Use of cellular automata-based methods for understanding material-process-microstructure relations in alloy-based additive processes

Matthew Rolchigo
Iowa State University

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Use of cellular automata-based methods for understanding
material-process-microstructure relations in alloy-based additive processes

by

Matthew Ryan Rolchigo

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

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The student author, whose presentation of the scholarship herein was approved by the
program of study committee, is solely responsible for the content of this dissertation. The
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Iowa State University
Ames, Iowa
2018

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<tr>
<td>b</td>
<td>Solidification constant (function of other parameters)</td>
</tr>
<tr>
<td>c</td>
<td>Lattice speed</td>
</tr>
<tr>
<td>$c_s$</td>
<td>Square root of the speed of sound on the lattice</td>
</tr>
<tr>
<td>C</td>
<td>Cell solute concentration</td>
</tr>
<tr>
<td>$C_L$</td>
<td>Liquidus composition *</td>
</tr>
<tr>
<td>$C_L'$</td>
<td>Binary alloy solute composition</td>
</tr>
<tr>
<td>$C_S$</td>
<td>Solidus composition *</td>
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<tr>
<td>$c_p$</td>
<td>Specific heat capacity **</td>
</tr>
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<td>D</td>
<td>Solute diffusivity</td>
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<tr>
<td>$e_i$</td>
<td>Unit vectors for velocity</td>
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<tr>
<td>E</td>
<td>Internal energy density</td>
</tr>
<tr>
<td>$E_{abs}$</td>
<td>Energy density absorbed by a cell</td>
</tr>
<tr>
<td>$E_{incident}$</td>
<td>Energy density incident on a cell</td>
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<tr>
<td>$E_S$</td>
<td>Strong scaling efficiency</td>
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<td>$\vec{F}$</td>
<td>Sum of melt pool forces</td>
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<td>$\vec{g}$</td>
<td>Acceleration due to gravity</td>
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<td>$g_d$</td>
<td>Mean grain diameter</td>
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<td>G</td>
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<td>$Iv$</td>
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<td>L</td>
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<td>$m_L$</td>
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<td>Preheat temperature</td>
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<td>Temperature difference</td>
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<td>$\gamma$</td>
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* May contain superscript “eq” for equilibrium value at a given temperature
** Superscripts “L” and “S” used for liquid and solid phase values, respectively
† If not explicitly written as a function of “V”, equilibrium value is assumed
††† Unless otherwise noted via superscript, volumetric density is used
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ABSTRACT

Deposition of metals through additive manufacturing has garnered research interest as of late due to the large range of potential industry applications. In particular, direct metal deposition processes such as Laser Engineered Net Shaping (LENS\textsuperscript{TM}) have the ability to construct near net shape parts, open cellular structures, compositionally graded parts, and parts with improved mechanical properties over those manufactured via traditional methods such as casting and forging. To utilize additive processes to their full potential, it is imperative that the relationships among process parameters, development of the molten pool, microstructure, and properties are understood. Our goal in applying computational modeling to this problem is to aid in our understanding of such relationships to guide future experiments towards sets of alloying additions and deposition conditions that produce preferred microstructures. Cellular Automata (CA) based modeling techniques provide a way to bridge the scales of the complex phenomena that occur during AM processes, reducing them to physics-based rules for the evolution of cell state variables; in particular, this makes these methods well-suited for large scale parallel computing problems and large ensembles of simulations. CA is applied at the scale of individual dendrites yielding quantitative agreement with analytical models for dendrite tip undercooling as a function of solidification velocity. For dendritic colonies, CA modeled microstructures yielded favorable quantitative and qualitative agreement with expected trends in primary arm spacing, side branching, solute segregation, and non-equilibrium growth phenomena such as solute trapping and banded growth morphology. CA is also applied at the scale of multiple grains to investigate the columnar to equiaxed transition in 2D and 3D with varied nucleation undercooling, alloying addition, and interfacial response function. The lattice Boltzmann (LB) method for fluid transport is combined with COMSOL Multiphysics simulations of melt pool dynamics and
the dendrite-scale CA for coupled simulation of fluid flow, solute transport, and solidification, yielding good agreement on microsegregation and dendrite arm spacing with experimental results for LENS™ alloy deposition. A thermal lattice Boltzmann (TLB) model of the melt pool is also developed and combined with the grain-scale CA for parallel, concurrent multi-scale simulation of fluid flow, heat transport, and grain growth for LENS™-representative conditions, showcasing the model’s ability to predict microstructure trends with changes in process conditions or alloying additions. The ability of CA to accurately predict many aspects of and trends regarding alloy solidification in additive processes show a promising future for using similar codes to augment experimental results for new alloy development, while the parallelizability and computational efficiency of CA show its potential for use in Exascale computing application codes.
CHAPTER 1. INTRODUCTION

1.1 Additive manufacturing of metals: overview

Additive Manufacturing (AM) for industrial part production has been referred to by The Economist as a “third industrial revolution”, promising to allow individualized production of parts economically and with low labor costs [12]. It has been suggested that AM will play a significant role in up to 42% of industrial, automotive, biomedical, and aerospace part production in the next 10 years [166]. The value of this market itself is predicted to grow to $26.5 billion by 2021 [217], with a total economic impact according to The Economist’s 2016 analysis of up to $550 billion by 2025. A variant of Rapid Prototyping, AM has matured to allow for more than just prototype development; the ability to make final parts on demand from a blueprint and feedstock material has made these processes appealing for many materials and for many industries. For low run part production, AM production routes are often cheaper than conventional manufacturing [250]. For alloys in particular, net shape or near net shape parts can be constructed with advantageous microstructural features [48, 67, 56] and/or improvement in the parts’ mechanical properties over those made through traditional alloy manufacturing methods [78, 171, 172]. Open cellular or honeycomb structures that would be difficult or impossible to produce with traditional manufacturing are also of interest for structural applications where light weight is desired [174, 265, 210], providing further materials cost savings. Though a wide variety of alloys, including Ni, Cu, Ti, Fe, Co, and Al-based systems, have been successfully deposited via additive production methods [57], our primary focus is primarily on the deposition of Ti alloys. Due to the high materials cost of Ti, the efficiency of material usage via AM (through production of specific geometry without the need for machining, recycling of unused powder feedstock,
and ability to produce open cellular structures) is particularly important. Titanium alloys’
low density and high strength is of particular interest for aerospace applications [151], while
their biocompatibility and corrosion resistance allows their incorporation into biomedical
applications [80].

Under the general umbrella of alloy-based AM are various process types. AM processes
for pure metals and alloy systems use a heat source to melt a feedstock material typically
consisting of a pure metal or pre-alloyed powder blend, though wire-fed processes such as
that of Sciaky, Inc. as described by [218] exist as well. Powder bed-based AM involves the
scanning of a heat source along a preset powder bed to melt and resolidify the material;
following the deposition of a layer, a new powder bed is placed atop the now-resolidified
powder and the process is repeated in a layerwise fashion. Partial melting, as is the case in
laser sintering, or complete melting as in most deposition processes, can be performed [80].
The energy source is often either a laser, as in the case of Selective Laser Melting (SLM), or
a focused electron beam, as in Electron Beam Melting (EBM). Alternative energy sources
include plasma arc and Joule heating, the latter of which is used commercially by Digital
Alloys, Inc. EBM and SLM are compared in detail by [173], and it is shown that differences
in operating environments, beam parameters, and preheat conditions generally lead to dif-
fences in observed microstructure. Other differences in process capability between electron
beam and laser-based processes exist as well; for example, electron beam-based processes
are more energy efficient than laser-based, but require operating under a vacuum of around
$10^{-4}$ Torr [107]. Common defects in powder bed-based AM processes include the balling
effect due to unstable melt pools and large surface tension, as well as delamination and
porosity between layers [157]. Direct deposition-based AM processes, in which the powder
feedstock is directly injected into the molten pool, have certain advantages relative to the
powder-bed based processes. The ability to alter the powder feedstock within a given layer
allows compositionally and functionally graded parts to be built in a simpler fashion than
with powder-bed based AM [153, 80, 49]. It can also be used for part repair, as well as
for construction of larger and more complex parts with closed-loop process control for some
direct metal deposition processes [80]. Direct deposition-based AM process’ weaknesses in-
clude melt pool instability from powder injection, as well as loss of energy deposition due
to laser-powder particle interaction [86, 15]. Laser Engineering Net Shaping (LENS™), an
example of a direct deposition AM process developed at Sandia National Laboratories in
the 1990s, is the focus of the present modeling effort. However, the physical and thermody-
namic phenomena along with the modeling strategies discussed throughout this thesis are
applicable to other AM processes as well, and solidification modeling under both LENS™
and the more extreme conditions of SLM are considered in later chapters. More details on
differences between specific alloy AM processes can be found in the review article of [57].

Despite recent progress regarding AM-deposition of custom Ti alloy parts with control-
lable properties and specified geometry, many challenges still remain regarding industrial
use of these processes for part production. Slow deposition rates may limit the size of parts
that can be economically produced, due to the trade off between deposition rate and resolv-
able feature size [207]. Surface roughness along part edges and along the top surface may
require machining, particularly if powder particles with large median size are used. Poor
feedstock quality can also lead to internal porosity within builds; such defects can lead to
crack formation and reduction in expected part strength [286, 105]. While porosity and sur-
face roughness are controllable to a degree, stochastic variations in these parameters across
a build will necessarily occur on the edges of the process window (i.e., sets of process param-
eters that allow for complete melting of the substrate and avoid other issues such as balling
of powder particles). Compositionally and functionally graded parts of interest may not be
possible for some material and process combinations with current technology, as mechanical
weakness resulting from poor substrate adherence or the development of internal strain due
to lattice mismatch can render parts useless [207]. For parts that avoid large defects such
as large porosity fractions or cracks during builds, properties will vary significantly based on
microstructure details, in particular the distribution of grain sizes, orientations, and solute
segregation within grains. Resulting microstructures both across a solidified molten pool and within individual grains are complex functions of the process itself and properties of the material used - as are the formation of defects such as pores and cracks [5, 21, 110]. As grain structure and other microstructural features directly affect part properties [17, 171, 267, 269], these relationships are of major importance for current and future AM design and production. Application of computational modeling to AM processes can be a useful augmentation to experimental results, allowing additional information on key relationships among process parameters, materials parameters, and resulting microstructures to be gathered. An effective model would reduce the need for costly trial-and-error experiments, where testing all possible sets of material and process conditions would not be efficient. The remainder of this chapter is broken down into two subsections: both of which broadly discuss thermodynamic, kinetic, and transport phenomena in and around the molten pool that develops during alloy-based AM processes. Chapter 2 describes modeling efforts regarding these phenomena in more depth, and describes the primary sets of physics and modeling methods applied through the rest of this thesis to better understand process-material-microstructure relationships of interest.

1.2 Physics in additive manufacturing

1.2.1 Process scale phenomena

Melt pool development and evolution in beam-based alloy AM processes depend on a myriad of transport and phase transformation phenomena that occur concurrently and often at different length and time scales. Figure 1.1 illustrates the complexities of these phenomena for powder bed fusion processes [157], though the relevant forces and transformations are present at least in some degree for direct deposition processes as well. The heat source, whether a laser or electron beam, typically (but not always) follows an axisymmetric Gaussian profile [57]. The absorption of this energy is a complex function of the process used [80],
the reflectivity of the material itself [232], and details of the feedstock material (particularly particle size and whether it is a powder bed or directly injected into the heat source) [57]. For prealloyed powder blends, it has been suggested that the heat of mixing may be an additional source of energy for the melt pool [46]. Powder particles directly under the beam or injected directly into the beam will undergo melting, while others may get heated and sinter without fully melting [154]. Most of the energy deposited, particularly for laser-based processes, will be absorbed by the material (whether solid or liquid) immediately at or just below the surface [157]. Heat diffusion in the liquid and conductivity in the solid allow the melt pool to grow, while heat loss from radiative cooling and convection occur at the top surface. Evaporation of material may occur at the melt pool surface; this evaporation is often material-dependent, and selective evaporation of elements within an alloy melt pool will lead to compositional inhomogeneity [55]. Directly under the beam, particularly for slow scan speeds and high beam powers, vaporization of material commonly occurs. As with evaporation, selective vaporization of specific alloying elements is common [87, 169]. Chemical reactions may occur in and around the molten pool, particularly oxidation at the surface when oxygen is present above a molten titanium or aluminum-based melt pool [147]. As the melt pool advances, solidification will proceed from the melt pool bottom and sides. The rapid cooling of material during solidification will typically involve shrinkage, inducing thermal stress and the development of dislocation structures and other lattice imperfections [80]. Phase change phenomena, whether melting, evaporation, vaporization, or solidification, will necessarily play a role in the heat transport of beam based AM processes.

Despite the relatively small size and short lifetime of the melt pools formed in additive processes, their behavior is highly dynamic involving several forces that induce strong fluid flow. In turn, this fluid flow will advect heat, altering the development and shape of the melt pool as well as the connectivity between multiple deposited layers [208, 157]. Much of this behavior can be attributed to the low viscosity and high surface tension of liquid metals [123]. For many laser-based additive processes that closely resemble welding conditions, it
has been suggested that the Marangoni force (also known as the thermocapillary force) is the primary driver of fluid flow [57]. This force arises due to the large temperature gradient at the liquid-gas interface and corresponding variation of surface tension with temperature. The colder melt pool surface near the solid-liquid interface typically has a significantly larger surface tension than the hotter melt pool surface near the region of energy absorption. As a result, fluid motion along the surface of the melt pool from the center to the edges is induced, leading to the development of convection cells as well as the formation of ripples along the melt pool surface [36]. The surface tension is also typically a function of composition, and the selective evaporation or vaporization of active elements at the melt pool surface can alter the Marangoni force-induced flow as well. An example of this is selective evaporation of sulfur in steels, which may pull fluid towards the melt pool center from the edges and reverse the direction of these convection cells [57, 163]. The recoil of the melt pool surface from evaporation and vaporization plays a major role in melt pool shape [87, 169]. For laser melting in particular, a vapor cavity may form beneath the incident beam leading to
a “keyhole” shaped cavity as the beam penetrates deeper into the material [157]. This is particularly true at large beam power and low scan speed, and can lead to a significant change in melt pool depth as the Marangoni force plus recoil pressure keep the keyhole stable, and multiple reflections trap incident energy density in the keyhole [228]. For electron beam melting under vacuum conditions, it has been suggested that capillary forces from melt pool and powder particle curvature may play a dominant role over the Marangoni force in melt pool shape and development [123]. For selective electron beam melting of powder beds, it has also been noted that the growth of melt pool is primarily related to wetting of powder particles rather than the Marangoni force [123]. The electrostatic force will play a role on melt pool development particularly in powder bed melting; the combination of the melt pool’s large surface tension and repulsive electrostatic interactions can lead to ejection of partially melted particles from the melt pool [36, 57]. While buoyancy and gravitational forces can play a significant role in the large melt pools formed in welding, they are often considered secondary effects on fluid flow in AM melt pools [157, 57].

The melt pool size, shape, and temperature distribution will necessarily vary from these phenomena, though the relative importance of different effects depend on the process used and process conditions. Keyhole formation at large energy densities can lead to porosity developing due to trapping of gas during keyhole collapse [114]. If input energy density is too small, such as at fast scanning speed, the elongated melt pool in the wake of the beam can separate due to capillary instabilities [122]. This effect, known as “balling”, can lead to melt pool inhomogeneity as well as pore formation. Defects due to incomplete melting at fast scan velocities are possible as well, such as gas porosity trapped in the melt pool due to lack of powder particle fusion [249]. Porosity formed via these different mechanisms can have different shapes [182]; however, there is often disagreement in the literature on exact mechanisms of porosity generation during solidification. Melt pool dynamics and temperature distributions within melt pools, though important, are difficult to measure experimentally. Temperature measurement is typically either performed with thermocouples [94, 212] or in-
Infrared thermography [56, 208, 93]. Work has also been performed using high-speed cameras to monitor the beam-material interaction and absorption [24]. Thermal gradients and cooling rates will necessarily depend on the location within the melt pool and the material used in addition to the specific AM process. For LENS™ specifically, [91] used a combination of thermal imagining and computational modeling to estimate thermal gradients and cooling rates for various process parameters, finding that cooling rates were typically on order of $10^3$ K/s and thermal gradients on the order of $10^6$ K/m at the melt pool boundary. However, there is still significant uncertainty in quantitative estimates of energy absorption, melt pool forces, and temperature profiles in and around the melt pool in AM processes, presenting a significant opportunity for the application of modeling to better understand these phenomena.

1.2.2 Microstructure development

Directly related to the thermal gradients and cooling rates in the wake of the advancing melt pool is the development of microstructure. As thermal profile will necessarily vary through a build, inhomogeneity in microstructure and properties are produced as well [176, 154]. Within the solid part are many grains that grow epitaxially through multiple deposited layers; due to the decreased energy barrier of solidification proceeding from an established surface (in this case, the tops of existing partially melted grains), epitaxial growth of grains has been observed for most common alloy systems. Epitaxial growth is discussed in depth in the review article by [16]. The growth of grains, primarily consisting of dendritic structures, will be a function of thermal conditions as well as solute diffusion. Dendrites with orientations more aligned with local thermal gradient directions will impinge those with less favorable orientations, leading to competitive growth of columnar dendrites [57]. Morphological details of these structures will depend on the phase diagram, solid-liquid interfacial energy, and solidification rates. An example of a non-dendritic grain morphology was shown by [252], where segregationless solidification of Ti-6Al-4V occurred due to the lack of so-
lute partitioning and small solidification range. For grains with cubic symmetry, the \(<001>\) growth directions dominate growth and a preferred texture is developed, typically perpendicular to the build axis. However, it has also been demonstrated that alloying additions can be used to produce a \(<110>\) texture \([27, 89]\). This texture developed during solidification tends to persist through cooling to room temperature and strongly influences part properties such as strength and ductility \([48]\). Melt pools of different shapes and sizes as produced through different processes or process parameters will necessarily have differences in resulting grain structures \([59, 231]\). Deposition of multiple layers through “back and forth” (bidirectional raster) scanning will lead to “zig-zag” type grain structures \([262, 48, 183]\); an example of such a grain structure is reproduced from \([59]\) in Figure 1.2a. A wide variety of textures have been produced through adjusting scan parameters \([262, 58, 10]\), and the ability to control the size and shape of grains through process parameter variation has been demonstrated \([117]\). Heterogeneous nucleation of grains away from the melt pool boundary can lead to competition with these columnar dendritic grains growing epitaxially from the previous layer, further complicating the issue of texture development. While columnar grain structures are the most common as grains growth through multiple deposited layers, equiaxed grains from nucleation events have been observed as well for different conditions \([16, 2, 15]\). In particular, as shown by \([256]\), equiaxed grains tend to appear at the top of melt pools, where the thermal gradients are the smallest. \([31]\) and \([191]\) provide examples of using alternative scan strategies (in this case, series of spot melts producing a large molten pool with reduced thermal gradient) to produce equiaxed grains. A pertinent result obtained by \([191]\) is reproduced in Figure 1.2b and c, showing columnar and equiaxed grain-dominated microstructures for variation in scan strategy. The presence of these equiaxed grains can also be brought about by changing alloy composition, as shown by \([23]\) with boride additions to Ti-6Al-4V, \([160]\) with W additions to Ti, and \([161]\) with trace C additions to Ti-6Al-4V. When compared to the columnar grains, equiaxed grains tend to be much more fine, though work also has been done with columnar grain refinement (including the work of \([187]\)) through scan strategy.
and alloying addition variation. While the columnar grains typically consist of cellular or dendritic structures, equiaxed grains are nearly always dendritic in nature.

Figure 1.2 Adapted from the works of [59] and [191]: Electron backscatter diffraction maps of AM grain structures, as produced with an (a) bidirectional raster scan pattern, (b) a spot scan pattern with low beam current, and (c) a spot scan pattern with high beam current. While the bidirectional raster was shown by [59] to produce the expected pattern of “zig-zag” shaped columnar grains, the spot scan patterns used by [191] produced either columnar or equiaxed grains depending on the beam current.

In addition to columnar grain texture and equiaxed grain formation, solidification of multiple solid phases from the melt can occur. [251] observed some stainless steel compositions to produce duplex ferrite and austenite microstructures on initial solidification. Other non-primary phase structures, such as eutectic [187] or oxide precipitates [193], can form in some systems as well. During further cooling of solid grains or during applied heat treatment, additional microstructural changes may occur. These include solid-solid phase transformations such as those observed in stainless steel [64], growth of existing single phase solid grains during reheating, and solute diffusion in and around existing grains. Many alloys precipitate intermetallic compounds during cooling cycles. This is particularly true for Ni-based alloys, which have shown significant volume fractions of precipitates [110, 183];
fractions and morphologies of such precipitates were shown to significant impact the material’s mechanical properties [178]. The rapid cooling of solid grains during AM processes can lead to diffusionless and non-equilibrium phase transformations as discussed in the review article of [48]. An example is the metastable ω phase that can form in some titanium alloys [14]. For the titanium alloy solidification focused on in this thesis, the grains upon initial solidification consist of the β phase (a body centered cubic, or BCC crystal structure). The final microstructure of these alloys will consist of metastable β grains stabilized at room temperature, with α colonies (a hexagonal closed packed, or HCP crystal structure) of varied volume fraction forming during cooling depending on the phase diagram and specific alloying additions [16, 120]. Rapid solidification at the interface can lead to non-equilibrium solute partitioning in the β phase due to the time scale of solute atom motion relative to that of interface advance. This is also true of the β to α transitions, as martensitic α′ can form when solute cannot diffusive fast enough to form equilibrium compositions of α and β phases [269].

Our primary focus is on the solidification of these original β Ti grains, and how their orientations and morphological details will vary with material and conditions. A secondary focus is given to solidification of single phase face centered cubic, or FCC, stainless steel and Inconel. While microstructure differences for a given alloy system can be observed and attributed to variables such as thermal gradient direction or alloying addition, controlling and predicting microstructure will require the use of computational modeling as trial-and-error experimentation for all possible conditions is not feasible even when limiting scope to the initial liquid-to-solid single phase solidification problem. Given that microstructure development and the fluid and heat transport phenomena in and around the melt pool are concurrent and codependent processes, successfully understanding these processes will require coupled modeling at the appropriate length and time scales.
CHAPTER 2. MODELING OF ADDITIVE-RELEVANT PROCESSES: LITERATURE REVIEW

2.1 Fluid and heat transport modeling

The heat transport occurring in and around the melt pool for all beam-based additive manufacturing processes has an inevitable effect on melt pool dimensions, porosity and keyhole defects, surface roughness, and as-solidified microstructure. As a result, much work has been applied to modeling this process over the last several decades. One of the simplest yet most useful approximations of these processes is given by the Rosenthal solution for a moving point heat source over a material surface, neglecting fluid flow, the latent heat of melting, and heat transport from the top of the melt pool [205]. This solution in 2D and 3D has been used to calculate thermal gradients \( G \) and solidification velocities \( V \) at different regions of the melt pool to relate process conditions to microstructure development [28, 29, 75, 144], and has also been used to benchmark or compare results obtained with other models [186]. More commonly used to model heat transport in these problems is the finite element (FE) method, in which the problem domain is broken down into small, geometrically simple pieces in which algebraic solutions to the more complex transport equations are calculated. Although the exact assumptions and solutions to the transport equations may vary depending on the method and model, in general the equation for diffusive heat transport

\[
\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + q_{\text{src}} - q_{\text{sink}} \quad (2.1)
\]

is solved, where the material density \( \rho \), thermal conductivity \( k \), and specific heat capacity \( c_p \) are often considered as functions of temperature and/or of local material porosity [44, 51, 196]. The volumetric heat source \( q_{\text{src}} \) includes energy absorbed from the beam and
is typically approximated as a Gaussian distribution of energy centered around the beam, which is either a 2D approximation of the 3D heat source (as described by [254]) or a fully 3D energy source. This term may also include the latent heat of phase transformation between solid and liquid. Not all models account for latent heat, some simply treat regions above and below the melting temperature with phase-dependent densities or conductivities [197], but as solidification for alloys tends to occur over a non-negligible range of temperatures, other models include this term or a similar one in some fashion [191, 287]. Modeling the energy absorption of the material has been handled in a variety of ways. Some simple solutions include a temperature-dependent or temperature-independent fraction of input energy absorbed by a given material, while others use exponential absorption of energy with increasing depth at the material surface [119, 189], while others yet use significantly more complicated ray-tracing procedures [228, 111]. Many models include the volumetric heat sink term $q_{snk}$ as well, which has the general form

$$q_{snk} = 2 h_c (T - T_a) + \epsilon \sigma (T^4 - T_0^4)$$

(2.2)

where $h_c$ is the heat convection coefficient, $T$ a local temperature, $T_a$ the ambient temperature, $\epsilon$ the emissivity, $w_0$ the substrate out-of-plane thickness and $\sigma$ the Stefan-Boltzmann constant. The two terms on the right hand side of Eq. (2.2) characterize out-of-plane heat loss via liquid convection and radiation at the top surface of the melt pool, and have been considered in the models of [83, 109, 254], among others. Calculations of material porosity from these FE models have been performed, with several models using material parameters and/or heat sink terms that are functions of calculated porosity [44, 51]. Microstructure prediction through obtained $G$ and $V$ values [191], comparison of temperature data with experimentally obtained values [91], comparison of melt pool dimensions with experiment [109], or understanding thermal stress and strain development [99] are commonly goals of FE heat transport models of these processes. Many authors have considered heat transport for multiple layer deposition [197, 253], showing how residual heat from previous layers affects $G$ and $V$ in successive layers. Other considerations include multicomponent deposition [50],
volume shrinkage on solidification \[52, 248\], and both evaporation and vaporization processes \[248, 191\]. \[257\] compared 2D and 3D models of LENS\textsuperscript{TM} thin wall geometry builds and found reasonable agreement with experiment, with only a small overestimation of melt pool length and underestimation of melt pool depth in 2D. \[248\] found that evaporation of melt from the top surface plays a vital role in accurately modeling melt pool dimensions and capping the maximum melt pool temperature where beam energy is absorbed.

FE models considering coupled fluid and heat transport were originally developed for welding processes, and have been expanded to model AM processes. This is often performed by solving the Navier-Stokes equation for an incompressible, Newtonian melt

\[
\frac{\partial \vec{u}}{\partial t} + (\vec{u} \cdot \nabla) \vec{u} = \nu \nabla^2 \vec{u} + \vec{F}
\]  

(2.3)

along with the mass conservation condition

\[
\nabla \cdot \vec{u} = 0
\]  

(2.4)

and a reformulated version of Eq.(2.1) including a term for heat transport in the liquid via advection and replacing temperature \( T \) with an internal energy density \( E \) (as modeling of the latent heat of phase transformation and the solid-liquid phase change is performed for nearly all of the fluid and heat transport models considered, this form of the equation is generally more useful)

\[
\frac{\partial \vec{E}}{\partial t} + \nabla \cdot (\vec{u}E) = \nabla \cdot (k \nabla E) + q_{\text{src}} - q_{\text{snk}}.
\]  

(2.5)

In Eq.(2.3), \( \vec{u} \) is the fluid velocity, \( \nu \) is the kinematic viscosity (equivalent to the dynamic viscosity divided by \( \rho \)), and \( \vec{F} \) is the vector sum of any external forces applied to the melt pool. Though the fluid is often approximated as incompressible, \( \vec{F} \) can include temperature-dependent forces under the assumption that there is some small density-dependence to temperature that induces melt pool flow, but not large enough to lead to significant differences in the solution of Eq.(2.3). As in Eq.(2.1), \( q_{\text{src}} \) in Eq.(2.5) is the volumetric heat source but no longer includes the latent heat of phase transformation as that is accounted for via use of
$E$ in place of $T$. The most commonly modeled melt pool forces in welding are the buoyancy force

$$F_{\text{buoyancy}} = \rho_0 (1 - \beta (T - T_{\text{ref}})) \vec{g}, \quad (2.6)$$

and the Marangoni force

$$F_{\text{Marangoni}} = -\frac{\partial \gamma}{\partial T} \frac{\partial T}{\partial x}, \quad (2.7)$$

where $\rho_0$ is the reference fluid density, $T_{\text{ref}}$ a reference temperature, $\beta$ the coefficient of thermal expansion, $\vec{g}$ the acceleration due to gravity, and $\frac{\partial \gamma}{\partial T}$ is defined as the thermocapillary coefficient, where $\gamma$ is the surface tension. As we are assuming the flow to be incompressible, deviations in fluid density $\rho$ from $\rho_0$ are assumed to be negligible yet enough to induce melt pool motion; this is known as the Boussinesq approximation. Eq.$\,(2.6)$ implies a force opposite the direction of $\vec{g}$ if fluid is less than the reference temperature, while Eq.$\,(2.7)$ implies a force from hotter to colder fluid along a liquid interface in the $x$ direction if the thermocapillary coefficient is less than 0 (as is often the case for the Ti alloys of interest). [125] modeled the 2D fluid flow in welds resulting from the Marangoni effect and found a significant increase in melt pool length and a decrease in depth when accounting for fluid flow. Other models of coupled heat and fluid transport in welding and laser cladding include the works of [36, 90, 159]. Some models relax the approximation of the liquid-gas interface as fixed, allowing it to deform as the fluid moves [185, 245]. [170] investigated the role of weld velocity in addition to Marangoni and buoyancy forces on the melt pool shape. Tracking of the fluid-gas interface in FE models of additive processes has been performed using the level-set method in 2D [86, 189] and 3D [227, 264]. Some more recent FE models account for curvature-dependent forces around melting powder particles [82, 167, 190]. The electromagnetic force on the powder particles and liquid is another force that can be considered as well [283]. Vaporization of material directly under the incident beam may lead to formation of a keyhole, a phenomenon that can be accounted for in free-surface tracking FE models [228]. Among the present FE models of fluid and heat transport with the solid-liquid phase change and a deformable liquid-gas interface in 3D, the arbitrary Lagrangian-Eulerian (ALE3D) code used by [112, 111] has
incorporated perhaps the most broad set of physics. This model includes evaporation of metal, recoil of the liquid due to material evaporation, and individual powder particles for long line scans in 3D. Such complex models tend to require massively parallel computers and large amounts of simulation time, but can also very precisely reproduce experimental observations on melt pool shapes, porosity, and surface roughness from partially melted powder particles.

An alternative to finite element-based methods, the thermal lattice Boltzmann (TLB) method has emerged as another way to model the complex fluid and heat transport encountered in beam-based additive melt pools. 2D implementations of this model have been applied to electron beam melting [122, 119], with consideration of curvature-dependent wetting and dewetting forces around particles as well as the gas pressure on the liquid surface. The TLB model has been applied to model porosity [119] and grain structure variation with scan pattern [88]. Work has been performed to expand this model to include evaporation [115], and later to include interface recoil dependent on local composition using a multicomponent TLB method [116]. Parallelization of the TLB method has been considered [121] and applied to the problem of interest [7], though unlike with the FE models, little TLB work has been performed in 3D due to the large computational costs [156]. The TLB method in 3D may still be more efficient than models that directly solve the Navier-Stokes equations, but direct comparison of computational efficiency between the methods in 3D has not yet been performed.

### 2.2 Alloy solidification fundamentals

Alloy solidification has been modeled analytically and empirically under a wide variety of conditions due to the importance that microstructure has on material properties. The primary problem of interest in this thesis is the solidification of $\beta$-Ti alloys, a single phase solidification problem in which a two-phase region exists on the equilibrium phase diagram between the liquid and solid body centered cubic (BCC) phase. However, this analysis also
holds for other single phase solidification problems, such as the solidification of austenitic (face centered cubic or FCC) stainless steel or the FCC matrix of Inconel Ni superalloys.

Consider a fine length scale at the edge of the advancing molten pool, where the solid-liquid interface can be locally approximated as a planar front. The mode for solidification advance, even when only considering a single phase, is a complex function of the thermal conditions present, solute diffusion, and interfacial energy. As the solidification front is constrained by the process conditions governing molten pool advance, we refer to this scenario as “constrained solidification”. It is assumed as in the analysis of [128] that the temperature gradient $G$ ahead of the solidification front, as well as the cooling rate $\dot{T}$ are controlled by the melt pool conditions, and not affected by the latent heat release at the solidification front. Generally, the solidification front’s advance rate $V$ (fixed under these circumstances as the quantity $\dot{T}/G$), is not fast enough for latent heat contributions to the solidification dynamics to become important at the length scales considered. We also introduce the following simplifying assumptions in this analysis: solute diffusion in the solid can be neglected at the time scale of interest relative to the rate of solute diffusion in the liquid, the solidus and liquidus curves can be approximated as straight lines of slopes $m_L$ and $m_S$, respectively, and the liquid far from the solidification front remains at the overall alloy solute composition $C_0$.

The solute partition coefficient, $k_p$, is defined as the ratio of $m_L$ to $m_S$ with the pure solvent melting point as the reference point. As shown in Figure 2.1, a low-velocity planar solidification front, low-velocity cells, dendrites, high-velocity cells, and a high-velocity planar solidification front are all possible modes for interface advance (regions A through F in the figure, respectively). These modes are governed by different physical and kinetic processes, and lead to significant differences in solute partitioning between the liquid and solid phases.

