a furnace with a known temperature gradient. The sample is oriented with the grain boundary normal to the temperature gradient. The grain boundary results in a cusp forming, which is revealed by quenching and polishing the sample, as seen in Figure 3.3.
The temperature-centric version of the Gibbs-Thomson equation for an infinitely long cylinder can be integrated along the direction of the temperature gradient to obtain:

\[ \int_{0}^{\infty} T(z) - T_m \, dz = \int_{0}^{\infty} \frac{\Gamma_T}{r} \, dz \]

where \( z \) is the position along the temperature gradient, \( T(z) \) is the temperature, which is known from the measured temperature gradient, \( T_m \) is the equilibrium melting temperature, \( \Gamma_T \) is the Gibbs-Thomson coefficient for temperature effects and \( r \) is the radius of the
cusp. Gündüz and Hunt used this method to determine a value of $\Gamma_T = 2.41 \times 10^{-7}$ K m for solid Al in an Al-Cu mixture at the eutectic composition and temperature.

This can be converted to the Gibbs-Thomson coefficient in the chemical potential or composition based Gibbs-Thomson equation using the following linear approximation of the liquidus line:

$$\Gamma_c = \Gamma_T \frac{m_l}{m_l}$$

where $m_l$ is the slope of the liquidus line. When dealing with the value of Gibbs-Thomson coefficient, it is important to remember that there are two commonly used definitions of the curvature: the mean curvature ($H = (\kappa_1 + \kappa_2)/2$) and what is typically just called the curvature ($\kappa = \kappa_1 + \kappa_2$). In this work, the mean curvature is used whereas the $\kappa$ curvature is used in [68]. Correcting for this results in a value of $\Gamma_c = 0.74$ nm when using weight fraction for the Cu concentration and $\Gamma_c = 2.23$ nm when using atomic fraction.

### 3.1.3. Diffusion coefficient

The diffusion coefficient of Cu in a near-eutectic Al-Cu liquid that is near the eutectic temperature has been measured experimentally several times [69, 70, 71, 72, 73, 74, 75, 76, 77], resulting in values between $2 \times 10^{-9}$ and $6 \times 10^{-9}$ m$^2$/s. One of the reasons for this large disparity in values is convection in the liquid can significantly affect the apparent diffusivity. One of the most thorough determinations is in [78], in which the diffusivity is calculated by quenching a solidification front in a Bridgman type furnace and measuring the composition gradient ahead of the interface. What is unique about this study is that
the measurements were performed using small diameter samples (from several mm down to 1 mm), which reduces the size of the convection cells that can develop and effectively eliminates the effect of convection. This method provided a diffusivity value of Cu at the eutectic temperature of $D_{Cu} = 2.4 \times 10^{-9} \text{ m}^2/\text{s}$.

Other notable methods include using small angle neutron scattering to determine diffusion coefficients in the liquid at several temperatures and extrapolating down to the eutectic temperature to obtain a value of $D_{Cu} \approx 3 \times 10^{-9} \text{ m}^2/\text{s}$ [79]. Another in-situ method uses X-ray radiography to estimate the composition of the liquid and solid phases in an isothermal diffusion couple, resulting in a value of $D_{Cu} \approx 1.8 \times 10^{-9} \text{ m}^2/\text{s}$ [80].

An alternative method of calculating diffusivity is provided in [66]. This method consists of using time-resolved microstructural evolution data from an isothermal coarsening experiment as an initial condition for a Cahn-Hilliard phase field model, evolving the phase field simulation and then comparing the evolution rates between the simulation and experimental data. This method results in a diffusivity value that is $D_{Cu} = 8.3 \times 10^{-10} \text{ m}^2/\text{s}$.

This has the advantage of not being post-mortem data with the accompanying uncertainty in quench effects and because the data is from an isothermal coarsening experiment, there are no temperature gradients that could affect the diffusivity. Another advantage of the phase field simulations used in this method use the value for the Gibbs-Thomson coefficient that was determined by Gündüz and Hunt in [68]. This is advantageous because the simulation and the analysis used in this work rely on the ratio of diffusivity to Gibbs-Thomson coefficient in the same way, which means that any experimental errors in one value or the other will be unimportant because the ratio will be correct. Because the

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1The data used in the paper is some of the same data that is used for this work
simulation-experiment comparison method in [66] most accurately represents the systems that are used here, the value of \( D_{Cu} = 8.3 \times 10^{-10} \text{ m}^2/\text{s} \) is used.

### 3.1.4. Phase densities and buoyancy

The densities of Al and Cu have vastly different values of \( \rho_{Al} = 2.70 \text{ g/cm}^3 \) and \( \rho_{Cu} = 8.96 \text{ g/cm}^3 \) [81]. This, when combined with the different chemical compositions of the phases, leads to convection in the liquid that makes accurate measurements of the diffusivity difficult and it also leads to buoyancy-driven motion of the phases. Assuming the phase densities can be calculated as a linear combination of the densities of the pure elements, the density of a phase can be calculated as:

\[
\rho^\theta = \left( \frac{f^\theta_{Al} \rho_{Al} + f^\theta_{Cu} \rho_{Cu}}{\rho_{Al} + \rho_{Cu}} \right)^{-1}
\]

where \( \rho^\theta \) is the density of phase \( \theta \), \( f^\theta_i \) is the weight fraction of element \( i \) in phase \( \theta \) and \( \rho_i \) is the density of element \( i \) in its pure state. The temperature dependent elemental densities are computed using the room temperature density and coefficient of thermal expansion to get temperature dependance. The liquid density is computed by assuming 5% volumetric expansion on melting. This results in phase densities at the eutectic temperature of \( \rho_l = 3.2 \text{ g/cm}^3 \) for the eutectic liquid and \( \rho_s = 2.7 \text{ g/cm}^3 \) for the solid at its maximum Cu content of 5.5 wt% Cu.

This density difference between the phases can result in sedimentation that is due to gravity and due to the rotation of the sample during the data gathering process. The
sedimentation due to gravity can be calculated by equating the buoyancy and viscous drag forces on a free floating spherical drop to obtain:

\[(3.5) \quad \vec{V} = \frac{2}{9} \sigma s - \rho l \frac{\mu}{\bar{g}} \vec{g} R^2 \]

where \(\vec{V}\) is the velocity of the particle, \(\mu\) is the viscosity of the liquid, \(\bar{g}\) is the acceleration due to gravity and \(R\) is the particle radius. Using values for the Al-Cu system and a particle size of 50 \(\mu\)m results in a settling speed of about 500 \(\mu\)m/s.

This sedimentation caused problems in the samples that contained less than 30 vol% solid, where dendrites would break off and float upwards. At solid fractions of 30 vol% and higher, the dendrites would form a rigid network that prevented sedimentation. In the solidification experiments, the dendrite would nucleate on the sidewall of the sample and stick to the wall.

The second type of sedimentation is that due to the rotation of the sample during the CT data collection process. If rate of sedimentation due to sample rotation is significantly smaller than that due to gravity, then it is assumed to be negligible both with respect to convection in the fluid and sedimentation of the liquid and solid phases. Therefore, the relevant quantity here is the acceleration due to rotation and how it compares to gravitational acceleration. This can be calculated by equating the force required to move a particle to the buoyancy forces for a hypothetical solid particle in liquid:

\[(3.6) \quad ma = m_e r \omega^2 \]
where \( m \) is the mass of a particle and \( a \) is its acceleration. For the buoyancy terms, \( m_e \) is the effective mass that is driving the buoyancy, \( r \) is the radius of rotation and \( \omega \) is the rotational speed. This can be reformulated in terms of phase densities and time to make a revolution (\( \Delta t \)) to obtain:

\[
a = \frac{\rho^s - \rho^l}{\rho^s} r \left( \frac{2\pi}{\Delta t} \right)^2
\]

(3.7)

Using the previously determined phase densities and upper-limit values of \( r = 0.5 \) mm and \( \Delta t = 1.0 \) seconds yields acceleration of about 0.01 \( m/s^2 \).

A second concern associated with rapid rotation of the sample is that the acceleration will be able to generate convective forces in the liquid. A similar argument to the rotation-based sedimentation can be used to show that this is also a negligible effect.

### 3.2. Sample preparation

Sample preparation consists of procuring the base alloys from high purity stock, directionally solidifying the materials and machining samples from the directionally solidified material.

The alloys are made by the Materials Preparation Center at Ames Laboratory. Starting materials are 99.99% purity elements which are melted using vacuum induction melting and cast into \( \frac{1}{2} \) inch diameter rods. Alloy compositions between 15 and 27 wt% Cu were used. These alloys were selected to give different volume fractions at the eutectic temperature. This method is preferable to varying the temperature for a single composition because it does not significantly affect the material parameters like diffusivity. Since the
material properties are the same between the different alloys, the results can easily be compared across different volume fractions. The alloys, expected and actual volume fractions of solid are listed in Table 3.1. The main reason for the difference between expected and actual solid fractions is that there are likely compositional differences between the individual samples since the samples are significantly smaller than the casting from which they were cut so any non-uniformities in the composition of the casting would lead to an off-chemistry sample.

The alloys used are listed in Table 3.1. The naming scheme used is comprised of a letter indicating whether the sample is used in a solidification (S) or coarsening (C) experiment, a number for the year in which the experiment was done and a second number for the nominal composition of the sample in weight percent copper. For the coarsening samples, both the expected and measured volume fractions of solid are listed because the nominal alloy compositions are not necessarily the same as the actual composition of each sample and comparing the two solid fractions gives an estimate of the composition of the sample.

Table 3.1. Alloy compositions and phase fractions.

<table>
<thead>
<tr>
<th>Name</th>
<th>Nominal composition (wt% Cu)</th>
<th>Solid fraction (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C08-26A</td>
<td>26</td>
<td>0.28</td>
</tr>
<tr>
<td>C12-27A</td>
<td>27</td>
<td>0.35</td>
</tr>
<tr>
<td>C08-26B</td>
<td>26</td>
<td>0.45</td>
</tr>
<tr>
<td>C08-20A</td>
<td>20</td>
<td>0.48</td>
</tr>
<tr>
<td>C12-19A</td>
<td>18</td>
<td>0.55</td>
</tr>
<tr>
<td>C08-15A</td>
<td>15</td>
<td>0.80</td>
</tr>
<tr>
<td>S13-24A</td>
<td>24</td>
<td>–</td>
</tr>
</tbody>
</table>

The alloys are directionally solidified using a Bridgman furnace at a speed of either 1.2 mm/min for samples C08-26A, C05-26B and C08-15A [82] or 2.4 mm/min for samples
C12-27A and C12-19A. The thermal gradient is measured to be approximately \(2.8^{\circ}\text{C/mm}\). This provides an initial secondary dendrite arm spacing of about 50 \(\mu\text{m}\) for the 2008 samples and 25 \(\mu\text{m}\) for the 2012 samples. The one exception to this is sample C08-20A, which was cast to produce equiaxed dendrites. The methods used to do this, as well as a comparison of interfacial normal directions between the equiaxed and directionally solidified samples can be found in [83].

The alloys from Ames Lab came in two groups: one in which the directional solidification step came immediately after the initial casting and a second group in that was swaged between casting and the directional solidification. In the group that was not swaged, there is porosity in approximately half of the samples whereas there is none in the swaged samples. The porosity has the potential to affect the results so the non-swaged samples with porosity are not used.

The directionally solidified rods were machined into 1 mm diameter by 5 mm long samples using electrical discharge machining with a brass wire at the Northwestern Instrument Shop. The diameter of the samples is chosen to work well with the data collection setup. The penetration power of 20 keV X-rays that are common at a synchrotron is limited to about 2 mm of these Al-alloys. Also, the field of view for the imaging setup is about 1.5 mm when the spatial resolution is on the micrometer level; since artifacts are introduced when the sample diameter is larger than the field of view, the samples are typically kept below a maximum diameter of 1.5 mm.

One of the samples, C08-26A, has a 2 mm diameter. This results in some artifacts that requires additional steps to account for; however, it is valuable because it is used as a test to see if the sample diameter has any effect on the dynamics of the system.
3.3. X-ray computed tomography

X-ray computed tomography (CT) data is collected by shining X-rays through a sample and recording the projection of the sample; this process is shown schematically in Figure 3.4. These projection images, like the one shown in Figure 3.5, will contain information about the entire microstructure but it is not directly useable because all of the information along the beam path is superimposed. In order to deconvolute the information along the beam path, the sample is rotated over $180^\circ$ and about 1000 projections are collected during the rotation. The microstructural information can be calculated from the projection data via a reconstruction method. This section will cover more details on how the projection images are formed, followed by information on the imaging and experimental setups used in this work.

![Figure 3.4. Schematic of the X-ray computed tomography process. X-rays come from the left, pass through the rotating sample and the projections are collected by the camera system.](image)

3.3.1. Contrast mechanism

The contrast in the projections is due to interactions between the incoming photon and the atoms. As the X-rays pass through the material, they will interact with the atoms and occasionally transfer their energy to the electron. When this happens, the beam
intensity in that location drops slightly and the material heated slightly [84]. The linear absorption coefficient, \( \mu \), of a pure material can be described by [84]:

\[
\mu = C \rho \lambda^3 Z^4 W
\]

where \( C \) is a constant, \( \rho \) is the density of the material, \( \lambda \) is the wavelength of the X-rays used, \( Z \) is the atomic number of the material and \( W \) is the atomic weight of the material. The strong \( Z \) dependence of absorption coefficient, combined with the large difference in atomic numbers between Aluminum (\( Z = 13 \)) and Copper (\( Z = 29 \)) and the large difference in Copper content between the liquid and solid phases provides good contrast in this system. This system also works well with X-ray CT because it has a relatively low average atomic number which enables the X-rays to pass through more material than if a higher \( Z \) system were used.

As the X-ray beam passes through a certain thickness of the material (\( dl \)), it will be attenuated by an amount that is proportional to the incoming beam intensity. This leads to an exponential decrease in the beam intensity as it propagates through the sample, which can be described by the Beer-Lambert law [84]:

\[
I_\theta(i) = I_0(i) \exp \left( -\int_1^i \mu(x) dl \right)
\]

where \( I_\theta \) is the projection of the transmitted intensity, \( \mu \) at angle \( \theta \) and \( I_0 \) is the projection image without the sample in the beam, this is known as flat-field image. Inside the exponential on the right hand side of this equation is a line integral of the attenuation
coefficient along a line, \( l \), that passes through point \( i \) on the detector; this integral is known as the mass-thickness. Since the goal of this method is to get the values of the attenuation coefficient, Equation 3.9 is inverted to get an expression that is linear with respect to the mass-thickness:

\[
- \ln \left( \frac{I_0(i)}{I_\theta(i)} \right) = \int_1 l \mu(\vec{x}) \, dl
\]

Examples of the a flat-field image, projection image and the normalized projection that is defined in Equation 3.10 are shown in Figure 3.5. The left hand side of Equation 3.10 will be referred to as the normalized projection data. This is the data that will be used in all reconstruction methods since it is proportional to the mass thickness.

![Figure 3.5](image)

Figure 3.5. An example of a (A) a projection image \( (I_\theta) \), (B) a flat-field image \( (I_0) \), and (C) the normalized projection defined by \( -\ln (I_\theta/I_0) \).

The normalized projections are converted into real-space data of the absorption density using a reconstruction technique. This process is discussed in the next chapter.
3.3.2. Synchrotron beamlines

Two synchrotron beamlines were used to collect the data that is used here: the TOMographic Microscopy and Coherent Radiology experiments (TOMCAT) beamline was used at the Swiss Light Source, Paul Scherrer Institut and the 2-BM beamline was used at Argonne National Laboratory’s Advanced Photon Source. The first set of experiments was led by Julie Fife in 2008 at the TOMCAT beamline. These experiments were focused on characterizing coarsening dynamics at a spatial resolution of about 1.5 µm and a temporal resolution of 2 to 4 minutes. A second set of experiments was performed in 2012 at the TOMCAT beamline. These experiments were also focused on coarsening and the main goal was to utilize improvements at the beamline to achieve temporal resolution of approximately 45 seconds, as well as to use a new furnace design that promised better temperature gradient control.

A final set of experiments were performed at the Advanced Photon Source in 2013. These experiments were focused on measuring the morphology of dendrites during solidification. These experiments provide the first 3D measurements of dendritic growth in a metal. This is made possible by a new concept for how to collect and process data, which will be discussed in subsequent computational methods sections.

3.3.3. Beamline setup

There are many parameters that must be chosen in a typical CT experiment that contribute to the overall quality of the data. Picking the setup that will give the highest quality data is difficult because there are competing objectives of image quality and speed of

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2Dr. Fife was a graduate student in the Voorhees group at the time and is now a beamline scientist at the TOMCAT beamline.
data acquisition. Projections that have high contrast and low undesirable signal\footnote{The undesirable signal is a combination of noise that is inherent to the imaging method, shot noise, variations due to differing gains of particular pixels, and all forms of background signal such as scattered X-rays.} will result in better spatial resolution in the reconstructions; however, getting these high quality projections usually requires increasing the total data acquisition time. This can result in serious artifacts if the structure of the object being measured changes significantly during the scan. This can be seen with the shrinking disk example in Figure 4.6, which shows how insufficient temporal resolution degrading the spatial quality of the data. Thus, there are cases when improving the temporal resolution also improves the spatial resolution. Because of these competing objectives of quality and speed, it is important to tune the various image acquisition parameters to obtain the best results.

One of the most important is the energy of the X-rays. The overall goal when choosing X-ray energy is to maximize the signal-to-noise ratio in the projections. The trade-off here is that the signal increases as a greater portion of the beam is attenuated (e.g. the statistics are much better for \( I(i)/I_0(i) \) values of 20% and 60% than if the values are 98% and 99%) but the baseline noise level in the image will be the same regardless of signal intensity, thus the signal-to-noise ratio will increase dramatically as the signal gets very low. For this reason, it is common to aim for transmission values of \( I(i)/I_0(i) \approx 0.2 \) \footnote{85}. For the Al-Cu alloys and sample sizes used here, this occurs with a beam energy around 25 keV. The photon flux at a synchrotron decreases with increasing beam energy when the energy is above the critical energy of the synchrotron. At the SLS this critical energy is less than 10 keV (see Figure 3.6) and at the APS the critical energy is around 20 keV \footnote{86}. Since
all experiments were run at beam energies above these values, there is incentive to keep the beam energy as low as possible to maximize the flux.

Figure 3.6. Photon flux of a monochromatic beam at the TOMCAT beamline at SLS. Note the decreasing flux with increasing energy, which has significant effects on exposure time. The significant drop around 20 keV due to a change in monochromator performance. Adapted from [87]

In some of the datasets, acquisition speed was prioritized over image quality. For these samples, a spread of energies was used rather than a single energy. This so-called polychromatic or white beam is created by bypassing the monochromator and instead passing the full beam intensity through a series of glass, aluminum or iron materials with thicknesses of between 1 and 10 mm to decrease the flux of relatively low energy X-rays. The photon flux profile for the conditions used in the 2012 experiments is shown in Figure 3.7.

Using a polychromatic beam results in much greater photon flux than the monochromatic beam but it suffers from a phenomenon known as beam hardening. Beam hardening occurs when there are multiple values of both beam energies and mass thickness. From
Equation 3.8, it is clear that if a polychromatic beam passes through a thick material, the low energy photons will be attenuated the fastest and the high energy photons will be attenuated the slowest\(^4\). This means that a thin section of material will permit nearly the full spectrum of X-ray energies through while a thick section will quickly damp all of the low energy X-rays. This leads to bright regions around the edges of the sample as can be seen in Figure 3.8.

To generate images from the transmitted X-rays, a scintillator is used to convert the X-rays into visible light, which is then magnified and saved as an image using a CCD or CMOS camera. A 20 µm thick Ce-doped yttrium aluminum garnet (Ce:YAG) was used in the 2008 experiments at SLS and a 100 µm thick Ce-doped lutetium aluminum garnet (Ce:LuAG) scintillator was used in the 2012 and 2013 experiments. The thickness of the scintillator is important because the amount of visible light produced increases with increasing scintillator thickness, which allows for reduced exposure times; however, the

\(^4\)The term beam hardening refers to the increase in average beam energy as it passes through material. Since high energy X-rays are known as hard X-rays, this process is called hardening.
Figure 3.8. An example of beam hardening that is due to X-rays of different energies being attenuated at the different rates. Note the relatively brighter ring around the edge of the sample compared to the center of the sample.

X-rays scatter as they pass through the scintillator so a thicker scintillator also results in some blurring of the image. Comparing 25 µm and 100 µm thick Ce:LuAG scintillators showed that the spatial blurring of the thicker scintillator did not significantly degrade the reconstructed image quality but it did produce an approximately four fold decrease in required exposure time. All exposure times are listed in Table 3.2.

Two cameras were used in the experiments, a PCO.2000 CCD camera was used in the 2008 experiments and a PCO.Edge 5.5 CMOS camera was used in the 2012 and 2013 experiments. The CCD camera has a resolution of 2048 × 2048 and pixel sizes of 7.4µm × 7.4µm; this camera is run in 2 × 2 binning mode, resulting in images that are 1024 × 1024. Images from the CMOS camera that are a maximum of 2560 pixels wide by 2160 pixels tall and the pixel size is 6.5µm × 6.5µm. Because of the way a CMOS camera works, any image sizes that are less than the maximum are done by cropping rather than
binning like the CCD. Data collected with this CCD camera resulted in very high signal-to-noise ratio reconstructions. The results when using the CMOS camera have a lower signal-to-noise ratio but the required exposure time is significantly lower than with the CCD. Table 3.2 contains information on the projection and reconstruction sizes as well as which camera is used and exposure time per projection.

Depending on the desired speed and pixel size, different magnifications were used. A continuously adjustable zoom system was used at the TOMCAT beamline at SLS to give magnification values between 4× and 10×; these values are listed in Table 3.3. The beamline at APS uses a fixed objective to magnify the image off the scintillator. An magnification value of 10× was used for all APS experiments.

Table 3.2. CT Parameters used for each sample. The much lower exposure times at APS are primarily due to the beamline staff recommending a lower total number of counts in the projection images.

<table>
<thead>
<tr>
<th>Name</th>
<th>Beamline</th>
<th>Beam energy (keV)</th>
<th>Camera</th>
<th>Exposure time (ms)</th>
<th>Projections per scan</th>
</tr>
</thead>
<tbody>
<tr>
<td>C08-26A</td>
<td>Tomcat</td>
<td>30</td>
<td>PCO.2000</td>
<td>400</td>
<td>721</td>
</tr>
<tr>
<td>C12-27A</td>
<td>Tomcat</td>
<td>poly.</td>
<td>PCO.Edge</td>
<td>18</td>
<td>501</td>
</tr>
<tr>
<td>C08-26B</td>
<td>Tomcat</td>
<td>25</td>
<td>PCO.2000</td>
<td>250</td>
<td>721</td>
</tr>
<tr>
<td>C08-20A</td>
<td>Tomcat</td>
<td>25</td>
<td>PCO.2000</td>
<td>250</td>
<td>721</td>
</tr>
<tr>
<td>C12-19A</td>
<td>Tomcat</td>
<td>poly.</td>
<td>PCO.Edge</td>
<td>18</td>
<td>501</td>
</tr>
<tr>
<td>C08-15A</td>
<td>Tomcat</td>
<td>20</td>
<td>PCO.2000</td>
<td>80</td>
<td>721</td>
</tr>
<tr>
<td>S13-24A</td>
<td>APS 2-BM</td>
<td>poly.</td>
<td>PCO.Edge</td>
<td>2</td>
<td>–</td>
</tr>
</tbody>
</table>

3.3.4. Furnace

One of the core components of this research is to be able to do in situ X-ray CT microscopy. This requires a specially designed furnace that has a way of inserting the sample that allows it to rotate and a path for the X-ray beam to pass through.
Table 3.3. Dimensions of each dataset. Dimensions are in voxels unless noted otherwise.

<table>
<thead>
<tr>
<th>Name</th>
<th>Pixel size (µm)</th>
<th>Projection dimensions</th>
<th>Reconstruction dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>C08-26A</td>
<td>1.44</td>
<td>1024 × 1024</td>
<td>1024 × 1024 × 1024</td>
</tr>
<tr>
<td>C12-27A</td>
<td>1.78</td>
<td>960 × 1360</td>
<td>960 × 960 × 1360</td>
</tr>
<tr>
<td>C08-26B</td>
<td>1.44</td>
<td>1024 × 1024</td>
<td>1024 × 1024 × 1024</td>
</tr>
<tr>
<td>C08-20A</td>
<td>1.44</td>
<td>1024 × 1024</td>
<td>1024 × 1024 × 1024</td>
</tr>
<tr>
<td>C12-19A</td>
<td>1.78</td>
<td>960 × 1360</td>
<td>960 × 960 × 1360</td>
</tr>
<tr>
<td>C08-15A</td>
<td>1.44</td>
<td>1024 × 1024</td>
<td>1024 × 1024 × 1024</td>
</tr>
<tr>
<td>S13-24A</td>
<td>0.65</td>
<td>2080 × 1000</td>
<td>2000 × 2000 × 1000</td>
</tr>
</tbody>
</table>

There are also strict thermal requirements on the furnace, particularly for the coarsening experiments. To avoid changes in the phase fractions, the temperature of the furnace must be very stable over long periods of time. Furthermore, the spatial gradients must also be very small\(^5\). This is because the equilibrium composition of the liquid phase is a function of temperature, so if there is a temperature gradient, there will be a composition gradient as well. This will cause solute to flow anti-parallel to the temperature gradient and result in interfacial motion that is not due to curvature-driven coarsening.

A maximum allowable temperature gradient can be determined by considering a spherical liquid droplet surrounded by solid. Assuming diffusion to occur only in the liquid and that the system is at steady-state conditions, the rate of solute flux due to the temperature gradient can be determined from the slope of the liquidus line, \(m_l\). This is related to the solute flux required for migration of the particle to obtain the rate at which the liquid droplet will migrate up the temperature gradient:

\(^5\)The axial gradient is the main concern since the diameter of the sample is relatively small and it is continuously rotating, so the radial gradients will be negligible.
\( V_z = \frac{D_l m_l}{C_s - C_l} \frac{dT}{d\bar{z}} \)  

where \( V_z \) is the droplet velocity in the z direction due to the temperature gradient, \( D_l \) is the diffusivity of copper in the liquid phase, \( C_s \) and \( C_l \) are the compositions of the solid and liquid phases and \( \frac{dT}{d\bar{z}} \) is the temperature gradient. Using values for the Al-Cu system at the eutectic temperature and with the temperature gradient in units of \( ^\circ C/mm \) results in:

\( V_z \approx \left( 2 \frac{\mu m}{\text{minute}} \right) \left( \frac{dT}{d\bar{z}} \right) \)

While this type of interfacial motion is not desired, it is fortunate that all interfaces move at the same rate regardless of particle size or curvature. This makes it possible to account for this motion by shifting datasets by an amount equal and opposite to the distance of interface migration. This is done using image registration concepts as is discussed in the Computational Methods chapter.

Three different furnaces were used for the 2008 SLS, 2012 SLS and 2013 APS experiments. The two used at SLS were designed by Dr Erik Lauridsen who was at Risø National Laboratory in Denmark at the time. The furnace used in the 2008 experiments (shown in Figure 3.9) did a nice job of keeping the temperature constant over the duration of the experiment but it had a slight temperature gradient along the axis of the sample. Using Equation 3.11 and the measured interfacial drift due to the thermal gradient, the temperature gradient in this furnace is estimated to be 0.25 \( ^\circ C/mm \).
The furnace used in the 2008 coarsening experiments contains three temperature zones, level with, above and below the sample. This allows for fine tuning of the temperature gradient. Over the 2 hour duration of the experiments, there is no noticeable temperature induced migration, indicating that the temperature gradient is less than 0.05 °C/mm. This furnace is shown in Figure 3.10.

Figure 3.9. The furnace used in the 2008 coarsening experiments. This is a single zone furnace with a relatively large sample chamber. The beam pathway is not visible in this photo. From [83]

Figure 3.10. The furnace used in the 2012 coarsening experiments. This furnace has a much smaller sample chamber and three temperature zones to better control the temperature gradients along the axis of the sample.
The furnace used in the solidification experiments at APS is a water cooled, copper-clad that contains resistive heating elements. This combination of both heating and cooling capabilities allows for controlled heating and cooling rates. The single-zone design of the furnace does not provide the kind of temperature gradients of the 2008 and 2012 furnaces; however, this is not a significant problem given that these experiments only last tens of seconds to a few minutes. This furnace is shown in Figure 3.11.

Figure 3.11. The furnace used in the 2013 coarsening experiments. The copper jacket is water cooled to provide greater control over the cooling rates
3.3.5. Experiment details

For the experiments, the sample is held in a boron nitride (BN) sample holder, which is supported on a 100 mm alumina rod. This assembly sits on a rotation stage, as shown in Figures 3.12 and 3.13, and is raised up into the bottom of the furnace.

Figure 3.12. Schematic of the sample and the BN sample holder that are placed on top of the alumina rod that is part of the rotation stage. The sample is a cylinder that is 1 mm diameter by 5 mm long.

The coarsening experiments are started by partially inserting the sample into the furnace to heat it to approximately 500 °C, then fully inserted to bring it up to a temperature that is just above the eutectic temperature. These experiments are run for between 2 and 12 hours, as listed in Table 3.4.
Figure 3.13. Photo of the rotation stage, alumina rod and BN sample holder. From [83]

Table 3.4. Duration of coarsening experiments.

<table>
<thead>
<tr>
<th>Name</th>
<th>Total experiment time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C08-26A</td>
<td>864</td>
</tr>
<tr>
<td>C12-27A</td>
<td>74</td>
</tr>
<tr>
<td>C08-26B</td>
<td>366</td>
</tr>
<tr>
<td>C08-20A</td>
<td>462</td>
</tr>
<tr>
<td>C12-19A</td>
<td>79</td>
</tr>
<tr>
<td>C08-15A</td>
<td>677</td>
</tr>
<tr>
<td>S13-24A</td>
<td>1</td>
</tr>
</tbody>
</table>

For the solidification experiments, the sample is heated to 650 °C, then cooled at 2 °C per minute. The duration of these experiments is limited by the software controlling the
rotation stage, which can only run for approximately two minutes at a time before having to be reset.

One significant difference between the solidification and coarsening experiments is the compositions of the liquid and solid phases at various points in the experiment. In the coarsening experiments, the compositions of the solid and liquid will be approximately $C_s = 5.5$ wt% Cu and $C_l = 32.5$ wt% Cu, which are the equilibrium values at a temperature that is just above the liquidus. The two phases will have these compositions regardless of the overall alloy composition. In the solidification experiments, the sample will start out as fully liquid at the overall alloy composition and once it reaches a sufficiently low temperature, solid phase will form at a composition that is dictated by the overall alloy composition and the amount of undercooling in the sample. This difference in compositions will typically be small relative to the coarsening datasets and it will increase with increasing Cu content in the alloy. This is important since the contrast in the resulting datasets is proportional to $Z^4$. For this reason, the solidification experiment must be done with a relatively Cu-rich (at least 20 wt% Cu) sample while the coarsening experiments have no such restrictions.
CHAPTER 4

Computational methods

Although this project is entirely experiment-based, it would not have been possible without a significant amount of computational work. The raw data from that is collected is in the form of many thousands of projections of the microstructure data. These projections need to be reconstructed into intelligible, real-space microstructure information. This data then needs to be segmented to identify which regions are solid and which are liquid. While the high contrast of the reconstructed data makes segmentation a relatively easy task, the huge volume of data being segmented (typically on the order of 100 billion data points per dataset) requires specialized computational tools to do it in a timely manner.

This chapter will be comprised of descriptions of the tomographic reconstruction methods that are used to obtain real space data from the CT projection data, then the segmentation method that provides interfacial locations based on the reconstructed real-space data and finally the analysis tools that are used to distill useful results out of the interfacial location data.

4.1. Reconstruction of computed tomography data

Reconstruction of the projections that are obtained from the CT process into useable, real-space data falls within the class of inverse problems, meaning that some known process happened (X-rays passing through the sample) to give some data (the projection images) but the data that is of interest (the microstructure information) must be inferred from
the collected data. This particular inverse problem is difficult because there is no linear transformation to obtain the desired data from what is measurable. Instead, non-linear inverse transform methods have been developed. These methods can be either one-step, direct methods or iterative methods; both types were used in this work and will be discussed here.

All CT reconstruction methods are computationally intensive. The main reasons for this are because 1) it is high dimensionality data and 2) there is a lot of data in each dimension. The microstructure data has three dimensions \((x, y, z)\) and the projection data also has three dimensions \((r, \theta, z)\). Since the \(z\)-axis is shared between the two, the 5 dimensional reconstruction process can be simplified to a 2D to 2D transformation of \((r, \theta)\) to \((x, y)\) that can be applied to each of the layers in the \(z\)-axis independently. The \((r, \theta)\) data is called a ‘sinogram’. Figure 4.1 shows a schematic of the 3D data and highlights the difference between a projection and a sinogram.

![Figure 4.1. Schematic of the difference between a projection (blue outline) and a sinogram (red outline).](image-url)
4.1.1. Filtered back projection

Filtered back projection (FBP) is has been the most common method of reconstruction since it’s development in 1960’s by Cormack and Hounsfield [89, 90, 91]. This one-step method is so common because it is relatively simple algorithmically and is one of the fastest methods available. FBP is based on applying an inverse Radon transform, or ‘back projecting’, the projection data, which is best described with an example. An object is represented in a $3 \times 3$ grid in Figure 4.2A. The CT process is simulated in Figure 4.2B to obtain the projection data from the object. The back projection is setup by replacing the object with a new empty array in which the reconstruction will be calculated in Figure 4.2C. In Figure 4.2D, the projections are prepared for back projection by dividing by the total number of projections, which is 2 in this case. The back projection is performed in Figures 4.2E and 4.2F. This consists of taking the projection data at the angle at which it was acquired and ‘smearing’ the data back across the reconstruction array. The algorithmic details of this back projection process are given in the implementation appendix.