The low velocity planar solidification front of region A involves very slow interface motion relative to the rate of solute diffusion in the liquid, and full equilibrium exists along the entire solidification front with the formation of the solidus composition for $C_0$ [215]. At faster $V$, this full equilibrium condition at the interface breaks down and a local equilibrium exists in
Figure 2.1 Modes of constrained single phase binary alloy solidification as a function of solidification velocity $V$, adapted from [239]. As the solidification front is cooled below the liquidus temperature, solute at the interface is partitioned into the solid and liquid phases as the solidification front takes the form of either low velocity cells, dendrites, or high velocity cells in regions B, C, and D, respectively. A planar solidification front, at very low $V$ as in region A or very fast $V$ as in region F, involves a flat solidification front at the overall alloy composition $C_0$. A banded microstructure as in region E involves oscillating planar front and cellular-dendritic solute morphologies. Solute partitioning and diffusion varies for each possible morphology.

its place. The temperature at the solidification front is no longer at the solidus, and while compositions along the liquidus and solidus are still formed at the solidification front itself, a region of liquid ahead of the solidification front is undercooled relative to the liquidus line (e.g., the local temperature and composition in this region are such that solid and liquid phases are favored, but only liquid exists). As shown in Figure 2.2, the finite speed of solute diffusion governed by the diffusivity $D$ in the liquid in conjunction with the imposed thermal gradient $G$ are important factors in determining whether this undercooled region exists: due to the fact that it arises from solute-related effects, this is typically termed constitutional or
solutal undercooling [53]. The critical velocity \( V_C \) for the solidification front, beyond which this constitutional undercooling exists, is given by

\[ V_C = \frac{GD}{\Delta T_0} \]

where \( \Delta T_0 \) is the equilibrium solidification range for the alloy of composition \( C_0 \) (i.e., the difference between \( T_L^{C_0} \) and \( T_S^{C_0} \)) and is equivalent to

\[ \Delta T_0 = \frac{m_L(k_p - 1)C_0}{k_p} \]

Figure 2.2 Depiction of solutal boundary layer development during constrained solidification of a binary alloy due to solute partitioning at the interface, resulting in the formation of a supercooled liquid region ahead of the solidification front where local equilibrium exists. Adapted from [53].

The limit given in Eq.(2.8) is equivalent to the limit that separates the planar solidification mode from the cellular and dendritic modes in Figure 2.1. This is due to the fact that any perturbations of this planar front due to stochastic variations in local solidification velocity will be extending away from the interface at local equilibrium and into undercooled
liquid, where there is a driving force for continued growth. Any one of such perturbations that is able to advance will lead to a pileup of solute at the base, where solute diffusion is less effective, leading to a locally smaller driving force in these regions and the formation of new perturbations adjacent to the original. As solute diffusion at cell or dendrite tips resulting from this process will be more rapid than at the planar front itself or at the perturbation bases, and the resulting regions of larger supersaturation (e.g., closer to \(C_0\) than the local temperature’s liquidus composition) will have a larger driving force for solidification, the cells and dendrites are able to outgrow the planar front and dominate the microstructure. While sharper perturbations will have more effective solute diffusion at the tips, their large interfacial area (and energy) will limit their rate of advance. More blunt perturbations will have less effective solute diffusion at the tips, but the energy penalty resulting from the creation of new solid-liquid interface will be less severe. As the radii of advancing cell or dendrite tips is closely related to the spacing of these perturbations at the unstable planar solidification front [135], mathematical modeling of this quantity is of interest. If the planar front consists of sinusoidal perturbations of wavelength \(\lambda\) and amplitude \(\epsilon_P\) small enough to have negligible effects on the solute and temperature fields, the temperature and concentration differences between the perturbation tips and depressions can be used to define an equation for the growth rate of these perturbations relative to the planar front growth velocity. From the analysis of [168], this relative perturbation growth rate \(\frac{\dot{\epsilon}_P}{\epsilon_P}\) is given by

\[
\frac{\dot{\epsilon}_P}{\epsilon_P} = \left( \frac{V}{m_L G_C} \right) \left( b - \frac{V}{D} \right) \left( - \left( \frac{2\pi}{\lambda} \right)^2 \Gamma - G - m_L G_C \right), \tag{2.10}
\]

where \(\Gamma\) is the Gibbs-Thomson coefficient (a measure of the solid-liquid interfacial energy), \(G_C\) the solute gradient in the undercooled liquid ahead of the interface (a function of solute diffusion), and the constant \(b\) from [128] is given by

\[
b = \frac{V}{2D} + \sqrt{\left( \frac{V}{2D} \right)^2 + \left( \frac{2\pi}{\lambda} \right)^2}. \tag{2.11}
\]

At very small \(\lambda\), the \(\Gamma\) term becomes very large and negative, leading to subzero values of \(\frac{\dot{\epsilon}_P}{\epsilon_P}\). As \(\lambda\) becomes very large, \(\frac{\dot{\epsilon}_P}{\epsilon_P}\) approaches zero (effectively the same as an unperturbed
planar solidification front). However, when $V$ is larger than the criteria of Eq.(2.8), a range of $\lambda$ under which $\frac{\epsilon_P}{\epsilon_p}$ is greater than zero exists, and the planar front becomes unstable. The analysis of Langer and Müller-Krumbhaar set the tip radius $R$ equal to the shortest wavelength perturbations that would cause the planar solidification front to destabilize (the “marginal stability criterion”), approximated for dendrites from the analysis of [168] as

$$\lambda_i = 2\pi \left( \frac{D\Gamma}{V\Delta T_0} \right)$$

or the geometrical mean of a diffusion length and a capillary length as per [128]. The value for $\lambda_i$ is typically also very close to the $\lambda$ that induces the maximum $\frac{\epsilon_P}{\epsilon_p}$, or the wavelength of the fastest growing planar front perturbations. This analysis also indicates an upper limit to the regime of cellular and dendritic growth where a planar front at the solidus will become stable once more, due to the larger and larger interfacial energies of finer dendrite tips dominating at large $V$ as discussed by [237]. This upper limit occurs when the solute diffusion distance (on order of $D/V$) approaches the solute capillary length (on order of $\Gamma/\Delta T_0$) and is given by [128, 132] as

$$V_A = \frac{\Delta T_0 D}{k_p \Gamma}.$$  

(2.13)

Note that in the absence of region D from Figure 2.1, $V_A$ separates the dendritic and high-velocity cellular region D from the high-velocity planar front region F. The banded region E, high-velocity planar front region F, and Eq.(2.13) will be returned to later in this subsection.

The difference between the low-velocity cells of region B and the dendrites of region C in Figure 2.1 lies in the shape and orientation of the perturbations, as low-velocity cells tend to be more coarse in length scale, lack secondary arm development, and grow parallel to the direction of $G$, while dendrites have a finer length scale, often develop secondary arms (via the same constitutional undercooling mechanism described), and grow in the preferred $<001>$ crystallographic orientation closest to the direction of $G$ [128]. However, since the formation of secondary arms (or lack thereof) depends on the exact alloy and conditions, and since the difference between the $<001>$ crystallographic orientation closest to the direction
of $G$ and the direction of $G$ itself are often nearly identical, the exact velocity dividing these structures can be difficult to determine. [242] used mathematical models and corroborating experimental results to determined the location of this transition regime as a function of $V$, $G$, and $C_0$; however, as both $V_C$ and this transition are far from the $G$ and $V$ conditions encountered during additive manufacturing solidification, they will not be discussed further. The solidification velocity range of $10^{-4}$ through $10^{-1}$ m/s, commonly encountered during alloy-based additive manufacturing, typically falls in regimes C and D of Figure 2.1, where unlike the cells of region B, the high-velocity cells of Figure 2.1 region D are simply dendrites too close together for secondary arms to fully develop. The relationship between $V$ and the steady-state undercooling $\Delta T$ at the solidification front (also known as the interfacial response function), as well as the relationship between $V$ and the spacing of primary dendrite arms along the planar front, are both of modeling interest. Both of these problems involve the approximation of the dendrite geometry (including any side branches) as a paraboloid of revolution to solve mathematically for the steady-state diffusion-limited solute field around the growing tips. The Ivantsov function, $I_v$, is commonly used [101], as in the analysis of [129] to solve for the interfacial response and primary dendrite arm spacing $\lambda_P$ (or PDAS). Several variations of the mathematical model for PDAS under these conditions exist, notably the analysis of [96] and later extension by [236]; one such equation for $\lambda_P$ is given by [128] and reproduced here as Eq.(2.14). It is noted that these mathematical models of $\lambda_P$ often do not agree with experimental results over large solidification ranges and for all alloys; this equation in particular is most valid for dendrites under “moderate growth rates” [128].

$$\lambda_P = \frac{4.3 (\Delta T_0 \Delta \Gamma)^{0.25}}{K^{0.25} \nu^{0.25} G^{0.5}}$$  \hspace{1cm} (2.14)

Use of the Ivantsov dendrite geometry and solute diffusion field with both the marginal stability criterion of Langer and Müller-Krumbhaar and the wavelength of the marginally stable wavefront of Mullins and Sekerka (Eq.(2.10)) can be used in the derivation of an interfacial response function. The analysis of Kurz, Giovanola, and Trivedi does just that,
describing the entire range of dendritic growth in terms of $R$, $V$, and composition of solid formed at the interface [130]. This model, often referred to as the KGT model in the literature, approximates binary alloy system between the bounds of Eq.(2.8) and Eq.(2.13). The operating point of a dendrite using the KGT model is given by

$$\frac{4\pi^2 \Gamma}{R^2} + \frac{m_L V C_0 (1-k_p) \xi}{D (1-(1-k_p) \nu \left( \frac{R V}{2D} \right))} + G = 0,$$

in which the function $\xi$ is given by

$$\xi = 1 - \frac{2k_p}{\sqrt{1 + \frac{4\pi D}{\lambda V^2} - 1 + 2k_p}}.$$ 

A simple approximation to the KGT model, valid outside of the rapid solidification regime ($V \leq 0.01 \text{ m/s}$), is shown by [128] as

$$\Delta T = m_L C_0 \left( 1 - \frac{1}{1 - (1-k) \pi \sqrt{\frac{V}{D \Delta T_0 k_p}}} \right).$$

In this approximation, the dendrite tip radius $R$ at steady state is predicted to be

$$R = 2\pi \sqrt{\frac{D \Gamma}{\Delta T_0 k_p V}}.$$ 

The aforementioned marginal stability criterion for determination of $R$ has been superseded by considering variation in a parameter $\sigma^*$, allowing for deviation from the parabolic dendrite shape due to interfacial energy and energy anisotropy effects [136, 239]. This “microsolubility” approach was first used for growth of dendrites in undercooled melts ($G = 0$) [141], but is commonly used in more recent derivations of interfacial response functions during directional constrained ($G > 0$ ahead of the solidification front) conditions [239]. A later extension of the KGT model allowed for modeling of alloy solidification under conditions in which solute partitioning is non-linear (i.e., $k_p$ is a function of $T$), as is often the case when considering large ranges of solute composition and phase diagrams that contain intermetallic compounds [238]. The effect of convection in the fluid on the solutal boundary layer ahead
of the growing dendritic front has also been included in numerical modeling efforts of non-rapid alloy solidification [241]. Another model of interfacial response was developed for rapid eutectic solidification [240]; this was later incorporated into a model of phase selection between dendritic and eutectic morphologies through comparing interfacial response functions for both morphologies and determining which morphology would occur at the larger interfacial temperature for a given set of conditions [131]. Multicomponent alloy solidification, in which more than one alloying addition is present, was considered in another extension to the KGT model [194]; more complex variations on this include the formation of multiple solid phases with additional interfacial response functions (for example, FCC and BCC dendrite growth in solidification of stainless steel [68]). Multicomponent solidification models can either treat the solutes as independent (including differences in $D$) and both playing a role in planar front breakdown and dendrite growth [97], or treat the segregation of one solute as dominant to approximate the system as a “pseudo-binary”, in which case segregation of the two solutes are not independent [164].

The KGT model and many of these extensions account for the dependence of $D$ on temperature over large solidification ranges, as well as the loss of local equilibrium at the solidification front during rapid solidification. The physical speed at which solute atoms in the liquid can diffuse is on order of 1 m/s [215]; once $V$ is within two orders of magnitude of this value, the assumption of $m_L$ and $k_p$ as constants from the equilibrium phase diagram needs to be revisited [132]. The solute diffusion field becomes more and more localized around the dendrite tip under these circumstances, and $m_L$ and $k_p$ become functions of $V$ itself as compositions other than that of the equilibrium phase diagram are present at the solid-liquid interface. This phenomenon is referred to as “solute trapping” as these non-equilibrium compositions are trapped by the rapidly advancing interface before enough time has passed for the solute to be partitioned into equilibrium liquidus and solidus compositions. This has been mathematically modeled in the literature [13]; in the present analysis, we use
equations for \( m_L(V) \) and \( k_p(V) \) from the analysis of [215] as

\[
\text{if } V < V_D \text{ then } k_p(V) = \frac{k_p^{eq} \left(1 - \frac{V^2}{V_D^2}\right) + \frac{V}{V_D}}{1 - \frac{V^2}{V_D^2} + \frac{V}{V_D}}
\]

\[
\text{if } V \geq V_D \text{ then } k_p(V) = 1
\]

(2.19)

and

\[
\text{if } V < V_D \text{ then } m_L(V) = m_L^{eq} \left(1 - k_p(V) + k_p(V) \ln \left[ \frac{k_p(V)}{k_p^{eq}} \right] \right)
\]

\[
\text{if } V \geq V_D \text{ then } m_L(V) = \frac{m_L^{eq} \ln \left[ \frac{1}{k_p^{eq}} \right]}{1 - k_p^{eq}}
\]

(2.20)

respectively. Here, \( V_{DI} \) and \( V_D \) are the physical rates at which solute atoms can diffuse at the interface and in the bulk liquid, respectively (on order of 0.1 and 1 m/s). Though their functional form may vary depending on the exact mathematical analysis and terms considered, \( k_p(V) \) should approach 1 and \( m_L(V) \) should approach a constant as \( V \) approaches \( V_D \). An example of this is shown in Figure 2.3; while the free energy minima compositions for liquid and solid would be formed at the interface under local equilibrium, the non-equilibrium compositions are formed instead. This is possible as per [239] if solidification still reduces the free energy of the system; in Figure 2.3 for a liquid composition less than the equilibrium value, there are a range of solid compositions that can be formed and still reduce the free energy of the system. As partitionless solidification is approaches (e.g., \( k_p(V) \) approaches 1), \( m_L \) must approach the \( T_0 \) line of Figure 2.3 as it is the warmest temperature at which partitionless solidification can occur and satisfy the thermodynamic free energy reduction constraint. In the case of some alloys with small equilibrium freezing ranges, \( V_A \) doesn’t significantly exceed 0.01 m/s and non-equilibrium effects play little role on interfacial response; fine cells governed by interfacial energy and solute diffusion in region D of Figure 2.1 transition into the planar solidification front of region E with little variation in \( \Delta T_0 \). For other alloys, the velocity-dependence of \( k_p \) and \( m_L \) may lead to a significant range of solidification velocities in which solute trapping occurs. Additionally, the variation
of $\Delta T_0$ and $k_p$ with $V$ in Eq. (2.13) will reduce the $V$ beyond which dendritic and cellular growth becomes unstable. As this introduces a range of $V$ at which no stable solidification morphology exists, a banded regime consisting of oscillation between a dendritic solidification front (governed by solute diffusion and interfacial energy) and a planar solidification front (governed by interface attachment kinetics for atoms joining the solid, containing no solute partitioning) will occur. The velocity values $V_{T_{\text{min}}}$ and $V_{T_{\text{max}}}$ of Figure 2.1 denote the lower and upper velocity limits of this metastable regime, as modeled with the banded structure interfacial response function of [34].

![Diagram](image)

**Figure 2.3** Adapted from [239]: free energy curves for a solid and liquid at temperature $T_i$ (less than the liquidus temperature $T_L$). While the most thermodynamically favorable transition for the alloy of composition $C_0$ is the formation of compositions $C_S^{eq}$ and $C_L^{eq}$ on the solid and liquid sides of the interface, respectively, this may not be possible during rapid solidification due to the finite speeds of solute diffusion and partitioning at the solidification front. Other compositions, of which $C_L$ and $C_S$ are an example, may be formed instead, as there is a range of possible phase compositions that can form and still decrease the free energy of the original system. If the liquid of composition $C_0$ is cooled below the $T_0$, it becomes thermodynamically possible to form solid at composition $C_0$ (e.g., partitionless solidification).
While completely partitionless solidification of Figure 2.1 region F, governed entirely by interface kinetics, lies outside the velocity range of interest for alloy-based additive manufacturing solidification, banded microstructures have been observed in laser processing [34, 77, 294]. [34] shows that the bands appear as oscillating light and dark regions parallel to the heat flow direction, and are shown by [294] to typically be on order of fractions of microns in width. A typical oscillatory cycle forming a banded microstructure under rapid solidification conditions is shown in Figure 2.4 [239]. As an alloy advancing with a dendritic morphology at point 4 in Figure 2.4 cools to point 1, it reaches the velocity-dependent solidus and rapidly accelerates to point 2 as partitionless solidification begins to occur at the dendrite tip, which broadens and advances as a planar solidification front. The liquidus approaches the $T_0$ line and $k(V)$ approaches 1 as per [34]; however, now growing as a planar solidification front, the interface slowly begins to heat up as it outruns the isotherms while moving at this rapid rate limited only by interface attachment kinetics [34, 294]. When point 3 is reached, the $T_0$ temperature is exceeded, and the interface rapidly decelerates to point 4, where the planar interface begins to cool again and break down into dendrites as solute segregation occurs. For $V$ values between points 1 and 3 of Figure 2.4, the metastable banded structure exists with the ratio of segregationless (planar) to segregation-laden (cellular-dendritic) regions inside of the microstructure increasing with $V$ [34]. While much of the work presented at present focuses on cellular and dendritic modes of solidification and neglects local non-equilibrium or banded morphologies, the thermodynamics and kinetics of these processes are often relevant in laser-forming processes such as Selective Laser Melting, though they would not be expected under the less rapid solidification conditions encountered in direct deposition additive processes such as LENS™.
Figure 2.4 From [239]: Schematic representation of the oscillatory cycle leading to banded microstructure formation under constrained rapid solidification of an alloy. The temperature at the solidification front would pass through points 1, 2, 3, and 4, with a dendritic front accelerating and becoming a planar solidification front with no solute partitioning between points 1 and 2, and the planar front decelerating and breaking down into cells or dendrites with solute partitioning between points 3 and 4.

A given sample of remelted alloy as produced through a beam melting process will typically consist of many grains. Within these grains there will exist sub-grain morphology (typically cells and dendrites with associated microsegregation of solute(s)) that develop via the mechanisms of the earlier discussion. The fastest growth direction for a grain consisting of aligned high-velocity cells or dendrites will be in the preferred crystallographic direction closest to the thermal gradient direction. However, in the case of changing thermal gradient directions and grains present with multiple orientations, competition between grains at the solidification front will necessarily occur. In the case of unidirectional beam scans such as welds, “preferred” orientations of grains will vary depending on local thermal gradients, and location-dependent texture can be modeled by solving the heat transport problem [194, 144]. As discussed in the previous chapter, more complex scan patterns and the dependence of advancing grain orientations on those of the previous layer (e.g., epitaxial growth) make the problem of texture and grain impingement modeling more challenging. This was explored in the work of [262], where modeling of the heat transport for various scan patterns was ap-
plied to help understand experimental differences in texture for an Ni based alloy. Another factor complicating microstructure development is the nucleation of new grains in the undercooled liquid ahead of the epitaxially-growing solidification front. While any liquid cooled below the liquidus temperature will have a bulk free energy driving force for solidification, the formation of new solid-liquid interface for small nuclei sizes creates an energy barrier that keeps nucleation from happening spontaneously in undercooled liquid. For homogenous nucleation of spherical nuclei, this barrier is such that the undercooling necessary to overcome it (typically on order of hundreds of Kelvin) is nearly always too large to reach in any practical solidification process [74]. The nucleation observed in AM processes is therefore not homogenous nucleation, but rather heterogeneous nucleation where nucleation proceeds from melt inhomogeneities. It is typically assumed that these inhomogeneities are debris of some sort, such as oxide precipitates [74], fragmented columnar grain dendrite arms that were carried into the undercooled zone [133], or partially unmelted powder particles [46]; however, there is debate in the literature regarding their exact nature in AM processes. Nevertheless, such inhomogeneities provide a solid surface from which nucleation can proceed with a dramatically reduced solid-liquid interfacial free energy penalty relative to the case of spherical nuclei. Under conditions in which sufficient nucleation events occur, growth of the nucleated grains (which ideally will have random orientations) will block the advance of the epitaxially-growing columnar grains, leading to a columnar to equiaxed transition (CET) in observed microstructure.

Whether epitaxial columnar grains or nucleated equiaxed grains dominate an alloy’s microstructure will depend on $G$ and the undercooling of the advancing solidification front. At large $V$, a larger undercooling at the columnar front is required to maintain steady-state growth and therefore the undercooled region of liquid ahead of the grains is larger; this gives more room for nuclei to grow and potentially block the columnar grains. When $G$ is small, the width of the undercooled zone is larger and growing nuclei have more time to grow. Depending on the exact solidification process and the desired microstructure, it may
be pertinent to carefully control the CET or avoid it entirely [133]. For this reason, modeling of the CET in alloy solidification has been heavily studied in the literature.

For commonly used alloys such as Ti-6Al-4V or stainless steel, approximate values of $G$ and $V$ at which columnar grains become mixed with and eventually become dominated by equiaxed grains are often known. The solidification of stray grains in the undercooled zone leading to the CET has been incorporated into models of weld texture as a function of location in weld pools, for example by [9]. A similar approach involves development of “process maps”, plotting local values of $G$ and $V$ at the melt pool boundaries determined from mathematical heat transport models into areas of columnar, mixed, or equiaxed grain structures [133, 28, 29, 75]. These process maps may also include the effect of alloy composition $C_0$ and include phase selection within $G$ and $V$ space [128, 132, 110], though the focus at present is for single-phase alloy solidification. Examples of such process maps from the literature are shown in Figure 2.5. [95] proposed a criteria that related the CET to the radius of growing nuclei in the undercooled zone: larger nuclei would be more likely to impede the progress of the columnar solidification front and yield a larger volume fraction of equiaxed grains for a given set of conditions. The calculation of these radii was based on the interfacial response function for the columnar front, $G$, the steady-state undercooling of the columnar front, and the undercooling at which the nuclei growth began to occur. This analysis was extended to include local non-equilibrium for solute and more complex versions of the interfacial response function [73]; it was found that the inclusion of non-equilibrium and kinetic undercooling components lead to the favorability of the columnar grains in a larger region of $G$ and $V$ space due to resulting changes to the interfacial response function. [158] explored the inclusion of a standard deviation to the nucleation undercooling on the CET boundary curves separating equiaxed, mixed, and columnar microstructure regions. Variation in grain structure due to process condition variation altering both the thermal gradient magnitude and direction within the molten pool in beam-based alloy additive manufacturing have also been observed experimentally [72, 88]. In addition to the CET’s dependence on thermal conditions and alloy
composition, the columnar grains’ misorientation relative to the thermal gradient direction may have an effect as well. For example, [165] found that the single crystal substrates with large misorientation to the thermal gradient direction had a higher volume fraction of equiaxed grains than the same conditions and a small misorientation. Understanding grain growth and texture development in additive processes, therefore, involves understanding both epitaxial growth and the CET for a very wide range of conditions.

![Figure 2.5 Examples of process maps for alloy solidification, showing expected structures as functions of key variables. (a) shows a simple solidification map for Ti-6Al-4V, adapted from [28], with columnar, mixed, and equiaxed dendritic grain structures under the large $G$ and $V$ conditions expected in alloy-based additive solidification. (b) shows a more complex solidification map developed by [98] for Fe-Ni, in which how the ratio $G/V$ and Ni composition can be varied to yield a variety of non-dendritic grain structures, including bands, planar front solidification, and two ($\delta$ and $\gamma$) solid phases.](image)

While the metallurgy of casting is not of direct interest, the principles and theories developed can be of use for understanding grain growth under the more extreme conditions of additive manufacturing. Research into modeling the CET and determining criteria for the occurrence of the CET as a function of variables like heat transfer coefficient and cooling rates has been also performed for casting solidification, for example in the work of [214].
Controlling grain size as a function of alloying addition via the nucleation and growth of new grains in the undercooled zone of existing grains is typically correlated with the supercooling parameter $P$,

$$P = \frac{m_L(k_p - 1)C_0}{k_p}$$

(2.21)

and the growth restriction factor $Q$

$$Q = m_L(k_p - 1)C_0.$$  

(2.22)

As clear from Eq.(2.21), $P$ is equivalent to the equilibrium solidification range of a binary alloy of composition $C_0$ (e.g., $\Delta T_0$ of Eq.(2.9)). $Q$, per [62], is equivalent to the rate of initial development of the constitutionally undercooled zone around a growing grain, and the addition of large-$Q$ alloying additions has been shown to dramatically reduce grain size in Al alloy casting. $Q$ is often preferred over $P$ for correlation with as-cast grain sizes as it typically varies over a smaller range and involves less scatter when compared to experiment [201]. Alternative definitions of $Q$ for multicomponent alloy solidification have also been established, for example by [209], where both positive and negative contributions to $Q$ are possible with alloying additions. The reason for the grain size reduction with large $Q$ lies in the development of “nucleation free zones” around growing grains due to the solutal boundary layer and resulting constitutional undercooling, zones that are reduced in size when $Q$ is large [220]. [188] analyzed the nucleation free zone for 1D, 2D, and 3D, showing the importance of precipitate shape and overlapping diffusion fields on grain sizes. Control of grain size in casting of inoculated Al melts has been shown to be possible via $G$ and $V$ variation and alloying addition. There have been attempts to develop modified versions of $Q$ for the prediction of as-welded grain size; the continuous growth restriction factor defined by [272] is one example. Alloying additions with large $Q$ such as boron and boride compounds have yielded some results in terms of grain refinement and the CET under additive thermal conditions [22, 23]. Tungsten, beryllium, and carbides have been other large $Q$ grain refinement candidates for which experimental work has been performed [21, 160,
However, there is often a large amount of uncertainty and experimental scatter when correlating experimental grain structures to solidification dynamics in alloy-based additive manufacturing.

2.3 Grid-based methods for intra-granular and inter-granular solidification modeling

In addition to mathematical models of interfacial response for dendrites, dendrite arm spacing, and the CET, several grid-based methods have been applied to various alloy solidification conditions to understand these physical processes. The most commonly used model for alloy solidification has historically been the Phase Field (PF) method. PF models rely on treating phases such as solid or liquid with continuous order parameters that vary across diffuse interfaces, and are evolved to lower the free energy of the system. The free energy functionals describe the state of the system (composition, phase, etc) at a fixed location and can come directly from thermodynamic databases such as those obtained via Calculation of Phase Diagrams (CALPHAD) to describe phase transformations. Evolution equations consist of calculating order parameter gradients and evolving order parameters to reduce the system’s free energy. The phase field method can be applied to a variety of phase transformation phenomena with free energy data for phases available. Isothermal dendritic solidification of binary alloys was considered by [260, 113], and heterogenous nucleation through PF was later introduced [213]. More complex alloy solidification conditions have been simulated through PF, some examples include multicomponent solidification [219, 63], solute trapping [26], solid-solid phase transformations [92], and solidification in the presence of convection [8, 18]. PF has also been coupled to the lattice Boltzmann (LB) method for fluid transport [30]. Recent review articles [26, 38] describe the wide array of phase transformation phenomena that have been simulated using PF methods in more depth. Application of PF specifically to thermal conditions encountered in alloy-based additive processes has
been performed [76, 3, 148], though the computational costs of solving the equations of this method often limit these simulations to small regions of actual additive melt pools or domains with representative undercooling or thermal gradient values [109]. While the method can simulate many problems with realistic thermodynamics through CALPHAD databases, the computational cost of doing so in 3D is a significant drawback. Additionally, PF solutions tend to be very dependent on handling of the phase interfaces described by order parameters that vary smoothly over computational grid points [106]. The dendritic needle network (DNN) model of [235] is one example of an alternative to the PF method for the modeling of dendritic solidification, involving rigorous tracking of tip velocities and radii for all branches of complex dendritic networks. These quantities are tracked and evolved as the tips interact with the surrounding diffusion field in the liquid, and are updated based on solute flux balances and surface tension anisotropy. The DNN model has shown agreement with PF results for the case of isothermal 2D binary alloy solidification, while retaining a significant computational advantage over the latter method [235]. The DNN model has also been applied to non-isothermal directional solidification in 2D [233] and 3D [234]. However, rigorously tracking dendrite tip velocities and radii as well as calculating solute diffusion fields for problems the size of melt pool solidification in additive problems will likely involve its own computational challenges and may not be feasible.

The cellular automaton (CA) approach to alloy solidification was originally pioneered by Gandin and Rappaz for modeling the solidification of square envelopes that approximate the shape of a grain with four-fold symmetry in 2D [195]. This was later expended on to include non-isothermal solidification of these grains using the decentered square algorithm to correct for grid anisotropy resulting from grains misaligned with the grid [69]. These CA calculations for tracking of the dendritic grain envelopes were coupled to an FE method for heat transport and included homogeneous and heterogenous nucleation of new grains in the undercooled liquid. This CAFE hybrid model was applied to 3D grain growth using a decentered octahedron algorithm for anisotropy-free growth of 3D grains with six-fold symmetry.
and large-scale solidification problems such as casting in 3D [71]. Following these original works, CA modeling of solidification split into two main development paths. The first of these continued treating grains as square or octahedral envelopes, neglecting the dendritic morphology within the grains and the solutal boundary layer around them. The growth velocity of these envelopes would be based on interfacial response functions (such as those mentioned in Section 2.2) that approximate the finer-scale dendrite tip growth behavior. The CAFE model at this scale has been applied to several materials and solidification processes including LENS\textsuperscript{TM} [79], continuous casting [244], and directional solidification [247]. More recently it has gained traction as a commonly used method for simulating the melt pool in additive manufacturing problems, as it can accurately model grains growing at multiple orientations relative to the grid direction. By neglecting the intricacies of solidification at the scale of individual dendrites as modeled in the DNN and PF methods, CA can quickly simulate these large solidification problems. A brief summary of recent work on CA and CAFE models as applied to solidification in alloy AM processes is shown in Table 2.1. Notably, [140] and [118] employed parallel computing for large-scale 3D simulations, with the latter of these large enough to look at grain growth through multiple layers with varied scan patterns. [192] used the thermal lattice Boltzmann method coupled to the CA calculations for grain growth in 2D, rather than coupling to finite element-based models for heat transport as performed in the other works. While the details of solute transport or dendrite branching may not be directly accounted for at this scale, non-equilibrium solute partitioning and/or additional solute components can be accounted for in changes to the interfacial response function [102, 282, 152]. The effect of fluid flow on the preferred grain growth directions can be accounted for by modifying local growth kinetics per [225]. The grain growth CA has recently been extended to account for 2D dynamic recrystallization processes [139, 39], solid-solid phase transformations [42], recrystallization in 2D with nucleation of new grains at existing grain boundaries [258], and 3D curvature driven grain growth [255]. Alternatives to the decentered square and octahedron algorithms for the reduction of grid anisotropy on
grain growth results have been proposed as well [155, 297], though the decentered square and octahedron algorithms remain the most heavily used.