The reconstruction shown in Figure 4.2F is the final reconstruction that is obtained from the back projection algorithm. This method recovers the central value of 1 correctly, but the neighboring values of 0.5 show that this method blurs the object. This blurring is only exacerbated when a more complex object is reconstructed. It is also important to note that it appears as if back projection correctly recovers the corner values of the reconstruction; however, this is merely an artifact of only using two orthogonal projections. If more projections had been used (for example, at a 45°), then the corners would also have had a slightly positive value.
Figure 4.2. The back projection method of reconstruction. (A) the sample. (B) Two projections of the sample. (C) Starting the reconstruction by with an empty array. (D) Adjusting the projections by dividing by the total number of projections. (E) Smearing the first projection values back across the reconstruction domain. (F) Smearing the second projection to obtain the final reconstruction. Note the blurring compared to the correct values in (A).
In order to reduce the blurring artifacts of back projection, a high pass filter can be applied to the projection data along the \( r \)-axis before back projecting; this is called filtered back projection. Figure 4.3 shows how the FBP algorithm works. The initial object and projection step are the same as back projection in Figure 4.2. The main difference is in Figure 4.3D where a high pass filter has been applied to the projections. The actual calculation of the reconstruction in Figures 4.3E and Figure 4.3F is the same except for the use of the filtered projection data.

The final FBP reconstruction in Figure 4.3F appears to be somewhat less blurred than the reconstruction in Figure 4.2F. The difference would be even more marked if more projections were used; as the number of projections goes to infinity, the FBP reconstruction will approach the initial object whereas the non-filtered back projection reconstruction will remain blurred. The complexity of the sample also has a significant effect on the amount of blurring in the reconstruction, as shown in Figure 4.4 where a real sample is used to compare the back projection and filtered back projection methods.

It is common to apply a low pass filter in along the \( r \)-axis when the high pass filter is applied to reduce the noise level in the reconstructions. This step is not done here because the reconstruction data will be smoothed during the segmentation process and the very high frequency noise that these low pass filters eliminate is quickly damped by the smoothing during segmentation. Thus, skipping the low pass filter makes the smoothing easier to control since it is done once during segmentation rather than during both reconstruction and segmentation.

An important parameter to pick when doing CT experiments is the number of projections, \( N_\theta \). The common guideline for the required number of projections to achieve
Figure 4.3. The filtered back projection method of reconstruction. Same steps as in Figure 4.2 except a high pass filter is applied to the projections in (D). This results in sharper interfaces in (F).
Nyquist sampling is to have $N_\theta$ be the same as the number of pixels of the object being reconstructed. When this condition is met, the exaggerated peaks and troughs in the filtered sinogram that occur as a result of the high-pass filter will align and cancel, resulting in a reconstruction with well defined edges. However, if fewer projections than this are used, the peaks and troughs will not cancel each other out, leaving behind alternating bright/dark lines extending from any edges in the sample. Another effect of being undersampled in projection space is that rounded features will appear as polygons. Both of these can be seen in Figure 4.5.

Another common artifact in CT data is due to the sample evolving during the scan. This is similar to the artifacts seen when too few projections are used since it is due to the amplified peaks and troughs in the filtered sinogram not aligning to cancel. This artifact is easily illustrated with a shrinking disk, as in Figure 4.6. These two artifacts of too few projections and motion during the scan are intertwined because increasing the number of projections increases the time required for a full scan and therefore increases the amount of
Figure 4.5. The effect of increasing the number of projections for a 1024 × 1024 domain that contains a disk with a diameter of 512 pixels. Number of projections used are: (A) 4, (B) 8, (C) 16, (D) 32, (E) 64, (F) 128, (G) 256 and (H) 512. The bright/dark fringes decrease and the disk becomes more round with increasing number of projections.

motion during the scan. Any 4D experiment that is run at or near the temporal resolution limits of the CT system, as are both the coarsening and solidification experiments in this work are, will have to be optimized to find the right balance of artifacts. The combined effects of these two sets of artifacts are shown with a shrinking disk and a variety of $N_{\theta}$ in Figure 4.7.

An alternative to FBP that is gaining in popularity is the ‘gridrec’ method [92]. This method does the non-linear transform from $(r, \theta)$ coordinates to $(x, y)$ coordinates in Fourier space according to the Fourier slice theorem. This provides some speed advantages over FBP at the cost of algorithmic complexity; however, it does not significantly change what is possible in terms of resolution or reconstruction quality.
Figure 4.6. Effect of an evolving object. The disk shown here was originally 512 pixels in diameter and shrunk by 5% during the data acquisition process, resulting in light and dark streaks coming off the edges of the sample.

Figure 4.7. The same scenario as in Figure 4.5 but now the disk is shrinking at a rate of 0.25 pixels per projection. The number of projections used are: (A) 4, (B) 8, (C) 16, (D) 32, (E) 64, (F) 128, (G) 256 and (H) 512. The optimal result here is somewhere around 16 to 32 projections.
4.1.2. Time-interlaced, model-based, iterative reconstruction

The need for better data processing algorithms has also motivated the computational content of this research. While there have been previous attempts to make in-situ measurements of microstructural evolution during solidification before [41], they have been limited by combination of insufficient temporal or spatial resolution[1]. Working with a research group at Purdue University, we have developed a new framework for collecting CT data and reconstructing it that can offer at least a 16-fold improvement in the temporal resolution with no degradation in the spatial resolution.

This method, called time-interlaced, model-based, iterative reconstruction (TIMBIR), combines two innovative techniques: interlaced view sampling and model based iterative reconstruction (MBIR). The typical method of collecting $N_\theta$ projections is rotate the sample so that the rotation angle is proportional to time, as shown in Figure 4.8A. An example of the interlaced method is shown in Figures 4.8B in which only every other angle is acquired in the first 180° rotation and the remaining projection angles are collected in a second 180° rotation. This example is characterized with $k = 2$, meaning the rotations are split into two sets. The second example in Figure 4.8C shows a $k = 4$ example in which every fourth rotation angle is acquired on the first rotation and the remainder are split among three other rotations.

It is important to note that both the standard progressive sampling and the interlaced methods measure projections at the same angles, so if $N_\theta$ meets the Nyquist requirement in the progressive sampling scheme, it will meet it using the interlaced method as well.

---

[1] The micrometer spatial resolution and the sub-second temporal resolution are possible independently with current state-of-the-art methods but not concurrently.
Figure 4.8. An example of (left) progressive sampling, (center) interlaced sampling with $k = 2$ and (right) interlaced sampling with $k = 4$.

Figure 4.9. Comparison of (A) filtered back projection with $k = 1$, (B) filtered back projection with $k = 16$, (C) model based iterative reconstruction with $k = 1$, and (D) time-interlaced, model based iterative reconstruction with $k = 16$. Arrows in (A) point to the areas where the differences are most evident.

The MBIR reconstruction technique is shown schematically in Figure 4.10. The liquid/solid sample (labeled as $x$) goes through the CT data collection process (‘physical system’) to produce the projection data ($y$). In the MBIR process, a reconstruction of the sample is made and labeled $\hat{x}$. This reconstruction is subject to a prior model, $p(x)$, in which various constraints can be imposed on the estimate data. In this case, the system
has only two phases so the majority of the pixels will have very similar values to their neighbors, so penalties are applied to any pixels that have greatly different values compared to its neighbors. The reconstruction is then processed through a forward model, \( f(x) \), which simulates the CT data collection process, including complex, non-linear effects like beam hardening and anomalous high energy X-rays, and the resulting data can be compared to the collected data, \( y \), highlighting any locations that the data and the reconstruction are inconsistent. Finally, the reconstruction can be manipulated so as to minimize the penalties in both the prior model and the forward model. More details of this technique, including information on the details of the prior model, forward model and the minimization scheme, can be found in [93].

The most important part of the TIMBIR method is how the interlaced view sampling and the MBIR reconstruction method are combined. If the interlaced sampling were used with no other modifications to the standard progressive sampling and filtered back projection reconstruction scheme, there would be very little improvement. If the progressive sampling method were used with MBIR, the spatial resolution and noise level in the reconstruction would improve but it would not deliver the desired improvements in temporal resolution.

The other alternative is to do interlaced view sampling and to perform reconstructions every \( \frac{N_{\theta}}{k} \) projections rather than every \( N_{\theta} \) projections. This would result in better temporal resolution by a factor of \( k \); however, it would also result in each of those reconstructions being done from fewer projections than specified by the Nyquist condition. This would result in significant artifacts when done with filtered back projection and is
unlikely to be worth the effort. Typical 3D MBIR methods would not work much better either due to the undersampling of the angles.

What is done in TIMBIR is to perform a MBIR reconstruction for every $N\theta/k$ projections but to add a temporal regularization to the prior model in MBIR. This allows each reconstruction to be focused on a narrow region in time but the regularization across different datasets that are performed with projections from different angles allows for complete Nyquist sampling.

![Figure 4.10. Schematic of model based iterative reconstruction (MBIR). From [94]](image)

### 4.2. Registration

The 4D data used here is made up of many 3D datasets. These are typically collected by acquiring projections as the sample rotates through 180°, then resetting the rotation stage to 0° and repeating the process (the exception to this is the solidification dataset, which is collected and reconstructed under the TIBMIR framework). Occasionally, the stage does not reset to the exact same starting position as the previous time and the two datasets will be rotated relative to each other by up to a degree, which can cause significant error when calculating the interfacial displacement between timesteps. These
misalignments are corrected for using a registration process. There are three components to the registration process: a transformation or set of transformations to apply to the datasets to bring them into alignment; a metric that quantifies how well the two datasets are aligned; and an optimization function that determines the amount of transformation that produces either the minimum or maximum value of the alignment metric.

Since the primary concern here is datasets that are misaligned by a rotation about the z-axis, this is one transformation that will be corrected. The second transformation is a translation along the z-axis. The translation is to correct for any drift of the interfaces due to thermal gradients. These transformations are determined using linear interpolation in each dimension.

The metric that is used to determine the quality of alignment between datasets is mutual information. Mutual information is a measure of the similarity between corresponding pixels between two arbitrary dimensionality datasets. It is defined using the difference between Shannon entropies of the individual images datasets, $H(A)$ and $H(B)$, and the joint entropy, $H(A, B)$, as follows:

\[
I(A, B) = H(A) + H(B) - H(A, B)
\]

The individual entropies for datasets $A$ and $B$ are defined using their histograms, $h_A(i)$ and $h_B(i)$, which are 1D sets of bins that contain the number of data points that have values $i$. The range and number of bins can vary depending on the data. Thus, the entropy for dataset $A$ is defined as:
where $N$ is the total number of data points in the dataset. The joint entropy is similarly defined using the joint histogram, $h(i, j)$, which is the probability of finding values $i$ and $j$ in corresponding locations in datasets $A$ and $B$. The joint entropy is then defined as:

$$
H(A, B) = - \sum_{i,j} \frac{h(i, j)}{N} \ln \left( \frac{h(i, j)}{N} \right)
$$

The resulting mutual information value is a nicely peaked function, as shown by Gulsoy in [95] (Figure 4.11). By having a well defined peak at the correct alignment of the data, mutual information is a very easy function to optimize. Another aspect of this problem that makes optimization relatively easy is that rotations are small – typically less than $1^\circ$ for rotations and less than 1 voxel in translations. As such, a quadratic polynomial fit was determined from 3 to 5 values to find the optimal transformation in each axis. An alternating scheme was used that optimized rotations first, then translations and repeated this sequence until the transformations were below a small threshold.

### 4.3. Segmentation

The goal of segmentation is to take the initial, noisy input data and to identify the ‘segments’ of the data by labeling each voxel as either solid or liquid. The difficult part of this segmentation is knowing what the ideal segmentation should look like. The
spatial resolution of the reconstructed CT data is typically quoted as 2 to 3 voxels\(^2\), thus, any segmentation that results in interfacial locations within a voxel of the CT data is considered accurate. The other form of accuracy that is considered is the consistency of the segmentation with what is known about the physics of the system. In this case, the surface energy will play a significant role in determining the morphology of the microstructure so it is clear that the interfaces will be relatively smooth. Thus, the goal is to find the structure that has the minimum possible total curvature and still matches the reconstruction data to within a voxel. An example of this smooth and accurate interfacial location that is desired is shown in Figure 4.12.

\(^2\)The spatial resolution is larger than the voxel size because of a combination of blurring that occurs in the image capture optics and also noise in the system. It is typically measured by the beamline by examining the frequency response of a known sharp interface sample.
Figure 4.12. A reconstruction and contour of the interface location after segmentation. Note how the contour is near the interface in the underlying image but also very smooth.

If a typical segmentation routine is used that produces binary data, the interface will look like a series of stair steps and the curvatures will be zero on the flat portions and infinite on the corners.

Instead of using binary data, a signed distance function (SDF) is used to represent the segments of the data. A SDF is a way of defining an interface at a sub-voxel level by having a positive value in one phase, a negative value in the other phase and a known, constant spatial gradient of $|\partial \phi / \partial x| = 1$ in the 1D case, where the SDF is represented by the variable $\phi$. A 1D example of this is shown in Figure 4.13.

A 2D or 3D SDF has very similar properties to the 1D case; principally, the spatial gradient is fixed as: $|\nabla \phi| = 1$. This makes the interface easy to locate at a sub voxel level and precludes the need for a triangulated mesh to be calculated as is common when trying to visualize or calculate the interfacial properties from binary data.
The alternative method of calculating curvature is to create a triangulated mesh of the surface, which is a series of \((x, y, z)\) points with each point connected to a set of neighbors so as to make many triangles that represent the interface. While this works well, it does introduce another step in which inaccuracies can be introduced and because the original data and the mesh are in different coordinate systems, it is very difficult to compare the interfacial locations between the two.

While it is possible to simply pick an iso-contour value in the data and extend a signed distance function from that iso-contour, the resulting interfaces are far too rough to accurately calculate curvature. Simple, single-step smoothing methods of diffusion smoothing and median smoothing were tried but neither produced interfaces that were sufficiently smooth without significantly shifting the interfacial locations compared to the original data.
More sophisticated segmentation methods such as expectation maximization/maximization of posterior marginals (EM/MPM) [96] and WEKA trainable segmentation [97, 98] were also tried. Both methods work quite well at segmenting the data but they results in binary data that must be smoothed in order to calculate curvatures. This additional smoothing step significantly degrades the accuracy of the overall segmentation method.

The method that is used for segmenting all the data in this work is an iterative method that is focused on creating a SDF that is both smooth and consistent with the input data. This method is based on methods presented in [99, 100, 101, 102] with modifications made for these particular datasets [103]. The common themes in all of these methods are starting data ($\rho$) that is comprised of a known, small number of intensity levels; estimating the input data as either a piecewise constant or piecewise smooth function ($\hat{\rho}$); and using a SDF to identify the interfacial locations. For segmenting a two-phase dataset using a piecewise constant approximation, the steps involved in this method are as follows:

- Pick an iso-contour value ($\rho_i$) for where the initial interfacial location will be
- Calculate the average intensity values for the two phases ($\rho_1$ and $\rho_2$)
- Calculate a SDF ($\phi$) with the interfacial locations at the iso-contour level defined by $\rho = \rho_i$
- Use $\phi$, $\rho_1$ and $\rho_2$ to calculate the piecewise constant approximation of the data ($\hat{\rho}$)
- Iterate over:
  - Calculate the error term: $\Delta \rho = \rho - \hat{\rho}$
  - Use $\Delta \rho$ to improve the accuracy of $\phi$
  - Smooth $\phi$
  - Reinitialize $\phi$

---

*Piecewise constant means that the image intensities are constant within each segment of the image. Piecewise smooth is similar but the intensities are allowed to vary within a segment albeit only at a very low spatial frequency.*
Recalculate $\rho_1$ and $\rho_2$

Recalculate $\hat{\rho}$

Figure 4.14 shows an overview of the segmentation process applied to a simple 2D dataset of a circle that has slightly blurred edges and some Gaussian noise so as to be similar to the actual data.

Figure 4.14. An overview of the segmentation method: (A and E) the initial intensity data, $\rho$; (B and F) the piecewise constant approximation, $\hat{\rho}$; (C and G) the signed distance function that locates the interfaces, $\phi$; (D) comparison of the initial (red) and final interfacial locations (blue); and (H) an enlarged view of $\rho$ and final $\hat{\rho}$ profiles at the interfaces of the disk.

4.3.1. Segmentation initialization

Picking the iso-contour value that defines the initial interface locations is done by comparing the values of the liquid and solid phases and picking a value that is half way between them to be the interface value, $\rho_i$. In the example shown in Figure 4.14, a value of $\rho_i = 0.5$ is selected based on the values in Figure 4.14E. With $\rho_i$ defined, it is possible to define the regions in space that belong to the two phases: $\Omega_1$ is the set of all pixels or voxels.
where \( \rho \leq \rho_i \) and \( \Omega_2 \) is the complimentary set where \( \rho > \rho_i \). The individual intensity values of the two phases are calculated using:

\[
\rho_1 = \langle \rho(\vec{x}) \rangle \quad \text{for} \quad \vec{x} \in \Omega_1 \tag{4.4}
\]

\[
\rho_2 = \langle \rho(\vec{x}) \rangle \quad \text{for} \quad \vec{x} \in \Omega_2 \tag{4.5}
\]

where \( \vec{x} \) is a vector indicating pixel or voxel location and \( \langle \ldots \rangle \) represents the mean value of the term in brackets. The estimate of the reconstruction can then be calculated as:

\[
\hat{\rho}(\vec{x}) = \begin{cases} 
\rho_1 & \text{for} \quad \vec{x} \in \Omega_1 \\
\rho_2 & \text{for} \quad \vec{x} \in \Omega_2 
\end{cases} \tag{4.6}
\]

The interfaces in the reconstruction data will have some finite width due to the blurring that inevitably occurs in data collection process. Therefore, the \( \hat{\rho} \) is smoothed using diffusion smoothing so that any differences between the \( \rho \) and \( \hat{\rho} \) data are due to the interfaces being in the wrong location and not due to differences in the interfacial width. An example of this estimate can be seen in Figure 4.14B and the finite interfacial width of both \( \rho \) and \( \hat{\rho} \) can be seen in Figure 4.14F. The diffusion smoothing process is defined as:

\[
\frac{d\hat{\rho}}{d\tau} = \frac{\partial^2 \hat{\rho}}{\partial x^2} + \frac{\partial^2 \hat{\rho}}{\partial y^2} + \frac{\partial^2 \hat{\rho}}{\partial z^2} \tag{4.7}
\]
where $\tau$ is an artificial smoothing time. This equation is evolved for a predetermined amount of time that is related to the interfacial width in $\rho$.

The reconstructed intensity values are used to calculate the initial conditions for the SDF as follows:

\begin{equation}
\phi_0 = \frac{\rho - \rho_i}{\rho_2 - \rho_1}
\end{equation}

Dividing by the difference between the intensity values of the phases ensures that the values of $\phi_0$ are order 1. The SDF must be calculated from $\phi_0$ and it also occasionally needs to be reinitialized to have the correct spatial gradient; these initialization and reinitialization operations are based on the descriptions in [104] and are described in detail in the Implementation Appendix.

### 4.3.2. Segmentation iterations

The first step in the iterations is to calculate the error between the original data and the estimate of the data that will be used to ensure the accuracy of the interfacial locations in $\phi$. This is done using:

\begin{equation}
\Delta \rho = \rho - \hat{\rho}
\end{equation}

Since $\rho$ contains noise, $\Delta \rho$ will also contain noise. It is undesirable for this to be transferred to $\phi$, so the $\Delta \rho$ array is smoothed using diffusion smoothing, similar to that described by Equation [4.7]. Diffusion smoothing works well here because it conserves the
total value of the array being smoothed. This means that if there are alternating positive and negative values that are characteristic of noise, these will be quickly damped by the smoothing; however, if there are many neighboring voxels with the same sign, as is the case when the interface is in the wrong position and needs to be moved, these values will only be slightly blurred. Since diffusion smoothing is a linear operator, this process can also be thought of as smoothing $\rho$ and $\hat{\rho}$ independently and then taking the difference between them.

After smoothing, $\Delta \rho$ is used to update the interfacial location array, $\phi$, as follows:

\begin{equation}
\phi = \phi + \Delta t \Delta \rho
\end{equation}

where $\Delta t$ is a timestep that is chosen based on based on the values of $\rho$ since $\Delta \rho$ will scale with the magnitude of $\rho$ and $\hat{\rho}$ but the values of $\phi$ that are near the interface will always be near 1.

The next step is to smooth the interfaces in $\phi$. This is done with either motion by mean curvature or diffusion smoothing. Motion by mean curvature smoothing is defined as:

\begin{equation}
\frac{d\phi}{d\tau} = H
\end{equation}

This works very well at smoothing the high frequency noise without overly affecting the interfacial locations. However, the mean curvature is a strongly non-linear term so the
evolution of this equation must be done with a very small timestep, which makes motion by mean curvature quite slow.

Since diffusion smoothing is a linear partial differential equation, it can be run with a timestep that is about two orders of magnitude larger than motion by mean curvature, which makes it significantly faster to calculate. It also has the advantage of being extendable to 4D smoothing as follows:

\[
\frac{d\phi}{d\tau} = D_x \frac{\partial^2 \phi}{\partial x^2} + D_y \frac{\partial^2 \phi}{\partial y^2} + D_z \frac{\partial^2 \phi}{\partial z^2} + D_t \frac{\partial^2 \phi}{\partial t^2}
\]

where \( \tau \) is again an artificial time used to evolve this equation. The diffusivities in the spatial and temporal dimensions are set with \( D_x, D_y, D_z \) and \( D_t \). Smoothing across timesteps can be quite advantageous with this data as the data is nearly constant in time for many data points and for those locations which an interface passes through during the experiment, the progress of the interface toward/away from the point is rather slow and predictable. This is shown in Figure 4.15 which shows the values of \( \rho \) and \( \phi \) for a fixed point in space over the duration of an experiment. Although the interface passing through the voxel is marked by sharp jumps in the \( \rho \) data, there is a very smooth and gradual change in \( \phi \) due to it being a distance function.

In practice, the best smoothing results come from motion by mean curvature smoothing the 3D datasets individually and using the 4D diffusion smoothing equation to smooth

\footnote{It should be noted that this is not a true diffusion equation since diffusion only operates spatially and this equation contains a temporal component. It is merely called a diffusion equation here due to the computational similarity to a true diffusion equation.}
through time only by setting $D_x$, $D_y$ and $D_z$ to zero. However, just 4D diffusion smoothing is significantly faster so this was commonly used for the coarsening datasets. The solidification datasets were done with 3D diffusion smoothing because the interfaces were moving significantly faster.

![Figure 4.15](image)

**Figure 4.15.** Profiles for a single voxel over time of the (A) reconstruction and (B) the signed distance function. Smoothing the SDF works much better since it is a smoothly varying function. From [103]

The final step in each iteration is to reinitialize $\phi$ and recalculate $\rho_1$, $\rho_2$ and $\hat{\rho}$. These are done the same way as in the initialization step. The segmentations were typically run for 25 iterations with the $\phi$ update timestep and the amount of smoothing adjusted to each dataset depending on their individual contrast and noise levels.

In a typical segmentation for a coarsening dataset, the individual phases will have intensities of $\rho_1 = 0.70$ and $\rho_2 = 1.18$; the estimate $\hat{\rho}$ will be smoothed for 1.0 artificial time units; $\phi$ will be smoothed for 0.15 artificial time units and reinitialized for 5.0 artificial time units; and $\Delta t$ will be set to 0.50.

Due to the size of the datasets that are being processed, a significant amount of memory, up to 1 TB, was required to perform the segmentations. To achieve this, the
segmentation code was written in Fortran 90 and parallelized using MPI. A parallel implementation of HDF5 was used to read, write and store the data, which reduced the data access times and also reduced the memory burden on the master process compared to single process read and distribute operations.

4.4. Analysis tools

There are two types of quantities that are examined here: global properties that are single values that describe the entire microstructure and local properties that describe the properties of a single interfacial patch\footnote{A patch is a small section of interface over which the properties are constant}. The global quantities are volume fraction of the solid phase ($f_s$) and the surface area per unit volume ($S_v$). In the coarsening experiments, the surface per unit volume of the sample is the relevant quantity whereas in the solidification experiment the surface area per unit volume of solid phase is a better description of the evolution since the interfacial area can increase due to either additional solid forming or due to coarsening and other morphological changes.

The local properties of interest are the patch area, normal velocity and curvatures. Since the interface is defined using a SDF, it is difficult to explicitly define the interfacial patches as individual, discrete entities. Instead, the interfacial properties are defined for all voxels in the computational domain and the properties are weighted by their distance to the interface with the weighting being greatest for the voxels closest to the interface and dropping off to zero over a specified distance. This is defined mathematically using a smeared delta function \([104]:\)
Figure 4.16. Convergence of $S_v$ as a function of volume sampled. Above sampled sizes of $10S_v^{-1} \times 10S_v^{-1} \times 10S_v^{-1}$, the $S_v$ values do not change dramatically; however, they continue to change slightly even at the largest box sizes used here.

\[
\delta(\phi) = \begin{cases} 
0 & \text{for } \phi < -\epsilon \\
\frac{1}{2\epsilon} \left(1 + \cos\left(\frac{\pi \phi}{\epsilon}\right)\right) & \text{for } -\epsilon \leq \phi \leq \epsilon \\
0 & \text{for } \epsilon < \phi 
\end{cases}
\]

(4.13)

A cutoff distance of $\epsilon = 1.5$ voxels is typically used in this work. This can be used to calculate $S_v$ by summing $\delta(\phi)$ for all the voxels and dividing by the total system size. The units of $\delta(\phi)$ will be pixels, which can be converted to real units using the grid spacing.

The interfacial normal velocity is calculated using:

\[
\vec{V}_n(\vec{x}) = -\frac{\nabla \phi}{|\nabla \phi|} \frac{d\phi(\vec{x})}{dt}
\]

(4.14)
In the analysis done for this work, the magnitude of the velocity is used more than the vector quantity. Taking the magnitude of both sides causes the two $\nabla \phi$ terms to cancel, resulting in:

\[ \mathcal{V}_n(\vec{x}) = -\frac{d\phi(\vec{x})}{dt} \]

The sign of the velocity is determined by the choice in the direction of the normal vector. Here, it is chosen to be pointing from the solid into the liquid, which results in a positive velocity when the solid phase is growing into the liquid phase. The derivative is calculated using a 3-point central difference method and the values are scaled to real units by using the grid spacing and the time between dataset scan times.

The interfacial curvatures are slightly more complicated in that there are multiple options for how to describe the curvature of an interface. The simplest way of describing curvatures is to find the principal radii of curvature, $R_1$ and $R_2$, which represent the smallest and largest radii of curvature on the interface; an example of the principal radii of curvature is shown in Figure 4.17. From these, the principal curvatures can be calculated using: $\kappa_1 = 1/R_1$ and $\kappa_2 = 1/R_2$. Here, the definition is used that $\kappa_2 \geq \kappa_1$, which is opposite to what is shown in Figure 4.17.

An alternative set of curvatures that has more utility than the principal curvatures are the mean and Gaussian curvatures, which are defined using:
Figure 4.17. The two principal radii of curvature ($R_1$ and $R_2$) of a patch ($p$). Since the radii of curvature are pointing the same direction as the normal vector, the curvatures will be positive. From [82]

\[
H = \frac{\kappa_1 + \kappa_2}{2} \quad (4.16) \\
K = \kappa_1 \kappa_2 \quad (4.17)
\]

where $H$ is the mean curvature and $K$ is the Gaussian curvature. The mean curvature is useful because it is the curvature that sets the chemical potential of an interface in the Gibbs-Thomson equation and will therefore drive the coarsening process. The Gaussian curvature describes the topology of the microstructure. Using the Gauss-Bonnet theorem
and the Gaussian curvature, it is relatively simple to determine the number of individual, non-connected features in a complex microstructure. The downside to the mean and Gaussian curvatures is that they are expressed in different length scales: the mean curvature has units of inverse length whereas the Gaussian curvature has units of inverse length squared.

Another set of curvatures are the curvedness and shape, as defined by Koenderink [105]:

\[
C = \sqrt{\kappa_1^2 + \kappa_2^2} \quad (4.18)
\]

\[
S = \frac{2}{\pi} \arctan \left( \frac{\kappa_2 + \kappa_1}{\kappa_2 - \kappa_1} \right) \quad (4.19)
\]

One advantage of these curvatures is the intuitiveness of relating their values to actual shapes, as shown with the shape curvature values listed in Table [105]. However, these curvatures do not have the nice link to the chemical potential in the way that the mean and Gaussian curvatures do.

Table 4.1. Example values of the shape curvature (S).

<table>
<thead>
<tr>
<th>Interfacial shape</th>
<th>S value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid sphere</td>
<td>−1.0</td>
</tr>
<tr>
<td>Liquid cylinder</td>
<td>−0.5</td>
</tr>
<tr>
<td>Saddle shape</td>
<td>0.0</td>
</tr>
<tr>
<td>Solid cylinder</td>
<td>+0.5</td>
</tr>
<tr>
<td>Solid sphere</td>
<td>+1.0</td>
</tr>
</tbody>
</table>

To calculate curvatures from a signed distance function, it is easiest to calculate the mean and Gaussian curvatures using the following equations [106]:

\[
\text{mean curvature} = \frac{1}{2} \left( \kappa_1 + \kappa_2 \right)
\]

\[
\text{Gaussian curvature} = \kappa_1 \kappa_2
\]
\begin{equation}
H = \frac{\phi_x^2(\phi_{yy} + \phi_{zz}) + \phi_y^2(\phi_{xx} + \phi_{zz}) + \phi_z^2(\phi_{xx} + \phi_{yy}) - 2\phi_{xx}\phi_y\phi_z - 2\phi_{yy}\phi_x\phi_z - 2\phi_{zz}\phi_x\phi_y}{2 |\nabla \phi|^3}
\end{equation}

\begin{equation}
K = \frac{\phi_x^2(\phi_{yy}\phi_{zz} - \phi_{yz}^2) + \phi_y^2(\phi_{xx}\phi_{zz} - \phi_{xz}^2) + \phi_z^2(\phi_{xx}\phi_{yy} - \phi_{xy}^2) - 2\phi_{xx}\phi_y(\phi_{xy}\phi_{zz} - \phi_{xz}\phi_{yz}) - 2\phi_{yy}\phi_z(\phi_{yz}\phi_{xx} - \phi_{xy}\phi_{xz})}{|\nabla \phi|^4}
\end{equation}

where the subscripts indicate partial derivatives, which are calculated using 3-point central difference stencils. From these curvatures, the principal curvatures and ultimately the \( S \) and \( C \) curvatures can be calculated.

Regardless of what pair of curvatures are used, the distribution of the curvatures are visualized using and interfacial shape distribution (ISD) \[39\]. The ISD is a 2D histogram showing the interfacial properties as a function of curvature. The ISD is typically used to plot the area of interfaces with a given pair of curvatures, which shows the relative proportion of the various interfacial shapes but it can also be used to show many other interfacial properties as a function of curvature. For example, it is possible to plot the average interfacial normal velocity as a function of curvature. In this case, the value of the ISD datapoint at specific curvature of \((\kappa_1^*, \kappa_2^*)\) is given by:
\[ (4.22) \quad \langle V_n \rangle (\kappa_1^*, \kappa_2^*) = \frac{\sum_{i \in \Omega^*} V_n(i) \delta(i)}{\sum_{i \in \Omega^*} \delta(i)} \]

where \( \Omega^* \) is the set of all points in the dataset for which \( \kappa_1 = \kappa_1^* \) and \( \kappa_2 = \kappa_2^* \). Thus, the right hand side of this equation provides an area weighted average of the interfacial normal velocity for all patches with curvatures that match the specified values of \( (\kappa_1^*, \kappa_2^*) \). A similar procedure can be done for any similar interfacial property.

Interfacial area ISDs created from each of the three sets of curvatures are shown for a single dataset in Figure 4.18. This figure demonstrates some of the merits of the various curvature expressions: in the \( (\kappa_1, \kappa_2) \) ISD, the lines of constant mean curvature run parallel to the \( \kappa_1 = -\kappa_2 \) line; this is particularly useful when visualizing the interfacial normal velocity since there will be a strong link between the mean curvature and the velocity in the coarsening datasets. The \( (H, K) \) ISD is harder to interpret due to the two curvatures having different units. The Gaussian curvature in particular is very compressed along the \( K = H^2 \) curve which bounds the range of possible curvatures. The \( (S, C) \) ISD is much better in this regard, spreading the values much more evenly throughout the plot. The \( (S, C) \) ISD makes it the most obvious that this structure is mostly comprised of solid cylinders \( (S = +0.5) \) to solid caps \( (S = +1.0) \) with a relatively high proportion of highly curved liquid cylinders \( (S = -0.5) \). Since the \( (\kappa_1, \kappa_2) \) and \( (S, C) \) ISDs each have advantages, they will both be used at various points in this work.

In the coarsening datasets, comparisons over time can be difficult since the curvature values decrease as the structure coarsens, leading to a general contraction of the ISD over time. Similarly to how the particle size distribution can be scaled by the average particle
radius to determine a time-independent distribution, the curvatures in the ISD can be scaled by $S_v$ \[107\], as has been done in Figure 4.18.

In the coarsening portion of this work, several important differential geometry principals are used. The first is the relationship between curvature ($H$), area ($A$) and volume ($V$) of a patch:

\[
H = \frac{\text{d}A}{\text{d}V}
\]
The rate of area change of volume due to interfacial motion can be determined from the area and normal velocity ($V_n$) of a patch:

$$\frac{dV}{dt} = AV_n \quad (4.24)$$

The properties in Equations 4.23 and 4.24 can be combined to determine the relationship between the rate of change in area of a given patch and its curvature and velocity:

$$\frac{dA}{dt} = HAV_n \quad (4.25)$$

This corresponds well with the source/sink concept in [54, 44], which noted:

$$\frac{dV}{dt} \propto R^2 \dot{R} \quad (4.26)$$
CHAPTER 5

Results

As in previous chapters, the solidification results will be presented first, followed by the coarsening results.