Table 2.1  Recent application of the grain growth CA in modeling additive microstructure

<table>
<thead>
<tr>
<th>Reference</th>
<th>Material and process simulated</th>
<th>Unique computational aspects or physics modeled</th>
</tr>
</thead>
<tbody>
<tr>
<td>[282]</td>
<td>Stainless steel 316, laser deposition</td>
<td>Heterogeneous nucleation, temperature and grain growth on different grids</td>
</tr>
<tr>
<td>[259]</td>
<td>Ti-6Al-4V, single point laser cladding</td>
<td>Non-linear interpolation of finite element temperatures to regular CA grid</td>
</tr>
<tr>
<td>[227]</td>
<td>Stainless steel 304, Electron Beam Melting</td>
<td>Keyhole formation in 3D melt pool model</td>
</tr>
<tr>
<td>[295]</td>
<td>Stainless steel 316 L, Selective Laser Melting</td>
<td>2D multilayer grain growth</td>
</tr>
<tr>
<td>[192]</td>
<td>Inconel 718, Selective Electron Beam Melting</td>
<td>Particle physics at melt surface</td>
</tr>
<tr>
<td>[145]</td>
<td>2024 Al, Selective Laser Melting</td>
<td>Benchmark with experimental grain sizes</td>
</tr>
<tr>
<td>[296]</td>
<td>Ti-6Al-4V, Selective Laser Melting</td>
<td>3D multilayer grain growth</td>
</tr>
<tr>
<td>[271]</td>
<td>Ti-6Al-4V, Selective Laser Melting</td>
<td>Heterogeneous nucleation, thermal cycling</td>
</tr>
<tr>
<td>[42]</td>
<td>Ti-6Al-4V, Electron beam melting</td>
<td>Solid-solid phase transition</td>
</tr>
<tr>
<td>[140]</td>
<td>Al-7Si, Selective Electron Beam Melting</td>
<td>Large scale parallelization</td>
</tr>
<tr>
<td>[118]</td>
<td>Inconel 718, Powder bed fusion</td>
<td>3D multilayer growth varied scan pattern</td>
</tr>
</tbody>
</table>

The second of the aforementioned two development paths for the CA involves calculation and tracking of the solutal boundary layer around growing dendrites as well as the curvature of individual dendrite tips, where local growth rates of cells at the solidification front depend on interfacial energy and solute supersaturation. The temperature field is typically either prescribed (e.g., constant cooling rate with a fixed thermal gradient) or calculated using another method on a coarser grid and interpolated to the CA grid. [177] performed these calculations for dendrites aligned with the grid direction, while [19] applied this to
dendrites aligned with the nearest and next-nearest neighbor directions on 2D grids. [20] later resolved some of the mesh anisotropy issues to allow for other 2D grain orientations; others have attempted to apply the aforementioned decentered square and octahedron algorithms to growth in this model as well, but the added complication of solute redistribution and transport makes grid anisotropy more prevalent at this scale. Single dendrite growth in an undercooled melt has been verified against analytical model solutions by several authors [290, 150]. Columnar growth, as well as the CET with variation in nucleation parameters or solidification velocity, have been studied using this model in both 2D and 3D [257, 61]. Work has been performed to relate changes in side branching (e.g., cell to dendrite transitions) and dendrite shapes to changes in parameters such as $C_0$, $\Gamma$, and interfacial energy anisotropy [137, 274]. Notable extensions to this model include additional solute elements [41], inclusion of CALPHAD databases for calculations of solute partitioning [284, 223], hexagonal crystal growth [276], and non-equilibrium solidification for large melt undercooling [285]. The solidification of second solid phases, including regular eutectic growth [289, 268] and divorced eutectic growth [33, 291, 266], has been modeled and in some cases compared experimentally to lamallae spacing [289], analytical models of eutectic formation [60], and both experimental CET observations and fractions of second phases [143]. A recent work used CA to model the solid-solid phase transformation in $\beta$-Ti as the $\alpha$ phase nucleates near prior $\beta$ grain boundaries and grows to dominate room temperature microstructure for Ti-6Al-4V [42]. Though the deleterious effects of grid anisotropy and the more computationally-intensive nature of this second development path has yielded fewer direct applications to melt pool solidification in additive manufacturing, small regions of the melt pool with known thermal conditions from process models have been simulated. Notable examples include the work of [280] simulating competitive dendrite growth along the boundary of a weld pool, and the work of [273], simulating location-dependent dendrite growth in different regions of a predicted LENS™ melt pool. Despite the relative simplicity of the CA method relative to PF, comparison of the two methods for problems with analytical solutions yields only a marginal
accuracy advantage for PF in 2D and a negligible one in 3D for square and cubic crystal growth [45]. The major disadvantage of the CA relative to PF came when simulating non-grid aligned dendrite growth, particularly on the hexagonal grid [279]. To take advantage of the less orientation-dependent growth of PF and the computational efficiency of the CA, hybrid CA-PF solidification models have been developed to model solidification in casting and additive manufacturing problems [226, 227].

A notable feature of the CA model for coupled solute transport and dendritic growth is that the local nature of solidification behavior allows natural coupling with the lattice Boltzmann (LB) method for fluid flow. This allows for modeling of both diffusive and advective solute transport, and coupled LB-CA models have been applied to single and multiple equiaxed dendrite growth problems in 2D [224, 274, 103] and 3D [66, 65]. Of note are simulations of directional solidification with fluid transport, as these conditions would be likely encountered at melt pool boundaries; side branching of dendrites opposite the direction of the fluid flow as well as a “lean” of primary dendrite arms towards the direction of flow have been observed [258, 292]. This is in particular seen for the 3D simulations, as fluid can flow around the dendrites rather than being blocked by dendrites near the fluid inlet [277]. The additional of thermosolutal convection, allowing fluid near dendrites to sink or rise depending on local solute composition, was observed to facilitate secondary arm development along dendrites and lead to both local remelting and the formation of solute channels as shown in 3D simulations [278]. As with the CA simulations in the absence of fluid flow, the LB-CA simulations have been extended to incorporate CALPHAD-based solute partitioning and ternary alloy solidification modeling [223].

The kinetic Monte Carlo method (KMC) for grain growth modeling is the least detailed of the methods described in this section, but is the simplest to implement and the most computationally efficient. Probabilistic rules for grains at the solidification front to change an adjacent liquid cell at the solidification front to solid are developed based on local undercooling values, and the calculation of these probabilities and generation of random numbers
are the primary computational expenses. The method has proven able to qualitatively re-
produce AM microstructures, but may lack quantitative agreement with grain orientation
distributions due to the relatively arbitrary nature of the state change rules for “solidifying”
liquid cells [199, 198]. The KMC method for solid-solid phase transformations and grain
densification following initial grain growth from the liquid has been incorporated into hybrid
KMC-CA models of solidification [258].

The variety of methods discussed in this section span detailed mathematical formulations
at the sub-micron scale of primary and secondary dendrite tips through the centimeter scale
of representative small parts produced via AM processes. This has included hybrid models
that attempt to account for details of a finer length scale while modeling the problem as a
whole at a coarser length scale. The choice of method for solidification modeling, whether
intricate, computation heavy methods such as PF or DNN, simple and efficient methods such
as KMC, or intermediate methods such as the CA approaches will depend on which details
of solidification a researcher is interested in. The tradeoff between how much computational
speed is willing to be sacrificed to achieve a given level of accuracy will type define the
appropriate type and scale of modeling for a given solidification problem.

2.4 Literature gaps

Extensive work has been performed applying computational modeling to heat transport,
fluid flow, phase change processes, and microstructure development in welding and additive
processes. While a wide range of FE models are available for understanding process scale
phenomena in the melt pool, these models are often constrained to the use of commercial
software packages. This limits their ability to be integrated into models of microscale be-
behavior, include new physics, or alter existing approximations. While some FE codes are
available through open source software, modifying the underlying physics or making signifi-
cant changes to the structure of such codes may be difficult. At the microscale, PF models
have been extensively applied to alloy solidification over wide ranges of conditions, but com-
putational challenges limit their applicability to model large sets of 3D microstructures over entire melt pools. On the opposite end of the computational efficiency-physical accuracy spectrum, KMC application to grain growth in additive processes has proven primarily qualitative and unable to account for dendrite scale solidification kinetics. While CA models for dendrite growth and solute transport represent a compromise between PF’s thermodynamic basis and KMC’s speed, they have thus far mostly been applied to single materials with little comparison across systems and primarily been applied to solidification conditions far from those expected in additive manufacturing. The assumption of local equilibrium for solute partitioning at the interface is nearly always made, despite many additive conditions lying outside this assumption’s working range, and questions remain on how accurately growth at non-grid orientations can be modeled when local curvature is explicitly calculated and solute diffusion is considered, as both of these will strongly affect growth at this scale. Macroscale CA, despite gaining traction as a credible method for simulating large scale grain growth problems in additive manufacturing, has rarely been applied to coupled heterogeneous nucleation and growth, often does not consider fluid flow, and no comparisons to date have been made for grain growth patterns across materials systems with alloy composition and process parameters as key variables. At scales of both individual dendritic colonies and grains, significant uncertainty on quantities such as solute diffusivity, phase diagram parameters, surface energies, and nucleation densities present issues for quantitative microstructure modeling that have thus far gone mostly unaddressed.

Using the CA-based TLB method for fluid and heat transport and CA methods for intra-granular and inter-granular microstructure development, our goal is to understand the coupling between process parameters and microstructure development. Particularly, we look to develop models that can simulate the primary physics of additive manufacturing, accurately reproducing trends in microstructure with changes to alloy composition, process parameters, and material parameters such as solute diffusivity. At the intra-granular scale, this includes modeling dendrite arm spacing and microsegregation for representative thermal conditions
and fluid flow of additive processes. Exploring what the CA can and cannot model as it has been developed, and the qualitative and quantitative accuracy of what it can model, will be performed for microstructure trends regarding cellular and dendritic growth as functions of variables such as $D$ and $\Gamma$. The use of CA in non-equilibrium solidification modeling will be discussed as well. The grain scale and nucleation CA will be used for comparison of 2D and 3D models, with elucidation of interfacial response and nucleation parameters roles’ on microstructure prediction. The 2D grain growth and nucleation model will be combined with a thermal LB model for a specific AM process (LENS\textsuperscript{TM}) to link process conditions with microstructural trends, with the further goal of being able to simulate large sets of conditions quickly for designing suitable sets of process conditions and alloy compositions for predictable microstructure development. The coupled TLB-CA model would be able to serve as a tool specifically for the LENS\textsuperscript{TM} process and titanium alloy microstructures, while the grain scale CA in general would be a tool that can be applied to many AM processes and alloys with appropriate process modeling. For both the standalone CA codes for intra-granular and inter-granular growth and for the coupled TLB-CA model, an additional goal is understanding the roles of materials parameter uncertainty and statistical variation of microstructure results with ensembles of CA runs that can bound this uncertainty. This will be performed by taking advantage of parallel computing and the inherent parallelizability of CA-based methods. Chapter 3 of this work details the LB and TLB methods, explaining their equations and assumptions with sample problems. Chapter 4 discusses the CA algorithms and equations used for solidification both at the intra-granular and granular scales, with solute transport and nucleation, along with example problems and model validation at both scales. Chapter 5 then uses the TLB and granular CA methods to develop a hybrid model for coupled fluid flow, heat transport, and grain growth. The results are split into “representative” additive conditions in Chapter 6, with realistic thermal gradients and cooling rates but no melt pool geometry, and “predicted” additive conditions in Chapter 7, where the melt pool geometry and temperature fields for specific AM processes are explic-
itly calculated and used in microstructure calculations. Chapter 8 concludes this work by discussing the impact and importance of the results obtained, potential uses for the models developed, computational challenges and physical limitations of the models as written, and future work that addresses these issues.
CHAPTER 3. THE LATTICE BOLTZMANN METHOD FOR TRANSPORT PHENOMENA

3.1 Choice of method and model abilities

The lattice Boltzmann (LB) method, an evolution of the lattice gas automata, provides an alternative to solving the full Navier-Stokes equations in computational fluid dynamics problems [43, 221]. Instead of modeling the fluid as a continuous entity on a mesh as in the Navier-Stokes equations, LB treats the fluid as a series of fictitious fluid particle distribution functions at each grid point. This consideration of particle distribution functions rather than discrete particles as in the lattice gas model allows the LBM to avoid the noise inherent to the latter approach [43, 81]. As it is based on both microscale particle behavior and satisfies mesoscale conservation and evolution equations for fluid, it provides a way to bridge the two scales [180, 35]. The fact that the LB is inherently a cellular automata-based method (with the evolution of fluid distribution functions relying on local environment-based rules) makes it well suited for parallel computing; parallelization of this method has shown good scalability for flow with free surfaces [121]. As shown later in this chapter, this method can be applied to fluid transport problems as well as both coupled fluid and heat transport (thermal lattice Boltzmann) and fluid and solute transport problems. It can also be coupled with other cellular automata-based methods for simulation of other phenomena; we explore the use of LB for fluid and solute transport as well as the thermal lattice Boltzmann method coupled to solidification problems later in this thesis. Perhaps the most significant advantage of LB over Navier-Stokes solutions is its treatment of boundaries, which are handled with simple rule changes regarding the evolution of fluid distribution functions, rather than complex remeshing and the application of explicit boundary conditions. For problems such
as solidification of a melt pool, in which these boundaries can both be complex and rapidly changing, LB would be expected to yield results much faster than Navier-Stokes solvers. Starting from an adapted version of the open-source Matlab script of [84], which originally validated the converged LB solution for fluid flow through an open channel against the analytical solution and found good agreement with fluid velocity as a function of height in the channel, inlet-driven flow around a series of dendritic grain-like obstacles is considered in Figure 3.1 to highlight this ability of the LB method. The top and bottom boundaries of the domain are walls that block the advance of fluid, while the left and right boundaries are periodic (i.e., fluid that leaves through the right boundary recirculates through the left side). The left boundary is held as a constant fluid pressure driving flow from left to right through this channel; details of this boundary condition are explained in Appendix A. In the case of low obstacle density in Figure 3.1a, there are many available paths for fluid to take around the obstacles. With increasing obstacle density, as in Figure 3.1b, there are fewer paths of lesser resistance through the obstacle array; as a result, a few favored paths appear with large regions of relative stagnant fluid between these paths and in regions blocked off by obstacles. This is even more evident in Figure 3.1c, where most of the fluid gets funneled through one or two main paths across the obstacle array, leading to locally fast fluid velocity in these channels and stagnant fluid in many other regions of the liquid. These results are similar to those obtained by [224] modeling fluid flow around six growing dendrites and observing large regions of moderate flow, and [103] with fluid flowing through a field of hundreds of dendrites and a few clear channels with rapid fluid flow. In general, more time steps were needed for the fluid flow field to converge for domains with more obstacles, but all fluid flow fields in these simulations did converge provided the inlet wasn’t completely blocked by obstacles.

Unless otherwise mentioned, the parameters in Table 3.1 are used throughout this work for thermal lattice Boltzmann and lattice Boltzmann with solute transport models. Values for Ti-6Al-4V from [122, 167] were used in place of unknown values for various alloy systems.
Figure 3.1 Fluid flow driven via a pressure gradient from left to right through series of obstacles, set to resemble growing dendritic grains. (a) shows flow through multiple channels around a low density array of obstacles, while (b) and (c) show fluid flow increasingly constrained to channels of low resistance through more densely packed obstacles.

Table 3.1 Lattice Boltzmann model parameters used in the present work

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid density</td>
<td>( \rho )</td>
<td>4000</td>
<td>( \text{kg/m}^3 )</td>
</tr>
<tr>
<td>Kinematic viscosity</td>
<td>( \nu )</td>
<td>( 1.25 \times 10^{-6} )</td>
<td>( \text{m}^2/\text{s} )</td>
</tr>
<tr>
<td>Thermal diffusivity (liquid)</td>
<td>( k_L )</td>
<td>( 9.93 \times 10^{-6} )</td>
<td>( \text{m}^2/\text{s} )</td>
</tr>
<tr>
<td>Thermal diffusivity (solid)</td>
<td>( k_S )</td>
<td>( 7.83 \times 10^{-6} )</td>
<td>( \text{m}^2/\text{s} )</td>
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<tr>
<td>Heat capacity (liquid)</td>
<td>( k_L )</td>
<td>1126</td>
<td>( \text{J/kg} \cdot \text{K} )</td>
</tr>
<tr>
<td>Heat capacity (solid)</td>
<td>( k_S )</td>
<td>670</td>
<td>( \text{J/kg} \cdot \text{K} )</td>
</tr>
<tr>
<td>Solute diffusivity (liquid)</td>
<td>( D )</td>
<td>( 2 \times 10^{-9} )</td>
<td>( \text{m}^2/\text{s} )</td>
</tr>
<tr>
<td>Latent heat of fusion</td>
<td>( L )</td>
<td>290</td>
<td>( \text{J/kg} )</td>
</tr>
<tr>
<td>Thermal expansion coefficient</td>
<td>( \beta )</td>
<td>( 2 \times 10^{-4} )</td>
<td>( \text{K}^{-1} )</td>
</tr>
<tr>
<td>Thermocapillary coefficient</td>
<td>( \frac{\partial \gamma}{\partial T} )</td>
<td>( -2.7 \times 10^{-4} )</td>
<td>( \text{N/m} \cdot \text{K} )</td>
</tr>
</tbody>
</table>
3.2 Equations and assumptions

3.2.1 The lattice Boltzmann method for fluid flow

A LB time step $\Delta t$ consists of solving the discrete Boltzmann equation for the distribution functions $f_i(\vec{x}, t)$ via successive collision and propagation steps on a regular lattice with spacing $\Delta x$. For 2D modeling, we use the D2Q9 lattice of Figure 3.2. The unit vectors for velocity, $\vec{e}_i$ are given by

$$
\vec{e}_i = \begin{cases} 
(0, 0) & \text{for } i = 0 \\
(\pm c, 0) & \text{for } i = 1, 2 \\
(0, \pm c) & \text{for } i = 3, 4 \\
(\pm c, \pm c) & \text{for } i = 5 - 8 
\end{cases} 
$$

(3.1)

and the lattice weights are given by

$$
\vec{\omega}_i = \begin{cases} 
\frac{4}{9} & \text{for } i = 0 \\
\frac{1}{9} & \text{for } i = 1 - 4 \\
\frac{1}{36} & \text{for } i = 5 - 8 
\end{cases} 
$$

(3.2)

where $c$ is the speed of moving one lattice site per time step, or $\frac{\Delta x}{\Delta t}$.

![Figure 3.2](image)

Figure 3.2 The D2Q9 lattice with unit vectors $\vec{e}_i$ representing the 9 discrete lattice directions for propagation of fluid density distribution functions $f_i(\vec{x}, t)$.
During the propagation step, the particle distributions located at position $\vec{x}$ and time $t$ are moved to positions $\vec{x} + \vec{e}_i$ at time $t + \Delta t$ through the expression

$$f_i^{in} (\vec{x} + \vec{e}_i, t + \Delta t) = f_i^{out} (\vec{x}, t). \quad (3.3)$$

If the next lattice site contains no fluid, either as a boundary or part of a growing solid, the directions of the distribution functions are reversed such that they will “bounce back” into the liquid on the next time step. Superscripts “in” and “out” refer to the distribution functions going into and out of the collisions at time $t$, respectively. Following the fluid propagation step and the application of any boundary conditions (see Appendix A for more details), conservation of mass and momentum yield the macroscopic fluid density

$$\rho = \sum_i f_i^{in} (\vec{x}, t) \quad (3.4)$$

and the macroscopic fluid velocity

$$\vec{u} (\vec{x}, t) = \frac{1}{\rho} \sum_i \vec{e}_i f_i^{in} (\vec{x}, t) \quad (3.5)$$

at the lattice sites $\vec{x}$. For an fluid approximated as incompressible, variations in $\rho$ will necessarily be small. During the collision step, the fluid at each site is evolved towards an equilibrium distribution; the fluid distribution functions coming out of the collision step are described by

$$f_i^{out} (\vec{x}, t) = f_i^{in} (\vec{x}, t) + \frac{1}{\tau_F} \left( f_i^{eq} (\vec{x}, t) - f_i^{in} (\vec{x}, t) \right), \quad (3.6)$$

with the equilibrium fluid distribution functions given by

$$f_i^{eq} (\vec{x}, t) = \omega_i \rho \left( 1 + \frac{\vec{e}_i \cdot \vec{u}}{c_s^2} + \frac{(\vec{e}_i \cdot \vec{u})^2}{2c_s^4} + \frac{\vec{u}^2}{2c_s^2} \right). \quad (3.7)$$

In Eq.(3.6), the Boltzmann equation collision operator is approximated using the Bhatnagar-Gross-Krook (BGK) single relaxation time $\tau_F$ for fluid. This relaxation time is related to the kinematic viscosity $\nu$ through

$$\tau_F = 3\nu + \frac{1}{2}. \quad (3.8)$$
in these equations is the speed of sound, given by $\frac{c^2}{\gamma}$. As the method approximates an incompressible Newtonian flow, these equations are only accurate for Mach numbers less than around 0.3 (the Mach number here is defined as $\frac{|\vec{u}|}{c}$) [122, 184]. It should be noted that a body force term $\omega_i F_i$ could be added to Eq.(3.6) to simulate the effects of an external force, such as buoyancy or surface tension [81, 122]. Such forces will be necessary to simulate the highly dynamic molten pool produced by AM processes. Finally, it has been shown that the incompressible Navier-Stokes equation, Eq.(2.3), can be recovered from the BGK lattice Boltzmann evolutions following a second-order Taylor series expansion about the left side of the propagation equation (Eq.(3.3)), a Chapman-Enskog expansion for the macroscopic quantities $\rho$ and $\vec{u}$, and proper selection of the lattice weights $\omega_i$ for selection of the equilibrium distribution functions [43].

### 3.2.2 Thermal and solutal lattice Boltzmann methods

Coupled fluid flow and heat transport can be simulated via various thermal lattice Boltzmann (TLB) models. One approach involves calculating local temperatures from additional moments about the fluid density distribution functions, and is known as the multispeed approach [6]. Though the implicit assumption of fixed Prandtl number (relating the fluid viscosity to heat diffusivity) has been worked around [230], the complexity, loss of the cellular-automata transport scheme, and common numerical instability are significant downsides [85, 243]. Another approach involves hybrid lattice Boltzmann solutions for mass and momentum transport with finite element schemes providing heat transport calculations [134, 162]. A disadvantage to this approach is more difficult parallelization [243]. Perhaps the most popular thermal lattice Boltzmann approach is the multi-distribution method [37, 181], which has been the only approach to the best of the author’s knowledge applied to modeling the coupled fluid flow, heat transport, and phase change problem in AM problems [122, 156, 7]. It is assumed that while the density distribution functions represented by $f_i$ model the fluid’s mass and momentum transport, an additional set of distribution functions
$g_i$ on the same lattice represents the internal energy density $E$. The equations used typically assume that the temperature is advected by the fluid flow as a passive scalar [122]. It also assumes that viscous heat dissipation and work done by the fluid can be neglected [211]. Both of these assumptions can be corrected in more complex formulations of the multi-distribution function approach [85], and multiple relaxation times can be used in place of the single relaxation time BGK collision operator as was assumed in Eq.(3.6) in cases where high precision is required [243, 184]. The propagation equation

$$g_i^{in}(\vec{x} + \vec{e}_i, t + \Delta t) = g_i^{out}(\vec{x}, t)$$  \hspace{1cm} (3.9)

is analogous to the fluid propagation equation, Eq.(3.3), while the collision equation

$$g_i^{out}(\vec{x}, t) = g_i^{in}(\vec{x}, t) + \frac{1}{\tau_G} \left( g_i^{eq}(\vec{x}, t) - g_i^{in}(\vec{x}, t) \right) + \omega \Phi$$  \hspace{1cm} (3.10)

is analogous to the fluid collision equation, Eq.(3.6). The term $\Phi$ in Eq.(3.10) represents energy absorption in the cell (e.g., from a heat source such as an electron beam). The equilibrium internal energy distribution $g_i^{eq}(\vec{x}, t)$, in analogous fashion to $f_i^{eq}(\vec{x}, t)$, is defined as

$$g_i^{eq}(\vec{x}, t) = \omega_i E \left( 1 + \frac{\vec{e}_i \cdot \vec{u}}{c_s^2} + \frac{(\vec{e}_i \cdot \vec{u})^2}{2c_s^4} + \frac{\vec{u}^2}{2c_s^2} \right).$$  \hspace{1cm} (3.11)

The relaxation time $\tau_G$ for internal energy density is related to the thermal diffusivity $k$ through

$$\tau_G = 3k + \frac{1}{2}$$  \hspace{1cm} (3.12)

in an analogous fashion to fluid viscosity’s relationship with $\tau_F$ in Eq.(3.8). As the thermal diffusivity $k$ will depend on whether the cell is treated as solid or liquid, for problems like beam melting, solid and liquid cells will use different $\tau_G$ values. In contrast to the fluid that bounces back at solid-liquid boundaries, the internal energy undergoes collision for all lattice sites, but with a $\tau_G$ value calculated with the appropriate $k$ value for the cell’s phase. The fluid velocity $\vec{u}$ in Eq.(3.11) is equal to zero for all solid cells (where heat transport is via diffusion only), but is given by Eq.(3.5) for liquid cells (where heat transport via diffusive
and advective modes is allowed). Analogous to Eq.(3.4) for the total fluid density at a given point, internal energy density $E(\vec{x}, t)$ following propagation and collision steps at a lattice point is given by

$$E = \sum_i h_i^{in}(\vec{x}, t).$$

(3.13)

Natural convection, also known as Rayleigh-Bénard convection, is presented as an example for validation of the thermal lattice Boltzmann model. This convection occurs when fluid in a confined space is heated from the bottom, with a top boundary maintained at a constant, colder temperature. Under certain conditions, small disturbances in temperature along the bottom boundary allow this hotter (and therefore less dense) fluid to rise towards the top boundary and displace the colder fluid. The previously stationary fluid breaks down into convection cells, increasing the overall rate of heat transport between the hot and cold walls relative to that of the stationary fluid (in which case heat transport occurred via diffusion only). Although the fluid in the model presented was assumed to be incompressible, a temperature-dependent force term $F_{buoyancy}$ can be added to the fluid collision equation. This allows for the simulation of convection under the Boussinesq approximation: the density variation with temperature is neglected in the evolution equations, but accounted for in the force term. While this assumption may be somewhat dubious over the large liquid temperature ranges expected to be encountered in AM melt pools, this approximation still tends to be made in models of laser melting conditions due to its simplicity [185, 1, 11]. The buoyancy force term described by Eq.(2.6) can be modified for incorporation into Eq.(3.6) as a body force term,

$$F_i = 3\omega_i \beta \rho \vec{g}(T - T_0),$$

(3.14)

as shown by [81]. For Rayleigh-Bénard convection, the reference temperature $T_0$ is equivalent to the average of the constant temperature hot bottom boundary and constant temperature cold top boundary. The details of these boundary conditions are explained in Appendix A. The sides are considered to be periodic, i.e., fluid or heat that streams out of the left boundary re-enters through the right boundary. As this problem does not consider phase changes,
temperature-dependent specific heat capacity, or temperature-dependence of fluid density (with the exception of the aforementioned approximation for $F_{buoyancy}$), $E$ is proportional to $T$ and $T$ can be used in its place in the TLB equations. Three simulations are performed with Ti-6Al-4V materials parameters, a temperature difference $T_D$ between boundaries fixed (set between the boiling point and liquidus temperature of the alloy), and varied chamber height $H$. By varying $H$, the Rayleigh Number $Ra$ for this setup - a measure of the instability of the layer of heated fluid - is varied through the expression

$$Ra = \frac{g \beta T_D H^3}{\nu k}$$

(3.15)
given by [81]. Each chamber is initialized with a small fluctuation in temperature at the bottom boundary to break the symmetry. As shown in Figure 3.3a, a small chamber will lead to the fluctuation slowly disappearing with a stationary fluid and linear temperature gradient as expected for purely diffusive heat transport. Convection is able to develop for the larger chamber size and larger $Ra$ value of Figure 3.3b, significantly increasing the rate of heat transport from the bottom to the top wall. More turbulent convection develops for the even larger $Ra$ value of Figure 3.3c. General trends regarding $Ra$ values for the formation of convection cells as well as the onset of more chaotic flow patterns as shown here agree with the literature results for Rayleigh-Benárd convection [81, 85].

The lattice Boltzmann method can be used to model coupled fluid flow and solute transport in a very similar fashion to the passive advection TLB model. A second set of distribution functions $s_i (\vec{x}, t)$ is used to describe solute concentration, and by performing collision and propagation steps consecutively for both fluid and solute, coupled transport of both quantities can be modeled. The propagation step for solute distribution functions is described by

$$s_i^{in} (\vec{x} + \vec{e}_i, t + \Delta t) = s_i^{out} (\vec{x}, t),$$

(3.16)

and the collision step and equilibrium distribution function for solute by

$$s_i^{out} (\vec{x}, t) = s_i^{in} (\vec{x}, t) + \frac{1}{\tau_s} \left( s_i^{eq} (\vec{x}, t) - s_i^{in} (\vec{x}, t) \right) + \omega_i \Delta S$$

(3.17)
Figure 3.3  Natural convection in Ti-6Al-4V with Rayleigh Numbers of (a) 20, (b) 20,000, and (c) 20,000,000; in (a), the low Rayleigh number did not allow for the development of convection, but for the larger Rayleigh numbers of (b) and (c), increasingly more rigorous convection was able to develop, in turn increasing the rate of heat transport between the hot lower wall and cold upper wall.

and

\[ s^e_i (\vec{x}, t) = \omega_i S \left( 1 + \frac{\vec{c}_i \cdot \vec{u}}{c_s^2} + \frac{(\vec{c}_i \cdot \vec{u})^2}{2c_s^4} + \frac{\vec{u}^2}{2c_s^2} \right), \quad (3.18) \]

respectively. Here, \( \Delta S \) is a term representing the change in solute concentration over the time step. In our model, this is calculated using the CA described in the next chapter. The macroscopic solute concentration at a given point (analogous to \( E \) in TLB) is calculated as

\[ S = \sum_i s^{in}_i (\vec{x}, t). \quad (3.19) \]

The solute relaxation parameter \( \tau_S \) (a function of solute diffusivity \( D \)) is given by

\[ \tau_S = 3\nu + \frac{1}{2}. \quad (3.20) \]

If the velocity field is set to zero everywhere, purely diffusive solute transport can be considered, while if the solute diffusivity is very small, \( \tau_S \) approaches 0.5 (very slow relaxation towards equilibrium) and purely advective solute transport can be modeled [11]. It is assumed that these solute distribution functions are passively advected by the fluid; they are
coupled to the fluid flow problem via the velocity $\vec{u}$ at each grid point and calculation of $s_i^{eq}(\vec{x}, t)$ in Eq.(3.18), but do not in turn affect the fluid flow field through additional body force terms. For a system in which the solute and solvent atoms have disparate density values, liquid density will vary based on the local amount of alloy addition present. Under those conditions this assumption will likely need to be revisited with a concentration-dependent force term added to the fluid collision equation (Eq.(3.6)).

In both the thermal and solutal LB methods, there is a range of $\Delta x$ and $\Delta t$ values outside of which either $\tau_F$ or $\tau_H/\tau_S$ will be too large; for a given $\Delta x$, $\Delta t$ must be carefully selected such that these relaxation parameters lead to a stable simulation. Either through using materials systems with thermal diffusivity, solute diffusivity, and kinematic viscosity within a few orders of magnitude (yielding similar $\tau_F$, $\tau_G$, and $\tau_S$ values [293] or through careful selection of $\Delta x$ and $\Delta t$ such that all phenomena occur at a reasonable rate [116], coupled fluid, heat, and solute transport can be simulated on the same grid. However, as solute diffusion and partitioning at the solidification front is generally orders of magnitude slower than the relaxation of fluid and energy fields and modeling the growth of individual dendrite tips under these conditions typically requires sub-micron scale $\Delta x$, these problems are generally better solved separately or with a multi-grid approach.
CHAPTER 4. CELLULAR AUTOMATA FOR ALLOY SOLIDIFICATION

4.1 Choice of method and model abilities

Of the three main classes of solidification models: Phase Field (PF), Cellular Automata (CA), and Kinetic Monte Carlo (KMC), Phase Field incorporates the most realistic and adaptable physics, but involves the most time-consuming set of equations to solve (especially in 3D). Kinetic Monte Carlo involves very simple and locally-based rules for the evolution of grain structures, but cannot model the dendritic growth inside of grains and is the least physical of the models. Cellular Automata-based methods for modeling solidification, as discussed in Chapter 2, can be applied both at the scale of individual dendrites (where its accuracy compares favorably to PF results) and at the scale of grain envelopes to model larger scale grain structures. It involves more physically-based capture rules than KMC, while retaining its computational efficiency and scalability. The ability of CA-based methods at either scale to take a complex set of physics down to a set of physically-based local rules for the evolution of a solute field, a dendrite tip, or a grain boundary, that can be parallelized for runs with large system sizes and ranges of conditions for experimental comparison, makes it an attractive choice for modeling solidification for additive processes. As there are many potential sources of uncertainty in the development of additive microstructures, especially with regard to variables such as nucleation rates and interfacial energies, the ability for CA-based solidification models to iterate through a wide range of possible input conditions to gauge uncertainty in final microstructure is of interest. Our goal is to use these methods to predict general trends in quantities such as dendrite arm spacing or grain aspect ratio, comparing them to other solidification models or experimental data trends, while also
exploring the limiting conditions of the models accuracy and proposing model extensions that could alleviate those limits.

Given that CA-based solidification modeling at the scale of individual dendrites and solute fields (referred to as the “Intragranular” model) and at the scale of grain envelopes (referred to as the “granular” model) make different assumptions and use different equations, they will be discussed separately. Subsection 4.2.1 will discuss the intragranular model (applied here only in 2D), while Subsection 4.2.2 will discuss the granular model (both the 2D “decentered square” and 3D “decentered octahedron” algorithms). The granular model includes an algorithm for the nucleation of new grains, which will be discussed in Subsection 4.2.2 as well. Section 4.3 contains sample problems to demonstrate the application of the models to some standard problems. In Subsection 4.3.1, the intragranular model is validated against the analytical solution for the case of a single isolated dendrite tip growing perpendicular to an applied thermal gradient. In Subsection 4.3.2, the intragranular model is then coupled to the lattice Boltzmann method for fluid and solute transport (see Subsection 3.2.2) to simulate growth of a single dendrite in an undercooled melt. Finally, the granular model in 2D and 3D is used to model the columnar to equiaxed transition for constrained grain growth under varied thermal conditions in Subsection 4.3.3.

4.2 Equations and assumptions

4.2.1 Intragranular solidification and solute transport

The intragranular solidification model requires coupling to a model of solute transport in the liquid (solute transport in the solid is almost always assumed to be negligible on the time scale of interest). In this case, we couple the model to the lattice Boltzmann method as described in Chapter 3; fluid streaming and collision can be considered for coupled diffusive and advective transport of solute, or neglected for purely diffusive solute transport. The solute source/sink term $\Delta S$ from Eq. (3.17) and local cell solute concentration in the liquid
phase $C_L$ from Eq. (3.19) link the two models; each time step, $\Delta S$ from the equations in this section is fed to Eq. (3.17) while the calculated $C_L$ of Eq. (3.19) affects the CA calculations for solidification. Both the LB and CA models use the same grid and time step, though it has been demonstrated that the CA can use a larger time step for slower solidification to speed up the calculations \[66\]. For now, we will make the assumption that all growing solidification structures have “preferred” growth directions (the 4 $<01>$ directions in 2D) aligned with the grid directions such that the problem of grid anisotropy is averted. In the case where this is not possible, e.g., solidification of dendrites belonging to grains with misaligned orientations, some modifications are made to the equations of this section; these modifications are detailed in Appendix B and used in the results of Section 6.2.

All cells on the grid are one of three types: solid, interface, or liquid. The solid fraction of a cell, $f_s$, of a liquid cell is 0, between 0 and 1 for an interface cell, and 1 for a solid cell. There are two primary rules: first, while an interface cell changes its type to solid upon reaching $f_s = 1$, a solid cell cannot transform back into interface or liquid (no remelting is considered). Second, a solid cell cannot have any of its four nearest neighbors be liquid; when an interface cell transforms into solid, any adjacent liquid cells must transform into interface. Each cell’s solute concentration, $C$, is a $f_s$-weighted average of its liquid solute concentration $C_L$ and its solid solute concentration $C_S$ through the expression

$$C = C_L(1 - f_s) + C_S f_s.$$ \hspace{1cm} (4.1)

As $C$ values aren’t used in the calculations themselves but typically printed as code output, this calculation is only performed at the end of a simulation and $C$ is not tracked in the code’s memory throughout. Other than $f_s$, $C_L$, and $C_S$, cells of type interface have additional variables that are re-calculated each time step. These variables are local interface curvature $\kappa$, and local interface orientation, $\phi$, and they are calculated using the local $f_s$ value of the cell in question as well as $f_s$ values of nearest and next-nearest neighbors on the grid using

$$\kappa = \left( \left( \frac{\partial f_s}{\partial x} \right)^2 + \left( \frac{\partial f_s}{\partial y} \right)^2 \right)^{-3/2} \left( 2 \frac{\partial f_s}{\partial x} \frac{\partial f_s}{\partial y} \frac{\partial^2 f_s}{\partial x \partial y} - \left( \frac{\partial f_s}{\partial x} \right)^2 \frac{\partial^2 f_S}{\partial y^2} - \left( \frac{\partial f_s}{\partial y} \right)^2 \frac{\partial^2 f_S}{\partial x^2} \right).$$ \hspace{1cm} (4.2)
and

\[ \phi = \cos^{-1} \left[ \frac{\partial f_s}{\partial x} \left( \left( \frac{\partial f_s}{\partial x} \right)^2 + \left( \frac{\partial f_s}{\partial y} \right)^2 \right)^{-1/2} \right], \tag{4.3} \]

respectively. In Eq. (4.2) and Eq. (4.3), \( f_s \) gradient values (e.g., \( \frac{\partial f_s}{\partial y} \)) are calculated using finite difference approximations. Once these quantities are calculated for all interface cells, the next step is to calculate the cell’s local equilibrium liquidus composition, \( C_{eq}^L \), through

\[ C_{eq}^L = \frac{T_{local} - T_{Ti}^m}{m_{eq}^L} + \kappa \Gamma (1 - \delta \cos(4(\phi - \theta))) \tag{4.4} \]

As we are not coupling this CA with a heat transport method, the local temperature \( T_{local} \) will be imposed externally and not affected by heat transport nor latent heat release on the CA grid. Eq. (4.4) shows that this calculation is not just a function of the cell’s undercooling relative to the liquidus temperature at local liquid solute composition \( C_L \) (\( T_{Ti}^m \) is the melting point of pure Ti) but is also dependent on interfacial energy (the right hand term). Here, \( \Gamma \) is the Gibbs-Thomson coefficient, a measure of the strength of the interfacial energy, \( \delta \) is a measure of the strength of the interfacial energy anisotropy, and \( \theta \) is the grain’s preferred orientation (always equal to zero here). The term \( 1-\delta \cos(4(\phi - \theta)) \) locally modifies the magnitude of this interfacial energy term such that it is somewhat larger if the interface’s orientation is more misaligned with the grid, or smaller if it is close to the alignment of the grid [274, 103]. The “4” within the \( \cos \) function accounts for the four-fold symmetry of cubic (e.g., FCC or BCC) crystal growth, though this term itself could be modified for other crystal symmetries or more complex interfacial energy anisotropies. Overall, the aforementioned interfacial energy term in Eq. (4.4) serves to shift the calculated value of \( C_{eq}^L \) towards \( C_L \) in regions of high local interfacial energy (due to curvature or interfacial energy anisotropy). Doing so reduces the local supersaturation and therefore the driving force for solidification, effectively mimicking the role of interfacial undercooling on solidification and controlling the dendrite tip radius and shape to a degree.

Based on the local supersaturation, \( C_{eq}^L - C_L \) relative to the maximum possible supersaturation for composition \( C_0 \), \( C_{eq}^L (1 - k_p^eq) \), a local change in \( f_s \) for interface cells can be
calculated through
\[ \Delta f_s = \frac{C_{eq}^L - C_L}{C_{eq}^L (1 - k_{eq}^p)}. \] (4.5)

While this quantity could technically be negative, we are not considering melting and any sub-zero \( \Delta f_s \) is not added to an interface cell’s \( f_s \) value. Additionally, while this quantity could reach as large as 1 (corresponding to solidification at the solidus, and a very large driving force for solidification), \( \Delta f_s \) values are capped at 0.1 prior to adding them to local \( f_s \) values to avoid cell capture-dependence on the iteration order through interface cells. This new increment of solid calculated using Eq.(4.5) will have a composition of \( C_{eq}^S \), as calculated via the phase diagram and using the expression
\[ C_{eq}^S = k_{eq}^p C_{eq}^L. \] (4.6)

If the solid within a given interface cell had solute composition \( C_S^* \) and solid fraction \( f_s \) at the previous time step, the cell’s solute composition in the solid following addition of increment \( f_s \), \( C_S \), is updated accordingly per
\[ C_S = \frac{f_s C_S^* + \Delta f_s C_{eq}^S}{f_s + \Delta f_s}. \] (4.7)

Finally, the solute composition change in the cell’s liquid, \( \Delta S \), is calculated based on the amount of solidification that occurred and the compositions formed via
\[ \Delta S = C_L (1 - k_{eq}^p) \Delta f_s. \] (4.8)

To reproduce naturally occurring local variation in solidification rate, the \( f_s \) value at which solidification of a cell is complete (e.g., it transforms into type solid) can be randomly selected for each interface cell to be some \( f_s^{\text{threshold}} \) value between 0.975 and 1.025. While the true \( f_s \) value used in any calculations involving this cell will be equal to \( f_s / f_s^{\text{threshold}} \), which is always between 0 and 1, the introduction of non-uniform values of solid fraction at which solidification is complete is necessary to reproduce natural stochasticity and the development of secondary dendrite arm perturbations.
For some simulations, the solidification velocity will be such that use of \( m_{eq}^L \) and \( k_{eq}^p \) in these equations is no longer a valid approximation, due to deviation from the equilibrium phase diagram. Under these circumstances, velocity-dependent solute partitioning coefficient \( k_p(V) \) and liquidus slope \( m_L(V) \) are needed in place of the equilibrium values, and Eq.\((2.19)\) and Eq.\((2.20)\) are used to calculate these quantities as functions of local calculated \( V \) values. For conditions in which solute partitioning depends on \( V \), consider an interface cell A, with some local solidification velocity \( V_{A_{local}} \) used to calculate local values for \( m_L(V) \) and \( k_p(V) \) during its solidification. When cell A transforms from interface to solid, a velocity \( V_{A_{calc}} \) can be calculated based on the time step \( t_S \) at which solidification started in the cell and the time step \( t_F \) at which solidification finished in the cell through

\[
V_{A_{calc}} = \frac{\Delta x}{\Delta t(t_F - t_S)}. \tag{4.9}
\]

If the solidification of cell A forced the transformation of an adjacent liquid neighbor, cell B, into a new interface cell, the local velocity \( V_{B_{local}} \) used to calculate \( k_p(V) \) and \( m_L(V) \) for cell B is given by the expression

\[
V_{B_{local}} = \frac{V_{A_{local}} + V_{A_{calc}}}{2}. \tag{4.10}
\]

Averaging \( V_{A_{local}} \) and \( V_{B_{local}} \) rather than simply setting \( V_{B_{local}} \) to \( V_{A_{local}} \) is done to minimize the spurious oscillations in solidification velocity that occur as a natural consequence of having local solidification behavior depend on the rate of solidification itself.

When selecting cell sizes (\( \Delta x \)) for this model, the primary concern is the need for smaller \( \Delta x \) at faster solidification rates \( V \). This is needed to accurate model dendrite tip curvature through Eq.\((4.2)\), as dendrite tip radii \( R \) decreases with \( V \). The prediction of \( R \) through Eq.\((2.18)\) is used to set a maximum bound for an acceptable \( \Delta x \) for a given simulation, though \( \Delta x \) less than 1 \( \mu m \) were never used regardless of \( R \). It was found that with larger \( \Delta x \), calculated dendrite curvature values on the grid were not accurate, leading to inaccurate undercooling values and unstable growth of secondary perturbations on the original dendrite surface. Unless otherwise mentioned, the smaller of 1\( \mu m \) and calculated \( R \) is set as a \( \Delta x \) value.
for each simulation. The time step $\Delta t$ must be selected such that it is not too large (too few time steps for a cell to solidify, leading to pileup of error) nor too small (for computational efficiency). The time step is set using the expression

$$\Delta t = \frac{\Delta x G}{N \dot{T}},$$  \hspace{1cm} (4.11)

where $N$ is the number of cycles taken for a cell to solidify at steady state (as $V$ is equivalent to $\dot{T}/G$) and should be between 40 and 400. However, to avoid error in calculation of the solute field in the liquid surrounding the dendrite, $\Delta t$ must also be selected such that the solute relaxation parameter from the LB calculations, $\tau_S$ is not too close to 0.50. Such over-relaxation of the solute field in the LB model is known to cause inaccuracy or instability in the solute fields for some situations [288]. When possible, $\Delta t$ is selected such that both Eq.(4.11) and $\tau_S > 0.525$ are satisfied. It is not possible to meet both criteria at $\Delta x$ values less than around 0.1 $\mu$m (required to resolve extremely fine cell or dendrite tips), in which case $\Delta t$ is selected to come as close to satisfying the second criteria as possible. If it is possible to meet both criteria, $\Delta t$ is selected using the chosen $\Delta x$ and $N = 50$, unless otherwise mentioned. We note that this implementation of the model has also been applied to dendrite growth at non grid-aligned orientations by combining the capture rules with the algorithms described in the following section [175, 40, 150], but as our focus is the application of this method for simulating constrained dendrite growth perpendicular to an applied thermal gradient in the grid direction, this is not performed here. All dendrites simulated with this method are assumed to be part of the same grain (e.g., one dendritic colony) unless otherwise mentioned. Additionally, the parameters in Table 4.1 are used with this CA unless otherwise mentioned, though several of these parameters will be varied in various results sections to explore their role on microstructure.
Table 4.1 Standard intragranular CA model parameters used in the present work, unless otherwise stated. The equilibrium liquidus and solidus slopes for all phase diagrams are approximated as constants

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
<th>Source</th>
</tr>
</thead>
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<tr>
<td>Solute diffusivity</td>
<td>D</td>
<td>$2 \times 10^{-9}$</td>
<td>m$^2$/s</td>
<td></td>
</tr>
<tr>
<td>Gibbs-Thomson coefficient</td>
<td>$\Gamma$</td>
<td>$5 \times 10^{-7}$</td>
<td>m·K</td>
<td></td>
</tr>
<tr>
<td>Surface energy anisotropy coefficient</td>
<td>$\delta$</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Solute diffusive speed at interface</td>
<td>$V_{DI}$</td>
<td>0.1</td>
<td>m/s</td>
<td>[215]</td>
</tr>
<tr>
<td>Solute diffusive speed in bulk liquid</td>
<td>$V_D$</td>
<td>1</td>
<td>m/s</td>
<td>[215]</td>
</tr>
<tr>
<td>Equilibrium liquidus slope:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-W</td>
<td>$m_{eq}^L$</td>
<td>59.40</td>
<td>K/(mol% solute)</td>
<td>[104]</td>
</tr>
<tr>
<td>Ti-Cu</td>
<td>$m_{eq}^L$</td>
<td>-18.41</td>
<td></td>
<td>[246]</td>
</tr>
<tr>
<td>Ti-Ni</td>
<td>$m_{eq}^L$</td>
<td>-26.590</td>
<td></td>
<td>[4]</td>
</tr>
<tr>
<td>Equilibrium solute partition coefficient:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-W</td>
<td>$k_{eq}^p$</td>
<td>3.56</td>
<td></td>
<td>[104]</td>
</tr>
<tr>
<td>Ti-Cu</td>
<td>$k_{eq}^p$</td>
<td>0.432</td>
<td></td>
<td>[246]</td>
</tr>
<tr>
<td>Ti-Ni</td>
<td>$k_{eq}^p$</td>
<td>0.333</td>
<td></td>
<td>[4]</td>
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</tbody>
</table>

4.2.2 granular solidification and nucleation

The decentered square algorithm for 2D growth and decentered octahedron algorithm for 3D growth are designed to model grain “envelopes”, with some approximation of the dendrite-scale detail within the envelopes. This makes the assumption that the length scale of solute transport at the solid-liquid interface is on order of the grid spacing, and therefore melt inhomogeneities arising from microsegregation at temperatures within the alloy’s equilibrium freezing range would be confined to the liquid immediately adjacent to the solidification front. Rather than treating the growing grains as series of dendrites with unique misorientations, solute distribution, and side branching patterns, these algorithms treat the four-fold symmetry of FCC or BCC growth in 2D as squares and the six-fold symmetry of cubic growth in 3D as octahedra. Though calculations using this approximation are more simple than those employed in the CA of Subsection 4.2.1, the approximation obscures mor-
phological details of the solidification front within the square or octahedral envelopes. The growth of these envelopes, whose orientations represent grain orientations, must be independent of the grid’s orientation. To accomplish this, three cell types are introduced: liquid cells, active cells, and inactive (solid) cells. Each active cell has its own “decentered” square or octahedron, at a misorientation relative to the grid direction that represents the grain’s overall orientation. The half-diagonal length of each active cell’s square or octahedron, defined as $L_d$, is updated each time step as $f_s$ values were for interface cells in the previous subsection. $\Delta T_{\text{cell}}$, the cell’s undercooling relative to the alloy’s liquid temperature, is used as an input to an interfacial response function that approximates the finer scale dendrite tip growth behavior inside of the envelope. In general, this relationship can come from results of a finer-scale solidification model, experimental observations, or other approximations; in this case, we will use the KGT approximation to constrained binary alloy solidification as discussed in Section 2.2. The relationship between solidification velocity and undercooling is fit to a cubic polynomial to calculate the dimensionless change in cell half-diagonal length $L_d$ over a time step via

$$
\Delta L_d = \frac{\Delta t}{\Delta x} \left( A\Delta T^3 + B\Delta T^2 + C\Delta T + D \right).
$$

(4.12)

In Eq.(4.12), constants $A$, $B$, $C$, and $D$ will depend on the alloy and polynomial fit to the approximated KGT interfacial response function, while $\Delta t$ is the time step and $\Delta x$ the cell size (1 $\mu$m unless otherwise mentioned). Note that while adjacent cells may be part of the same grain (in which case their squares or octahedra have the same orientation relative to the grid), their half-diagonals grow independently based on local $\Delta T_{\text{cell}}$ values. As with calculation of $\Delta f_s$ from Eq.(4.5), the value of Eq.(4.12) must be greater than 0 as remelting is not considered and is capped at 0.1 to avoid cell capture dependence on the iteration order through active cells. $\Delta t$ is selected by solving Eq.(4.11) with $N = 25$.

First, we detail the capture procedure for the decentered square algorithm. An active cell has both a physical “center” as well as center coordinates for its decentered square, which may or may not be the same. This is schematically illustrated in Figure 4.1a, where the
active cell with physical center $C_A$ has an associated decentered square with center $S_A$ and four half-diagonal lengths $L_A$. The square, of orientation $\theta$ relative to the grid direction, gets larger each time step as the half-diagonal length grows. When the square’s boundaries overlap the physical center of an adjacent liquid cell, as in Figure 4.1b with the cell center $C_B$, that liquid cell is captured by the growing grain, becoming active and receiving its own decentered square also at orientation $\theta$. The decentered square center coordinate and initial half-diagonal length, however, still require calculation. If the closest corner of the captured cell center to the original decentered square is $C_1$, and the next-closest corner captured cell center to the original decentered square is $C_2$ (as labeled in Figure 4.1b), the lengths $L_1$ and $L_2$ can be defined as the distances between the captured cell’s physical center and these two corners. The captured cell’s decentered square half-diagonal length is given by

$$L_{new} = \sqrt{2}(\min\left(\frac{L_1}{\sqrt{2}}, \sqrt{2}\Delta x\right) + \min\left(\frac{L_2}{\sqrt{2}}, \sqrt{2}\Delta x\right)),$$

which is the starting value for $L_B$ in Figure 4.1c. The center of this new decentered square is placed such that one corner overlaps the closest corner of the original active cell’s decentered square (i.e, $C_1$). Given the half-diagonal constraint of Eq. (4.13) and the square orientation $\theta$, the new decentered square’s center coordinates (i.e., $S_B$ in Figure 4.1c) can be calculated. It is noted that this procedure may place the new active cell’s decentered square center coordinates such that they do not overlap with the physical cell center, or may even lie outside of the physical cell boundaries entirely. Once the new active cell’s decentered square coordinates are calculated, “critical” half-diagonal length values needed to capture each of its remaining liquid neighbors are calculated. If this decentered square’s half-diagonal length reaches one of these critical half-diagonal length values at some later time step and the corresponding neighboring cell is still liquid, this capture procedure repeats itself. If an active cell no longer has any liquid neighbors, it becomes inactive and its decentered square growth is no longer tracked. It is also noted that active cells will always separate liquid and inactive cells through the first and second nearest neighbors. More details about the
decentered square capture procedure, including diagrams, can be found in [192] and in the original work [69].

Figure 4.1 Schematics of a capture event using the decentered square algorithm. (a) An active cell with center coordinates \( C_A \) and associated square with center at \( S_A \) and half-diagonal length \( L_A \) grows along the four square directions (blue arrows) oriented with angle \( \theta \) relative to the grid direction. (b) \( L_A \) reaches a critical value \( L_A^{\text{crit}} \), at which one of the square sides engulfs the center coordinates \( C_B \) of an adjacent liquid cell. The closest and next-closest corners of the original decentered square to \( C_B \) are calculated as \( C_1 \) and \( C_2 \), respectively, and the lengths \( L_1 \) and \( L_2 \) are defined. (c) Using \( \theta \), \( L_1 \), and \( L_2 \), the now activated liquid cell’s square center (\( S_B \)) and initial half-diagonal length (\( L_B \)) are calculated such that the new active cell’s square overlaps the nearest corner of the old active cell’s square.

While the decentered octahedron algorithm is more complex, the general rules are the same. General schematics for the capture process of a liquid cell with center coordinates \( C_B \) by growth of an interface cell with center coordinates \( C_A \) are shown in Figure 4.2, while more details can be found in the work in which the algorithm was originally developed [70]. Rather than being characterized by a single misorientation variable \( \theta \), active cells each have an octahedron characterized by a set of three Euler angles. The center of the active cell \( C_A \) may or may not be the same as the center of the associated octahedron \( O_A \). From the octahedron’s orientation, six “grain unit vectors” (red arrows in Figure 4.2) are calculated to represent the six growing half-diagonals of the octahedron (which start at length \( L_A \) in Figure 4.2a). When \( L_A \) reaches some critical half-diagonal length at which the active cell’s
octahedron engulfs the center of a liquid cell (for example, when $L_A$ reaches $L_A^{\text{crit}}$ in Figure 4.2b, the liquid cell center $C_B$ is located on the octahedron face), that liquid cell becomes a new active cell. The new interface cell then obtains its own decentered octahedron with the same orientation (same grain unit vectors) as the original. The initial half-diagonal length of this new octahedron, $L_B$, is calculated through several steps. First, the equation of the original octahedron’s face that captured the new physical cell center is determined; this face is an equilateral triangle, bounded by three of the grain unit vectors as highlighted in red in Figure 4.2b and isolated in Figure 4.2c. The coordinates of this face’s three corners in order of proximity to the physical cell center of the captured cell are then calculated as $S_1$, $S_2$, and $S_3$. The projections of the physical cell center of the captured cell ($C_B$) on the segments $S_1S_2$ and $S_1S_3$ are used to define points $I$ and $J$, respectively. Finally, the lengths of segments $IS_1$, $IS_2$, $JS_1$ and $JS_2$ are calculated and fed into

$$L_{12} = \frac{1}{2} \left[ \left( \min \left( \frac{IS_1}{\sqrt{3}}, \sqrt{3}\Delta x \right) \right) + \left( \min \left( \frac{IS_2}{\sqrt{3}}, \sqrt{3}\Delta x \right) \right) \right]$$ \hspace{1cm} (4.14)$$

and

$$L_{13} = \frac{1}{2} \left[ \left( \min \left( \frac{JS_1}{\sqrt{3}}, \sqrt{3}\Delta x \right) \right) + \left( \min \left( \frac{JS_3}{\sqrt{3}}, \sqrt{3}\Delta x \right) \right) \right],$$ \hspace{1cm} (4.15)$$

which in turn are used to calculate the initial half-diagonal length of the captured cell’s decentered octahedron through the expression

$$L_{\text{new}} = \sqrt{2} \cdot \max (L_{12}, L_{13}). \hspace{1cm} (4.16)$$

The calculated $L_{\text{new}}$ value is the initial octahedron half-diagonal length $L_B$ for the new active cell’s octahedron, as shown in Figure 4.2d. As with the decentered square algorithm, the new octahedron is placed such that one corner overlaps with the closest corner of the capturing cell’s octahedron ($S_1$); this condition along with the calculated $L_{\text{new}}$ value constrains the coordinates of the new active cell’s octahedron center, $O_B$. Again, this octahedron center may or may not align with the physical center of the active cell $C_B$, and may lie outside the cell altogether. Using the grain unit vectors and the new octahedron center, critical half-diagonal length values for the capture of any adjacent liquid neighbors (through third nearest
neighbors, totaling 26) are calculated. If the octahedron’s half diagonal length exceeds one of these critical half diagonal lengths and the corresponding neighbor cell is still liquid, this capture procedure is repeated.

Figure 4.2 Schematics of a capture event using the decentered octahedron algorithm. (a) An active cell with center coordinates $C_A$, associated octahedron center $O_A$, and half-diagonal length $L_A$ grows along the six unit vector directions (red arrows). (b) $L_A$ reaches a critical value $L_A^{crit}$, at which one of the octahedron faces (highlighted in red) engulfs the center coordinates $C_B$ of an adjacent liquid cell. (c) The three corners of the capturing face of the original active cell’s octahedron are labeled as $S_1$, $S_2$ and $S_3$ in order of their proximity to $C_B$, with points $I$ and $J$ calculated through projection of $C_B$ onto the face edges $S_1S_2$ and $S_1S_3$. (d) Using the calculated coordinates of the face corners and cell center projections, the now activated liquid cell’s octahedron center ($O_B$) and initial half-diagonal length ($L_B$) are calculated such that the new active cell’s octahedron overlaps the nearest corner of the old active cell’s octahedron.

It should be noted that for both of these algorithms, the interface between two grains will necessarily be jagged; such a representation of a grain boundary, while reasonable as simple simulation output, may need to be modified when using these microstructure results as input in a micromechanics code to estimate the microstructure’s mechanical properties. While information on quantities like dendrite arm spacing or microsegregation both within
grain envelopes and at grain boundaries is lost using this method, these assumptions do allow for realistic grain growth and large-scale microstructure simulation. Additionally, nucleation in the undercooled liquid cells for both the decentered square and octahedron algorithms can be considered, where a nucleation event consists of changing a liquid cell to active with a new decentered square or octahedron of random orientation. We apply the method of [273], among others, in which a Gaussian nucleation density distribution as a function of undercooling is parameterized by a mean nucleation undercooling $\Delta T_N$, a standard deviation $\Delta T_\sigma$, and a maximum nucleation density $N_{\text{max}}$ (equivalent to the area under the Gaussian curve). As a cell with volume $V_{\text{cell}} = (\Delta x)^3$ undergoes a change in undercooling from $\Delta T_1$ to $\Delta T_2$ over some time step, the probability of a new nucleus forming in that volume over that time step is related to the change in nuclei density over the change in undercooling through

$$P_N = \frac{N_{\text{max}} V_{\text{cell}}}{\sqrt{2\pi} \Delta T_\sigma} \int_{\Delta T_1}^{\Delta T_2} \exp \left( -\frac{\left( \Delta T - \Delta T_N \right)^2}{2 (\Delta T_\sigma)^2} \right) d(\Delta T).$$ (4.17)

If a randomly generated number for the cell is less than the nucleation probability of Eq.(4.17), a random orientation is generated along with a decentered square or octahedron, and the cell is transformed from liquid into an active cell. While picking a random orientation in 2D is trivial (consisting of selecting a random $\theta$ between 0 and 90 degrees), it is more complex in 3D. We select 2 random numbers $[0, 2\pi)$ and $[0, \pi)$ corresponding to a random $\theta$ and $\phi$ on the unit sphere, yielding a vector. The intersection of the plane perpendicular to this vector with the unit sphere forms a circle; selecting a random point on the circle yields a direction perpendicular to the first. Taking the cross product of these two vectors yields a third mutually perpendicular vector, and these three vectors together give a random 3D crystallographic orientation. This crystallographic orientation can be converted back into the standard Euler angle convention via rotation matrices. Finally, we note that $\Delta t$ is always selected to be small enough such that the integral of Eq.(4.17) can be easily approximated using the trapezoid rule (e.g., the average of the integral values at $\Delta T_1$ and $\Delta T_2$). Table 4.2 shows values for the parameters used in calculation of the interfacial response function, including phase diagram values for different alloying additions in
Ti and standard nucleation parameters used in the simulations (unless mentioned otherwise for a specific subset of results). Alloying addition-dependent liquidus slopes and partition coefficients for Ti-Mo, Ti-Cu, and Ti-Fe were taken from [160], while values for Ti-Ta were estimated from [108]; \( m_{eq}^L \) and \( k_{eq}^p \) are approximated as constants, which appeared to be a valid for these phase diagrams particularly as alloying additions were generally kept under 10 weight percent solute.

Table 4.2 granular CA simulation parameters used in presented results unless otherwise stated.

<table>
<thead>
<tr>
<th>Interfacial response function</th>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid solute diffusivity (all alloys)</td>
<td>( D )</td>
<td>( 3 \times 10^9 )</td>
<td>m/s</td>
<td></td>
</tr>
<tr>
<td>Gibbs-Thomson coefficient (all alloys)</td>
<td>( \Gamma )</td>
<td>( 5 \times 10^{-7} )</td>
<td>m·K</td>
<td></td>
</tr>
<tr>
<td>Equilibrium liquidus slope (Ti-Mo)</td>
<td>( m_{eq}^L )</td>
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<td>K/wt.%</td>
<td></td>
</tr>
<tr>
<td>Equilibrium liquidus slope (Ti-Ta)</td>
<td>( m_{eq}^L )</td>
<td>3.8</td>
<td>K/wt.%</td>
<td></td>
</tr>
<tr>
<td>Equilibrium liquidus slope (Ti-Fe)</td>
<td>( m_{eq}^L )</td>
<td>-18.0</td>
<td>K/wt.%</td>
<td></td>
</tr>
<tr>
<td>Equilibrium liquidus slope (Ti-Cu)</td>
<td>( m_{eq}^L )</td>
<td>-10.6</td>
<td>K/wt.%</td>
<td></td>
</tr>
<tr>
<td>Equilibrium partition coefficient (Ti-Mo)</td>
<td>( k_{eq}^p )</td>
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<tr>
<td>Equilibrium partition coefficient (Ti-Ta)</td>
<td>( k_{eq}^p )</td>
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<tr>
<td>Equilibrium partition coefficient (Ti-Fe)</td>
<td>( k_{eq}^p )</td>
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<td>none</td>
<td></td>
</tr>
<tr>
<td>Equilibrium partition coefficient (Ti-Cu)</td>
<td>( k_{eq}^p )</td>
<td>-0.39</td>
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<table>
<thead>
<tr>
<th>CA simulation conditions</th>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
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<tr>
<td>Max nucleation density (3D)</td>
<td>( N_{max} )</td>
<td>( 1 \times 10^{12} )</td>
<td>m(^3)</td>
<td></td>
</tr>
<tr>
<td>Mean nucleation undercooling</td>
<td>( \Delta T_N )</td>
<td>5</td>
<td>K</td>
<td></td>
</tr>
<tr>
<td>Standard deviation of nucleation undercooling</td>
<td>( \Delta T_{sigma} )</td>
<td>0.5</td>
<td>K</td>
<td></td>
</tr>
</tbody>
</table>

4.3 Examples

4.3.1 Single dendrite tip growth

As an estimate of the CA model’s accuracy, calculations of the relative undercooling of an isolated dendrite tip at steady state and at multiple solidification rates for the constrained solidification of a Ti-1.5 mole percent W system and a Ti-1.5 mole percent Cu system are compared to those predicted by the Kurz, Giovanola, and Trivedi (KGT) model described
in Section 2.2 [130]. The relative undercooling is defined as the difference between the local temperature at the dendrite tip and \( T_{\text{L}}^C \) (which is alloy dependent). We will evaluate the tip undercooling-solidification rate relationship under the assumption of local equilibrium for solute (i.e., with \( k_p = k_p^{\text{eq}} \)), noting that this assumption will begin to break down at the faster solidification velocities.

For each simulation, the thermal gradient, \( G \), is set to 100,000 K/m with cooling rates, \( \dot{T} \), of 10, 50, 100, 500, 1000, and 5000 K/s, giving solidification rates, \( V = \dot{T}/G \), in the range of 0.0001 to 0.05 m/s. A planar solidification front parallel to the direction of \( G \) is initialized with one perturbation in local \( f_s \) values, which develops into a single isolated columnar dendrite for each simulation. The system size is chosen large enough such that the dendrite tip reaches a steady-state temperature, at which point the undercooling of the tip is calculated.

![Graph](image)

**Figure 4.3** Comparison of the present CA model prediction of steady-state dendrite tip undercooling for varied solidification velocity with the KGT analytical model (solid curves) for (a) Ti-1.5 Cu and (b) Ti-1.5 W. The CA model is generally within about 5% of the analytical model solution at low and moderate solidification rates, with more variability as the rapid solidification regime is approached. Error bars represent uncertainty in the CA model prediction due to grid discretization error.
Figure 4.3 shows the resulting calculations of dendrite tip undercooling at multiple solidification velocities for both systems compared to the KGT solution. For solidification velocities under 0.01 m/s, the CA prediction is generally within around 5% of the analytical solution. A larger discrepancy occurs at the faster solidification rates, likely related to deviation from the ideal Ivatsov geometry assumed in the KGT model and the inability of the 2D grid based model to capture a complex 3D shape. Possible discretization error resulting from the solute transport and solidification being modeled at the same length and times scales may also be a reason for the loss of accuracy at faster solidification rates. Discretization errors from the grid and inexact dendrite geometry notwithstanding, the CA model produces the KGT solution for these alloys with acceptable accuracy.

4.3.2 Lattice Boltzmann-CA for isothermal single dendrite growth

The intragranular CA model can be combined with the lattice Boltzmann method of Subsection 3.2.2 for modeling coupled fluid flow, solute transport, and solidification. This allows for simulation of growth when solute transport around growing dendrites can occur via both diffusive and advective modes. As a simple test problem, a single dendrite with preferred growth directions aligned with the grid is initialized at the center of a Ti-1.5 mol.% Cu melt of constant undercooling of 4 K (or around 11% of $\Delta T_0$ for the alloy) both with and without consideration of fluid flow. The domains consisted of a 750 by 750 array of cells with $\Delta x = 0.75 \mu m$ and $\Delta t = 2.9 \mu m$, with 1.5 s of growth for each. The inlet velocity in the simulation considering fluid flow was 0.25 mm/s, driven from left to right across the domain. All non-inlet boundaries were considered to be periodic. Figure 4.4 shows the resulting dendrite growth pattern and solute transport field both in the absence of (a) and with consideration of (b) fluid flow. As expected, in both cases the four primary arms aligned with the grid direction extended outward from the initial seed as solute diffusion at the dendrite tips was faster than in the regions between dendrite arms where the solute-enriched liquid became trapped to a certain degree. The solid was formed at the fixed composition
$C^eq_S$ for the 4 K undercooling, while compositions near $C^eq_L$ were formed on the liquid side of the interface (the exact equilibrium liquidus composition, as per Eq. (4.4), depends on local curvature values). Without fluid flow, the four arms were symmetrical as was the solutal boundary layer, which tapered off from compositions near the liquidus towards $C_0$ far from the solidification front. With fluid flow, however, the introduction of advective solute transport allowed for faster solute transport and thus faster solidification at the arm opposite the fluid flow direction. The transverse arms were relatively unaffected, while the build up of solute advected towards the arm on the right hand side lead to a locally stunted solidification rate. It can also be seen that the solute concentration gradient in the liquid for the leftmost arm of Figure 4.4b is much steeper than that of the arms of Figure 4.4a, while the opposite is true for the rightmost arm of Figure 4.4b. These results match those obtained in equivalent LB-CA models of isothermal single dendrite growth [224, 223].