5.1. Solidification

Interfacial locations of sample S13-24A are shown for four early times in the solidification process are shown in Figure 5.1. These images show that there is a nucleation point on the side of the sample that results in a dendrite that grows out across the sample with its corresponding four-fold symmetric arms growing near the sample walls. Because the main arm that is growing across the sample is the first to grow into the melt, it will be growing into a liquid that is uniform in both temperature and composition. The rate of growth of this dendrite arm is much faster than the cooling rate of the sample so it can be assumed that the undercooling of the melt is constant as well. Since this dendrite is not interacting with neighboring dendrites, it is a free-growing dendrite, which makes it comparable to the theoretical work on growing dendrites.

Some 2D slices of the X-ray CT reconstructions are shown in Figure 5.2. These images have been rotated and cropped to show just the free growing dendrite and demonstrate what is and isn’t possible to determine with the current data. The shape of the primary and secondary dendrite arms are relatively easy to resolve except for in the region near the tip. Near the tip of the dendrite, the very fast evolution of the shape results in blurring
Figure 5.1. Isosurfaces of four of the early solidification datasets. The transparent blue surface is the sample bounds and the yellow surface is the liquid/solid interface. The images are from consecutive reconstructions and are at times of approximately (A) 3.6s, (B) 5.4s, (C) 7.2s, and (D) 9.0s after the start of growth.

since the CT process averages the structure over the 1.8 seconds that it takes to collect a dataset. The features that are moving relatively slowly, such as the secondary dendrite arms in the later times like Figures 5.2D and 5.2E, are very well resolved with sharp, clear interfacial locations.

The inability to determine the tip shape is disappointing since the majority of the theoretical predictions of dendrite properties (e.g. tip growth speed and scaling properties as a function of distance from the tip) involve the dendrite tip radius. Instead, the tip
radius is estimated in two ways: 1) by fitting a parabola to the resolvable points on the dendrite and 2) by using the theoretically-derived Equation 2.7. The fit, shown in Figure 5.3, is done using points at the roots of the secondary dendrite arms since these are evolving relatively slowly and therefore well resolved. This results in a tip radius of 1.0 µm.

To calculate the dendrite tip radius from marginal stability theory, Equation 2.7 is used with mass diffusivity since the growth process in an alloy will be controlled by solute diffusion rather than thermal diffusion. A diffusivity value of $D = 8.3 \times 10^{-10} \text{mm}^2/\text{s}$ is used along with a capillary length value of $\Gamma_c = 2.27 \times 10^{-9} \text{m}$, which is different from what was reported in the Experimental Methods chapter because it is based on atomic
fraction here and mass fraction in the earlier section. A marginal stability parameter value of $\sigma^* = 0.025$ is used. The tip velocity is measured as $V = 69 \mu m/s$. These give an expected tip radius of $\rho = 1.5 \mu m$.

It is possible to calculate the tip growth velocity despite the relatively poor resolution of the tip because the amount of blurring is consistent between all timesteps. Thus, picking an intensity value in the image and tracking its position over time gives a good estimate of the displacement of the dendrite tip between times. This results in a growth speed of $V \approx 69 \mu m/s$. While there are theoretical predictions for the tip growth speed, it is difficult to compare the experiments and theory because the theories predict a growth
speed as a function of both tip radius and undercooling; neither of which are possible to accurately measure with the current experimental setup.

Figure 5.2 show that the secondary dendrite arms are not growing perpendicularly to the primary dendrite arm; instead, they are growing at a slight angle in the main growth direction. This is likely due to the preferential growth conditions in the growth direction due the other secondary dendrite arms in this direction being smaller than those in the opposite direction.

It is also evident in Figure 5.2 that the secondary arms on the left and right sides are growing at different rates. These differences are due to convection currents that are generated by the growing dendrites growing and rejecting solute, which creates density gradients and drives convection. This will affect the two sides of the dendrite differently because the secondary dendrite arms on the right side of the primary arm are growing in the direction of gravity and the secondary arms on the left side are growing opposite to the direction of gravity (this can be seen in Figure 5.1). This is consistent with studies done on succinonitrile, as seen in Figure 2.13.

The solid fraction and surface area per unit volume of solid are shown in Figure 5.4. The solid fraction increases in a two-step manner as the melt is initially undercooled when the solid nucleates, which leads to rapid initial solidification during the recalescence period that lasts for approximately the first 30 seconds, then steady-state growth takes over and growth occurs at a slower rate.

The $S_v$ data in Figure 5.4 is quite interesting in that it seems to follow a single path over the initial 70 seconds of solidification despite this significant change in the overall solidification rate.
Figure 5.4. Solid volume fraction \( (f_s) \) and surface area per unit volume solid \( (S_v) \) for sample C13-24A that is cooling at 2\(^\circ\)C/minute.

In order to understand the evolution of a single dendrite, the initial dendrite arm that can be seen growing across the sample in Figure 5.1 is isolated and analyzed as a function of distance from the dendrite tip \( (\hat{Z}) \). This is similar to the work of Li and Beckerman in [36] but here the analysis is performed on a 3D data compared to 2D projections; the 3D data makes it possible to calculate important quantities like the interfacial area and volume fraction solid. Since the dendrite tip radius cannot be measured in the 3D data, direct comparisons between the datasets are not possible; however, the growth behavior can still be compared by looking at the exponents in the power laws\(^1\).

The total volume of solid, \( V_s \), solid/liquid interfacial area, \( A_{s/l} \), interfacial area per unit volume of solid, \( S_v \), and the average value of curvedness, \( \langle C \rangle \) are measured and plotted against \( Z \), which is axial position along the dendrite using a fixed coordinate system, in Figure 5.5 and against \( \hat{Z} \), which is adjusted so that the dendrite tip is always

\(^1\)The tip radius estimates can be used, but it is important to note that these are rough estimates compared to the careful measurements of Li and Beckerman.
at $\hat{Z} = 0$, in Figure 5.6. Both plots are made using a rolling average over 15 $\mu$m, which is approximately the secondary dendrite arm spacing; this averaging is done because the area measurements over a very thin section can be misleading. In Figure 5.5, it can be seen that there is an initial portion of the data where the solid volume and interfacial area increase smoothly and a second portion further back from the tip where the growth rate of certain secondary arm growth increases rapidly. This is seen most clearly in the solid volume plot around $Z = 300 \mu$m and $Z = 425 \mu$m where a small bump in either the solid volume or the interfacial area term at an early time will be significantly amplified over time. This is because the initial small bump is due to a secondary arm will start to grow more than its neighbors at one time and this growth will be significantly amplified in the subsequent times. This is due to the competitive nature of secondary dendrite arm growth and the more favorable growth conditions that are present farther from the main dendrite arm.

The data in Figure 5.6 has been shifted so that the dendrite tip is at the same place for all times. This data is shown with the power law fits that are listed in Equations 5.1 – 5.4.

In all of these plots, the four times that are shown collapse to a single curve for approximately the first 225 $\mu$m with deviations due to rapid secondary arm growth. This seems consistent with Li and Beckerman’s description of linear and non-linear regions of sidebranching behavior; however, the change from linear to non-linear regions is expected to occur near $Z/\rho \approx 1/P$, where $P$ is the Péclet number, resulting in a change over occurring at $Z \approx 25 \mu$m. Instead, these spikes in the solid volume and interfacial area curves could be secondary dendrite arms reaching far enough from the main arm to become
Figure 5.5. Total solid volume ($V_s$), total solid/liquid interfacial area ($A_{s/l}$), surface area per unit volume of solid ($S_v$), and average values of the curvatures $C$ and $H$ as a function of axial position along the dendrite ($Z$).
free of the solute rejection of the initial dendrite and thus become free-growing dendrites themselves.

\begin{align*}
V & \propto \dot{Z}^{1.44} \\
A_{s/l} & \propto \dot{Z}^{1.32} \\
S_v & \propto \dot{Z}^{-0.12} \\
\langle C \rangle & \propto \dot{Z}^{-0.16} \\
\langle H \rangle & \propto \dot{Z}^{-0.21}
\end{align*}

The volume and interfacial area relationships are much closer to linear than those reported by Li and Beckerman of \( V \propto \dot{Z}^{2.10} \) and \( A_{s/l} \propto \dot{Z}^{1.92} \) in [36]. This difference is due to a combination of the behavior of the Al-Cu alloys used here compared to the pure SCN used by Li and Beckerman, the measurements being 3D instead of 2D with approximations made for volume and area. Given the complex morphology seen in the dendrites here, it seems likely that the simple cylinder-and-spherical-cap models used could be a significant source of error.

In [36], it was noted that the \( Z \) dependence in these equations could be turned into a temporal dependence by using the relationship \( Z \approx V_n t \). It was also noted that using this relationship shows that \( S_v \) is not evolving with a coarsening-like \( t^{1/3} \) dependence, which shows that there are process involved in the evolution of the secondary arms other than coarsening; however, there was some ambiguity as to whether this was in fact the case or was the relationship between \( S_v \) and \( t \) inaccurate due to the measurements not capturing
Figure 5.6. Similar plots to Figure 5.5 but with the dendrite tip positions at a constant position of $\tilde{Z} = 0$. 
the full complexity of the secondary arm shapes. Since the 3D measurements of $S_v$ here
match well with the 2D measurements in [36], it confirms that the observation that there
are more processes than coarsening occurring is accurate.

One possible source of error in the measurements here is the dendrite leaving the field
of view of the experiment, as seen in Figures 5.1 and 5.2. This does not seem to be a
significant effect as the $V_s$ and $A_{t/s}$ curves from the $t = 5.4 \, s$ and $t = 7.2 \, s$ data, which
were not cut off by the field of view, line up very well with the data from $t = 9.0 \, s$ and
$t = 10.8 \, s$, which had secondary arms leave the field of view.

One method of analyzing the sidebranching behavior is by calculating ISDs for sub-
Volumes of the dendrite, as is shown in Figure 5.7. These ISDs are calculated for 75 $\mu$m
thick slices in the $Z$ direction and give an insight into the local secondary dendrite arm
properties. The two slices highlighted are from $\hat{Z} = 125 \, \mu$m where there are primarily
only secondary arms and $\hat{Z} = 250 \, \mu$m where there are both secondary and tertiary arms.

The ISD at $\hat{Z} = 125 \, \mu$m has a peak around $C = 0.1 \, \mu$m$^{-1}$. Since this peak is on the
$S = 0.5$ line, it is indicating that the primary features at this location are solid cylinders
with diameters of approximately 15 $\mu$m. This peak is representative of the secondary
dendrite arms since they are the predominant features in this region.

In the ISD that is centered at $\hat{Z} = 250 \, \mu$m, the peak is still along the $S = 0.5$ line
but has stretched out to $0.05 \, \mu$m$^{-1} < C < 0.15 \, \mu$m$^{-1}$. This means that the predominant
microstructural features are solid cylinders with diameters between 10 $\mu$m and 30 $\mu$m.
The sidebranches of the dendrite in this location are much more complex than those in the
region centered at $\hat{Z} = 125 \, \mu$m. These dendrite arms have generally become flatter rather
than cylindrical in cross section and tertiary arms have started to grow. The growth of
these tertiary arms will be controlled by morphological fluctuations, which will only form when the existing surfaces reach a size that is large enough to support these fluctuations. The appearance of the tertiary arms in the ISD that is centered at $\hat{Z} = 250 \, \mu m$ can be used to conclude that when the secondary dendrite arms grow to a diameter to approximately 20 to 25 $\mu m^{-1}$, they can support morphological fluctuations that will grow into tertiary arms.

Looking at the secondary arms in more detail reveals that they are not all as uniform and circular in cross section as in transparent organic analogues. Figure 5.8 shows a few

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2This is very similar to the morphological fluctuations that will form on an advancing planar interface that causes it to break up into an array of dendrites.
examples of a doublon or split tip dendrite arm formation, starting with Figures 5.8A and 5.8B that are a secondary dendrite arm growing off of the free growing dendrite just before and after the tip splitting occurs. The two split tips will continue to grow but the groove in between them does not change significantly; this is shown in Figure 5.8C which is a different doublon that is shown at two times. Note that there is significant growth of the one visible dendrite tip but there is very little motion of the base of the groove between the tips. Several other doublon examples are shown in Figure 5.8D.

Figure 5.8. The view direction in A, B, and C are parallel to the growth direction; in D, the growth direction is up. The scale bar applies to all images. From [108]

A doublon or split tip dendrite is a dendrite arm that has two advancing tips instead of a single one. The groove that exists between these split tips fills with solute that is rejected from the growing dendrite. Because of the shape of this groove, the solute is trapped, which prevents significant growth of the solid phase into the groove. This has the overall effect of the groove not significantly evolving over time.

Doublons have been reported before in theoretical calculations [109, 110], in phase field simulations [111, 112] and in experiments involving transparent organic analogues [113].
There has also been evidence that tip splitting occurs in metals based on post mortem microscopy [111] but there are no reports of the formation mechanism or the morphology of doublons in metals.

It has been proposed that a twin forming along a $(1 1 1)$ plane of a dendrite growing in the $(1 1 0)$ direction limits the growth rate of the dendrite arm at the twin, resulting in the formation of two alternate dendrite tips [112, 115]. This twin would form a cusp due to interfacial energetics and result in two tips forming and growing. A pile-up of solute in the groove would prevent the groove from growing. While this is a satisfactory explanation for dendrites growing along $(1 1 0)$ directions, it cannot apply to the experimental work here since the dendrites are growing in $(1 0 0)$ directions and there are no possible twin planes perpendicular to the $(1 0 0)$ growth direction.

An alternate mechanism that could be responsible for this transition is a morphological instability along the broad, low curvature arc of the relatively broad sidebranch, as in Figure 5.8A. This type of morphological instability is identical to that which causes a flat interface to morph into a dendritic array; as such, there is some minimum dendrite tip radius as is described by the Mullins-Sekerka marginal stability criterion.

To determine if this mechanism is feasible, an estimate of the stable curvature can be made and compared to the radius of the dendrite arm in Figure 5.8A. The relevant stability limit[3] is estimated from the ISDs in Figure 5.7. These have already been used to determine that when the secondary arms reach a diameter of approximately 20 $\mu$m, they will be large enough to support morphological fluctuations that evolve into tertiary arms.

[3]The stability limit will be dependent on the materials properties of the sample as well as local properties like undercooling and solute gradients; therefore, it is important that the stability limit be determined from a very similar region.
Since the formation of tertiary arms is very similar to the splitting of a single growing tip into the two tips of a doublon, this same criterion can be used for the single-tip to doublon transition.

This theory cannot be tested perfectly since the surfaces in Figures 5.8A and 5.8B, which are from consecutive timesteps, show the dendrite arm sometime before and sometime after splitting but there is no indication exactly when the splitting occurred or exactly what the morphology of the single tip dendrite arms was like when the splitting occurred. However, this theory is at least consistent with the surfaces in Figure 5.8 since the pre-split dendrite arm is less than 20 µm wide and the main body of the post-split arm is slightly over 25 µm wide.

Figure 5.8D shows several more examples of these split tip dendrite arms as well as broad but not split tip dendrite arm. These broad arms are the key to the formation of the split tip arms and they are also a significant departure from transparent organic analogues which typically have circular cross section arms. The flatness of the sidebranches that is seen here is likely due to diffusional interactions between the sidebranches.

5.2. Coarsening

Isothermal coarsening is studied by heating samples to just above the eutectic temperature and watching the evolution of the resulting liquid/solid mixture. By using different alloys that provide a variety of different solid fractions, it is possible to see how differences in distances between interfaces that come with the changes in solid fraction affect the dynamics of coarsening. This is also useful in that the different solid fraction samples
have significantly different initial microstructures that adds to the variables that can be examined and their effect on coarsening.

The solid fraction will influence the distance between the interfaces and therefore the diffusion distances. In systems of spherical particles, it has been shown that the shorter diffusion distances that occur in high solid fraction samples can cause a significant increases in the coarsening rate of the systems (see Figure 2.22).

The solid fractions of all the samples are shown in Figure 5.9 as a function of time. This shows the differences in solid fraction between the different samples and also that there is an initial equilibration time for some of the samples of approximately 50 minutes. The initial non-equilibrium solid fraction would be caused by non-uniformities in composition that form during solidification and by cutting out a small sample from a much larger as-solidified rod. Changes in the volume fraction solid affect the distances between interfaces and will therefore have an effect on the dynamics of coarsening; however, the changes in
solid fraction during this time are very slight so it is not likely that they would significantly affect the coarsening dynamics.

The initial and coarsened microstructures are described individually in order of increasing solid fraction, followed by figures showing $(500 \, \mu m)^3$ views of the microstructures at an early, intermediate and late stage in the experiment which shows how the different solid fraction samples evolve. Since the experiments had significantly different durations, these three sets are not necessarily comparable across the different samples. Instead, they show how each of the different samples evolves over time to the greatest extent possible.