![Figure 4.4](image)

**Figure 4.4** Comparison of isothermal dendrite growth without (a) and with (b) fluid flow as per the lattice Boltzmann- cellular automaton model. While fourfold dendritic growth proceeded symmetrically with purely diffusive transport in (a), the advective transport of solute in (b) lead to locally increased solidification rates at the leftmost dendrite tip and locally decreased solidification at the rightmost dendrite tip.
4.3.3 Grain impingement and the columnar to equiaxed transition

Given that 3D simulations will necessarily be much more memory and time-intensive than their 2D counterparts, a comparison of the 2D and 3D granular CA models was performed to determine how much of a difference the third dimension makes in the results. Here, 2D and 3D domains initially consisted of 529 grains along the bottom surface; these were 7 cells wide in 2D and 7 by 7 cells in area in 3D. Five sets of results were obtained for each model, in which different random seeds were used to generate random initial grain orientations in each version of the simulation. The domain heights were 500 µm, and growth in the vertical direction was performed at a constant rate per time step. The 2D and 3D results are presented in Figure 4.5a, showing the impingement of grains with height in the simulation, and Figure 4.5b, showing the mean orientation of the non-impinged grains as they advance towards the domain top.

![Figure 4.5a](image1.png)  
![Figure 4.5b](image2.png)

**Figure 4.5** Comparison of the 2D and 3D model predictions for (a) fraction of grains impinged as a function of domain height, and (b) mean orientation of non-impinged grains as a function of domain height.

From Figure 4.5a, around 93% of the grains from the original solidification surface in 2D compared to nearly 98% in 3D were impinged before reaching the domain top. The vast majority of this impingement took place within the first 250 µm or so of growth, with a slow
asymptotic decline of the number of grains remaining as the top surface was approached. This discrepancy is related to the geometry of impingement in 2D and 3D; misoriented grains in 3D can be impinged from both the X and Y directions, while misoriented grains in 2D can only be impinged by adjacent grains in the X direction. Another factor is that the maximum possible misorientation between the growth direction of the grains and the growth direction in the domain in 2D is 45 degrees, compared to 54.7 degrees in 3D; this was the primary factor in the differences seen in Figure 4.5b. Overall, the small differences in fraction of grains impinged and orientation of remaining grains versus domain height for 2D and 3D seem logical; however, we note that this was essentially a 1D solidification problem and for a solidification problem with 3D thermal gradients (e.g., in additive processes), the full 3D range of possible orientations for grains would seem necessary to accurately model microstructure.

Given the differences in grain orientation and impingement when moving from 2D to 3D, the implications of these variations on modeling the columnar to equiaxed transition (CET) were explored under $G$ and $V$ values likely to induce such a transition while also reasonably within LENS$^\text{TM}$ process space. For the 3D simulations, the standard nucleation parameters from Table 4.2 were used. However, it was noted that there can be significant differences in 2D and 3D grain sizes when modeling nucleation [263]. For the 2D simulations, one of two approaches was taken: either no changes were made to $N_{\text{max}}$ or $V_{\text{Cell}}$ within Eq.(4.17), or a corrected $N_{\text{max}}^{2D}$ and $A_{\text{Cell}} = \Delta x^2$ replaced $N_{\text{max}}$ and $V_{\text{Cell}}$ in Eq.(4.17), respectively. To convert from $N_{\text{max}}$ to $N_{\text{max}}^{2D}$ for the latter of these two approaches, the relationship

$$N_{\text{max}}^{2D} = \left( \frac{N_{\text{max}}}{\sqrt{\frac{\pi}{6}}} \right)^{\frac{2}{3}}$$

from [297] was used. For each set of $G$ and $V$, randomly oriented grains were initialized on the bottom surface in 3D. For the equivalent 2D simulations, domains of width 1600 $\mu$m and height 625 $\mu$m were used with initial randomly oriented grains of width 100 $\mu$m. As shown in Figure 4.6 for the 3D results, the columnar grains dominate the microstructure at high $G$. 

and low $V$, while with increased values of $V$ nucleated grains are shown embedded within
the columnar microstructure (typically elongated in the thermal gradient direction). As $G$
is reduced for the larger values of $V$, these nucleated grains tend to more effectively blocked
the original columnar grains and take on more equiaxed shapes. As expected based on the
solidification literature, the CET occurred at small $G$ and large $V$.

Table 4.3 shows how the percentage of the top solidification front consisting of nucleated
grains varied when moving from the 3D to the 2D simulations. For each case (3D, 2D without
 correction, and 2D with use of Eq.(4.18)), this percentage increased with decreasing $G$
and increasing $V$ as expected. However, with no correction in 2D (red numbers in Table
4.3), the nucleation rate was severely underestimated as was the percentage of nucleated
grains at the top boundary relative to the 3D case (black numbers in Table 4.3). When
the correction was used (blue numbers in Table 4.3), the opposite issue occurred, and the
nucleated grains dominated at too large $G$ and too small $V$ relative to the 3D prediction.
This may be because there is a smaller range of possible orientations in 2D and all nucleation
is confined to a single plane, both factors greatly increasing the probability that a nucleated
grain in the liquid can impinge the columnar grains at the initial solidification front. The
fact that the 2D model overestimates both nucleation rate in plane as well as impingement
is important for future application of the method to 2D modeling of 3D solidification phe-
nomena, showing that some additional correction is required to quantitatively model the
CET in 2D. In general, the ability of the 3D version of the model to show this transition
between columnar to equiaxed microstructures in the range of thermal conditions expected
in additive manufacturing processes shows promise for future application of the model to
realistic microstructure prediction in such processes.
Figure 4.6  3D modeled microstructures for varied thermal gradient and solidification velocity under constrained alloy solidification conditions. Color represents grains’ crystallographic orientation, where blue is aligned with the thermal gradient (vertical) direction and red is the maximum misalignment.
Table 4.3  Percentages of the initial columnar front blocked by nucleated grains for fixed alloy and varied thermal conditions. Red text represents values for 2D solidification without the prefactor correction as per Eq.(4.18), black text represents values for 3D solidification, and blue text represents values for 2D solidification with the prefactor correction of Eq.(4.18).

<table>
<thead>
<tr>
<th></th>
<th>Solidification velocity (m/s)</th>
</tr>
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<tr>
<td></td>
<td>0.002</td>
</tr>
<tr>
<td>250,000</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
</tr>
<tr>
<td>86</td>
<td>60</td>
</tr>
<tr>
<td>200,000</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>74</td>
<td>1</td>
</tr>
<tr>
<td>89</td>
<td>74</td>
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<tr>
<td>150,000</td>
<td></td>
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<tr>
<td>2</td>
<td>0</td>
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<td>2</td>
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<tr>
<td>96</td>
<td>77</td>
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<td>100,000</td>
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</tr>
<tr>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>85</td>
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</tr>
<tr>
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CHAPTER 5. THERMAL LATTICE
BOLTZMANN-CELLULAR AUTOMATA HYBRID MODEL

The thermal lattice Boltzmann (TLB) method of Chapter 3 can be combined with the grain growth CA of Chapter 4 to simulate coupled fluid flow, heat transport, and grain growth for LENS™ solidification. Temperature values calculated through the TLB model are used to update CA cell states using the intergranular CA, while the interface position calculated using the CA is used by the TLB model to determine whether cells act as solid or liquid. Section 5.1 discusses the details of coupling the two models, including the boundary conditions used and how energy absorption at the top surface is handled. Section 5.2 discusses how the model is parallelized and its parallel performance, while Section 5.3 applies the parallelized TLB-CA model to an example problem with a stationary beam allowing a spot melt pool to develop, reach steady-state, and solidify. The hybrid TLB-CA model is used more extensively in the results of Section 7.2.

5.1 Equations and assumptions

The TLB model described in Subsection 3.2.2 for modeling the evolution of internal energy density \( E \) on the same lattice at fluid transport, can implicitly be extended to consider the solid-liquid phase change using the method of [192], which relates \( E \) values calculated through Eq.(3.13) to temperatures \( T \) through the expression

\[
T = \begin{cases} 
\frac{E}{\rho c_p^S} & E \leq \rho c_p^S T_S \\
T_S + (T_L - T_S) \left( \frac{E - \rho c_p^S T_S}{\rho c_p^S (T_L - T_S) + L} \right) & \rho c_p^S T_S < E < \rho c_p^S T_S + L \\
T_L + \frac{E - L - \rho c_p^S T_L}{\rho c_p^L} & E \geq \rho c_p^S T_S + L 
\end{cases} 
\]  
(5.1)

Here, \( T \) is a piecewise function of \( E \), and depends on the fluid mass density \( \rho \), solid specific heat capacity \( c_p^S \), liquid specific heat capacity \( c_p^L \), liquidus temperature \( T_L \), solidus tempera-
ture $T_S$, and latent heat of the solid-liquid phase change $L$. At the scale of this fluid and heat transport problem, the liquid is assumed to be uniform in concentration and therefore $T_L$ and $T_S$ are constants. However, inhomogeneities in the melt resulting from incomplete melting of particles or microsegregation during solidification may challenge this assumption under certain conditions; we assume that such inhomogeneities are confined to the growing CA cells, and that liquid cells ahead of the solidification front have local compositions near that of the overall alloy ($C_0$).

Simulation domains are initialized with left, right, and bottom boundaries set at a preheat temperature $T_{preheat}$, and dimensions of sufficient size as to accurately model the temperature distribution from the laser. A fixed fraction $f_{abs}$ of the beam power $P_{beam}$ is considered to be absorbed by the material, and a 2D slice of the 3D Gaussian energy distribution of width $W_{beam}$ is converted into values of incident energy $E_{incident}$ for top surface cells (necessarily a function of cells’ lateral position relative to the beam at a given time step). The heat sink terms of Eq.(2.2) and the force terms of Eq.(2.6) and Eq.(2.7) are considered at the top boundary, but neither liquid-gas phase changes nor deformation of the top melt pool surface are accounted for. These assumptions along with the lack of heat dissipation out of the 2D plane lead to a modeling challenge: without any evaporation or vaporization at the center of the incident beam, the melt pool temperature will reach non-physically large values. However, capping energy absorption or the melt pool temperature will lead to a melt pool that is unreasonably small. To model realistic temperature distribution and melt pool size without including the additional physics required for liquid-gas phase changes, evaporation, or forces relating to melt pool curvature, an ad-hoc method of modeling energy absorption is introduced as a stand-in. Cells at the top surface will only absorb $E_{abs}$ (a fraction of $E_{incident}$ depending on local temperature), where superheating is allowed but the melt pool temperature is still capped by shutting off energy absorption above 3700 K (around 150 K
above the boiling point for Ti-6Al-4V). $E_{abs}$ is given by

$$E_{abs} = \begin{cases} 
E_{incident} & T < 3450K \\
E_{incident} \cdot (1 - 0.004 \cdot (T - 3450)) & 3450K \leq T \leq 3700K \\
0 & T > 3700K 
\end{cases}$$

(5.2)

If $E_{incident} > E_{abs}$ for a cell in the top row, 10% of this remaining energy will have a chance to be absorbed by cells immediately below the top row (while the remainder is assumed to be lost through reflection or liquid-gas phase change processes). $E_{incident}$ for a cell in the second row is therefore found by taking 10% of the difference between $E_{incident}$ and $E_{abs}$ of the adjacent top row cell. $E_{abs}$ for the second row will again depend on the local temperature of these cells through Eq.(5.2). As laser energy absorption is primarily confined to the immediate surface, no additional energy absorption is considered beyond the first two rows. By allowing cells in these top rows to superheat but capping the amount of energy they can absorb, these “pseudo-liquid” cells allow for a reasonable amount of energy absorption without reaching unrealistic temperatures. In reality, these cells having been heated beyond the vaporization temperature would be devoid of material and part of a keyhole-shaped vaporization cavity at the melt pool surface, as opposed to just allowing a certain amount of energy to pass through. This procedure can be empirically tuned to model reasonable melt pool sizes for a set of process conditions. Increasing the heat capacity of liquid as $T$ approaches the boiling temperature, rather than allowing the liquid to superheat, would yield a similar result for energy absorption while avoiding the non-physical temperatures and such an approach is used later in this work.

Selection of $\Delta x$ and $\Delta t$ in this model require further consideration. Too small of a $\Delta x$ for the TLB model will lead to very large domain sizes and unreasonably long computational time, while too large of a $\Delta x$ will yield Marangoni forces on the melt pool surface (proportional to temperature gradient over a cell width) that are too large to allow for a convergent fluid flow field. $\Delta x$ for the CA model should be around 1 $\mu$m, as values significantly larger than this will not allow the temperature field to be modeled as continuous (i.e., temperatures
of adjacent CA cells will be far apart), resulting in inaccurate grain growth modeling. The ∆x for the TLB model of 2.5 µm was chosen not because such a small ∆x was required for modeling the fluid flow (∆x of 5 µm was used in the TLB model of [123] for a similar beam melting process), but rather so that interpolation of temperatures onto the CA grid (which used ∆x = 1.25 µm to avoid the aforementioned temperature field discontinuity) would be less calculation-intensive during each time step. Use of this 2:1 ratio of TLB to CA grid sizes allowed for a relatively simple bilinear interpolation of temperatures onto the CA grid, as shown schematically in Figure 5.1a. Cell types determined through the CA model were by the TLB model as a basis for whether a cell behaves as solid or liquid. As illustrated in Figure 5.1b, if all four CA cells that made up a TLB cell were liquid, the TLB cell would be treated as liquid; otherwise, the TLB cell would be treated as solid.

The substrate to undergo melting and resolidification is generated using the 2D CA algorithm, where randomly oriented nuclei are randomly placed and allowed to grow and claim all available cells. This allows the generation of an equiaxed substrate with an average grain diameter \( g_d \) related to the number of nuclei placed and the domain size. The relatively large preheat temperature of \( T_{preheat} = 800 \) K was selected to approximate the residual heat expected from previous layers’ deposition. Unless otherwise mentioned, the parameters of Table 5.1 are used for the TLB-CA model.

<table>
<thead>
<tr>
<th>Parameter name</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam power</td>
<td>( P_{beam} )</td>
<td>500</td>
<td>W</td>
</tr>
<tr>
<td>Beam width</td>
<td>( W_{beam} )</td>
<td>0.0003</td>
<td>m</td>
</tr>
<tr>
<td>Fraction of power absorbed at top surface</td>
<td>( f_{abs} )</td>
<td>0.5</td>
<td>N/A</td>
</tr>
<tr>
<td>Heat convection coefficient</td>
<td>( h_c )</td>
<td>50</td>
<td>W/(m^2·K)</td>
</tr>
<tr>
<td>Emissivity</td>
<td>( \epsilon )</td>
<td>0.4</td>
<td>None</td>
</tr>
<tr>
<td>Substrate thickness</td>
<td>( w_0 )</td>
<td>0.002</td>
<td>m</td>
</tr>
<tr>
<td>Preheat temperature</td>
<td>( T_{preheat} )</td>
<td>800</td>
<td>K</td>
</tr>
<tr>
<td>Mean grain diameter</td>
<td>( g_d )</td>
<td>25</td>
<td>µm</td>
</tr>
<tr>
<td>Time step (TLB and CA)</td>
<td>( \Delta t )</td>
<td>0.15</td>
<td>µs</td>
</tr>
<tr>
<td>Cell size (TLB)</td>
<td>( \Delta x_{LB} )</td>
<td>2.50</td>
<td>µm</td>
</tr>
<tr>
<td>Cell size (CA)</td>
<td>( \Delta x_{LB} )</td>
<td>1.25</td>
<td>µm</td>
</tr>
</tbody>
</table>
Figure 5.1 Schematic of interpolation between TLB and CA grids. (a) Interpolation from the TLB grid (red outline) to the CA grid (black outline); for the shaded CA cell, the temperature as calculated for the location marked with the black dot uses bilinear interpolation from the four nearest TLB cell centers (red dots). (b) Interpolation from the CA grid to the TLB grid; as liquid TLB cells must contain four liquid CA cells, only the top right TLB cell would be considered liquid, while the other three in this schematic would be treated as solid.

5.2 Model parallelization and scalability

Larger problems, such as simulation of a moving beam over a long substrate, can be simulated with the current model through use of parallel computing. One modification to the present model that can save computational time is applying the TLB and CA models only to regions that can feasibly melt (within a reasonable distance from the beam). While the domain itself will still need to be large enough to accurately estimate cooling rates and thermal gradients in the melt pool, the large region of space between $T_{preheat}$ at the boundaries and $T_{solidus}$ around the melt pool does not need to be simulated using lattice Boltzmann distribution functions. Based on prior simulations and the model parameters chosen, the size of the TLB and CA domains are chosen while temperatures in the remainder of the domain are calculated by solving the heat transport equation (Eq. (2.1)) using the finite
difference (FD) method. Assuming that the solid-liquid interface does not reach the edges of the TLB portion of the overall domain, the LB-FD interface is handled by using FD to calculate temperature and internal energy density, then setting the internal energy density distribution functions to the equilibrium distribution with $\vec{u} = 0$. Parallelization of this model is performed via domain decomposition, in which the number of columns on the TLB grid is divided up evenly among the available processors. Given that all calculations are local and only depend on values of variables at neighboring cell sites, all processors can independently perform calculations for both the LB and CA portions of the model over a given time step. However, cells for which some neighbors are handled on one processor and other neighbors are handled on a different one require further discussion. Consider a domain of 2000 LB columns and 2 available processors for calculations. If columns 1 through 1000 were used by rank 0 and columns 1001 through 2000 by rank 1, cells in columns 1000 and 1001 would have some neighbor cells with unknown states. This problem is handled by using “ghost nodes”: rank 1 would have a copy of the information on rank 0’s column 1000, and rank 0 would have a copy of the information on rank 1’s column 1001. After propagation of distribution functions, recalculation of fluid density, velocity, and internal energy density, and collision of distribution functions, the ghost nodes on rank 1 are replaced with rank 0’s calculated values of these quantities for column 1000, and the ghost nodes on rank 0 are replaced with rank 1’s calculated values of these quantities for column 1001. The same procedure is taken following CA calculations of grain growth with the variables of cell type, grain orientation, decentered square position, and decentered square diagonal length.

The Intel message passing interface (MPI) library was used for communications among processors. As these communications will necessarily increase computational time, at least somewhat offsetting the performance improvement of parallelizing the program, the code was designed to minimize time spent on processor-to-processor communications. Given that the moving beam problems in 2D will require many more columns than rows, a column-centric domain decomposition in which each processor would need to communicate with at most
two others was preferable to a column and row-based domain decomposition. As nearly all communications will require a simultaneous sending and receiving of information between pairs of processors containing adjacent regions of the domain, the point-to-point command “MPI_SENDRECV” was used in place of individual “MPI_SEND” and “MPI_RECV” command pairs whenever possible for computational efficiency. To minimize the number of individual “MPI_SENDRECV” commands used, data was not sent as individual variables (e.g., one command each for sending fluid and energy distribution functions) but as packaged buffers in which all pertinent information was copied and placed. This allowed the number of “MPI_SENDRECV” steps (exchanging ghost node data with either one or both processors with adjacent regions of the domain) to be reduced to two: one for the TLB variables, and one for the CA variables. For further optimization, the compiler flag “-fast” was used in program compilation as suggested by the Iowa State High Performance Computing tutorials.

To test the strong scaling of the program (computational speed for a fixed problem size and varied number of processors), a TLB domain of 7232 rows and 600 columns and a partially overlapping FD grid of 7500 columns and 1000 rows was initialized. Over the course of $10^7$ time steps, a beam was moved across the domain from left to right at the speed of 0.01 m/s. Nucleation and the writing of output files were not considered. The program was run on Iowa State University’s Condo Cluster, consisting of SuperMicro nodes each containing two, 8-core Intel Haswell processors. As the serial code would take much too long to run, the program was run on one node (16 processors), two nodes (32 processors), etc., through eight nodes (128 processors). The strong scaling efficiency, $E_S$, of the program would typically use the serial performance as a baseline, but in this case used the single node (16 processors) wall clock time (707,306 seconds) as shown in the expression

$$E_S = \frac{(16 \text{ processors}) \times (707,306 \text{ seconds})}{N_p t_N} \times 100,$$

in which $N_p$ is the number of processors used and $t_N$ is the wall clock time in seconds for the $10^7$ time steps to complete. Table 5.2 shows $E_S$ as a function of the number of nodes.
and processors used; with up to four nodes, the strong scaling efficiency is above 90%, with the decrease primarily due to the increasing overhead for inter-processor and inter-nodal communication. With between four and seven nodes, the strong scaling efficiency is still above 80%, with the most notable drop in efficiency between 7 and 8 nodes used. As the fixed number of TLB columns is divided up among more and more processors, there are diminishing returns in computation time saved per processor while the parallel overhead continues to increase with more nodes communicating. If more processors were used beyond 128, the scaling efficiency would likely continue to drop as communication among processors would becoming even more significant relative to the time used for calculations on the processors. To improve the computational speed of the code further, shrinking the TLB grid to encompass only areas that are near the solidus temperature (rather than all cells that could feasibly melt during the simulation) and having that TLB grid move with the melt pool itself would likely be the best approach rather than adding more processors or altering the structure of the calculations performed. Nevertheless, the ability of the present model to simulate a long line scan problem such as this in just over one day (around one day and seven hours) using eight nodes as opposed to over a week (around eight days and four hours) with one node will allow for the simulation of larger problem sizes with parallel computing than would otherwise be possible in feasibly amount of time.

Table 5.2 Strong scaling of the present TLB-CA model for a moving beam simulation on the Condo Cluster

<table>
<thead>
<tr>
<th>Number of nodes</th>
<th>Number of processors</th>
<th>Wall time (s)</th>
<th>Strong scaling efficiency ($E_s$)</th>
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<td>1</td>
<td>16</td>
<td>707,306</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>32</td>
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<td>5</td>
<td>80</td>
<td>167,159</td>
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<tr>
<td>8</td>
<td>128</td>
<td>112,100</td>
<td>79</td>
</tr>
</tbody>
</table>
5.3 Stationary heat source example problem

As a test problem, a stationary Gaussian beam, using parameters from Table 5.1, is allowed to heat a preheated substrate until a steady-state melt pool is formed. The steady-state melt pool size and fluid flow pattern was obtained after $2 \times 10^6$ time steps (0.3 seconds), with the temperature and fluid velocities fields are shown in Figure 5.2a. Temperatures near the boiling point of the alloy were confined to the region immediately adjacent to the incident beam, with large thermal gradients between the beam absorption region and the melt pool boundary. Thermal gradients on order of magnitude of those expected in LENS™ melt pools were found ahead of the melt pool boundary, though the thermal gradient was significantly smaller in the “mushy zone” between the liquidus and solidus temperatures as to be expected from the effect of latent heat. The melt pool contained two Marangoni force-driven fluid flow cells to either side of the incident beam, as the thermal gradient at the top boundary lead to the flow of fluid away from the energy source with fluid flow velocities between 0.1 and 1 m/s at the top surface. The order of magnitude of these fluid velocities, as well as the general fluid recirculation pattern, match those expected based on fluid and heat transport modeling in the welding literature. After the steady-state melt pool size was formed, the energy source was turned off to allow solidification of the melt pool, a process which took approximately $4 \times 10^5$ additional time steps. Nucleation of new grains was not considered during this solidification. The resulting grain structure shown in Figure 5.2b shows grains that grew in the direction of the thermal gradient, which was generally concentric around the region of heat absorption but elongated in the horizontal direction both due to the finite width of the laser and the Marangoni flow. At the bottom of the melt pool, this lead to grains generally oriented in the vertical direction (-20 to +20 degrees of misalignment) growing towards the melt pool center, while grains with larger misalignments grew inward from the melt pool sides, where the thermal gradient direction was closer to the diagonal (+/- 45 degrees of misalignment) directions.
Figure 5.2 TLB-CA results for a stationary heat source melting and solidification problem. (a) shows the temperature distribution around a stationary energy source, with arrows representing fluid velocities in the melted region, while (b) shows the grain structure resulting from resolidification of the substrate through epitaxial growth of grains at the boundary.

The temperatures in the melt pool can be compared to an equivalent control simulation without the Marangoni or buoyancy forces. Fluid flow and control simulation temperatures as a function of depth below the melt pool center and as a function of position along the melt pool's top surface are shown in Figure 5.3a and Figure 5.3b, respectively. As shown in Figure 5.3a, the region below the melt pool center is significantly (up to 200 K) colder when these forces are considered relative to the control simulation. The melt pool was also slightly more shallow in the simulation with the forces applied. Figure 5.3b shows that the regions along the top surface are significantly (up to 300 K) hotter when considering melt pool forces, with a melt pool width increase of around 400 µm compared to the control simulations. The magnitude of the thermal gradient at the melt pool surface is reduced in the case where
fluid flow is considered due to the advective heat transport, a notable result as the thermal
gradient magnitudes and directions in the liquid affect solidification behavior. Overall, the
differences in melt pool temperature profile and shape between the two simulations appear
reasonable as the fluid flow is expected to advect heat laterally along the melt pool surface,
extending its length, while less heat is available to diffuse towards the bottom of the melt
pool. The vertical force due to buoyancy on the very hot fluid at the melt pool center further
limits its ability to transfer heat to the melt pool bottom, though as expected the Marangoni
effect played the primary role in the differences between these simulation results.

Figure 5.3  Comparison of melt pool temperature profiles with and without consider-
atution of Marangoni and buoyancy forces. (a): Temperature as a function
of melt pool depth beneath the heat source for a stationary beam melt-
ing problem, showing a reduction in temperature below the surface when
fluid flow is considered (b) Temperature as a function of lateral position
at the melt pool surface for the stationary beam melting problem, show-
ing a significant extension of the melt pool and larger temperatures to
the sides of the absorption region when fluid flow is considered.
CHAPTER 6. MODEL APPLICATION TO REPRESENTATIVE ADDITIVE CONDITIONS

The results obtained using the CA methods, as well as the coupled LB-CA method, are separated into the categories “representative” additive conditions (this chapter) and “predicted” additive conditions (next chapter). By representative conditions, it is meant that the thermal gradients, cooling rates, and solidification velocities used are generally representative of those encountered in AM processes, but exclusively rectangular domains with fixed thermal conditions are considered for the simulations. Section 6.1 discusses solidification at the scale of individual dendrites, which are all assumed to be growing perpendicular to the thermal gradient direction $\vec{G}$ to represent the condition at the melt pool boundary [126, 261]. These simulations include diffusive solute transport, and are meant to give representative dendrite arm spacings and solute segregation profiles within a given grain. Section 6.2 employs a coupled LB-CA method to simulate fluid and solute transport in small domains along a melt pool boundary, with representative conditions predicted by a COMSOL Multiphysics approximation of temperature and fluid flow expected during LENS™ deposition. Local thermal gradients, cooling rates, and fluid flow conditions are used to estimate location-dependent microsegregation and dendrite arm spacing, which are compared to experimental observations. Section 6.3 then discusses solidification using the granular CA, approximating 2D and 3D growth with square and octahedral envelopes as representative of individual dendrite colonies at length scales more representative of melt pool heights in AM processes. More details regarding results shown in Section 6.1 and Section 6.2 can be found in the papers [202] and [204], respectively. Results shown in Section 6.3 are pending publication [203] (preprints available upon request).
6.1 Intragranular near-rapid and rapid solidification

6.1.1 Development of dendrite arm spacing and morphology

As a single perturbation of an initially planar interface for alloy solidification may grow into an elongated cell or dendrite, multiple perturbations of the interface may develop into a series of cells or dendrites, referred to as a colony. A colony will have a characteristic primary dendrite arm spacing (PDAS), solute segregation profile (e.g. mean solute compositions both within primary arms and in interdendritic regions), as well as the presence or absence of primary arm side branching. Experimentally, many of these quantities are non-uniform and involve significant variation for a given set of conditions [61]; it is of interest, therefore, to explore the statistical variation in these quantities as a function of initial conditions.

First, we explore the role of initial perturbations in the solid fraction \( f_s \) for cells at the initial solidification front. The alloy used was Ti-1.5 mol.% W, the cooling rate \( \dot{T} = 50 \text{ K/s} \), and thermal gradient \( G = 100,000 \text{ K/m} \). All simulations were initialized with liquid domains and a row of interface cells at the bottom (see Subsection 4.2.1 for the discussion on cell types in the CA). Starting with a row of interface cells at exactly the same \( f_s \) value may not break the symmetry of the simulation. This would result in dendrites not forming under conditions in which they would be favored; a non-physical result. To initialize simulations with conditions more representative of the naturally occurring stochasticity regarding breakdown of the initially planar interface, two approaches are taken. The first (“Approach 1” in Table 6.1) involves spreading the interface out over the two rows. For each column, a random number \( R \) is generated between 0 and 1. If \( R < 0.5 \), the bottom cell in this column is set to be an interface cell with \( f_s = R \) and cell immediately above it to be a liquid cell. If \( R \geq 0.5 \), the bottom cell in this column is set to be solid and the cell above it to be an interface cell with \( f_s = R - 0.5 \). The second approach (“Approach 2” in Table 6.1) involves initializing a single row of interface cells at the bottom of the domain, with \( f_s \) for each column set equal to a random number chosen from a truncated Gaussian distribution between 0.1 and 0.9.
These differences in initialization (Approach 2 having a much more smooth initial interface than Approach 1) will lead to differences in local curvature calculation and also therefore changes in the early stage solidification of the potential dendrites. The use and absence of $f_s^{\text{threshold}}$ values other than 1 that simulated natural fluctuations in growth rate of growing cells or dendrites (as described in Subsection 4.2.1) were considered as well.

Approach 1 and Approach 2, each with and without the presence of the aforementioned natural fluctuations via $f_s^{\text{threshold}}$ variation, were used for 5 model runs each (20 simulations total). Each run was based on different initial conditions through selected random number generator seeds in obtaining $R$ values. Table 6.1 shows mean, minimum, and maximum primary dendrite arm spacing (PDAS) calculated for each set of initial conditions. The inherent variability in modeled PDAS for each set is represented by a spread of around 8 $\mu$m. Use of Approach 1 with the sharper initial perturbations resulted in a slightly smaller mean PDAS as well as less PDAS variation with selected random number generator seed than Approach 2. Inclusion of the random fluctuations through non-unity $f_s^{\text{threshold}}$ lead to some additional secondary arm development along primary cells, but yielded little change in PDAS. As faster cooling conditions lead to finer cell and dendrite tips and therefore require smaller $\Delta x$ values, the sharper perturbations of Approach 1 yielded more consistent results while the smooth perturbations of Approach 2 often failed to initiate the breakdown of the perturbed planar solidification front. As a result of this, and the fact that the natural fluctuations induced via the inclusion of $f_s^{\text{threshold}}$ made negligible difference in modeled PDAS, simulations in later sections of this thesis used Approach 1 with the fluctuation procedure.

Second, we explore the role of varied solidification velocity $V$ and initial interfacial undercooling $\Delta T_{\text{init}}$ on the modeled PDAS for Ti-1.5 mol.% W and Ti-1.5 mol.% Cu solidification. The maximum bound on $\Delta x$ was set to be either 1 $\mu$m or the predicted tip radius as per Eq.(2.18), while the time step was selected using Eq.(4.11) with $N = 50$. For each alloy and for $V$ values of 0.0001, 0.0005, 0.001, and 0.005 m/s, 5 runs were performed at randomly
Table 6.1  Primary dendrite arm spacing (PDAS) with two approaches for interface initialization, with and without inclusion of random fluctuations through non-units $f_{\text{threshold}}$ values. The mean PDAS is reported at the top of each table cell, while the minimum and maximum are in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>PDAS ($\mu$m)</th>
<th>PDAS ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No Random Fluctuations</td>
<td>Random Fluctuations</td>
</tr>
<tr>
<td>Approach 1</td>
<td>27.3</td>
<td>26.1</td>
</tr>
<tr>
<td></td>
<td>(23.8 – 31.7)</td>
<td>(23.8 – 29.7)</td>
</tr>
<tr>
<td>Approach 2</td>
<td>28.6</td>
<td>30.1</td>
</tr>
<tr>
<td></td>
<td>(26.4 – 31.7)</td>
<td>(29.7 – 31.7)</td>
</tr>
</tbody>
</table>

selected $\Delta T_{\text{init}}$ values between 0 and $\Delta T_0$. Domain sizes were chosen to ensure a sufficient number of primary dendrite arms to calculate a statistically significant PDAS, and the results compared to the empirical PDAS relationship of Eq.(2.14) are shown in Figure 6.1.

While the CA predicted PDAS values for both alloys follow the same general decreasing trend and functional dependence of the Eq.(2.14) prediction, there is a fair amount of quantitative disagreement between the models. One example is that the CA predicts Ti-1.5 mol.% Cu to have the finer PDAS for all $V$, while the Kurz and Fischer model predicts Ti-1.5 mol.% W to have the finer PDAS for all $V$. There is also a variability of about 10 $\mu$m on each CA predicted PDAS value due to the PDAS dependence on model initial conditions. For more quantitative agreement, a multi-grid method allowing coarsening or refining of local $\Delta x$ values would likely be needed to more accurately calculate local interface curvature. This would more effectively model the planar front breakdown, which plays a significant role in the development of primary dendrite arms. However, as the analytical models of PDAS often disagree with both each other [128] and experimental results [236], the present model appears sufficient for qualitatively modeling PDAS trends with solidification conditions.

It was noted that for $\Delta x$ values smaller than around 0.6 $\mu$m, a stable primary dendrite arm spacing may not result from simulations with too small or too large $\Delta T_{\text{init}}$. This sensitivity of dendrite arm development to $\Delta T_{\text{init}}$ at small $\Delta x$ is related to the large interfacial energy of the initial planar front perturbations; because of the large curvature and corresponding
Figure 6.1  Predicted primary dendrite arm spacing (PDAS) for Ti-1.5 mol.% Cu (black line) and Ti-1.5 mol.% W (blue line) via the model of Kurz and Fischer in Eq.(2.14) relative to CA modeled PDAS for the same alloys (black and blue points, respectively). The points each represent averages of 5 PDAS values initialized with different initial interface undercooling values, while the error bars indicate PDAS variation from the different initial undercooling values.

large interfacial energy of a single cell size perturbation, a larger driving force is necessary to precipitate its advance. If the $\Delta T_{\text{init}}$ is too small for this to occur, the initial perturbations will disappear, and a representative PDAS will not be achieved in a reasonable amount of simulation time. Additionally, the development of secondary arms along primary dendrite stems (or lack thereof) seemed to be strongly dependent on the cell size, $\Delta x$, and the initial undercooling of the solidification front, $\Delta T_{\text{init}}$. When a small $\Delta x$ is used, cell-width perturbations along primary arms will have large interfacial energies and will be unlikely to grow, particularly if the initial undercooling at the interface is very large (which heavily favors rapid growth of the initial primary arms, with little room between them). This cell size-dependence of PDAS calculation and secondary branching is something that should be
accounted for when relying on this CA for rapid solidification microstructure results, and is taken into consideration further in Subsection 6.1.3. The selection of $\Delta x$ in this CA is a complicated issue, as it has been noted that inaccurate results may be achieved if $\Delta x$ is either too large or too small for a given set of conditions [127], and that the CA tends to “prefer” developing dendrites with radii close to the cell size itself [45]. A dynamic mesh coarsening and refinement might be necessary to resolve the issue completely.

6.1.2 Variation of dendrite growth with solute and interfacial energy parameters

For a fixed thermal gradient $G$, solidification velocity $V$, and alloy solute composition $C_0$, small variation in solute diffusivity $D$ (often not known for solute elements in molten Ti, particularly unusual additions such as W) can play an important role in solute partitioning and dendrite morphology. This is particularly true for phase diagrams containing large solidification ranges, in which the dependence of $D$ on temperature may not be negligible [239, 128, 130]. Although solute diffusivity as a function of temperature is not detailed here, variation in $D$ within an order of magnitude of the expected value of $10^{-9} \text{ m}^2/\text{s}$ for solute in a molten alloy near its liquidus temperature is shown here (along with the overall alloy composition $C_0$) to have a significant role on microstructure development. We select $\dot{T}$ to be 2000 K/s and $G$ to be 750,000 K/m (e.g., conditions representative of AM processes such as LENS™ [273, 91]). We also use domains wide enough such that the error in calculated PDAS values was on the order of the grid spacing. Figure 6.2 shows how changes to $C_0$ and $D$ can noticeably affect the modeled microstructure. Increasing $C_0$ lead to coarser microstructures with more room for secondary arms to develop between primary cells, while decreasing $D$ leads to the further destabilization of both initial planar front perturbations (leading to finer PDAS) and additional secondary and even ternary arm growth. Table 6.2 shows that the coarsening of PDAS with increase in $D$ and $C_0$ occurs both for Ti-W and Ti-
Cu, matching the qualitative trend in PDAS expected based on mathematical relationships between these quantities in the literature [95, 236].

Figure 6.2 Ti-W solidification microstructure results for varied alloy concentration and solute diffusivity, showing differences in primary arm spacing and secondary branching. (a) $D = 2 \times 10^{-9} \text{ m}^2/\text{s}$, $C_0 = 0.75$, (b) $D = 2 \times 10^{-9} \text{ m}^2/\text{s}$, $C_0 = 1.50$, (c) $D = 2 \times 10^{-9} \text{ m}^2/\text{s}$, $C_0 = 3.00$, (d) $D = 1 \times 10^{-9} \text{ m}^2/\text{s}$, $C_0 = 3.00$.

As with solute diffusivity, the Gibbs-Thomson coefficient, $\Gamma$, and anisotropy coefficient, $\delta$, characterizing the solid-liquid interfacial energy are also often not known precisely for varied alloying addition and crystal structure. As $\Gamma$ and $\delta$ values have previously been shown to impact the shape and branching of dendrites modeled with CA in undercooled melts [274], their impact on Ti-1.5 mol% W growth under approximated LENS$^{\text{TM}}$ conditions ($\dot{T} = 1250 \text{ K/s}$ and $G = 250,000 \text{ K/m}$) is investigated here. As smaller $\Delta x$ values were needed to model fine dendrite tips at smaller surface energies, more cells were required to simulate solidification over the same physical domain size. As branching during early stages of interface breakdown may look different than that during growth closer to the steady-state condition, the simulation domains had heights such that the steady-state was reached before calculating solute compositions along dendrite stems. As $\Gamma$ was decreased and $\delta$ increased, the magnitude of the interfacial energy in the preferred growth (grid) direction was decreased through
Table 6.2  Simulated PDAS for Ti-1.5 mol.% W and Ti-1.5 mol.% Cu systems, showing variation with solute diffusivity and overall solute composition.

<table>
<thead>
<tr>
<th>Ti-1.5 mol.% W calculated primary dendrite arm spacing, in µm</th>
<th>( D = 1 \times 10^{-9} ) m(^2)/s</th>
<th>( D = 2 \times 10^{-9} ) m(^2)/s</th>
<th>( D = 3 \times 10^{-9} ) m(^2)/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_0 = 0.75 ) mol</td>
<td>2.7</td>
<td>5.4</td>
<td>6.8</td>
</tr>
<tr>
<td>( C_0 = 1.50 ) mol</td>
<td>4.7</td>
<td>7.9</td>
<td>8.3</td>
</tr>
<tr>
<td>( C_0 = 3.00 ) mol</td>
<td>7.5</td>
<td>9.4</td>
<td>11.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ti-1.5 Cu mol.% calculated primary dendrite arm spacing, in µm</th>
<th>( D = 1 \times 10^{-9} ) m(^2)/s</th>
<th>( D = 2 \times 10^{-9} ) m(^2)/s</th>
<th>( D = 3 \times 10^{-9} ) m(^2)/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_0 = 0.75 ) mol</td>
<td>3.1</td>
<td>4.8</td>
<td>5.8</td>
</tr>
<tr>
<td>( C_0 = 1.50 ) mol</td>
<td>4.0</td>
<td>5.6</td>
<td>6.8</td>
</tr>
<tr>
<td>( C_0 = 3.00 ) mol</td>
<td>4.4</td>
<td>7.1</td>
<td>8.8</td>
</tr>
</tbody>
</table>

Eq.(4.2), which lead to finer primary arms and more secondary and ternary arm development. The development (or lack thereof) of side branches along with the presence of grid effects around the most narrow dendrite tips somewhat obscures the trend in primary dendrite tip radii, but the variation of the interfacial component in the undercooling’s effect (the right hand term of Eq.(4.4)) can be seen in the change in solute composition at the dendrite tips, as Eq.(4.4) and Eq.(4.6) relate total undercooling to equilibrium solute composition in the solid. Table 6.3 shows the mean solute concentration within primary dendrite stems for each \( \Gamma \) and \( \delta \) value. As decreasing \( \Gamma \) and increasing \( \delta \) reduces the interfacial component of the undercooling (and also, therefore, the magnitude of the total undercooling), solidification proceeds at smaller supersaturation and forms solid at a larger solute composition (due to the positive slope of the solidus for Ti-W). Although variation in these interfacial energy parameters should also affect the primary dendrite arm spacing based on empirical models, this was not the case here; which may be due to the grid dependence of the model’s curvature calculations and variation in PDAS from initial undercooling and \( f_s \) values at the interface.
Table 6.3  Average solute concentration (in mol.% W) at the steady-state dendrite tips for varied interfacial energy parameters and constant solidification conditions. As the liquidus slope for Ti-W is positive, decreasing the interfacial energy through increase in the anisotropy coefficient or decrease in the Gibbs-Thomson coefficient results in a smaller interfacial component to the tip undercooling and thus a larger steady-state dendrite tip solute concentration.

<table>
<thead>
<tr>
<th>δ</th>
<th>$\Gamma = 2 \times 10^7$ m·K</th>
<th>$\Gamma = 5 \times 10^7$ m·K</th>
<th>$\Gamma = 8 \times 10^7$ m·K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.86</td>
<td>2.53</td>
<td>2.33</td>
</tr>
<tr>
<td>0.4</td>
<td>2.91</td>
<td>2.68</td>
<td>2.50</td>
</tr>
<tr>
<td>0.8</td>
<td>3.01</td>
<td>2.77</td>
<td>2.62</td>
</tr>
</tbody>
</table>

6.1.3 Rapid solidification and local non-equilibrium at the solidification front

For rapid solidification conditions, very small $\Delta x$ and $\Delta t$ are required to model the increasingly fine cell and dendrite tips. To achieve results for domain sizes that require a large number of cells and time steps, the solidification front in this subsection is initialized to the expected steady state undercooling of the dendritic front as predicted through Eq.(2.17). This obscures the details of the actual interface breakdown from a planar front to fine cells, but allows modeling of steady-state rapid solidification microstructure in smaller amounts of simulation time. As was noted in Subsection 6.1.1, the final microstructure can be sensitive to the initial front undercooling $\Delta T_{init}$, and $\Delta T_{init}$ values too far from steady state may not yield representative steady state dendrite arm development. Figure 6.3 shows Ti-1.5 mol.% W cells solidifying at 0.01 and 0.05 m/s, velocities near the upper limit of the dendritic front’s stability range (0.07 m/s per Eq.(2.13)). Increasingly fine cell spacings are seen as the solute composition within the cells approaches $C_0$. As the dendritic front’s upper stability limit is approached, fine cellular microstructures beginning to closely resemble a planar front. This result was also observed in the Phase Field model of [229]. Though the upper limit of stable dendritic solidification will vary based on the phase diagram, as shown in Eq.(2.13), its value will typically fall between 0.01 and 0.5 m/s for most binary phase diagrams and alloy compositions; beyond this limit, a planar solidification front below the alloy’s solidus temperature would be expected to occur in the absence of deviation from local equilibrium.
Figure 6.3 Ti-1.5 mol.% W solidification microstructure results for (a) 0.01 m/s and (b) 0.05 m/s solidification rates; the fine cellular structures begin to resemble a planar solidification front as the front temperature approaches the solidus and the velocity approaches the absolute stability limit.

For solidification velocities near and beyond the aforementioned upper limit of dendritic front stability, the effect of local non-equilibrium at the solidification front will begin to become important in predicting interfacial solute compositions in both dendrite stems and interdendritic liquid. For Ti-1.5 mol.%W, local non-equilibrium did not have a major impact on the resulting microstructure as the absolute stability limit for rapid dendritic growth was reached at a very similar velocity to that where local non-equilibrium effect become relevant.

To look at local non-equilibrium using the CA, we use Ti-1.5 mol.% Ni, which has a larger upper limit for dendritic front stability and also, therefore, a larger range of solidification velocities in which local non-equilibrium at the interface affects solute redistribution. $V_{DI}$ and $V_D$ values of 0.1 and 1 m/s are used, which are on the low range of what might be expected but not unreasonable [215, 216]. For $G = 100,000$ K/m and two solidification velocities, the solute concentration profile for a single dendrite of Ti-1.5 mol.% Ni is shown in Figure 6.4, with and without accounting for local non-equilibrium in calculation of $k_p$ and $m_L$. At the slower solidification velocity of 0.006 m/s (Figure 6.4a), $k_p(V)$ and $m_L(V)$ in Eq.(2.19) and Eq.(2.20) are near their equilibrium values, and deviation from the equilibrium interface compositions is small. At the faster solidification velocity of 0.04 m/s (Figure 6.4b), the increase in $k_p(V)$ along the rapidly growing dendrite stem leads to solute trapping and a larger Ni concentration...
relative to the same simulation without accounting for $V$-dependence of $k_p$ and $m_L$. The change in $m_L(V)$ under these conditions also lead to less solute being incorporated into the liquid surrounding the dendrite relative to the local equilibrium case. These local non-equilibrium effects becoming significant in calculation of the solute profile at $V$ around two orders of magnitudes less than $V_D$ matches what has been modeled for rapid solidification in the literature [215, 216]. At faster solidification rates, the velocity-dependent or “kinetic” solidus temperature may be surpassed due to the large undercooling at dendrite tips. Neither a dendritic microstructure with solute trapping nor a planar solidification front will be stable under these conditions, and a banded microstructure consisting of alternating planar front and dendrites is formed as shown in Figure 6.4d-f. The oscillation between dendrites with partial solute trapping and a planar solidification front with complete solute trapping, as well as the increase in the ratio of planar to dendritic region area with solidification velocity as seen in Figure 6.4, are both qualitatively correct when compared with previous analytical models and experiments [239, 77, 34]. Although these banded microstructures can be reproduced qualitatively with the CA model as it is, the grid’s cell size and time step artificially limit the velocity at which the planar solidification front can advance. This velocity would normally be limited by attachment kinetics for atoms in the liquid joining the solid, and could be up to an order of magnitude larger than the largest velocity permitted by the CA on this grid. As a result, the spacing of the bands is not quantitatively correct. Quantitatively modeled banded microstructures using the CA would require separate rules (and also likely separate grids and time steps) for the planar front’s advance. It is also noted that while the modeled cellular-dendritic to banded transition occurred between 0.04 and 0.06 m/s, as shown in Figure 6.4c and Figure 6.4d-f, it is observed experimentally at velocities up to an order of magnitude higher $V$. Discretization error in the solute field as the solutal boundary layer became very small and selection of relatively small $V_D$ and $V_{DI}$ values likely played roles in the $V$ range in which banded structures appeared in the present model.
Figure 6.4  Rapid solidification predictions for Ti-1.5 mol.% Ni using the CA. Solidification of a single dendrite at velocities (a) 0.006 m/s and (b) 0.040 m/s under constrained growth conditions both with (blue) and without (black) the assumption of local equilibrium at the interface show an increasing importance to non-equilibrium solute partitioning in and around the dendrite as solidification velocity is increased. (c) through (f) show rapid solidification microstructures for multiple initial dendrites at $V$ of (c) 0.04 m/s, (d) 0.06 m/s, (e) 0.08 m/s, and (f) 0.10 m/s. In (c), a fine cellular structure with solute trapping along dendrite stems is observed while (d)-(f) show banded microstructures in which alternations between a cellular solidification front with solute partitioning and a partitionless planar solidification front occurred.
6.2 LB-CA modeling for predicted LENS\textsuperscript{TM} conditions

As shown in the sample problem in Subsection 4.3.2, coupled transport of solute with fluid flow and solidification can be modeled using CA-based methods. Under conditions common to additive manufacturing, however, solidification does not typically proceed from nucleated grains but from a series of epitaxially-growing grains or dendritic colonies constrained by the walls of the melt pool, more resembling the initial conditions of Section 6.1. However, as shown in the simulation results of [277] and [54] and in the experimental work of [241], fluid flow can still play a role in solute redistribution and dendritic growth under these conditions, leading to secondary arm growth, locally increased dendrite tip advance rates, and variation in tip shape or growth direction.

To obtain more realistic thermal profiles and fluid flow estimations for the melt pool boundary in LENS\textsuperscript{TM}, the commercial software package COMSOL Multiphysics was used to simulate fluid and heat transport in spot melting of a preheated substrate. The fluid flow and heat transport modules of this program were used to solve the 2D coupled equations for energy, momentum, and mass conservation. The fluid flow module accounts for buoyancy and the Marangoni effect assuming laminar flow and a Newtonian fluid, while the heat transport module considers conduction, convection, and radiation as modes of transport. As the relevant materials parameters for Ti-1.5 mol.% W (equivalent to about Ti-5.5 wt.% W) were not available, thermocapillary coefficient, temperature-dependent density, thermal conductivity, and heat capacity values for comparable Ti alloy systems with more available data (such as Ti-6Al-4V) or for pure Ti were used. While this wouldn’t be expected to have a large effect on the results, this approximation could lead to minor differences in fluid flow velocities or local thermal gradients. Table 6.4 contains COMSOL and LB-CA model parameters used in this section. The same approach used by [167] was used to model the Marangoni effect in this work; more specifically, through applying Eq.(2.7) to the top boundary of the melt pool. For each of the 3 laser powers investigated (183 W, 259 W, and 367 W, referred to as low, middle, and high from this point on), scanning electron microscopy...
images of LENS melt pool cross-sections were used to estimate the melt pool size as melting and solidification were not explicitly considered by COMSOL. Although simulations were performed in mole percent W, results were converted to weight percent W in this section for ease of experimental comparison.

Table 6.4 Parameters used in the process-scale COMSOL model (some as functions of temperature) and the microscale LB-CA model

| COMSOL parameters | | | | |
|-------------------|----------------|----------------|----------------|
| Parameter name    | Symbol | Value | Units | Source(s) |
| Solid heat capacity | $c_p^s$ | 403.04 - 0.215T | J/kg·K | [47] |
| Solid heat capacity | $c_p^s$ | 412.7 + 0.1801T | J/kg·K | [47] |
| Solid density     | $\rho^s$ | 4461.1 - 0.1419T | kg/m$^3$ | [47] |
| Solid density     | $\rho^s$ | 4462.6 - 0.1425T | kg/m$^3$ | [47] |
| Solid thermal conductivity | $k^s$ | 1.2595 + 0.0157T | W/m·K | [47] |
| Solid thermal conductivity | $k^s$ | 3.5127 + 0.0127T | W/m·K | [47] |
| Liquid heat capacity | $c_p^l$ | 0.831 | J/kg·K | [47] |
| Liquid density    | $\rho^l$ | 5227.6 - 0.688T | kg/m$^3$ | [47] |
| Liquid thermal conductivity | $k^l$ | -12.752 + 0.024T | W/m·K | [47] |
| Thermocapillarity | $\gamma$ | -2.4 x 10$^{-4}$ | N/m·K | [167] |

| LB-CA parameters | | | | |
|-------------------|----------------|----------------|----------------|
| Liquidus slope    | $m_L$ | 59.4 | K/mol.% | [104] |
| Partition coefficient | $k$ | 3.56 | none | [104] |
| Alloy solute concentration | $C_0$ | 1.5 | mol.% | |
| Pure Ti melting point | $T_{m}$ | 1943 | K | [104] |
| Gibbs-Thomson coefficient | $\Gamma$ | 2.4 x 10$^{-7}$ | m·K | [224] |
| Surface energy anisotropy | $\delta$ | 0.6 | none | [103] |
| Liquid density    | $\rho$ | 4865 | kg/m$^3$ | [100] |
| Kinematic viscosity | $\nu$ | 4.66 x 10$^{-7}$ | m$^2$/s | [47] |

Owing to the assumptions made by COMSOL, solidification using the LB-CA model was simulated for specific subdomains and for short time periods at the melt pool boundary. For each laser power, the same general fluid flow pattern developed with two large convection cells on the left and right sides of the melt pool and some minor fluid flow in the central portion of the melt pool just below the energy source. This general convection pattern, with two main cells driven by surface forces and slower fluid flow below the region of energy absorption, has been seen in 2D models of welding and AM processes and arises primarily
Figure 6.5  Typical COMSOL simulation results for temperature (a) (in K) and fluid velocity (b) (in m/s) under conditions representative of the LENS™ process. The black outline represents the fixed molten pool geometry considered. Because of the effects of the strong Marangoni convection, the temperature field is not symmetric about the region where beam absorption occurred, which lead to significant differences in thermal gradient and fluid flow pattern between subdomain A, represented by the red square, and subdomain B, represented by the blue square. 

from the Marangoni effect [124, 185, 1]. The size and relative velocity of the fluid within these convection cells was observed to be significantly larger at higher beam powers because of the larger thermal gradients present under these conditions. For our analysis, we consider two square subdomains within the COMSOL melt pool (0.1 mm per side), along the melt pool walls and aligned with the thermal gradient; these are highlighted in the plot of COMSOL temperature shown in Figure 6.5a and the plot of COMSOL fluid flow velocity shown in Figure 6.5b. The analogous regions to the highlighted regions of Figure 6.5 are used for each of the three power levels, though the exact X and Y coordinates will vary since the melt pool size is a function of the applied power. For subdomain A, just beneath the large convection cell on the left side of the melt pool and highlighted in red in Figure 6.5, the fluid flow is parallel to the wall. To model this region for a given power, the fluid is initialized everywhere to the COMSOL value for the magnitude of the fluid flow in the region. Since there is additional solidification occurring on both sides of this location, periodic boundary conditions are used for the LB fluid, solute, and solidification. The top boundary is held
at constant fluid velocity in the X direction with a magnitude equal to that found in the COMSOL calculation. For subdomain B, at the bottom of the melt pool and highlighted in blue in Figure 6.5, the fluid flow is perpendicular to the interface, diverging to either side as it approaches the subdomain bottom. For this region, the top boundary is held at a constant velocity in the negative Y direction as determined with COMSOL, while the left and right boundaries have zero-concentration gradient and outlet boundary conditions. In both cases, the top boundary is held at constant concentration $C_0$, providing a source of solute for the growing solid.

Local $G$ and $\dot{T}$ vary not only as a function of laser power, but also as a function of subdomain. For subdomain A, the large convection cell mixes the heat effectively enough to locally reduce the thermal gradient relative to those present in the rest of the melt pool. As heat from the top of the melt pool is mixed into this region, the cooling rate is also somewhat low relative to the rest of the melt pool. In subdomain B, the local thermal gradient and cooling rates are larger on average due to the rapid heat conduction into the underlying solid. The expected trends of decreasing $G$ and $\dot{T}$ with increasing laser power generally held for subdomain A, but subdomain B has the slowest cooling rate occur for the middle power. At higher powers, increased fluid flow advects heat towards the sides and away from the bottom of the melt pool. As only the first 0.10 seconds of $G$ and $\dot{T}$ data was required for the solidification of these subdomains, COMSOL-calculated local $G$ and $\dot{T}$ values were fit to parabolas and straight lines, respectively. While changes in $G$ in the subdomains during solidification were considered using location-dependent cooling rates, the thermal gradient was always assumed to be linear and perpendicular to the solidification front. More details on how temperature fields were fit to to the calculated temperature profiles as a function of time for the subdomains can be found in [202].

Subdomain A microstructures for low, middle, and high powers at 37.5 and 97.5 percent solidification are shown in Figure 6.6. As expected, time for solidification increased with laser power because of the decrease in cooling rate and the corresponding decrease in steady state
dendrite tip velocity. With the decreased dendrite growth rate, the solute concentrations within dendrites increased as well; smaller tip velocities required smaller undercooling, which correspond to higher values for $C_{eq}^S$. Finer microstructures (smaller primarily dendrite arm spacing, or PDAS) were formed in the low power case because of a slower cooling rate than those found in the middle and high power cases. Relative to control simulations that did not consider fluid transport (e.g., all solute transport was via diffusion in the liquid) there were negligible differences in solidification time, PDAS, or composition of the dendrites. Unlike in the sample problem of Subsection 4.3.2, the left to right flow was not driven by an inlet at the left boundary but by a constant velocity condition at the top surface. This scenario is more similar to the dendrite arms perpendicular to the fluid flow in Subsection 4.3.2. The fluid velocity at the solidification front tended towards zero and did not have sufficient vertical motion to effectively mix solute that was ahead of the growing dendrites. Considering this problem in 3D, in which the fluid can flow around growing dendrites rather than being blocked as it is in 2D, has suggested a more notable effect of fluid flow on the microstructure [277, 258]. Additionally, inclusion of local composition-dependent buoyant forces in the fluid would allow for more vertical fluid motion, potentially leading to solute mixing around the dendrites as well [222, 149].

Subdomain B, in which fluid flow perpendicular to the top boundary supplies solute-rich fluid to the interface as the solidification process consumes it, is under conditions more closely resembling the tip facing the fluid flow in the example problem of Subsection 4.3.2. Subdomain B microstructures at 99% solidification are shown in Figure 6.7 alongside their control (no fluid flow considered) counterparts. For the low power case, the flow is not strong enough to have an effect on the microstructure and for the high power case, the local undercooling near steady state is close enough to the equilibrium solidus value that supplying more solute did not significantly increase the driving force. Because of this effect and the relatively small fluid velocity, the difference between the low power microstructure and its control counterpart is only visible at the domain bottom (corresponding to solidification early
Figure 6.6 Model results for solute concentration profiles of representative subdomain A microstructures (see Figure 6.5 for subdomain definitions). Arrows represent fluid velocity for cells that have not completely solidified. At partial domain solidification (a-c), more time is needed to reach the same solidification threshold with increasing input power (boxed times). At complete domain solidification (d-f) this is again true; a larger solute concentration in the dendrite arms is also seen as the input power is increased.

On in the simulation, prior to reaching larger undercooling values). The 99% solidification threshold is reached at approximately the same time for calculations with and without fluid flow. The high power case, with its faster fluid flow, shows a larger region near the bases of the dendrites where concentration is noticeably larger than the control counterpart. However, the high power case too has the majority of solidification taking place near the constitutional undercooling limit, and the 99% threshold is reached only slightly faster with the addition of fluid flow. The middle power case, for which fluid flow had the greatest effect on the results, is examined in more detail in Figure 6.8. The fluid, initially moving in the direction of the front, is pushed to the side and out of the domain. The fluid flow goes from primarily vertical to primarily horizontal as the fluid velocity at the solidification front approaches zero. However, the domain is small enough, and the time period in which the fluid was supplying solute to the solidification front long enough, that a significant difference in early
solidification rate and solid concentration is seen. The presence of these small variations in solute partitioning arising from fluid flow in constrained solidification have also been seen in mathematical models of directional solidification under the influence of fluid flow [25].

Figure 6.7 Model results for solute concentration profiles of representative subdomain B microstructures (see Figure 6.5 for subdomain definitions). (a-c) represent the microstructure without fluid flow for the low, middle, and high powers, while (d-f) represent the microstructure with fluid flow at the same powers. The most notable difference is the tendency for more solute to be incorporated into the dendrite arms near the dendrite bases, as fluid from the top boundary is driven toward the solidification front allowing some mixing of the solutal boundary layer.

As performed in Section 6.1, cross sections of solute composition across the dendrite arms can be used to calculate PDAS and to plot solute composition profile at different heights in the simulation domain. The PDAS results are shown in Table 6.5; in general, the arm spacing tended to be smaller for subdomain B, as expected due to the faster cooling in this region. The arm spacings, plotted in Figure 6.9 for three Y positions within subdomain B, show how the W concentration was larger during the early stages of solidification (low Y) and decreased as the steady state undercooling was approached (close to the constitutional limit). Experimental data through energy-dispersive X-ray spectroscopy (EDS) line
Figure 6.8  Model results for solute concentration profiles of representative subdomain B microstructure (see Figure 6.5) at the middle input power. (a-c) represent the solute field (color) as well as the fluid velocity (arrows) for various times during solidification, while (d-f) represent the same times for a control run done in the absence of fluid flow. The early solidification occurs faster and at higher solute concentrations with fluid flow, as it allows mixing of the solutal boundary layer with the addition of relatively solute-rich liquid from the top boundary.

scans for W concentration is shown in Figure 6.9, showing variations in solute concentration with periodicity very near that predicted by the CA simulations (corresponding to a PDAS near 7 \( \mu \text{m} \))[160]. While the predicted peaks and valleys of the concentration profile resemble the simulation results for dendrite stems and interdendritic regions, uncertainty in solidification parameters such as Gibbs-Thomson coefficient and the approximations of the LENS\textsuperscript{TM} process made in the COMSOL simulations (no explicit movement of the melt pool boundaries, no moving beam or 3D temperature profiles) prevents these simulations from predicting location-dependent composition profiles and PDAS with more accuracy. Overall, the present model’s ability to predict experimental PDAS from COMSOL temperature and fluid flow conditions appears promising, and a more complex process model accounting for interface motion and the moving beam, coupled with a 3D version of this CA model would
likely yield more precise composition and PDAS profiles as a function of position in the melt pool.

Table 6.5  Primary dendrite arm spacing (PDAS) values for the two subdomains and varied COMSOL simulation power, in µm

<table>
<thead>
<tr>
<th></th>
<th>Low power</th>
<th>Middle power</th>
<th>High power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subdomain A</td>
<td>9.1</td>
<td>14.3</td>
<td>14.3</td>
</tr>
<tr>
<td>Subdomain B</td>
<td>5.3</td>
<td>9.1</td>
<td>5.3</td>
</tr>
</tbody>
</table>

Figure 6.9  (a) Variation in solute concentration as a function of X position in the domain, for three different Y positions in the modeled microstructure for subdomain B. The peaks represent dendrite arms, while the valleys represent the solute-depleted interdendritic liquid, allowing an estimate of primary dendrite arm spacing. As the dendritic front advanced, the solute concentration within the dendrite arms decreases as the local temperature decreases and the solidification front approaches a steady-state velocity. (b) EDS results on a Ti-5.5 wt.% W as-deposited sample fabricated via LENS™, showing a similar concentration profile at the same length scale [160]
6.3 granular CA modeling of nucleation and growth

6.3.1 Role of solute concentration on microstructure development

As shown in Subsection 4.2.2, the granular CA model successfully predicted the columnar to equiaxed transition (CET) at small $G$ and large $V$, with nucleation occurring at large $V$ and said nucleation events dominating the microstructure and becoming more equiaxed in nature at small $G$. Here, we investigate the role played by the interfacial response function in microstructure development for fixed $G$ (50,000 K/m), $V$ (0.01 m/s), and solute element (Mo), but with variation in solute concentration $C_0$. Altering $C_0$ affects both $P$ and $Q$ via Eq.(2.21) and Eq.(2.22), respectively, but also affects the interfacial response function relating solidification velocity to undercooling at the solidification front. As a result, $C_0$ will have a significant impact on the simulated solidification behavior. Figure 6.10 shown the interfacial response function and corresponding microstructure variations with changes to Mo composition in simulations of directional solidification. As $C_0$ is increased, the steady-state undercooling needed to drive growth at any given solidification velocity ($\Delta T_S$) is larger. However, the general shape of the interfacial response function is similar for all $C_0$ values. Figure 6.10’s shaded region corresponds to the range of undercooling over which nucleation is possible ($\Delta T_{NR}$), in which the darkest shading centered on the mean nucleation undercooling $\Delta T_N$. While adding 2 wt.% Mo yields no nucleation and a fully columnar microstructure (as expected, since $\Delta T_S$ is below the range $\Delta T_{NR}$ at this composition), the addition of 4 wt.% Mo allows $\Delta T_S$ to surpass the majority of $\Delta T_{NR}$. As a result, the Ti-4 wt.% Mo microstructure displays nucleated grains. However, since the $\Delta T_S$ isotherm is so close to the range $\Delta T_{NR}$, the nucleated grains are physically very close to the columnar front and have little time to grow before either becoming impinged by the bottom surface’s growing columnar grains (if at an unfavorable orientation relative to the preferred growth direction) or absorbed into the columnar front (becoming a grain of columnar shape). This situation is similar to that seen in Figure 4.6 at large $G$ and large $V$. Ti-6 wt.% Mo and Ti-8 wt.%
Mo have interfacial response functions with $\Delta T_s$ being somewhat further from the $\Delta T_{NR}$ range and as a result, nucleation events have more time to grow prior to impingement. The nucleated grains may come to dominate the simulation volume despite orientations often misaligned with the thermal gradient direction and, as in the case of Ti-8 wt.% Mo, even block the bottom surface’s original columnar grains from advancing entirely. Table 6.6 shows the quantitative details of this transition with increasing Mo content. As the steady state undercooling is further increased with Mo addition, both the percentage of the original columnar front blocked by the nucleated grains as well as the percentage of the simulation volume as a whole consisting of nucleated grains increase, reaching and approaching 100% respectively. These nucleated grains became more and more equiaxed (aspect ratio closer to 1) as the Mo concentration was increased. It is also of note that the number of nucleation events that occurred in the simulation domain quickly saturated as $\Delta T_s$ surpassed $\Delta T_{NR}$, suggesting that while simply adding more solute may aid in producing smaller, equiaxed grains, the grain refining effect saturates after enough solute is added. As $P$ and $Q$ are proportional to $C_0$ and an increase in these quantities can be linked to grain refinement, this result corroborates the expected experimental dependence on $P$ and $Q$.

Table 6.6  Variation in microstructural parameters with alterations to Mo content in constrained 3D solidification simulations.

<table>
<thead>
<tr>
<th>Wt.% Mo</th>
<th>Number of nucleation events</th>
<th>Aspect ratio of nucleated grains</th>
<th>Percentage of original solidification front blocked by nucleated grains</th>
<th>Percentage of overall domain consisting of nucleated grains</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>N/A</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>51</td>
<td>3.96</td>
<td>1.7</td>
<td>0.8</td>
</tr>
<tr>
<td>3</td>
<td>110</td>
<td>2.92</td>
<td>11.7</td>
<td>11.4</td>
</tr>
<tr>
<td>4</td>
<td>110</td>
<td>2.40</td>
<td>46.0</td>
<td>33.6</td>
</tr>
<tr>
<td>5</td>
<td>110</td>
<td>1.99</td>
<td>78.9</td>
<td>53.3</td>
</tr>
<tr>
<td>6</td>
<td>110</td>
<td>1.76</td>
<td>94.3</td>
<td>66.1</td>
</tr>
<tr>
<td>7</td>
<td>110</td>
<td>1.59</td>
<td>100.0</td>
<td>73.6</td>
</tr>
<tr>
<td>8</td>
<td>111</td>
<td>1.49</td>
<td>100.0</td>
<td>76.3</td>
</tr>
<tr>
<td>9</td>
<td>111</td>
<td>1.47</td>
<td>100.0</td>
<td>79.0</td>
</tr>
</tbody>
</table>
Figure 6.10 Interfacial response function for Ti-X wt.%Mo solidification, with modeled representative microstructure for constrained solidification of Ti-2 wt.% Mo, Ti-4 wt.% Mo, Ti-6 wt.% Mo, and Ti-8 wt.% Mo. The gray shaded region represents the range of undercooling in which nucleation is possible, with the maximum of the probability distribution shaded the darkest over the mean nucleation undercooling. As the steady-state grain undercooling becomes larger than the nucleation undercooling range, nucleation ahead of the seeded grains at the bottom surface becomes possible. As the undercooling becomes larger yet, the nucleated grains are more likely to block the initial columnar grains, leading to the observed columnar to equiaxed transition.