ISDs are also shown for each sample; the $S$ and $C$ curvatures are used in these because they have the most intuitive relationship to the interfacial shapes of liquid spheres ($S = -1.0$), liquid cylinders ($S = -0.5$), saddle shapes ($S = 0.0$), solid cylinders ($S = +0.5$) and solid spheres ($S = +1.0$). The curvatures in the ISDs are scaled by $S_v$ where appropriate to make comparisons across time easier and give an idea of what is happening in the entire sample, not just the small $(500 \, \mu m)^3$ views of the microstructures that are only 10% to 20% of the total sample volume.

5.2.1. C08-26A

At 28 vol% solid, sample C08-26A is the lowest solid fraction sample. It is initially comprised of long, cylindrical dendrite arms with spherical caps, as shown in Figures 5.10A. This is seen in the ISD in Figure 5.10B as the majority of the patches being between 0.0 and 1.0 with a peak around $S = +0.5$.

As the sample evolves, the features become larger, as seen in Figures 5.10C and 5.10E. The ISD shows that the overall distribution of shapes does not change significantly. There
is a slightly larger share of saddle shaped interfaces in the later times; these saddle shapes form as dendrite arms coalesce.

5.2.2. C12-27A

Sample C12-27A was one of the two samples run in 2012. These experiments of this 35 vol% solid sample were focused on the early evolution of dendritic microstructures. As a result, this experiment was relatively short in duration but started from a relatively fine structure. The faster evolution of the fine structure made it possible to almost achieve a doubling of $S_v$ in a relatively short experiment.

The fine initial structure of this sample can be seen in Figure 5.11A. The initial microstructure is a classical dendritic microstructure with many secondary and tertiary arms shown in the field of view. Over the duration of the experiment, these arms coalesce and become more spherical. This can be seen in the microstructure images and also the ISDs where the peak shifts from about $S = +0.5$ to almost $S = +1.0$.

5.2.3. C08-26B

The evolution of C08-26B, which contains 45 vol% solid, is very similar to the two preceding samples. It is initially dendritic but, interestingly, with much shorter dendrite arms than sample C12-27A, as seen in Figure 5.12A. Something that is different about this sample is that the ISD is nearly constant over the coarsening process. This sample is also different in that much of the coarsening is less affected by coalescence of dendrite arms.
5.2.4. C08-20A

Sample C08-20A is different from the rest in that it was originally solidified in such a way as to provide a microstructure with minimal directional preference unlike the directional solidification techniques used for the other samples. Like sample C08-26B, this sample starts with the dominant feature in the ISD being solid cylinders and spheres and evolves to have a slight preference for cylinders over spheres.

Sample C08-20A contains 48 vol% solid, which is very close to that of C08-26B and makes it possible to compare these two samples that have very different initial microstructures.

5.2.5. C12-19A

Sample C12-19A, at 55 vol% solid, is the first sample that is over 50 vol% solid. The view direction of this sample in Figure 5.14 is aligned with a secondary dendrite arms and shows a series of tertiary arms growing in the upward direction. In the early time, these tertiary arms have already coalesced, leaving behind a series of bumps and ridges on these coalesced features. These ridges where the arms have coalesced in particular can be seen in the ISDs, where they appear as liquid cylinders near $S = -0.5$. These bumps and ridges smooth out over time, as can be seen in the relatively smooth features in Figure 5.14E and the lower prominence of the $S = -0.5$ features in the ISD in Figure 5.14F.

5.2.6. C08-15A

The highest solid fraction sample, C08-15A, at 80 vol% solid shows very different morphologies than the other samples. It initially contains many liquid tubes that link several
liquid walls. These walls run along the axis of the sample and are likely a result of the directional solidification process. This can be seen in Figure 5.15A and in the ISD in Figure 5.15B where the liquid tubes are seen as a peak near $S = -0.5$ and the liquid walls are the broad peak at the low-$C$ values.

As coarsening progresses, the tubes pinch in the middle and shrink away into the walls while the walls reduce in number to just a few main walls in the latest times. The ISD in Figure 5.15D shows that the liquid tubes are growing in relative area fraction. The liquid walls are represented by the peak near $S = +0.5$. This has a slight solid-cylinder-like character because the liquid walls are a result of the solid phase growing in large columns along the axis of the sample; thus, the walls are on average concave towards the solid phase.

The decomposition of the tubes results in many liquid droplets that are trapped within the solid phase that can be seen in Figures 5.15C and 5.15E. This appears in the ISD in Figure 5.15F as a very high peak near $S = -1.0$. While the intensity of this peak is quite high, the reason is not because there is a lot of area associated with these liquid droplets; instead, it is because the liquid droplets are isolated from the rest of the structure by the low-diffusivity solid phase so any coarsening simply results in these droplets becoming more spherical. This results in nearly all of the liquid droplets having an identical value of the shape curvature and the formation of a very high peak on the ISD.

### 5.2.7. Cahn-Hilliard phase field simulation

Because there is some experimental uncertainty in the curvature and velocity data that is used here, microstructural data from a phase field simulation is used as a comparison
tool to ensure that the velocity-curvature relationships that are observed are real and not an artifact of noise in the measurements. Interfacial locations and an ISD for this data are shown in Figure 5.16. This two phase mixture contains 50 vol% of each phase and the phases have equal diffusivities. The initial conditions for this microstructure is random numbers that result in spinodal decomposition and subsequent coarsening. This results in highly connected interfaces that are mostly saddle shaped, as seen in the ISD in Figure 5.16. It is notable that the microstructure of this sample is highly symmetric about the $S = 0$ line, which coincides with the $H = 0$ line.
Figure 5.10. Sample C08-26A (28 vol% solid) at times of (A, B) 17.0 minutes, (C, D) 199.7 minutes, and (E, F) 858.5 minutes and $S_v^{-1}$ values of (A, B) 56.7 $\mu$m, (C, D) 97.2 $\mu$m, and 144.2 $\mu$m.
Figure 5.11. Sample C12-27A (35 vol% solid) at times of (A, B) 3.0 minutes, (C, D) 26.7 minutes, and (E, F) 60.6 minutes and $S^{-1}$ values of (A, B) 34.1 $\mu$m, (C, D) 46.9 $\mu$m, and 60.6 $\mu$m.
Figure 5.12. Sample C08-26B (45 vol% solid) at times of (A, B) 11.6 minutes, (C, D) 109.0 minutes, and (E, F) 362.1 minutes and $S^{-1}_v$ values of (A, B) 33.7 $\mu$m, (C, D) 58.7 $\mu$m, and 81.7 $\mu$m.
Figure 5.13. Sample C08-20A (48 vol% solid) at times of (A, B) 11.6 minutes, (C, D) 127.3 minutes, and (E, F) 359.8 minutes and $S^{-1}$ values of (A, B) 56.8 $\mu$m, (C, D) 72.0 $\mu$m, and 84.9 $\mu$m.
Figure 5.14. Sample C12-19A (55 vol% solid) at times of (A, B) 3.0 minutes, (C, D) 30.0 minutes, and (E, F) 78.2 minutes and $S_v^{-1}$ values of (A, B) 39.3 µm, (C, D) 49.9 µm, and 61.2 µm.
Figure 5.15. Sample C08-15A (80 vol% solid) at times of (A, B) 7.3 minutes, (C, D) 143.1 minutes, and (E, F) 597.4 minutes and $S_v^{-1}$ values of (A, B) 42.8 $\mu$m, (C, D) 70.7 $\mu$m, and 94.2 $\mu$m.
Figure 5.16. Cahn-Hilliard phase field simulation. $S^{-1}_v = 23.5$ voxels and the box size of the data shown is $216 \times 216 \times 216$ voxels.
There are several interesting ways in which these results contrast to published results of coarsening in systems of spherical particles. The first difference is in the concept of self-similarity, which occurs in many systems including theoretical predictions of zero volume fraction of the coarsening phase and measurements of real systems with a finite amount of the coarsening phase.

The analog of the steady-state particle size distribution of spherical particles in these complex morphology systems is the ISD. It is clear from Figures 5.10 – 5.15 that some of the ISDs here are evolving and some are relatively constant over the evolution of the experiments. Therefore, these samples either do not evolve self-similarly or they have not yet reached the steady-state regime that occurs at long coarsening times.

The second interesting comparison is that of the coarsening rate and how it varies as a function of the fraction of the coarsening phase present. One way of comparing the coarsening rates is to use the temporal power laws that relate the $S_v$ vs $t$ data. Since the power law $S_v^{-3} \propto t$ has been seen many times, so it will be used here. Plots showing the fits of this equation to each of the datasets is shown in Figure 5.17.

The red line showing the fit in Figure 5.17 is plotted for all time values that were used in the fit and thus, it shows which data points were used in the fit. The initial portion of the data is not used in the fit because there is some amount of equilibration time required before steady-state coarsening begins. An example of this fit for sample C08-26A is:

\begin{equation}
S_v^{-3} - 63.6^3 = 3210 \frac{\mu m^3}{\text{min}} t
\end{equation}
Figure 5.17. Evolution of surface area per unit volume for samples (A) C08-26A, (B) C12-27A, (C) C08-26B, (D) C08-20A, (E) C12-19A, and (F) C08-15A.
The constant of $63.6^3$ in this equation has relatively little value since it is simply
the extrapolation of the linear portion of the data to the start of the experiment. The
time-dependence coefficient is much more important since it is a function of the material
properties and should be transferrable to other samples with similar compositions. The
remaining time-dependence coefficients are listed in Table 5.1 and plotted in Figure 5.18.

Table 5.1. Temporal dependence coefficient ($A$ in $S_v^{-3} \propto At$) for the different samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solid fraction</th>
<th>Temporal dependence coefficient ($\mu m^3/min$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C08-26A</td>
<td>0.28</td>
<td>3201</td>
</tr>
<tr>
<td>C12-27A</td>
<td>0.35</td>
<td>2576</td>
</tr>
<tr>
<td>C08-26B</td>
<td>0.45</td>
<td>1345</td>
</tr>
<tr>
<td>C08-20A</td>
<td>0.48</td>
<td>1017</td>
</tr>
<tr>
<td>C12-19A</td>
<td>0.55</td>
<td>2207</td>
</tr>
<tr>
<td>C08-15A</td>
<td>0.80</td>
<td>1174</td>
</tr>
</tbody>
</table>

The high solid fraction sample, C08-15A, could have a different exponent due to
its exceptional microstructure. The liquid spheres in particular would not coarsen like
solid spheres since they are isolated from the rest of the sample by the solid phase that
encapsulates them.

Sample C08-20A is also different from the rest of the samples. It takes quite a long
time to reach a steady state, $S_v^{-3} \propto At$ regime. This is likely a byproduct of how it
was solidified, which resulted in this sample having the largest initial feature size. Since

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4In several of the C08-15A reconstructions, there are significant motion artifacts, which cause the drops
in the $f_s$ and $S_v$ plots in the first 200 minutes of the experiment. It seems likely that these were due
to very brief changes in the furnace temperature, causing brief periods of melting/freezing. The affected
times are not useable; however, the $S_v$ plot shows that these events did not have significant effects on the
overall coarsening rates so the rest of the data is still useable.
any non-uniformities in the composition of the solid phase would have to equilibrate via diffusion, and since diffusion in the solid phase is quite slow, the larger size of the solid particles would mean that this sample would take longer to reach steady state behavior.

Figure 5.18. Temporal dependence coefficient \((A \propto S_v^{-3})\) for the different samples.

An alternative method of examining the coarsening rate that allows for more comparison of the solid fraction effects is to plot \(dS_v^{-1}/dt\) against \(S_v\); this is shown in Figure 5.19. This plot simplifies the data to coarsening rate \((dS_v^{-1}/dt)\) as a function of the average feature size \((S_v)\). There is significant scatter in the data due to the finite difference method that is used in calculating \(dS_v^{-1}/dt\) but it clearly shows that as the features become larger, the coarsening rate slows. It also shows that there is very little solid fraction dependence. The lowest volume fraction solid sample, C08-26A, shows a higher coarsening rate than the other samples but within the remaining five samples, there is very little difference.
The different behavior of sample C08-26A could be due to experimental uncertainty associated with its 2 mm diameter, which caused a significant portion of the sample to be outside of the 1.5 mm field of view.

Significantly, there is no trend that follows the solid fraction data; for example, the slowest evolving sample is C08-26B, which is in the middle of the range of solid fractions while the lowest solid fraction sample, C08-15A, is in the middle in terms of coarsening rate.

This is contradictory to what is seen with spherical particles (see Figure 2.22) and it is not intuitively expected since increasing the solid fraction will reduce the distance between the interfaces. However, the diffusion takes place in the liquid phase and it is quite clear from comparing the microstructures of the 28 vol% solid C08-26A and the 80 vol% solid C08-15B samples that increasing solid fraction makes the liquid pathways much more tortuous. Thus, there is a complex relationship between the solid fraction and the overall coarsening rate.

The deviation from the classical $S_v^{-3} \propto t$ law and the lack of a clear volume fraction dependence calls into question whether or not these samples are in the steady state coarsening regime, which is surprising given the long coarsening times of up to 14 hours. This steady state regime seems to be independent from self-similarity since sample C12-27A follows a $S_v^{-3} \propto t$ law even though it has a continuously evolving ISD but conversely, sample C08-20A does not follow a $S_v^{-3} \propto t$ relationship even though the ISD does not change significantly over the duration of the experiment. Furthermore, for sample C08-15A, with a solid fraction of 80 vol%, it is unclear if there is or ever will be a steady state coarsening regime due to the formation of isolated liquid droplet domains.
5.2.8. Individual interface evolution

To evaluate the evolution in more detail requires considering the data on a per patch of interface level. This is done using attributes like the curvatures and velocities of the interface instead of overall attributes like solid fraction that has been done up to this point. In doing this, it is important to use samples that are at the same point in the coarsening process to make sure that any comparisons between the samples are just comparing differences caused by composition and solid fraction and are independent of effects from faster or slower evolution that is due to the samples being at different stages in the coarsening process. This is done by selecting a certain $S_v$ value and only comparing samples when they are at that common value. Figure 5.20 shows isosurfaces for the samples at a constant value of approximately $S_v^{-1} = 55 \mu m$. 

Figure 5.19. The coarsening rate of the sample ($\frac{dS_v^{-1}}{dt}$) as a function of the average size scale of the sample ($S_v$). Note that all samples bar C08-26A are very similar despite a variety of solid fractions.
Figure 5.20. Samples (A) C08-26A, (B) C12-27A, (C) C08-26B, (D) C08-20A, (E) C12-19A, and (F) C08-15A at the same average feature size of $S^{-1} \approx 55 \mu m$. The volumes shown are $(500 \mu m)^3$ in size.
Figure 5.21. ISDs of the six samples shown in Figure 5.20.
One of the most important relationships in coarsening is that of interfacial curvature and velocity. The simplest case is to note that mean curvature drives coarsening and therefore there should be a relationship between the mean curvature and the interfacial normal velocity that is the response that enables coarsening. This is examined by plotting these for the six samples in Figure 5.22. While this shows a definite trend of $V \propto -H$, there is also a broad distribution to the data in these plots; this is particularly evident when looking at the range of velocities for a single curvature value (typically about $2dS^{-1}/dt$) which is a significant portion of the total spread of velocities (about $4dS^{-1}/dt$).

There is also a problem that the size of the distribution for a given $H$ value does not seem to vary in a consistent manner between samples. Samples C12-27A, C08-20A and C12-19A have greater scatter than samples C08-26A, C08-26B and C08-15A. Since there is no obvious trend with solid fraction, it is likely that the differing amounts of scatter are related to the details of the microstructure and therefore need to be examined in more detail than the mean curvature alone.

A more sophisticated approach is to look for a well defined theoretical expression for the relationship between velocity and curvature. This is done by looking at the derivation of coarsening rates that is described in the Background chapter. In systems of spherical particles, this relationship can be derived analytically by assuming the spheres are interacting with a mean field and by taking advantage of the simple relationship between solute mass flow and growth rate for a sphere. This results in:

$$\frac{dR}{dt} = \alpha \frac{1}{R} \left( \frac{1}{R_c} - \frac{1}{R} \right) \tag{5.7}$$
Figure 5.22. Scaled interfacial normal velocity and mean curvature histograms of the six samples shown in Figure 5.20. The double peak in the C08-15A result is due liquid spheres that are isolated from the rest of the system.
Figure 5.23. ISDs showing the average interfacial normal velocity for each pair of curvatures for each of the six samples shown in Figure 5.20.
where $\alpha$ is a constant that is dependent on the materials system, as described in Equation 2.23.

In a system with a more complex microstructure like those studied here the mean field approach needs further justification if it is going to be used. In a complex microstructure, it is clear that the composition of the liquid with which an interface interacts will be influenced by the surrounding patches. The only way for a mean field approach to be valid in this scenario is if the all interfacial patches are surrounded by an environment that is similar to the average for the microstructure. This is investigated by creating ISDs for particular sets of shapes. This is done by picking a range of curvatures to consider and identifying all patches that are within that range, then creating an ISD of all patches that are within a certain physical distance of the patches with the curvatures of interest.

For example, when calculating the ISD bin for $\kappa_1/S_v = -1$, $\kappa_2/S_v = +1$ with a bin size of $\Delta \kappa = 1$, the patches that meet the criteria $-1.5 < \kappa_1/S_v < -0.5$ and $0.5 < \kappa_2/S_v < 1.5$ be known as $P_{\kappa_1, \kappa_2}$. The typical ISD is calculated by going to every point on the interface and adding its area to an ISD bin according to the curvature of the patch; however, in this case the ISD is calculated by going to every point within $P_{\kappa_1, \kappa_2}$ and then finding all patches within a certain radius of each of those points which will be used to calculate the ISD. Several of this type of ISD are shown in Figure 5.24.

These ISDs in Figure 5.24 show both similarities and differences between the different locations in $\kappa_1$, $\kappa_2$ space. The individual ISDs are different from each other in that they tend to follow their source point; for example, the ISD of patches near solid spheres has a distinct preference for solid sphere like shapes and the same is true for the other shapes. There is also a significant influence from the overall ISD; this is most evident in the ISD
of patches near $\kappa_1 = -2$, $\kappa_2 = 0$ where there is a peak corresponding to similar liquid cylinders and a peak corresponding to the peak in the overall ISD.

Another way in which the ISDs are similar is in their average mean curvature values. While this will vary between the ISDs shown in Figure 5.24, the variation is significantly smaller than the difference in mean curvatures of the origin points. Because of this, the neighborhood effect on coarsening rate to be secondary to the curvature of the patch itself and therefore it is reasonable to use a mean field approximation to describe coarsening in these complex microstructures.

Since the mean field approximation can be used, Equation 5.7 is a good starting point in looking for a velocity/curvature relationship. In this expression, the $(1/R_c - 1/r)$ term comes from the Gibbs-Thomson equation for a sphere. This is relatively easy to generalize since the inverse particle radius becomes mean curvature in the Gibbs-Thomson equation for arbitrary morphology. The preceding $1/r$ term in Equation 5.7 comes from the solution to the diffusion equation for a sphere. By examining the solution to the diffusion equation for various other shapes, it is apparent that $1/R$ can be replaced with the curvedness, $C$, which is defined in Equation 4.18. Making these changes results in a relationship between interfacial curvature and velocity that applies to arbitrary shapes, as was proposed in [116]:

\begin{equation}
V_n = \alpha C (H_c - H)
\end{equation}

where $V_n$ is the interfacial normal velocity, $C$ is the curvedness, $H$ is the mean curvature, and $H_c$ is the critical mean curvature that splits which interfaces grow and which shrink.
The α term contains properties of the alloy system; values for these properties can be found in the Experimental Methods chapter. This is similar to what DeHoff proposed in \cite{57} with the connected neighbor theory; however, in place of the generic diffusion length of $1/\lambda$ used by DeHoff that is a property of both the interfacial patch geometry and also its surroundings, we have used $C$, which is dependent only on the patch geometry.
Equation 5.8 is tested against experimental data in Figure 5.25 using sample C12-19A. The experimentally measured and the theoretically predicted average velocities in this plot match up very well, indicating that this expression is quite accurate.

Figure 5.25. Comparison of Equation 5.8 with experimental data for sample C12-19A. The colors and the red contours represent the experimentally measured velocity and the blue contours are the theory.

While this expression gives a very good estimation of the average velocity value of a patch with a given curvature, it does not account for the spread of velocities for individual interfaces. This spread is due to the different neighborhoods of individual patches; for example, there could be two interfacial patches with identical curvatures but if one is surrounded by large, positive mean curvature patches and the other is surrounded by large, negative curvature patches, the liquid surrounding these two patches will have very different chemical potentials and will result in different velocities of the two patches.

This spread can be examined by considering the distribution of velocities for a narrow range of curvatures. These distributions are shown for a few different curvatures in
Figure 5.26 for sample C12-27A. These distributions are calculated curvatures bin sizes of $\Delta \kappa / \zeta_v = 0.05$, so for a particular distribution at $(\kappa_1^* = -1.0, \kappa_2^* = +1.0)$ the velocities in the distribution are all of those with curvatures of $-1.025 < \kappa_1 / \zeta_v < -0.975$ and $+0.975 < \kappa_2 / \zeta_v < +1.025$.

Figure 5.26. Distributions of the velocity scaled by $dS_v^{-1}/dt$ using sample C12-19A for a few different curvatures, as indicated by the white boxes on the area ISD. The red dashed lines are fits of Gaussian distributions. The box sizes representing which curvature values are used in the distributions are enlarged compared to where the data is taken from for better visibility.

What is rather remarkable about these distributions is that they are very nearly Gaussian in shape, as shown by how close the distribution is to the Gaussian distributions that are fit to each dataset. This is true for curvatures that are near the peak on the ISD or far from the peak. This is significant because a patch that has curvatures near the ISD

\[ \frac{dS_v^{-1}}{dt} \]
peak is likely to be surrounded by neighbors that have very similar curvatures to itself. This is opposed to a patch that is far from the ISD peak in curvature space is likely to be surrounded by patches that have very different curvatures. In the non-peak curvature case, the surrounding patches will likely be close to the average curvatures of the system, therefore the distribution of curvatures of the surrounding patches will be highly skewed towards the average curvatures of the system. It is therefore reasonable to expect that the velocity distribution of these patches that have far-from-average curvatures would have highly skewed velocity distributions but they actually have very symmetric, Gaussian velocity distributions similarly to the nearly-average curvature patches.

It is possible that these unanticipated Gaussian distributions are the product of noise in the microstructural data, which would cause random noise in the measured velocities. To account for this, microstructural data from a Cahn-Hilliard phase field simulation is used for comparison. Six velocity distributions for this data are shown in Figure 5.27 along with their positions on the ISD using the same methodology and same bin size as is done for sample C12-19A. These distributions show less deviation from the Gaussian distributions than the experimental data; however, this data largely confirms that the distributions seen in the experimental data are real and not byproducts of noise in the measurements.

One notable trend in Figures 5.26 and 5.27 is for the standard deviation to increase with increasing distance from the origin. This can be seen with greater curvature resolution by plotting the standard deviation of the velocity distributions as a function of the curvatures, as in Figure 5.28. The experimental data in Figure 5.28A is very symmetric about the $H = 0$ line given how asymmetric it is in both it’s area ISD (in Figure 5.26).
Figure 5.27. Distributions of the velocity scaled by $\frac{dS_v}{dt}$ for a few different curvatures using the Cahn-Hilliard simulation data.

and the average velocity (Figure 5.25). The phase field simulation results are also very symmetric about the $H = 0$ line, but this is expected since it also has a very symmetric ISD.

The standard deviation values almost scale with the curvature $C$, which is proportional to the distance from the ISD origin. In the experimental data, this is most evident for the higher values of standard deviation, specifically the bright green and red regions in Figure 5.28A. The simulation data also appears to scale with $C$; however, there is clearly an additional influence here as the distribution appears to be compressed along the $H$-axis.
The causes of the relationship between the standard deviation and $C$ are not clear, nor are the causes for the differences between the experimental and simulation results. One possible, though speculative, cause for the standard deviation–$C$ relationship is that the high $C$ interfaces are necessarily associated with smaller features since they have a high curvature, therefore, they are closer to non-similar interfaces compared to a small $C$ interface, which is big and probably surrounded by very similar interfaces to itself.

Figure 5.28. Standard deviations of the fit Gaussian distributions for (A) sample C12-19A and (B) the phase field simulation data.

A final analysis that is possible with this data is to examine the total rate of change of area of all patches with a given curvature. The rate of area change of individual patches using the differential geometry property is calculated using:

\[
\frac{dA}{dt} = HVA
\]

This can be used to calculate an average property ISD in the same way that was done for the interfacial normal velocity. The resulting ISD shows the total $\frac{dA}{dt}$ value for all patches with the specified curvature values. These plots answer the question of which
affects the rate of coarsening more: the rare but highly curved and therefore rapidly evolving patches or the lower curvature, slowly evolving but very common patches.

Figure 5.29. Total $\frac{dA}{dt}$ values as a function of curvature. The gray lines are ISD contours and the red dashed is the average mean curvature.

These ISDs are shown for the different samples in Figure 5.29. Specifically, these plots show the scaled $\frac{dA}{dt}$ values where each bin value is the total amount of area change for all patches with those $\kappa_1$, $\kappa_2$ values, with a bin size of $0.016S_v^{-1} \times 0.016S_v^{-1}$. ISD contours are overlaid on these plots to compare where the amount of interfacial area in each bin
with its rate of change. The average mean curvature is indicated with a dashed line on the plots.

There are two common trend among the samples: 1) the rate of area change goes to zero just outside of the lowest area ISD contour, and 2) the maximum area change occurs near the outer limits of the area ISD. This indicates that it is the faster moving interfaces, rather than the more common ones that are near the peak of the area ISD, that dominate the coarsening dynamics. In fact, it is common for there to be a net increase in the interfacial area of the flatter interfaces. This is due to the interfacial velocity passing through zero near $H = \langle H \rangle$; therefore, the product of $H$ and $V$ will be positive in the region between $H = 0$ and $H = \langle H \rangle$.

This is most likely due to the requirement of zero net interfacial normal velocity for the sample that is imposed by the constant volume fraction. This means that in order for these high curvature, high velocity interfaces to move, an equal and opposite volume change must occur elsewhere in the system.
CHAPTER 6

Discussion

There are several interesting topics in this research that have not been done; some due to the lack of data and some due to lack of time to analyze the existing data. While the solidification data that is presented here is quite likely the highest spatial and temporal resolution 3D data of dendritic solidification in a metal, it is still not sufficient to see the shape of the dendrite tip or the rest of the near-tip region. This is a significant shortcoming of this dataset since the majority of theories and previous experiments of dendritic solidification are normalized by the tip radius. Fortunately, in March of 2014, we collected many datasets that are similar to this one but with a temporal resolution of 0.25 seconds instead of 1.8 seconds. This should allow for a much better view of the rapidly evolving regions of the dendrite. This data is not included in this thesis due to time constraints and will be examined by another student.

In the current 1.8 second resolution data, the interfaces move by a significant amount between datasets. With this increase in temporal resolution, the displacement of the interfaces will be significantly smaller. If the displacement is small enough that the normal direction of the interface does not change significantly, it will be possible to calculate interfacial velocities. This will make it easier to understand what is driving the interfacial motion in much more sophisticated ways than are currently possible.

It will also be useful to use this data to be able to look at the early times in more detail as well as look at the longer time evolution of $S_e$ to try to determine why it seems to follow
a single path in Figure 5.4 even though the solid fraction evolution follows two distinctly different slopes during undercooling-driven and then cooling-rate-driven solidification.

There are further possibilities for the coarsening data as well. The theories of Drew [55] and DeHoff [57] could be tested. Drew’s theories on the evolution of interfacial curvature could be used to determine the evolution of the ISD by determining the rate of change of curvatures for every interfacial patch and averaging these values for all patches of the same curvature. This results in a vector quantity for each point on the ISD that represents the rate of change of area based on the evolution of curvatures; this is called the curvature flow. Something similar was done by Mendoza but instead of using the experimentally measured curvature flow, a phase field simulation was used in which the initial conditions were an experimentally derived microstructure [65]. These results are shown in Figure 6.1 for an Al-15 wt% Cu sample at two times. This method is quite successful as the early time data shows a significant flux of curvatures towards $\kappa_1/S_v \approx 2.5$, $\kappa_2/S_v \approx 0$, which does in fact have a much higher propensity in the later times. We now have the experimental and computational tools available to calculate the curvature flow from the experimental data.

In [57], DeHoff proposed that the interfacial velocity during coarsening could be described by:

\[
V = \alpha \frac{1}{\lambda} (H_n - H)
\]

where $\alpha$ is a constant, $\lambda$ is the distance between the interface and a neighboring interface, $H$ is the mean curvature of the interface and $H_n$ is the mean curvature of the neighboring
interface. There are examples given in [57] of coarsening of spherical particles. In this case, it is relatively simple to determine $\lambda$ because the individual particles can be treated as discrete points with a constant mean curvature over the surface of the particle. However, in the case of complex morphologies, the distances would have to be calculated between every pair of patches. The simplistic way of doing this is to calculate the distances between every pair of patches such that if there are $10^6$ patches in the system, there would have to be $10^{12}$ distances computed. The more sophisticated and more correct method is to determine the line-of-sight paths through the liquid phase between all pairs of interfaces. This would give more accurate distances and would limit the number of pairs to be calculated due to screening effects. Neither of these methods have been tried either due to the computational burden of calculating $10^{12}$ distances in the simple case or due to the complexity of calculating lines-of-sight in the more advanced case.
Even though this work on coarsening has used the largest sample volumes to my knowledge\footnote{Previous analysis of the 2008 data presented here used 0.13 mm$^3$ subsets of the data whereas this work uses 1.7 mm$^3$, which is nearly the full sample volume. Other works, such as \cite{62} used approximately 0.29 mm$^3$.}, there are still questions about the sample size being sufficient. It is odd that sample C08-26A is the only 2 mm diameter sample in this work and it shows the fastest coarsening rate in Figure 5.19. This sample is also the lowest solid fraction and the only sample in which the field of view is smaller than the sample diameter; any one of these could be causing the faster than expected coarsening rate so it is impossible to determine whether or not the sample diameter is having an effect.

Similarly, there are lingering questions about the rate of change of $S_v$ that could be answered by longer duration experiments. The most recent experiments, C12-19A and C12-27A, were started with a finer microstructure than the 2008 experiments. This allowed them to achieve a doubling in $S_v^{-1}$ in a relatively short period of time and the experiments were stopped after this happened. While the finer microstructure caused these samples to reach steady-state conditions faster than the coarser microstructures, there still was not sufficient time in the steady-state regime to determine the time exponent in the equation $S_v^n \propto t$, which is a much more difficult task than showing that the data is consistent with the classical $S_v^{-3} \propto t$.

These shortcomings, combined with advances in what is possible in terms of X-ray computed tomography, make a good case for additional experiments. The development of the TIMBIR algorithm in particular would make it possible to achieve sub-micrometer spatial resolution with 10 second temporal resolution, compared to the previous best for the coarsening experiments of 2 $\mu$m spatial resolution and 45 second temporal resolution.
These improvements would make it possible to start with finer microstructures, which would decrease the amount of time to reach steady-state conditions and also increase the rate of evolution. This would make it possible to achieve a much greater increase in $S_v^{-1}$ in the same amount of time as the experiments presented here. Additional experiments would also allow for more tests of large diameter samples like sample C12-26A to see if the sample diameter is having an effect.
CHAPTER 7

Conclusions

A summary of the solidification results is provided here, followed by a summary of the main coarsening results.

7.1. Solidification

The work here on solidification has shown:

- It is possible to obtain time-resolved, 3D data of dendritic growth during solidification using a novel data gathering and processing method.

- The growth of a dendrite in a uniformly undercooled, hypo-eutectic Al-Cu alloy is measured with spatial and temporal discretization sizes of 0.65 µm and 1.8 seconds, respectively.

- Power laws that describe various attributes of the growing dendrite as a function of distance from the dendrite tip (\( \hat{Z} \)) are determined:
  
  \begin{itemize}
  \item Total volume of solid: \( V \propto \hat{Z}^{1.44} \)
  \item Liquid/solid interfacial area: \( A_{l/s} \propto \hat{Z}^{1.32} \)
  \item Surface area per unit volume: \( S_v \propto \hat{Z}^{-0.12} \)
  \item Average mean curvature: \( \langle H \rangle \propto \hat{Z}^{-0.16} \)
  \end{itemize}
- Average net curvature $\langle C \rangle \propto \hat{Z}^{-0.21}$

- The secondary dendrite arms are significantly flatter and more plate like than the relatively cylindrical secondary arms seen in transparent organic analogues.

- The formation of a split-tip dendrite arm is observed, which makes it possible to conclude that it forms because of a morphological instability that is due to the pre-split shape of the dendrite arm.

- Interfacial shape distributions have been calculated for 75 $\mu$m thick sections of the dendrite and show that the dendrite is not self similar with distance back from the tip; these can also be quantitatively compared to phase field simulations.

The successful characterization of dendritic solidification in a metal is a significant accomplishment of this work. Until recently, it has not been possible to characterize an opaque, metallic sample with the necessary spatial and temporal resolution to measure dendritic growth; thus, the development and application of the time-interlaced, model-based iterative reconstruction method is a significant accomplishment.

This method and the resulting data is used to determine power laws that characterize the evolution of solid fraction, liquid/solid interfacial area and curvatures as a function of position along the dendrite. These results, particularly the solid fraction, could be useful in theories involving liquid feeding during solidification since it will link the distance a dendrite grows with its solid fraction.

The 3D nature of the data has made it possible to calculate interfacial curvatures and interfacial shape distributions. The ISDs are useful in analyzing the growth behavior; for

\[ \text{The net curvature is defined in Equation 4.18} \]
example, it can be seen in the ISDs that there is a point in the growth of the dendrite at which the secondary arms are large enough to support tertiary arms. These ISDs will also be very useful for validating simulation results since they provide a concise, quantitative description of the morphology of a growing dendrite.