6.3.2 Role of solute element on microstructure development

We next examine the effects of simultaneously varying solute element and quantity, which alters the quantities $P/C_0$ and $Q/C_0$. Table 6.7 shows that solutes with larger $P/C_0$ show a larger fraction of the columnar front blocked, and a smaller nucleated grain aspect ratio for a given $C_0$. It is also readily seen that adding more of any solute also yields a larger fraction of the columnar front blocked, as was the case in the previous subsection for Ti-x wt.% Mo. The difference in simulated microstructure with solute element can be rationalized through
Figure 6.11a, which shows how adding the same amount of different solutes can lead to differences not only in the steady-state solidification velocity for a given undercooling, but also in the shape of the interfacial response function. As expected, alloying additions that produce interfacial response functions with larger $\Delta T_S$ (relative to the $\Delta T_{NR}$) are more likely to produce the CET. However, we note that the decrease in nucleated grain aspect ratio and increase in fraction of the columnar front blocked by nucleation does not necessarily correlate with increase in $Q/C_0$ (particularly when Ta is the alloying addition). This is despite previous work suggesting that $Q$ strongly correlates with smaller and more equiaxed grains experimentally in many solidification processes [272]. Noting this, we compare Ti-2.764 wt.% Fe and Ti-4 wt.% Ta interfacial response functions in Figure 6.11b. While Ti-2.764 wt.% Fe and Ti-4 wt.% Ta have the same steady-state undercooling for the imposed thermal conditions and very similar $P$ values, Ti-4 wt.% Ta has a $Q$ value nearly 8 times larger than that for Ti-2.764 wt.% Fe. With the same thermal gradient for both simulations, Figure 6.11b indicates that a nucleation event at a given undercooling for Ti-2.764 wt.% Fe will grow faster than an equivalent nucleation event for Ti-4 wt.% Ta, despite being the same distance from a columnar grain front growing at the steady state velocity of 0.01 m/s (which occurs at between 8 and 9 K of undercooling for both alloys). The faster growth of nuclei in the Ti-2.764 wt.% Fe system is represented in the larger percentage of the columnar front blocked by nucleated grains and the larger percentage of the domain consisting of nucleated grains as shown in Table 6.8. In theory, the slower growth of nuclei in the Ti-4 wt.% Ta system relative to Ti-2.764 wt.% Fe should lead to more nucleation events, as fast growth of nucleated grains will lead to extinction of new potential nucleation sites in the undercooled zone. The Ti-4 wt.% Ta, with a much larger $Q$ value, did have slightly more nucleation events occur and a slightly smaller mean aspect ratio for nucleated grains; however, because of the slow growth of the nucleation events, they were actually less effective at precipitating the CET compared to Ti-2.764 wt.% Fe. This suggests that while larger $P$ and $Q$ in general tend to correlate with grain refinement and furthering the CET, as suggested in the literature for
these thermal conditions, their role may be more complex for certain alloy systems – and the roles of heterogenous nucleation sites, nucleation rate, and nucleation undercooling on this problem should be understood as well. Because of this complexity, alternative definitions of $Q$ have been defined, and grain refinement models that take into account nucleant potency and density have been developed [272, 62, 209].

Table 6.7  Variation in $P/C_0$ and $Q/C_0$ for different solute elements, along with the fraction of the columnar solidification front impinged by nucleated grains and the aspect ratio of nucleation grains with these alloying additions and concentrations.

<table>
<thead>
<tr>
<th></th>
<th>Mo</th>
<th>Ta</th>
<th>Fe</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P/C_0$</td>
<td>3.0</td>
<td>3.2</td>
<td>4.8</td>
<td>16.6</td>
</tr>
<tr>
<td>$Q/C_0$</td>
<td>4.5</td>
<td>20.0</td>
<td>3.8</td>
<td>6.5</td>
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</tbody>
</table>

Fraction of columnar front impinged

<table>
<thead>
<tr>
<th>Wt. %</th>
<th>Mo</th>
<th>Ta</th>
<th>Fe</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.227</td>
<td>0.229</td>
<td>0.871</td>
<td>1.000</td>
</tr>
<tr>
<td>3</td>
<td>0.427</td>
<td>0.395</td>
<td>0.983</td>
<td>1.000</td>
</tr>
<tr>
<td>4</td>
<td>0.707</td>
<td>0.691</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>5</td>
<td>0.900</td>
<td>0.790</td>
<td>1.000</td>
<td>1.000</td>
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</tbody>
</table>

Nucleated grain aspect ratio

<table>
<thead>
<tr>
<th>Wt. %</th>
<th>Mo</th>
<th>Ta</th>
<th>Fe</th>
<th>Cu</th>
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</thead>
<tbody>
<tr>
<td>2</td>
<td>2.53</td>
<td>2.86</td>
<td>1.99</td>
<td>1.26</td>
</tr>
<tr>
<td>3</td>
<td>2.64</td>
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<td>1.67</td>
<td>1.23</td>
</tr>
<tr>
<td>4</td>
<td>2.17</td>
<td>2.21</td>
<td>1.49</td>
<td>1.24</td>
</tr>
<tr>
<td>5</td>
<td>1.86</td>
<td>2.03</td>
<td>1.41</td>
<td>1.20</td>
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</tbody>
</table>

Table 6.8  Variation in microstructural parameters for alloys with similar supercooling parameters $P$ but disparate growth restriction factors $Q$.

<table>
<thead>
<tr>
<th>Alloying addition</th>
<th>$P$</th>
<th>$Q$</th>
<th>Number of nucleation events</th>
<th>Aspect ratio of nucleated grains</th>
<th>Percentage of original solidification front blocked by nucleated grains</th>
<th>Percentage of overall domain consisting of nucleated grains</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti- 2.764% Fe</td>
<td>13.3</td>
<td>10.5</td>
<td>110</td>
<td>2.52</td>
<td>95.2</td>
<td>61.1</td>
</tr>
<tr>
<td>Ti- 4% Ta</td>
<td>12.7</td>
<td>80.1</td>
<td>112</td>
<td>2.49</td>
<td>40.1</td>
<td>34.5</td>
</tr>
</tbody>
</table>
Figure 6.11 Interfacial response functions for (a) Ti-3 wt.% X and four different solute additions, with varied shape and solidification velocity value at $V = 0.01$ m/s, and for (b) A Ti-Fe and a Ti-Ta alloys with the same steady state undercooling for solidification at $V = 0.01$ m/s, but very different shapes. As the Ti-Fe and Ti-Ta alloys have similar $P$ values as shown in Table 6.8, the difference in $Q$ is most likely related to these different function shapes.

### 6.3.3 Role of nucleation parameters on microstructure

While carefully choosing alloying elements and concentrations can bring about the CET for a set of thermal conditions, there is often a practical limit on how much solute can be added without changing material properties or introducing intermetallic or other compounds from the phase diagram. The solute additions explored in the previous section were effective at inducing the CET at $G = 50,000$ K/m, on the low end of thermal gradients expected during LENS$^\text{TM}$ (generally only occurring near the top of the melt pool), and it may not be possible to induce this transition at larger $G$ with compositional changes alone. Decreasing $\Delta T_N$ is one possibility that would clearly lead to an increase in space between the $\Delta T_S$ and $\Delta T_{NR}$ isotherms, therefore giving nucleated grains a larger available region in which they can operate and, thus, an increased chance to impinge the columnar grains. However, if this is not possible, and it is desired to induce the CET for a situation in which the large $G$ cannot be
reduced and the material is limited to a binary alloy of fixed composition, another possibility is increasing $N_{\text{max}}$ (possibly through introducing external nucleant particles to the system). An example is shown in Figure 6.12, in which $N_{\text{max}}$ is varied by many orders of magnitude for the thermal gradient of $G = 250,000 \text{ K/m}$ (more typical of solidification in LENS$^\text{TM}$). There is a clear transition between a fully columnar microstructure and a mixed equiaxed and columnar structure as a function of $N_{\text{max}}$. For $N_{\text{max}} = 10^{13} \text{ m}^{-3}$, the original bottom surface grains were entirely blocked off, though nucleated grains of favorable orientation (blue) tended to grow rapidly into new columnar grains. Within this structure, however, grains of less favorable orientation (red) can be shown to have more equiaxed shapes, and have been impinged by the nucleated grains with more favorable orientations. Simulating with this same large $N_{\text{max}}$ and the smaller $G$ of 50,000 K/m showed an equiaxed structure with a much finer grain size than the equivalent simulations at smaller $N_{\text{max}}$, suggesting that if grain refinement is desired under conditions in which the CET already occurs, the addition of more nucleation sites through melt inhomogeneity would be a more effective strategy than increasing $Q$. It is also noted, however, that decreasing nucleation density for thermal conditions in which the CET is expected to occur (e.g., $G = 50,000 \text{ K/m}$ but $N_{\text{max}} = 10^{10} \text{ m}^{-3}$) can lead to a more columnar structure, which suggests that in addition to favorable selection of variables such as $G$, $V$, and alloy composition, the nucleation density in the melt is another required condition to induce the CET. Additionally, large $N_{\text{max}}$ values can lead to a mixed columnar and equiaxed microstructure even for unfavorable thermal conditions.

### 6.3.4 Parameterization of the role of alloying addition, thermal gradient, and nucleation undercooling on the CET

Thus far, it has been seen that smaller $G$ and larger $V$ correlate with more equiaxed microstructures, as does larger $C_0$ and, in general but not always, larger $P$. As $P$ tends to correlate with increased $\Delta T_S$ (which comes from $V$ and the interfacial response function), this
Figure 6.12 Comparison of microstructure predictions (with varied nucleation density) at the thermal gradient of $G = 50,000$ K/m (relatively small for LENS$^{\text{TM}}$ solidification) with those at the thermal gradient of $G = 250,000$ K/m (more typical for LENS$^{\text{TM}}$ solidification).

A larger difference between $\Delta T_S$ and $\Delta T_{NR}$ is likely the responsible factor for more equiaxed microstructure formation. As was seen in Table 6.8 and Figure 6.11b, the area under the interfacial response function between equivalent $\Delta T_S$ and $\Delta T_{NR}$ values affects the CET as well. Given this information and based on the previous analysis of [95], we propose a parameter “$\alpha$”, defined as

$$\alpha = \frac{1}{G} \int_{\Delta T_{N,\text{min}}}^{\Delta T_S} V(\Delta T) \, d(\Delta T), \quad (6.1)$$

that would be expected to correlate with the fraction of the top surface area consisting of nucleated grains, which we define as $f_N$. In Eq.(6.1), $\Delta T_{N,\text{min}}$ is approximately the smallest undercooling at which significant nucleation occurs; for $\Delta T_\sigma = 0.5$ K, this is about $3\Delta T_\sigma$ below $\Delta T_N$. A total of 64 simulations were performed with randomly chosen alloying addition (Ta, Mo, Fe, or Cu), solute composition (2, 3, 4, or 5 weight percent), $V$ (0.006 to 0.010 m/s), $G$ (50,000 K/m to 200,000 K/m), and $\Delta T_N$ (3 to 8 K). All other parameters were held
constant, and each simulation was run four times with different random number generator seeds. All input parameters were chosen such that the value of $\alpha$ would be positive, as no nucleation occurs for simulations with negative $\alpha$. Figure 6.13 plots $f_N$ as a function of the calculated value of $\alpha$ for each of the four data points obtained with the different random number generator seeds, represented as different marker shapes. As might be expected, scatter occurs in part due to the relatively arbitrary nature of this measure of the CET (depending on where the domain “top” is, and how many grains happened to nucleate close to the layer defined as the top, this value will fluctuate). The scatter is in particular noticeable near the $f_N = 0.5$ threshold, at which the solidification front transitions from more than half columnar grains to more than half nucleated grains. $\alpha$ values near 0 yielded little to no equiaxed grains at the solidification front, as any grains that nucleated so close to the main solidification front would almost always be impinged by the more favorably oriented grains growing from the bottom surface of the simulation. The largest factor on this statistical variation appeared to be the orientation of the initial columnar grains, with more misoriented grains in the initial microstructure leading to a larger fraction of blocked columnar grains. Since each marker represented a different random number generator seed, the seeds that produced more favorably oriented initial grain structures also produced lower $f_N$ value data points on average. This is seen in Figure 6.13 as the triangular marker type tended to be the lower bound on the $f_N$ range, while the square and circle markers are near the upper bound, and the diamond markers in between. Considering all data points with $f_N$ between 0 and 1, a strong correlation is seen with increasing $\alpha$ and an increased fraction of the columnar front impinged by nucleated grains ($R^2$ value of 0.824 for a linear fit). Despite this scatter in the region where columnar and equiaxed grains coexisted, the nucleated grains always blocked the entirety of the solidification front beyond an $\alpha$ value of about $0.8 \times 10^{-6}$. Use of $\alpha$ values to select conditions under which the CET would be likely to occur both for mixed and equiaxed microstructure formation should also be extendable to other interfacial response functions, such as those for ternary alloy systems. It is a
similar approach to “process maps” developed in the literature, relating columnar, mixed, and equiaxed microstructures to $G$ and $V$ encountered in various additive processes, but accounts for the role of alloying addition and nucleation undercooling on the microstructural transitions. To relate specific $\alpha$ values to the experimental microstructural transitions would require data on real nucleation densities and nucleation undercooling for the various alloys. However, the use of such a parameter that ties thermal conditions, nucleation, and the phase diagram into the likelihood of equiaxed grains in a microstructure would prove useful in alloy and process design for tunable grain structure.

![Figure 6.13](image)

Figure 6.13  Fraction of the columnar solidification front impinged ($f_N$) as a function of the parameter $\alpha$, which incorporates variation in solidification velocity, thermal gradient, mean nucleation undercooling, and alloying addition. The marker shape of the points plotted (circle, square, diamond, and triangle) represent points obtained with a common number generator seed for initial microstructure and nucleated grain orientations, showing how different a given seed tended to produce smaller or larger than average $f_N$ values over the range of $\alpha$.

Another important part of the problem is that while a favorable $\alpha$ value is needed to induce the CET, the nucleation density needs to be large enough such that the transition actually occurs. A lack of nucleation sites in a small simulation volume (e.g., the melt pool formed in LENS™) could lead to too few nucleated grains, and thus columnar growth despite
favorable conditions for the CET. We also note that applying the present model to larger \(G\)
and/or \(V\) conditions will require decreases in \(\Delta x\) and \(\Delta t\) to ensure that the temperature field
remains continuous a function of both space and time. As the octahedra model grain “en-
velopes” consisting of multiple dendrites growing in a preferred direction, \(\Delta x\) should clearly
be smaller than measured dendrite arm spacing values (which will approach the 1 \(\mu\)m used
in the present simulations for \(\Delta x\) during rapid solidification) for the grain results to have
physical meaning. As the primary purpose of the present work was to investigate constitu-
tional effects on the interfacial response function and the CET, an approximated interfacial
response function that assumed a dominant constitutional undercooling term was used in
Eq. (2.17). However, under larger \(G\) and \(V\) conditions (particularly close to and beyond \(V = 0.01\) m/s), the dendrite tip geometry shifts away from the hemispherical cap assumed
in Eq. (2.17), dendrite tips become more narrow with larger interfacial contributions to the
tip undercooling, and both \(m_L\) and \(k_p\) become dependent on the rate of solidification (e.g.,
loss of local interfacial equilibrium) [130, 128, 239]. These factors (among others) will need
to be considered when modeling larger ranges of solidification conditions in order to more
accurately estimate both the interfacial response function and microstructure development
as a whole.
CHAPTER 7. MODEL APPLICATION TO PREDICTED ADDITIVE CONDITIONS

The granular CA model, having been studied in rectilinear domains in Chapter 6, is applied in this chapter to more realistic melt pool geometries. Section 7.1 applies 2D and 3D versions of the CA to melt pool temperature profiles as a function of time, reading input files for temperature data for use in solidification calculations. Section 7.2 employs the coupled TLB-CA method of Chapter 5 to simulate and fluid and heat transport of the melt pool for a specific additive process while simultaneously modeling grain growth using the granular-scale CA. Unlike the one-way information passing of Section 7.1, this hybrid TLB-CA model includes separate length scales for TLB and CA calculations, with communication between the two models.

7.1 granular modeling of SLM microstructure solidification

7.1.1 2D CA modeling of grain growth in SLM

The 2D CA developed in Subsection 4.2.2, verified against a benchmark CET problem in Subsection 4.3.3, and explored further in Section 6.3, can be applied to melt pool geometry and thermal conditions as predicted by the multi-physics software tool ALE3D. This code, developed at Lawrence Livermore National Laboratory, uses a hybrid finite element-finite volume method to solve heat and mass transport problems on an unstructured grid [179]. The use of arbitrary-Lagrangian Eulerian meshes (the origin of the “ALE” potion of the name) leads to a wider range of simulation physics that can be incorporated relative to Lagrangian-only or Eulerian-only approaches, while also offering scalable parallel performance for large and complex simulations [179]. The use of unstructured grids allows the code
to handle mesh distortion caused by the melting particles and melt pool surface motion, as energy is absorbed by the powder bed and the dynamic melt pool develops [112]. From line scan output obtained by Saad Khairallah at Lawrence Livermore National Laboratory, 2D “slices” of these simulation domains, both parallel and perpendicular to the beam direction, were extracted and interpolated in time to be used as input for the 2D CA model. These simulations were performed for stainless steel 316L. However, as the CA requires a structured grid that does not change in time, and a cell size much smaller than that of the ALE3D data (1 \( \mu \text{m} \) is typically used in the literature for CA modeling of additive solidification and used here as well, while the ALE3D data around the melt pool was at around 3 \( \mu \text{m} \)), several additional steps are needed for data interpolation. An example is discussed here for a longitudinal (parallel to the beam scan or positive Y direction) slice of the melt pool data.

As the ALE3D output consists of both structured and unstructured grid data, a filter is applied to remove all data outside of the specific XZ plane (e.g., not at the specific Y value selected for the cross section) as well as all data not corresponding to the structured grid (mostly at the melt pool surface). The data is converted from cartesian coordinates to coordinates of the type (row, column) on the CA grid’s length scale. The region of the ALE3D slice area that undergoes melting is further selected from the filtered data. Next, bilinear interpolation is done from the coarse ALE3D temperature values to fill the remaining CA cells with temperature values, noting that regions with no material (e.g., outside of the region bounded by the data points representing the melt pool top) are ignored. However, as removing points not on the structured grid lead to a jagged appearance to the top melt pool surface, further interpolation in the triangular regions bounded by liquid was required to recreate the melt pool shape in a more realistic manner. Schematics of this interpolation process are shown in Figure 7.1. This process is repeated for each new input file (representing the melt pool at different times in the ALE3D simulation), with temperatures between file time steps interpolated linearly to the CA time step. For a ternary alloy interfacial response function, we use the approximation made by [194], which assumes that the solidification
front’s behavior is primarily controlled by Ni diffusion and approximate the stainless steel’s composition as Fe-12.5 Ni. Parameters from [146] were used in the interfacial response function of [244] for this pseudo-binary system. As nucleation is not considered, the exact form of the interfacial response function is not of as much importance as it was in Section 6.3.

![Figure 7.1 Schematic showing the process of converting the raw ALE3D output temperature data on the 3D grid to spatially interpolated temperature in a 2D plane of interest on the CA grid.](image)

Two notable changes to the CA rules are required for these simulations. First, as the melt pool advances, solid or interface cells that reach temperatures above the alloy’s liquidus temperature are converted to liquid and lose their grain orientation and their decentered square attributes. However, as a layer of interface cells through second-nearest neighbors is always required to separate solid and liquid cells, an additional check is needed to create new interface cells out of solid cells that find themselves at the melt pool boundary following melting of their neighbors. Second, as the top surface of the melt pool moves due to fluid flow, an additional cell type of “blank” is introduced for cells that contain no material. Any
cell, whether solid, liquid, or interface that gets converted to blank loses all solidification and temperature attributes. A blank cell can be converted to liquid if material flows into it, triggering a check to ensure that the new liquid cell does not border a solid cell. If it does, that solid cell is converted into new interface. As the beam velocity in the simulation was 1.335 m/s, the time step was selected to be $7.49 \times 10^{-8}$ seconds, such that the max rate of diagonal growth on the grid ($0.1 \Delta x/\Delta t$) was equivalent to the fastest steady state solidification velocity at the interface. A “first pass” simulation for a given slice involved initializing each CA cell as a different grain with a random orientation (effectively a grain size equivalent to the CA cell size), and the output in Figure 7.2 for two latitudinal simulation runs and one longitudinal run show the preferential growth of grains with orientations aligned with the local thermal gradients of the liquid.

For more realistic initial conditions, grains in subsequent simulations were initialized as columns with widths and orientations based on the output from the previous simulation, which simulates growth of additional layers on top of a previous layer. The process of feeding width and orientation distributions into the initialization of additional runs of the CA with the same ALE3D input was performed for seven layers, the results of which are shown in Figure 7.3 and Table 7.1. The median grain width in each layer increased as more of the unfavorably orientated grains were impinged, eventually converging near a grain width of 10 $\mu$m. This grain width convergence, as well as the bimodal distribution of grain widths (some grains growing wider with height in the domain, while others slowly get impinged by their neighbors) was close to what was seen experimentally for grain widths of as-deposited SLM samples under these conditions [200]. The orientation distribution showed a similar trend as the median grain orientation became more aligned with the vertical direction with additional layer simulation; this was as expected and has been seen experimentally due to the flat shape of the melt pool and the thermal gradient close to the vertical direction but rotated slightly towards the beam scan direction [270]. The latitudinal cross sections also show the growth of multiple orientations and impingement as the rounded melt pool boundary moves.
Figure 7.2  Grain growth results for a longitudinal (parallel to beam movement) and two latitudinal (perpendicular to beam movement) melt pool cross sections using interpolated ALE3D temperature data. Grains more closely aligned with the local thermal gradient advanced and impinged less favorably oriented grains, leading to a decrease in grain width from bottom to top of the simulation domains. For the longitudinal slice, this thermal gradient was vertical across the majority of the melt pool at it was mostly flat, and red and blue grains closely aligned with the vertical direction tended to advance to the top surface. As the thermal gradient was more radial for the latitudinal slices, grains of all misorientations are represented along the curved melt pool boundaries.

towards the centerline, with qualitative similarities to experimental microstructure in beam cross sections [200]. We note that non-equilibrium phases in solidification were neglected, as austenite appeared to dominate the experimental microstructure for this material, but the nucleation and growth of a second phase (for example, ferrite) is something that could be incorporated with an additional interfacial response function.
Figure 7.3  CA microstructure for SLM line scans using an initial condition where each site is a different grain (layer 1), and where the initial grain widths and orientation distribution come from the previous layers’ top surface grain widths and orientations (layer 7). In both cases, some grains decreasing in width with height in the solidified region while others increased in width with height in the solidified region due to orientation-dependent impingement were observed.

Table 7.1  CA-predicted grain widths and orientations for solidification using an ALE3D thermal profile prediction.

<table>
<thead>
<tr>
<th>Layer number</th>
<th>Median grain width projected onto the X axis (µm)</th>
<th>Median grain orientation (degrees rotated clockwise from Y axis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.5</td>
<td>16.8</td>
</tr>
<tr>
<td>2</td>
<td>4.6</td>
<td>12.6</td>
</tr>
<tr>
<td>3</td>
<td>6.7</td>
<td>11.8</td>
</tr>
<tr>
<td>4</td>
<td>9.7</td>
<td>17.1</td>
</tr>
<tr>
<td>5</td>
<td>10.0</td>
<td>10.2</td>
</tr>
<tr>
<td>6</td>
<td>10.6</td>
<td>6.8</td>
</tr>
<tr>
<td>7</td>
<td>10.1</td>
<td>6.8</td>
</tr>
</tbody>
</table>
7.1.2 3D CA modeling of grain growth in SLM

To model 3D solidification, the 3D version of the CA can be applied to SLM conditions with spatial and temporal interpolation of temperatures from the output of another code in the same manner as in 2D. The OpenFOAM computational fluid dynamics code was used to simulate these conditions; unlike ALE3D, the output of this code is in a standard finite element format, in which mesh geometry files map points to faces and finite element grid cells. The procedure for mapping temperatures on the finite element to the CA grid is relatively straightforward as both meshes involve regular 3D arrays of cells, and the bilinear interpolation scheme from Subsection 7.1.1 can be extended into 3D with ease. The OpenFOAM simulation data was obtained by Alex Plotkowski at Oak Ridge National Laboratory, for spot melt and line scan data sets representative of SLM conditions for Inconel 625. As these simulations did not include interface motion, the “blank” cells from Subsection 7.1.1 were not required, although the procedure for remelting solid cells was retained.

Two additional modifications are made to simulate these conditions. First, an interfacial response function representing solidification of this alloy (a single phase) is required; the polynomial representation of the interfacial response used by [192] for Inconel 718 solidification is used as an approximation to Inconel 625. Second, an initial microstructure for each simulation domain is required. This is done by starting with an all-liquid domain of the same size, randomly placing nuclei at a spacing representative of the grain size in realistic baseplates for SLM, and letting them grow at a constant rate until all liquid cells were claimed by a grain. 40 μm was chosen as the starting grain size in these simulations, estimated from the baseplates of the AM bench data collected at the National Institute of Standards and Technology and available online [138]. The orientations of these randomly placed nuclei can be random, as in the case of the spot melt result of Figure 7.4a, or taken from a biased distribution over-representing a preferred orientation, as in the case of the spot melt result of Figure 7.4b with \(<001>\) orientations. The most significant microstructural change arising from differences in initial grain orientation distribution is the larger number
of grains originating from the melt pool bottom advancing to the top surface in the textured substrate case, as the misaligned grains that grew in from the melt pool sides in the equiaxed case were no longer there to impinge them. In Figure 7.4c, we show histograms for both of these spot melt simulations showing the difference in the orientations of grains represented at the top of the simulation domain. In the case of the textured substrate, a significant number of grains were forced to grow at unfavorable misalignments relative to the thermal gradient direction. These differences in orientation distributions of grains show the importance of the previous layer’s microstructure on successive layers. In particular, as larger undercooling is required to drive growth of grains more misoriented with the local thermal gradient, it is possible that the columnar to equiaxed transition could take place under $G$ and $V$ conditions that would not normally be favorable for a substrate consisting of low misorientation grains.

![Figure 7.4](image.png)

Figure 7.4 As-solidified microstructure using OpenFOAM thermal profiles of spot melt pool geometries. The equiaxed substrate (a) and <001> textured substrate (b) produced different final microstructures, as grain growth proceeded from different regions of the melt pool boundary. The histogram plotting the frequency of grain orientations represented in the area of the melt pool top (c) shows a large number of grains growing at unfavorable orientations relative to the thermal gradient direction (10-20 degrees off the $+Z$ direction) in the case of the textured substrate.
Simulations with the equiaxed substrate were applied to three different sets of conditions: one with the standard conditions used for the spot melt shown in Figure 7.4, one with the same conditions but neglecting fluid flow, and one with the same conditions but with an increased energy absorption efficiency. The parameters needed to model the force on the melt pool surface and energy absorptivity of the material tend to have a large amount of uncertainty. Thus, performing simulations for ensembles of predictions and comparing to experiment will help understand these processes better. As shown in Figure 7.5, neglecting fluid flow leads to a significantly different melt pool shape as well as a wider (but only slightly more shallow) melt pool. As a result of the difference in melt pool geometry, the local thermal gradients in the liquid and, therefore, the modeled microstructure, are significantly different. Compared to the grain structure that primarily originated from the melt pool bottom and lower sides in Figure 7.5a, the grains of Figure 7.5b along the melt pool top tended to grow inward from the steep upper melt pool sides. Grains along the bottom surface in the case without fluid flow were mostly impinged by these grains growing inward from the sides, leading to clear differences in number, size, and shape of grains at the melt pool top. The histogram of Figure 7.5c shows the differences in top surface grain misorientation relative to the positive Z direction for the fluid flow, no fluid flow, and fluid flow with increased energy absorption cases. As might be expected, there are more grains represented at the top surface for the high absorption efficiency case (as it has the largest melt pool). Of note is that the bimodal distribution of grain misorientations that showed relatively equal numbers of low misorientation and high misorientation grains for the no fluid flow and fluid flow cases was significantly skewed towards high misorientation grains when more energy was absorbed. As different misorientation grains are represented in different regions of the melt pool, these results highlight the importance of melt pool geometry on texture development in representative melt pools.

Though the melt pool in these spot melt simulations was too small to observe the columnar to equiaxed transition at the melt pool top (where the thermal gradients would be the
Figure 7.5  As-solidified microstructure using OpenFOAM thermal profiles of spot melt pool geometries, without inclusion of fluid flow (a) and with inclusion of fluid flow (b). The number of grains as well as the grain shape vary due to the change in melt pool geometry brought on by the presence of flow, with more grains growing in from the sides of the deeper and steeper melt pool walls in (a) relative to (b). The histogram (c) plots the number of grains with specific orientations at the top surface of the melt pool, showing a bimodal distribution but significantly more highly misorientated grains in the fluid flow case, particularly in a simulation in which fluid flow and a larger energy absorption efficiency were considered.

(smallest), some simulations with very large nucleation densities and an increased absorption efficiency (which lead to increased melt pool size) were performed for ranges of values for the mean nucleation undercooling $\Delta T_N$ and the maximum nucleation density $N_{\text{max}}$. As the thermal gradients present were still very large, values of $\Delta T_N$ that were near the steady state undercooling for grain growth left nucleated grains with too little room to grow or significantly impinge the epitaxial grains. As shown in Figure 7.6, $N_{\text{max}}$ of $10^{18}$ m$^{-3}$ was required to see significant nucleation in the melt pool, and $10^{19}$ m$^{-3}$ to see the nucleated grains significantly impinge the advance of the epitaxial grains of the melt pool sides and bottom.
Even at the large nucleation densities, small values of $\Delta T_N$ were needed for this transition to take place, showing the importance on microstructure of both nucleation density and the undercooling values at which nuclei are activated. Though problems like these simple simulations of transient melt pools from a stationary energy source one are somewhat trivial, being able to model these simple test problems for small melt pools and spot melt scenarios is a necessary step towards future work modeling more complex and larger melt pool geometries. In particular, the formation of melt pools of unusual shapes through varied scan pattern in 3D is of interest due to the possibility of large misorientations between grains in adjacent layers leading to the columnar to equiaxed transition, as is the use of experimental results to estimate realistic nucleation parameters for simulations; these are subjects of planned future collaboration with Alex Plotkowski and collaborators at the national laboratories.

Figure 7.6 3D CA simulated spot melt cross sections as functions of nucleation density and mean nucleation undercooling, showing more refined and equiaxed microstructures as nucleation density is increased and mean nucleation undercooling decreased. The blocking of the original grains by nucleated grains is quantitatively shown in the percentage of epitaxially growing grains represented at the top surface (boxed numbers).
7.2 Coupled thermal LB-CA applied to LENS\textsuperscript{TM} transport and solidification

The hybrid thermal lattice Boltzmann-cellular automata (TLB-CA) model discussed in Chapter 5 can be applied to modeling coupled fluid flow, heat transport, nucleation, and grain growth for the LENS\textsuperscript{TM} process using varied beam parameters, substrate conditions, and materials properties. Simulation of a moving beam over an elongated substrate with varied beam velocities (0.002, 0.006, and 0.01 m/s, corresponding roughly to the range of beam velocities common to LENS\textsuperscript{TM}) was performed to yield single pass microstructure results. Figure 7.7a shows the difference in melt pool shape and size for the smallest and largest of the aforementioned beam velocities, with the beam moving from left to right across the domains. $N_{\text{max}} = 1 \times 10^{11}$ m$^3$ (converted into a 2D nucleation density with use of Eq.(4.18)), $\Delta T_N = 5$ K, and $\Delta T_\sigma = 0.5$ K were the nucleation parameters used, and Ti-6 wt.% Mo the alloy used. It can be readily seen that the melt pool resulting from the 0.01 m/s scan speed was more shallow and wider than that resulting from the 0.002 m/s scan speed. As indicated by the arrows in both cases of Figure 7.7a, the two convection cells from the stationary beam test problem of Figure 5.2 are still present, but are asymmetrical with the cell ahead of the moving beam smaller and with faster fluid flow, and and cell behind the moving beam elongated and with slower fluid flow. As expected, the thermal gradients ahead of the moving beam for the 0.01 m/s case are larger, and the thermal gradients in the wake of the moving beam smaller than those in the 0.002 m/s case. The differences in melt pool geometry, thermal gradient direction, and thermal gradient magnitudes in the wake of the moving beam lead to the differences in microstructure development shown in Figure 7.7b. For the slowest scan velocity, the rounder shape of the melt pool lead to more grains advancing from left to right across the length of the melt pool, generally dominating those that grew from the melt pool bottom. These grains generally had orientations rotated clockwise from the horizontal direction (positive degrees, colored green), and nucleated grains were generally
confined to the rightmost region of the scan path (where the beam was turned off, and faster solidification under the transient thermal conditions occurred). The 0.006 m/s scan velocity shows a similar result, though with more nucleated grains near the top surface and therefore slightly more variation in grain orientation. The 0.01 m/s scan velocity, which produced a more elongated melt pool with a flat bottom, was not dominated with grains growth from left to right but rather by grains growing from the melt pool bottom. These grains tended to be aligned with the vertical direction or slightly rotated in the direction of the beam movement (yellow and light green in color). Additionally, the faster solidification rates and smaller thermal gradients in the wake of the beam for the 0.01 m/s scan velocity gave rise to more nucleated grains dominating the top half of the resolidified grain structure. The two main qualitative findings from these microstructure results at different beam velocities - epitaxial growth of grains from different regions of the melt pool depending on the melt pool geometry, and nucleation of new grains at the top of the melt pool where the magnitude of the thermal gradient was smaller - were both expected based on alloy solidification theory and show the importance of beam velocity on predicting grain structures in LENS™ solidification.