Finally, the data has been used to see the formation of doublons or split tip dendrite arms. This is the first observation of the formation of these structures in a metal, which made it possible to attribute their formation to a morphological instability that happens when the tip of the dendrite arm becomes sufficiently blunted.

7.2. Coarsening

The coarsening portion of this work has focused on describing the behavior of individual interfaces and how the curvature of an interface relates to its normal velocity. These relationships are examined for a variety of alloy compositions, which provided a range of solid volume fractions of between 28% and 80%. This is used to show:

- The evolution behavior of the interfacial shape distributions and overall morphology for six samples with solid volume fractions of 28%, 35%, 45%, 48%, 55%, and 80%.

- The rate of evolution of the microstructure, as measured by surface area per unit volume, does not significantly depend on the volume fraction of solid.

- There is a correlation between the normal velocity of an interface and its mean curvature, but there is a significant amount of scatter in this relationship.
A mean field approximation is developed that relates the interfacial normal velocity to the net curvature\(^2\) as well as the mean curvature that does a good job of predicting the average interfacial velocity for a given interfacial shape.

For a given interfacial shape, the distribution of individual interfacial velocities about the mean is Gaussian for almost all interfaces examined.

The interfacial shapes that contribute the most to coarsening are the relatively high curvature, fast moving interfaces rather than the more common, slower moving interfaces.

The interfacial mean curvature and normal velocity should be related since the mean curvature sets the chemical potential of an interface and the velocity is its response that enables coarsening. These variables are compared using a 2D histogram to show their relationship. While this shows a definitive correlation between the mean curvature and normal velocity, there is too much variability in the relationship to make it very useful.

A more successful approach is to plot the normal velocity as a function of two principal curvatures. This reveals an additional dependence on the net curvature, \(C\). It is found that a mean field model to describe this dependence works very well for predicting the average normal velocity of a piece of interface based on its curvature and materials parameters with no fitting parameters required.

While this equation describes the \textit{average} interfacial velocity for a given curvature, we find that it does not predict the actual velocity of every piece of interface in the system. That is because there is a distribution of velocities for a given curvature. By examining these distributions, we show that they are Gaussian shaped. A phase field simulation

\(^2\)See Equation 4.18 for a description of net curvature.
result is used to show that this is not merely an artifact of noise in the velocity data. The standard deviations of these distributions are examined and shown to be correlated to the curvedness but there are clearly other factors that influence it.
References


APPENDIX A

Implementation

A.1. Radon transform

Both the Radon transforms and the inverse Radon transforms described here are done in 2D; however, it is a simple process to extend them to 3D. The inverse Radon transforms that are used in the filtered back projection reconstructions are done to relate the projection data that is in terms of an angle of rotation of the sample, $\theta$, and a pixel location on the detector, $r$, to real-space coordinates $x$ and $y$. This work are done by looping over all angles ($\theta$), then looping over all $x$ and $y$ values and determining which detector pixels are aligned with that particular ($x$, $y$) point at that angle.

The computational domain is centered around the center of rotation of the sample in the ($x$, $y$) coordinates, which makes determining the rotations of the sample relatively easy. However, the relationship between the center of rotation of the sample and the pixel locations on the detector are not know. It is initially assumed that the reconstruction domain and the detector are aligned in the middle. This makes it possible to determine the relationship between the projection space and real space:

\begin{equation}
(A.1) \quad r(\theta, x, y) = x \sin(\theta) + y \cos(\theta)
\end{equation}
In order to make this more useful, it is important to define how these quantities relate to the data as it is stored on a computer. The variables $x$, $y$, and $r$ are in coordinates that are zero at either the center of the reconstruction or the center of the detector. New variables are defined that are zero at the computational origin of the data and with unit spacing. These are identified with an $i$ subscript to indicate that they are integer quantities:

\begin{align*}
    x_i &= \frac{x}{\Delta x} - \frac{n_x}{2} \\
    y_i &= \frac{y}{\Delta y} - \frac{n_y}{2} \\
    r_i &= \frac{r}{\Delta r} - \frac{n_r}{2}
\end{align*}

where $\Delta x$ is the grid spacing along the $x$-axis and $n_x$ is the number of pixels along the $x$-axis. The variables for $y$ and $r$ are defined similarly. These new variables can be inserted into Equation A.1 to obtain an expression for $r_i$ in terms of $\theta$, $x_i$, and $y_i$; however, this will give a non-integer value for $r_i$. The simplest solution to account for this is to round to the nearest integer. A more accurate and only slightly more difficult solution is to do a linear interpolation. This is done by determining the integers that are nearest to the estimate for $r_i$ provided by Equations A.1 and A.4:

\begin{align*}
    r_{i,lo}^i &= \text{floor}(r_i) \\
    r_{i,hi}^i &= r_{i,lo}^i + 1
\end{align*}
Then determining weighting factors for each of these locations:

\[ w_{lo} = r_{hi}^i - r_i \]  
(A.7)

\[ w_{hi} = 1 - w_{lo} \]  
(A.8)

These concepts can be combined to calculate the reconstruction, \( \rho(x, y) \), from the normalized projection data, \( P(\theta, r) \):

```plaintext
foreach \( \theta \) do
    foreach \( x, y \) do
        Find \( r_i \) with Equation A.1
        Find \( r_{lo}^i \) and \( r_{hi}^i \) with Equations A.5 and A.6
        Find \( w_{lo} \) and \( w_{hi} \) with Equations A.7 and A.8
        \[ \rho(x, y) = \rho(x, y) + w_{lo} P(\theta, r_{lo}^i) \]
        \[ \rho(x, y) = \rho(x, y) + w_{hi} P(\theta, r_{hi}^i) \]
    end
end
```

While this is not the only possible method of performing the inverse Radon transform, there are some benefits to doing it this way. In particular, it is important that this method loops over every \((x, y)\) point. In any transformation operation, it is important to loop over the destination array and use that location information to get information from the input array rather than the other way around. If the input array is looped over, it is possible that rounding errors and other inaccuracies (for example, due to simplifications or estimations) in the algorithm could lead to pixels in the output array mistakenly not being filled.

In this particular implementation, the \( \theta \) values are looped over first and the \((x, y)\) values second. There is no significance to this decision; it is merely done because it works
better with the way in which the data is stored from a memory access point of view. This
decision will be dependent on both the memory layout and the language used since that
will change how the multi-dimensional array is serialized and stored in memory.

The Radon transforms performed for this work are based on the ‘slant stacking’ method
presented in [117]. This is very similar to the inverse Radon transform except for an
additional decision being made about whether the reconstruction is better aligned with the
and projection data along the $x$-axis or along the $y$-axis. This is done as follows:

\[
\begin{align*}
\text{foreach } \theta \text{ do} \\
\quad \text{foreach } r_i \text{ do} \\
\quad\quad \text{if } |\sin(\theta)| < 0.5 \text{ then} \\
\quad\quad\quad \text{foreach } x_i \text{ do} \\
\quad\quad\quad\quad \text{Find } y_i \text{ with Equation A.1} \\
\quad\quad\quad\quad \text{Find } y_{i}^{lo} \text{ and } y_{i}^{hi} \\
\quad\quad\quad\quad \text{Find } w_{i}^{lo} \text{ and } w_{i}^{hi} \\
\quad\quad\quad\quad P(\theta, r_i) = P(\theta, r_i) + w_{i}^{lo} \rho(x, y_{i}^{lo}) \quad P(\theta, r_i) = P(\theta, r_i) + w_{i}^{hi} \rho(x, y_{i}^{hi}) \\
\quad\quad\quad \text{end} \\
\quad\quad \text{end} \\
\quad\quad \text{else} \\
\quad\quad\quad \text{foreach } y_i \text{ do} \\
\quad\quad\quad\quad \text{Find } x_i \text{ with Equation A.1} \\
\quad\quad\quad\quad \text{Find } x_{i}^{lo} \text{ and } x_{i}^{hi} \\
\quad\quad\quad\quad \text{Find } w_{i}^{lo} \text{ and } w_{i}^{hi} \\
\quad\quad\quad\quad P(\theta, r_i) = P(\theta, r_i) + w_{i}^{lo} \rho(x_{i}^{lo}, y) \quad P(\theta, r_i) = P(\theta, r_i) + w_{i}^{hi} \rho(x_{i}^{hi}, y) \\
\quad\quad\quad \text{end} \\
\quad\quad \text{end} \\
\quad \text{end} \\
\end{align*}
\]

where $x_{i}^{lo}$, $x_{i}^{hi}$, $y_{i}^{lo}$, $y_{i}^{hi}$, $w_{i}^{lo}$, and $w_{i}^{hi}$ are found in a very similar manner to the values
for $r_i$ in Equations A.5 to A.8.
A.2. Signed distance function reinitialization

To reinitialize the SDF, it is useful to start from the definition that a SDF has a constant spatial gradient of \(|\nabla \phi| = 1\):

\[
|\nabla \phi| = 1
\]

Figure A.1. The blue line is a 1D SDF that needs reinitializing because it has the wrong gradient. The green line is what the correct SDF should be and the arrows indicate in which direction the blue line needs to evolve to be correct.

From this, it is possible to formulate a partial differential equation to describe the evolution of \(\phi\) that is necessary to turn it into a SDF. One component of this PDE is the deviation from the correct slope \((1 - |\nabla \phi|)\). The other component of the PDE comes from the ‘signed’ aspect of the signed distance function that causes the positively and negatively signed regions to behave differently. This sign related difference is shown in
Figure A.1 where the positive and negative points have the same gradient but different signs and therefore need to go in opposite directions. Combining these, the reinitialization equation is:

\[
\frac{\partial \phi}{\partial t} = S(\phi_0)(1 - |\nabla \phi|)
\]

(A.10)

where \( t \) is an artificial evolution time and \( S(\phi_0) \) is a sign function. In the simplest implementations, \( S(\phi_0) \) is a smeared or smoothed version of a sign function:

\[
S(\phi_0) = \frac{\phi_0}{\sqrt{\phi_0^2 + (\Delta x)^2}}
\]

(A.11)

where \( \Delta x \) is the grid spacing. This results in a sign function far from the interface with the values going to zero at the interface. This is done to prevent \( \phi \) from moving by stopping its motion as it approaches a grid point. While this approach is easy to implement, it does not do a good job of keeping the interface in the correct location. This is due to the different speeds at which \( \phi \) evolves depending on how close it is to the interface. For example, imagine two neighboring cells with an interface between them and values of \( \phi(x = 0) = -0.1 \) and \( \phi(x = 1) = +0.4 \). Clearly, the correct values for this to be a SDF are \( \phi(x = 0) = -0.2 \) and \( \phi(x = 1) = +0.8 \). Since the value at \( x = 0 \) is closer to the interface, and will therefore have a lower, it will evolve more slowly than the point at \( x = 1 \). This will result in the point at \( x = 1 \) moving more than it should and the point at \( x = 0 \) moving less than it should which will has the effect of incorrectly moving the interface.
This $S(\phi_0)$ function can be improved using the subcell interface method from [120]. This method uses a more accurate computation of the values near the interface, with the values that are on the border of an interface (as determined by taking the product of the SDF value and its neighbors; if any of these products are negative, then the pixel is on the border of an interface) as follows for a 2D example:

\begin{equation}
\frac{\partial \phi}{\partial t} = \frac{\phi_0}{\sqrt{g_x^2 + g_y^2}} - S(\phi_0) |\nabla \phi|
\end{equation}

where $t$ is the integration time, $S(\phi_0)$ is a sign function and $g_x$ and $g_y$ are the gradients as defined by:

\begin{equation}
g_x(x, y) = \max\left(\frac{\phi(x+1, y) - \phi(x-1, y)}{2\Delta x}, \frac{\phi(x+1, y) - \phi(x, y)}{\Delta x}, \frac{\phi(x, y) - \phi(x-1, y)}{\Delta x}, 10^{-9}\right)
\end{equation}

and similar for $g_y$. The remaining non-boundary voxels are updated according to Equation A.10 with $S(\phi_0)$ being a plain sign function.

The gradient term, $|\nabla \phi|$, in Equation A.10 can not be computed with simple central differencing or something similar. This is because the information should always be passed from the interfaces outwards. For example, in Figure A.1 the far outside data points should not affect the values of the two inner data points. Instead, the distance from the interface should set the values of the inner data points and the values of the inner data points should set the values of the outer data points. In order to achieve this, an upwind scheme is used that uses data that are only from data points that are ‘upwind’ of the
point of interest. The standard method of doing this is Godunov’s method \[121\]. This consists of determining the spatial derivatives using forward and backward differencing and using only the one that is closer to the interface. For 1D SDF with for which \( \phi > 0 \), this is done as follows:

\[
\frac{\partial \phi}{\partial x} = \max \left( \left( \max \left( 0, \frac{\phi(x) - \phi(x - 1)}{\Delta x} \right) \right)^2, \left( \min \left( 0, \frac{\phi(x + 1) - \phi(x)}{\Delta x} \right) \right)^2 \right) 
\]

If a higher dimension SDF is being calculated, the gradients for those dimensions are calculated in a similar way and \( |\nabla \phi| \) is calculated from the resulting upwind gradients.

A different method of determining the upwind gradients that ultimately results in less motion of the interface during reinitialization and ultimately smoother curvatures, is using the weighted, essentially non-oscillatory (WENO) method of calculating gradients. This uses the same method of determining the interface boundary values as described in Equation \[A.12\] but the spatial gradients that are calculated by computing many two-point finite differences near the voxel of interest, determining the amount of oscillation associated with each of these gradients, and using this to weight the gradients in a way that picks the smoothest possible gradient. Similarly to Godunov’s method, both the forward and backward differences are calculated and the one that is the upwind difference is selected from these two. For the backward difference, the individual two-point differences are calculated as:
\[ V_1 = \frac{\phi(x - 2) - \phi(x - 3)}{\Delta x} \]

\[ V_2 = \frac{\phi(x - 1) - \phi(x - 2)}{\Delta x} \]

\[ V_3 = \frac{\phi(x + 0) - \phi(x - 1)}{\Delta x} \]

\[ V_4 = \frac{\phi(x + 1) - \phi(x + 0)}{\Delta x} \]

\[ V_5 = \frac{\phi(x + 2) - \phi(x + 1)}{\Delta x} \]

For calculating the forward differences, these The overall backward difference is calculated using a

\[ \frac{\partial \phi}{\partial x_{\text{back}}} = \text{WENO}(V_1, V_2, V_3, V_4, V_5) \]

where \( \text{WENO}(\ldots) \) is a function that is dependent on several quantities:

\[ S_1 = +\frac{13}{12} (V_1 - 2V_2 + V_3)^2 + \frac{1}{4} (V_1 - 4V_2 + 3V_3)^2 \]

\[ S_2 = +\frac{13}{12} (V_2 - 2V_3 + V_4)^2 + \frac{1}{4} (V_2 - V_4)^2 \]

\[ S_3 = +\frac{13}{12} (V_3 - 2V_4 + V_5)^2 + \frac{1}{4} (3V_3 - 4V_2 + V_5)^2 \]
\begin{align*}
A_1 &= \frac{0.1}{(S_1 + \epsilon)^2} \\
A_2 &= \frac{0.6}{(S_2 + \epsilon)^2} \\
A_3 &= \frac{0.3}{(S_3 + \epsilon)^2}
\end{align*}

where \( \epsilon \) is a small floating point value. The weighting factors are calculated with:

\begin{align*}
W_1 &= \frac{A_1}{A_1 + A_2 + A_3} \\
W_2 &= \frac{A_2}{A_1 + A_2 + A_3} \\
W_3 &= \frac{A_3}{A_1 + A_2 + A_3}
\end{align*}

\begin{align*}
G_1 &= \frac{1}{6}(2V_1 - 7V_2 + 11V_3) \\
G_2 &= \frac{1}{6}(-1V_2 + 5V_3 + 2V_4) \\
G_3 &= \frac{1}{6}(2V_3 + 5V_4 - 1V_5)
\end{align*}

Finally, the WENO(\ldots) function can be calculated with:

\begin{equation}
\text{WENO}(V_1, V_2, V_3, V_4, V_5) = W_1G_1 + W_2G_2 + W_3G_3
\end{equation}
A very similar method is used for calculating the backward difference, except the individual two-point differences are calculated as:

\[(A.34) \quad V_1 = \frac{\phi(x + 3) - \phi(x + 2)}{\Delta x}\]
\[(A.35) \quad V_2 = \frac{\phi(x + 2) - \phi(x + 1)}{\Delta x}\]
\[(A.36) \quad V_3 = \frac{\phi(x + 1) - \phi(x + 0)}{\Delta x}\]
\[(A.37) \quad V_4 = \frac{\phi(x + 0) - \phi(x - 1)}{\Delta x}\]
\[(A.38) \quad V_5 = \frac{\phi(x - 1) - \phi(x - 2)}{\Delta x}\]

And the overall forward gradient is calculated using:

\[(A.39) \quad \frac{\partial \phi}{\partial x_{fwd}} = WENO(V_1, V_2, V_3, V_4, V_5)\]

With both the forward and backward differences calculated, the upwind difference is calculated using Godunov’s method as in Equation \([A.14]\).