![Figure 7.7](image)

**Figure 7.7** Temperature and velocity fields for steady state melt pools formed at two beam scan velocities (a), and microstructure results for the solidification of melt pools formed at three beam scan velocities (b). The more elongated melt pools formed at faster scan speed lead to flatter melt pools and more growth from the melt pool bottom, along with faster solidification allowing more nucleation to occur.
As was performed using the 3D CA in Subsection 6.1.1, the effect of alloying addition on the microstructure through induced variation in the interfacial response function can be explored using the TLB-CA model. We simulate a single pass from left to right of a beam moving at 0.01 m/s for three different Mo concentrations: 2, 5, and 20 weight percent Mo. It is noted that the approximations used from Eq.(2.17), particularly the dilute alloy approximation of linear liquidus slope $m_L$ and solute partition coefficient $k_p$ will likely lose validity upon addition of 20 weight percent Mo; it is shown here merely for demonstration purposes. The nucleation parameters of $N_{max} = 5 \times 10^{11} \text{m}^3$ (converted into a 2D nucleation density with use of Eq.(4.18)), $\Delta T_N = 5 \text{K}$, and $\Delta T_\sigma = 0.5 \text{K}$ were used.

Grain orientations for the three alloy compositions as shown in Figure 7.8 use two different colormaps: grains that grew epitaxially from the substrate use the grayscale colormap, while those that nucleated ahead of the epitaxial grains use the chromatic colormap. For Ti-2 wt.% Mo, fewer nucleation events occurred relative to the other two alloys as the steady state undercooling of the epitaxial front grains was similar to the undercooling at which nucleation occurred, leading to the extinction of some nucleation sites via growth of epitaxial grains. The nucleated grains were almost exclusively found in the region in which the final melt pool solidified, under transient solidification conditions following the end of the scan, and had an equiaxed nature due to the small thermal gradients in this region. Those that did nucleate during the larger thermal gradient conditions of steady state beam movement and solidification tended to be very close to the solidification front, becoming impinged and embedded in the epitaxial grains or becoming part of the epitaxial front itself. This is also the case for Ti-5 wt.% Mo, though more nucleation events occurred due to the larger undercooling at the epitaxial front and as a result, more nucleated grains appear in the microstructure. Equiaxed nucleated grains appear mostly at the top of the domain, while nucleated grains closer to the melt pool bottom tended to be more columnar in shape. Ti-20 wt.% Mo had the largest number of nucleated grains due to the even larger steady state undercooling of the epitaxial front, and the nucleated grains dominated the majority of the
solidified melt pool. These nucleated grains still tended to be columnar in shape apart from at the top of the melt pool and in the region at the end of the scan path, but the grain shapes overall tended to be more equiaxed for Ti-20 wt.% Mo than for Ti-5 wt.%. Though a more exact interfacial response function for Ti-20 wt.% Mo would alter this result to some degree, the ability of alloying additions to induce changes to the interfacial response function that result in more equiaxed microstructures is clearly demonstrated using this model. Although the microstructure even for Ti-20 wt.% Mo is more mixed columnar and equiaxed rather than fully equiaxed, and the equiaxed grains at the top of the solidified melt pool would likely be remelted during deposition of additional layers, the modeled ability of these nucleated grains to impede the epitaxially growing columnar grains and reduce the mean grain width has been seen in the literature as discussed in Section 2.2. These results demonstrate that the use of interfacial response functions with this TLB-CA model has the potential to aid in the design of both process conditions as well as alloying additions to predict trends in grain shapes and sizes, noting again that more complex functions would be required for alloys with less linear phase diagrams or ternary systems.

Figure 7.8 TLB-CA modeled grain structures for a single left-to-right beam pass at 0.01 m/s and varied solute composition. The grayscale colormap is used for substrate grains, while the chromatic colormap is used for grains that nucleated from the liquid. As Mo content is increased, changes to the interfacial response function allow for more nucleation events, and nucleated grains constitute more of the solidified melt pool.
Modeling of multilayer solidification can be considered using the TLB-CA model through repositioning the substrate within the simulation domain between layers. A given number of rows (200 CA cells in the cases shown here) consisting of new equiaxed grains is placed at the top of the simulation domain following the end of solidification for a scan path, the temperature of the substrate is reset to \( T_{\text{preheat}} \), and the heat source position is reinitialized. Through using this procedure, unidirectional scans in which the beam moves left to right for each layer, and bidirectional scans in which the beam’s position does not reset but its direction alternates between layers, are considered. For the unidirectional and bidirectional scan patterns, \( 7.5 \times 10^6 \) time steps were used with a beam moving at 0.01 m/s. As Ti-5 wt.% Mo was the material used, and nucleation of new grains primarily affected the top of resolidified layers in the previous results (which in turn would be remelted during subsequent layer deposition), heterogeneous nucleation was neglected. In addition to the line scan patterns, we also considered a “multi-spot scan” pattern for microstructure simulation in this section, in which five beams of truncated Gaussian shapes spaced with centers 700 TLB cells apart are pulsed on and off for each layer. For the multi-spot scan pattern, the beams heated the substrate for \( 2 \times 10^6 \) time steps per layer. Solidification of the multipot melt pool was performed with and without consideration of heterogeneous nucleation, using \( N_{\text{max}} = 5 \times 10^{11} \text{ m}^3 \) (converted into a 2D nucleation density with use of Eq.(4.18), \( \Delta T_N = 5 \text{ K}, \) and \( \Delta T_{\sigma} = 0.5 \text{ K} \). Schematics of these scan patterns are shown alongside the modeled grain orientations following deposition of four layers in Figure 7.9.
Figure 7.9 Scan pattern schematics (left) and modeled microstructure for multilayer LENS™ solidification as a function of scan pattern (right). In (a), the beam moved only from left to right, while in (b), the beam switched direction every other layer. Grain shapes and widths varied depending on the different thermal gradient directions induced by scan pattern variation. (c) considered five beams that pulsed on and off to create a wide, single melt pool for each layer, yielding more changes in grain widths and orientations relative to the cases of (a) and (b) due to the more static thermal gradient direction that developed in the absence of beam motion. (d) differs from (c) by including heterogenous nucleation of new grains in the undercooled liquid ahead of the solidification front, showing a finer and more equiaxed microstructure as the epitaxial grains that grew from the melt pool bottom and dominated the simulation in (c) were blocked from advancing.
The grain structures resulting from the unidirectional and bidirectional scan patterns showed the expected epitaxial grain growth from the substrate, with impingement of less favorably oriented grains in each layer resulting in wide (on the order of a few hundred microns) columnar grains at the top surface. These are around an order of magnitude wider than the substrate grains’ average diameter. The unidirectional scan pattern, as clear from Figure 7.9a, resulted in an average grain width at the top surface of around 27% smaller than that of the bidirectional scan pattern in Figure 7.9b. This is due to the fact that as the thermal gradients evolved in an identical manner in each layer for the unidirectional pattern, impingement occurred only to a modest degree as all advancing grains had relatively favorable orientations. For the bidirectional scan pattern, however, every other layer involved sharp changes in thermal gradient direction; this lead to a larger number of impinged grains and the “zig-zag” appearance to the grain structure in Figure 7.9b relative to the single scan direction “lean” of the grains in Figure 7.9a. The multispot scan strategy as shown in Figure 7.9 lead to an even more narrow average grain width, nearly 45% smaller than those of the bidirectional scan pattern. The thermal gradient that developed in the long, flat melt pool was more static than that of the moving beam melt pools and held a primarily vertical orientation across the melt pool boundary, leading to the advance of many grains very closely oriented with the vertical direction. For more exact comparisons to experimental grain widths and orientations, more quantitative estimates of initial grain sizes and orientation distributions as well as the simulation of additional layers would be needed. Residual heat could also be included by using a “dwell time” between the solidification of a layer and the start of a new layer, during which heat diffusion would be calculated rather than resetting the material to the preheat temperature.

Unlike the line scan simulations with varied Mo composition, in which nucleated grains coexisted with columnar grains and only dominated the microstructure at the top surface, the transient melt pool conditions that developed during the multispot scan lead to a fully equiaxed microstructure when heterogeneous nucleation was included as shown in Figure
7.9d. The difference between the line scan and multispot thermal profiles was responsible for this, as the spot melt pool was deeper and involved smaller thermal gradients with relatively static direction during solidification. This deep melt pool allowed nucleated grains the ability to grow closer to the melt pool bottom relative to nucleated grains in the line scan patterns; these equiaxed grains in the multispot pattern case were able to dominate through multiple layers rather than remelting entirely. These results showed in addition to the factors affecting solidification of the melt pool resulting from a single beam pass, the chosen multilayer scan strategy plays an important role in grain growth for AM processes. The qualitatively and quantitatively reasonable grain widths, orientation distributions, and shapes achieved with the multilayer TLB-CA model showcase the potential for the model to continue developing into a tool for understanding grain growth trends with material and process conditions in AM processes. More quantitate comparisons with experimentally determined grain aspect ratios and orientation trends for the process of interest (LENS\textsuperscript{TM}) with the inclusion of heterogeneous nucleation will likely require some empirical tuning of nucleation parameters and energy absorption, and potentially a 3D implementation of the model. Such comparisons and the tuning of the model parameters for more accurate simulation of LENS\textsuperscript{TM} process conditions are the subject of planned future collaboration with Richard LeSar and Peter Collins at Iowa State University.
CHAPTER 8. CONCLUSIONS AND FUTURE WORK

8.1 Abilities and potential uses for the CA and LB-CA models in additive problems

In this thesis, variants of the lattice Boltzmann method and cellular automata (CA) for alloy solidification were applied to conditions representative of additive manufacturing processes for alloys. Two specific forms of CA were considered for microstructure modeling: one in which solute partitioning was explicitly calculated and local solidification was a result of local constitutional undercooling and interface curvature, and a second in which grain envelopes were considered in lieu of specific details of dendrite morphology and solute partitioning. The first CA was mostly used to simulate solidification morphology within single grains (the “intragranular” scale). It demonstrated good quantitative agreement with the analytical solution for dendrite tip velocity as a function of solidification rate in the range of thermal conditions common to AM processes for Ti-1.5 mol.% W and Ti-1.5 mol.% Cu. Statistical variation in the growth of multiple dendrites from an initially planar interface was performed for varied initial conditions, and primary dendrite arm spacing values compared reasonably well with analytical relationships of arm spacing as a function of cooling rate. The primary dendrite arm spacing for Ti-W was modeled with varied solute diffusivity and solute composition, showing the expected qualitative trends and producing a test of the sensitivity of the results to parameter variation. Secondary branching of dendrites was shown to strongly depend on the interfacial energy and interfacial energy anisotropy, both also having an effect on the solute concentration in dendrite stems. Decreasing dendrite arm spacing was modeled as dendrite tips under rapid solidification conditions approached the solidus temperature, and a model extension to include non-equilibrium solute partitioning for Ti-
1.5 mol.% Ni allowed for the modeling of solute trapping along dendrite stems. The banded morphology beyond the upper velocity of dendritic front stability was observed during rapid solidification modeling of Ti-1.5 mol.% Ni, within which the solidification front oscillated between dendrites with solute trapping and a planar, segregationless solidification front in qualitative agreement with analytical models and experimental rapid solidification results. Additionally, the CA model was coupled with the lattice Boltzmann method for simultaneous simulations of fluid flow, solute transport, and solidification. When applied to isothermal dendrite growth, fluid flow had a notable impact on solidification. When the COMSOL Multiphysics-predicted thermal gradients, cooling rates, and fluid flow conditions were used to approximate Laser Engineered Net Shaping (LENS\textsuperscript{TM}) process conditions, a lesser impact of fluid flow at the solidification front was seen as the most dynamic flow tended to be at the top melt pool surface as opposed to the solidification front itself. Nevertheless, the model’s predictions for Ti-1.5 mol.% W microsegregation and primary dendrite arm spacing closely matched experimental energy-dispersive spectroscopy (EDS) microstructures from LENS\textsuperscript{TM} builds of this alloy, showing a promising ability of the present model to accurately model details of dendritic microstructure for this process.

The second form of CA considered (the “granular scale”) was applied to constant thermal gradient and cooling rate conditions representative of those encountered in the LENS\textsuperscript{TM} process for the simulation of directional growth of grains. The columnar to equiaxed transition (CET) was successfully modeled at fast solidification velocities and reduced thermal gradients. The interfacial response function – relating the growth velocity of grains to local cell undercooling values – was varied through changing solute element and solute amount for several $\beta$-Ti alloys. It was shown that through larger quantities of alloying additions, the resulting changes to the interfacial response function can be used to bring about the CET in the model results. Different alloying additions were more effective than others at enhancing grain nucleation and consequent blocking of the columnar grain front’s advance, which was found to be closely related to the shape of the interfacial response function and
the supercooling parameter $P$. Nucleation density was varied to show that the CET requires not only a sufficiently small thermal gradient, but a sufficient concentration of nuclei as well. Large nucleation density can yield either fine equiaxed grains or small equiaxed grains embedded within large columnar grains depending on the thermal gradient. The CET as a function of several model parameters was parameterized, relating the spatial extent of the undercooled zone ahead of the solidification front and the integral of the interfacial response function from the minimum required undercooling for nucleation to the steady state front undercooling to a parameter that correlated well with the fraction of columnar grains blocked by nucleation events. The CA was also applied to temperature profiles as functions of time in 2D and 3D predictions of Selective Laser Melting (SLM) melt pool evolution, and predicted quantitatively reasonable grain widths and qualitative features of grain growth consistent with experimental observations. The ability of CA to predict coupled nucleation and growth for various set of conditions in a relatively simple manner should prove useful for ensembles of simulations that can capture uncertainty in experimental quantities such as nucleation undercooling or density, and potentially help to predict such values. The grain growth CA is general and, with accurate 2D or 3D thermal data for a given material and an interfacial response function, a resulting microstructure can be calculated. The model could be expanded to easily incorporate additional physics specific to an alloy system as well. Examples of this include the $\beta$ to $\alpha$ transition in Ti, nucleation and growth of the ferrite phase from the liquid for two-phase steels, or solid phase grain growth.

The coupled thermal lattice Boltzmann-CA (TLB-CA) model, developed specifically for LENS$^\text{TM}$ solidification, allows for simulation of fluid and heat transport in a qualitative manner while simulating nucleation and grain growth on a separate length scale (or time scale, though that wasn’t done in the present work). Changes in beam scan speed and solute composition were directly shown to affect the fluid flow and temperature fields of the melt pool as well as predicted grain structures. The scan pattern in 2D was varied and shown to have significant effects on grain orientations and shapes. Simulation of large line scans and
multiple layers of solidification was possible through use of the message passing interface (MPI) library for parallelization, in which a domain decomposition was performed to take advantage of the local nature of the CA-based methods’ calculations. Locally calculated thermal gradient and cooling rate values from this model could be fed to the intragranular-scale CA for qualitative estimates of dendrite spacing, morphology, and microsegregation as well. Although experimental validation has not yet been performed, through use of empirical tuning of unknowns such as beam absorption and nucleation parameters, this model would likely serve a useful role in designing a set of LENS\textsuperscript{TM} process conditions and $\beta$-Ti alloying additions that would produce predictable microstructures. Despite the fact that the model does not simulate all relevant physics (e.g., only approximating the formation of the keyhole, no deformation of the liquid-gas interface), the present CA models have already proven useful in correlating materials parameters and solidification dynamics to microstructure changes, and further optimization and parallelization would yield an even more useful tool for linking key trends and relationships among material, process parameters, and microstructure.

8.2 Computational and physics challenges for CA and LB-CA in additive problems

While the present model has been able to demonstrate many aspects of AM melt pool formation and solidification trends qualitatively and qualitatively, there are still several issues that need to be addressed to achieve more accurate calculations. The intragranular scale, despite the corrections proposed in the literature, still struggles to quantitatively model dendritic growth at off-grid orientations; growth will be biased towards the nearest neighbor or next nearest neighbor directions, which will affect microstructure prediction when applying this model at scales beyond that of a single grain. Additional consideration of solute redistribution ahead of the solid-liquid interface and more complex capture rules will likely be required to address this issue. The challenge of interface curvature estimation from discrete
solid fraction values of cells is another major issue that will need to be addressed for more quantitative comparisons with dendritic microstructures across wide ranges of conditions and alloys. Under and overestimation of interface curvature can lead to dendrites not developing when they should, or artificial growth of secondary dendrite arms due to grid effects. The best way to solve this issue with CA would be a multi-grid method in which solidification at multiple length scales can be considered depending on local conditions, in conjunction with improvement in the algorithm for estimation of interface curvature. Alternatively, the Phase Field (PF) method or hybrid PF-CA models could be used at this scale to resolve this issue.

At the granular scale, the effect of ignoring the solutal boundary layer on grain impingement and nucleation have not been considered. The decentered square and octahedron algorithms do not account for the effect of surface energy anisotropy on growth, which would lead to differences in grain shape particularly when grains are growing with a large misorientation between the grain unit vectors and the thermal gradient direction. Such considerations will be important when differentiating between body-centered cubic (BCC) and face-centered cubic (FCC) solidification, the two primary solid phases formed on liquid to solid phase transformation in binary and ternary Ti, Fe, and Ni alloys. There is the opportunity for significant computational and experimental work on reducing uncertainty in parameters governing nucleation, interfacial energies, and solute transport, as these parameters have been shown to play significant roles on microstructure development and are often only known within an order of magnitude.

The proposed modifications for the intragranular scale CA, particularly if performed in 3D, might lead to a large increase in computational cost. The TLB model, even without full inclusion of interface physics and liquid-gas phase changes, would also likely have a high computational cost in 3D even with large-scale parallelization. For modest computing resources, the 2D TLB model coupled to the 2D granular CA model yielded results in a reasonable amount of time. However, when expanding the TLB-granular CA model to 3D, other computing approaches may be required for computational speed. Use of parallel
GPU computation can significantly accelerate LB calculations, and has been used in large scale thermal LB calculations [32] and coupled LB-PF calculations [206]. Multigrid LB methods have been developed and applied to fluid flow problems, and a multigrid method for the thermal LB method with a smaller cell size at the interface and larger cell sizes elsewhere in the simulation may provide faster computation time. More coarse LB grid spacing with a more rigorous temperature interpolation scheme to connect to the CA scale could also be used. As 3D modeling of this problem will be needed for full comparison of grain growth results with experiment with more complex scan patterns, a concurrent multiscale and parallel TLB-granular CA with these modifications would provide better performance than modeling solute transport and growth of individual dendrites with the intragranular CA across the entire melt pool. Local thermal gradient and cooling rate values from the TLB model could be used as input for calculations using the intragranular CA for estimation of primary dendrite arm spacing, morphology, and solute segregation for selected grains or regions of the melt pool.

8.3 Use of CA for additive manufacturing-based exascale computing problems

Exascale computing, or computers capable of performing $10^{18}$ floating point operations per second, has been a goal of international supercomputing initiatives. The Exascale Computing Project (ECP), funded by the US Department of Energy, highlights modeling of materials and transport phenomena in additive manufacturing processes as a potential application for exascale computing. The development of codes suitable for exascale computing and applied to modeling fluid and heat transport, microstructure, and part behavior to aid AM material and part qualification is the goal of the Transforming Additive Manufacturing through Exascale Simulation, or ExaAM, initiative. The 3D granular CA, with inherently local behavior and simple rules governing solidification and nucleation of cells, is well suited
to be incorporated into large-scale parallel frameworks used by the ExaAM project. Such a model would have the ability to run concurrently with a fluid and heat transport model on the appropriate length and time scales to simulate microstructures across an entire part, which could then be fed to micromechanical codes to link grain structure to material behavior. As the granular CA model using OpenFOAM thermal profiles for melt pool cross sections have already yielded qualitatively consistent grain structures with those seen experimentally from benchmark experiments performed at NIST, as shown in Figure 8.1, the ability of a parallelized model directly coupled to heat transport calculations to predict trends in grain sizes, orientation, and texture during complex scan patterns is of interest. Additional physics such as solid-solid grain growth and phase transitions have been performed with this CA and could naturally be included in such a model as well. With appropriate corrections to the intragranular CA, exascale computing could make modeling of individual dendrite growth and solute segregation feasible in 3D across the scale of entire parts as well, provided that appropriate adjustments are made with multiple grids and calculations of interface curvature.

The Adaptive Mesh Refinement for Exascale computing (AMReX) framework provides a pathway for incorporating the existing CA algorithms for solidification – at the scale of dendrites or grain structures – into large-scale parallel simulations. Similar to the domain decomposition strategy employed in the MPI TLB-CA simulations introduced in Section 5.2, AMReX is a block-structure adaptive mesh refinement framework that breaks the domain up into regions, with the size of the regions depending on where computational efforts are focused. The parallelization is handled automatically. Such a framework would provide a very useful way of introducing multiple grids into the intragranular CA model. It also could provide a more efficient parallelization of the 3D granular CA model for simulations of AM melt pools relative to simple geometrical domain decompositions, as nearly all calculations are performed at interface cells, and this framework could naturally load balance the number of interface cells per processor. The “multifab” and “particle” data types defined by AMReX are naturally suited for handling variables such as grain identification (which
Figure 8.1 An experimentally obtained secondary electron microstructure image of a chemically etched cross section of an SLM cross section (a), and an electron backscatter diffraction image of the same area showing the grain structure (b), obtained by the AM benchmark experiments performed at NIST [138]. A qualitatively similar result using granular CA simulation of an OpenFOAM-predicted SLM thermal profile is shown in (c).

defines a grain’s orientation) and decentered octahedra attributes such as coordinates and size; the ability to create or delete particles in this framework provides an effective way to manage the program’s memory. In addition to MPI parallelization, the AMReX framework supports OpenMP parallelization and hybrid MPI/OpenMP parallelization, which could further improve the code’s performance. As of Fall 2018, the 2D decentered square algorithm for nucleation and growth has been incorporated into the AMReX framework and applied to some simple directional growth problems with fixed thermal conditions. Future work includes expanding this work to 3D and directly incorporating calculations of heat transport and cell temperatures, rather than reading files of temperature values from another code’s output. Scoping out improvements to the intragranular CA for coupled solute segregation
and dendritic growth calculations for potential use in the AMReX framework is also of inter-

est. Whether at the scale of individual dendrites, grain structures across melt pools, or modeling of AM fluid and heat transport phenomena coupled to solidification problems, CA-based methods for modeling AM processes are proving to be a versatile tool that show promise for better understanding material-process-microstructure relationships as well as designing materials suited for predictable microstructure development.
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APPENDIX A. LATTICE BOLTZMANN BOUNDARY CONDITIONS

Fluid boundary conditions

Three types of boundary conditions for fluid were applied in this thesis: bounce-back at solid walls, constant velocity, and constant density (i.e., an inlet or outlet for fluid). Bounce-back at a wall, where slip is not considered and the fluid velocity must be zero, is the most simple of these. Consider a cell at lattice location \( \vec{x} \) that is either a solid cell or part of a wall. Following propagation of distribution functions at time \( t \), the boundary condition is applied by reversing the directions of the distribution functions; for the D2Q9 lattice of Figure 3.2, the rewritten distribution functions \( f_{i}^{\text{in}}(\vec{x}, t) \) as a function of the distribution functions post-propagation step \( f_{i}^{\text{in\ast}}(\vec{x}, t) \) are

\[
 f_{i}^{\text{in\ast}} = \begin{cases} 
 f_{0}^{\text{in}} & i = 0 \\
 f_{2}^{\text{in}} & i = 1 \\
 f_{1}^{\text{in}} & i = 2 \\
 f_{4}^{\text{in}} & i = 3 \\
 f_{3}^{\text{in}} & i = 4 \\
 f_{7}^{\text{in}} & i = 5 \\
 f_{8}^{\text{in}} & i = 6 \\
 f_{5}^{\text{in}} & i = 7 \\
 f_{6}^{\text{in}} & i = 8 
\end{cases} \quad (A.1)
\]

where \( f_{i}^{\text{in}} \) is an abbreviation for \( f_{i}^{\text{in}}(\vec{x}, t) \) and \( f_{i}^{\text{in\ast}} \) an abbreviation for \( f_{i}^{\text{in\ast}}(\vec{x}, t) \). The constant velocity and constant density boundary conditions are handled as described by [298], and schematically described in Figure A.1. Consider a case for which a constant fluid velocity
of $u_{fixed}$ in the X direction and zero in the Y direction is imposed at the left boundary, as shown in Figure A.1a. Following the propagation step, $f_{1}^{in*}$, $f_{5}^{in*}$, $f_{8}^{in*}$, and $\rho$ are unknown (as shown in Figure A.1b) while all other $f_{i}^{in*}$, having streamed from other lattice sites, are known. Using Eq. (3.4) and Eq. (3.5), $\rho$ can be determined as

$$\rho = f_{0}^{in*} + f_{2}^{in*} + f_{4}^{in*} + 2 (f_{3}^{in*} + f_{6}^{in*} + f_{7}^{in*}) . \tag{A.2}$$

By making the assumption that the bounce back rule is still correct for the non-equilibrium part of the distribution function as done by [298], the unknowns can be solved for as

$$\begin{cases} 
    f_{1}^{in*} = f_{3}^{in*} + \frac{2}{3} \rho u_{fixed} \\
    f_{5}^{in*} = f_{7}^{in*} - \frac{1}{2} (f_{2}^{in*} - f_{4}^{in*}) + \frac{1}{6} \rho u_{fixed} \\
    f_{8}^{in*} = f_{6}^{in*} + \frac{1}{2} (f_{2}^{in*} - f_{4}^{in*}) + \frac{1}{6} \rho u_{fixed}
\end{cases} \tag{A.3}$$

Figure A.1 Illustration of a constant velocity boundary condition at the left boundary of a lattice Boltzmann domain prior to (a) and following (b) propagation of distribution functions $f_{i}$. The boundary itself is highlighted in red, while lattice sites adjacent to the boundary are within the blue shaded region. Following propagation, the distribution functions highlighted in red must be rewritten as a function of the known distribution functions (black) to preserve the boundary condition.
The constant pressure boundary condition is similar, but with $u_x$ unknown and $\rho_{\text{fixed}}$ a known quantity. Again using Eq.(3.4) and Eq.(3.5), $u_x$ can be determined as

$$u_x = 1 - \left( \frac{f_{0}^{\text{in}} + f_{2}^{\text{in}} + f_{4}^{\text{in}} + 2 \left( f_{3}^{\text{in}} + f_{6}^{\text{in}} + f_{7}^{\text{in}} \right)}{\rho_{\text{fixed}}} \right) \left( f_{\text{in}} - f_{\text{in}}^{*} \right).$$  \hspace{1cm} (A.4)

Making the same assumptions made in the derivation of the constant velocity boundary condition, the unknowns can be solves for as

$$f_{i}^{\text{in}} = \begin{cases} 
    f_{1}^{\text{in}} = f_{3}^{\text{in}} + \frac{2}{3} \rho_{\text{fixed}} u_x \\
    f_{5}^{\text{in}} = f_{7}^{\text{in}} - \frac{1}{2} \left( f_{2}^{\text{in}} - f_{4}^{\text{in}} \right) + \frac{1}{6} \rho_{\text{fixed}} u_x \\
    f_{8}^{\text{in}} = f_{6}^{\text{in}} + \frac{1}{2} \left( f_{2}^{\text{in}} - f_{4}^{\text{in}} \right) + \frac{1}{6} \rho_{\text{fixed}} u_x
\end{cases} \hspace{1cm} (A.5)$$

**Energy boundary conditions**

Two types of boundary conditions for internal energy density are required: constant temperature at stationary walls ($\vec{u} = 0$, as used at the top and bottom walls of Figure 3.3) and adiabatic boundaries (used at the melt pool surface in the TLB-CA model). We apply the procedure of [142] for these conditions. For applying a constant temperature condition (equivalent to some constant internal energy density $E_{\text{fixed}}$ through Eq.(5.1)), for example at a top surface wall where $g_{4}^{\text{in}}$, $g_{7}^{\text{in}}$, and $g_{8}^{\text{in}}$ are unknown, we consider these unknown values to be equivalent to the sum of their known directional opposites ($g_{2}^{\text{in}}$, $g_{5}^{\text{in}}$, and $g_{6}^{\text{in}}$, respectively) plus a correction term $\omega_{i}G$, where $G$ is defined using the definition of $E$ in Eq.(3.13) as

$$G = \frac{E_{\text{fixed}} - \left( g_{0}^{\text{in}} + g_{1}^{\text{in}} + g_{3}^{\text{in}} + 2 \left( g_{2}^{\text{in}} + g_{5}^{\text{in}} + g_{6}^{\text{in}} \right) \right)}{\omega_{1} + \omega_{2} + \omega_{3}}. \hspace{1cm} (A.6)$$

This allows the unknown energy density distribution functions to be solved for via the expressions

$$\begin{cases} 
    f_{4}^{\text{in}} = f_{2}^{\text{in}} + \omega_{4}G \\
    f_{7}^{\text{in}} = f_{5}^{\text{in}} + \omega_{7}G \\
    f_{8}^{\text{in}} = f_{6}^{\text{in}} + \omega_{8}G
\end{cases} \hspace{1cm} (A.7)$$

Adiabatic boundaries, where no temperature gradient exists at the interface, are handled in the same way but require an estimation of the value for $E_{\text{fixed}}$ at the boundary. This could
be performed, for example, with a simple finite different approximation using the known $E$ values for the row of cells adjacent to the boundary cells. Following this estimation, Eq.(A.6) and Eq.(A.7) are solved as in the same way as they were for the constant temperature boundary condition.
APPENDIX B. DENDRITIC GROWTH WITH GRID MISORIENTATION

For solidification on a 2D grid, it is well known that consideration of the Von Neumann (4 nearest neighbor cells) and Moore (4 nearest and 4 next nearest neighbor cells) neighborhoods induces an artificial anisotropy in dendritic growth, biasing the growth pattern in either the nearest or next-nearest neighbor directions respectively [19, 20]. The most common approach to address this for grain growth is the decentered square algorithm of Gandin and Rappaz [195], later modified for the coupled solute transport and solidification problem [257]. In the simulations of Section 6.2 that considered multiple grains along a planar solidification front, the method of [281] was used to reproduce growth for multiple dendrite orientations. This method effectively expands the local neighborhood for interface cells, considering a multi-layer mesh consisting of 2 by 2 cell “clusters”. Each grain is originally its own 2 by 2 cluster at the solidification front, and its local liquid composition $C_L$ used in solidification calculations consists of the mean values of the four smaller cell values. The larger cell’s local curvature is still calculated using Eq.(4.2), but accounting for the larger cell’s expanded local neighborhood. Each grain’s orientation $\theta$ is randomly assigned by generating two integers “$m$” and “$n$” (where $m > n$ and neither integer is larger than 5) and calculating using

$$\theta = \arctan \left( \frac{n}{m} \right)$$

Upon solidification of the cluster cell, the locations of the next clusters along the orientation axes using $m$ and $n$ are calculated. If any of the new interface cells are along an orientation axis, the new cluster is “activated” and begins solidifying as did the original cluster. If the new interface cells are not along an axis, they solidify as a normal interface cells as described in Subsection 4.2.1. A schematic of this growth process for the case of $m = 2$ and $n = 1$ is shown in Figure B.1.
Figure B.1 (from [281]): (a) Schematic of growth for a cluster nucleus with $m = 2$ and $n = 1$. (b) Upon the cluster becoming solid, the nearest neighbor cells are captured as normal interface cells. (c) Interface cells along the orientation axes become new cluster cells, while other interface cells proceed to solidify normally. (d) Upon solidification of the new cluster cells, this process repeats itself allowing growth along the grain axis directions.

For simulation of LENS™ solidification, the rapid cooling and large thermal gradients primarily allow only the grains closely aligned with the grid to advance. The algorithm had difficulty with the fast rate of solidification, also causing some of the grains with large $m$ and $n$ to lose their preferred orientation and grow aligned with the grid direction. For consideration of growth for multiple dendritic colonies across the scale of entire LENS™ melt pool boundaries rather than small regions with locally unidirectional thermal gradient, a different algorithm such as a modified version of the decentered square algorithm may be necessary due to the current method’s limitations.