Theoretical modeling of cellular and dendritic solidification microstructures

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Abstract of Dissertation

Interface pattern formation during solidification of a liquid material is important to decide final microstructures, which are related to properties of the final solid materials [51, 165, 37]. Hence, in order to understand microstructural pattern formation during solidification processes, experiments have been carried out, and various theoretical approaches have been suggested to model interface dynamics. Recently, the phase-field (PF) approach has emerged as a method of choice to investigate solidification. This method is rooted in continuum models of phase transitions. It circumvents the notorious difficulty of front tracking by making the solid-liquid interface spatially diffuse and can model quantitatively the spatiotemporal evolution of interfaces of arbitrarily complex shapes in three dimensions.

In this dissertation, we use three-dimensional (3D) PF modeling to investigate (i) 3D solid-liquid interface dynamics observed in microgravity experiments, and (ii) array patterns in a thin-sample geometry. In addition, using the two-dimensional (2D) dendritic-needle-network (DNN) model, we explore (iii) secondary sidebranching dynamics.

Recently, solidification experiments are carried out in the DSI (Directional Solidification Insert) of the DECLIC (Device for the study of Critical LIquids and Crystallization) facility aboard the International Space Station (ISS). Thus, the directional solidification experiments are achieved under limited convective currents, and the experimental observations reveal unique dynamics of 3D microstructure in a purely diffusive growth regime. In this directional solidification setup, a temperature field between heat sources could evolve due to two main factors: (i) heat transfer within an adiabatic zone and (ii) latent heat rejection at the interface. These two thermal effects are phenomenologically characterized using a time-dependent thermal shift [116]. In addition, we could quantitatively account for these thermal factors using a numerical calculation of the evolution of temperature field. We introduce these phenomenological and quantitative thermal representations into the PF model. The performed simulations using different thermal descriptions are compared to the experimental measurements from the initial planar interface dynamics to the final spacing
The DECLIC-DSI experimental observations exhibit complex grain boundary (GB) dynamics between large grains with a small misorientation. In the observations, several large grains with a small misorientation with respect to the temperature gradient are formed during solidification. Specifically, at a convergent GB, a localized group of misoriented cells penetrates into a nearby grain, which yields the morphological instability of grain boundaries. Remarkably, while the invasion process starts with a group of cells, the leader cell can detach itself from the group and grow continuously as a misoriented solitary cell in the other grain with a different misorientation. We use PF simulations to investigate the GB morphology and dynamics of a solitary cell.

Solidification experiments on earth are typically performed in a thin-sample geometry to avoid fluid convection. Thus, we consider various influences on cellular and dendritic array patterns in thin samples.

First, we explore the influence of crystal orientation. When a grain in a thin-sample geometry is misoriented with respect to the temperature gradient, primary cells and dendrites drift laterally in both experiments and simulations. At the same time, grain boundaries are systematically formed at the edges of the misoriented grain. The misoriented primary branches move away from the divergent grain boundary. At this boundary, cells/dendrites are generated continuously, and their spacings are larger than the dynamically selected spacings \[66, 52, 61, 53, 49, 48\]. Primary branches run into the other convergent GB, which leads to their elimination. Thus, at a stationary state, a spacing distribution is uniform with the spacing selected at the divergent GB until it decreases near the convergent GB. We perform simulations to illustrate the global evolutions of a primary spacing. In addition, we suggest a simple geometrical model and a nonlinear advection equation for the dynamics of the primary spacing evolution, which can predict the slow evolution of a primary spacing in a quasi-2D array.

Experimental observations point out that the primary spacing selection could be affected
by the sample thickness [137]; however, the detailed description for the link between the primary spacing selection and a sample thickness is still missing. Here, we use PF simulations to investigate the primary cellular and dendritic spacing selection mechanisms under the influence of a sample thickness.

A thin-sample geometry can limit thermal and solutal convective currents effectively. However, as the sample thickness increases, the convective currents can influence the solid-liquid interface dynamics. Then, the microstructure selection mechanisms can be different from the classical theories that are valid in a diffusive regime [157, 66, 91, 72]. We propose a simple approach for the PF model to demonstrate the microstructure selection when liquid convection is present. These simulations are compared to experimental results.

Columnar microstructures with cells and dendrites typically form polycrystalline materials during directional solidification. Then, convergent and divergent grain boundaries form systematically between grains, which are misoriented with respect to the temperature gradient. Moreover, the GB is dynamically selected during the competition between two nearby misoriented grains. In order to investigate the GB orientation selection, we carry out 3D PF simulations in a thin-sample geometry. These simulations reveal the influence of the 3D GB bi-crystallography on grain competition. The results highlight the importance of considering the orientation of the orthogonal planes containing secondary branches in addition to the growth direction of primary branches.

Finally, we propose three growth steps to demonstrate the secondary sidebranching growth dynamics under isothermal dendritic growth condition. When a secondary sidebranch is created near the primary dendrite tip, it typically screens out the other neighbors. Then, the branch passes through a progressive sidebranch elimination regime. If it survives the second elimination regime, it transitions to a growth regime free from the influence of any neighboring branches. We carry out DNN simulations to validate the proposed growth scenario for a secondary branch.
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C.1 This figure contains copyright permissions of Ref. [154] from the publisher.

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<td>Cu</td>
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<td>DECLIC</td>
<td>DEvice for the study of Critical Liquids and Crystallization</td>
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<td>DNN</td>
<td>Dendritic-Needle-Network</td>
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<td>DSI</td>
<td>Directional Solidification Insert</td>
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<td>FCC</td>
<td>Face Centered Cubic</td>
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<td>FTA</td>
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<td>GB</td>
<td>Grain Boundary</td>
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<td>GPU</td>
<td>Graphic Processing Unit</td>
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List of Symbols

\( a_s(n) \) Anisotropy function

\( c \) Concentration of solute

\( c_\infty \) Nominal composition

\( c_p \) Heat capacity of an alloy

\( d_0 \) Capillary length

\( D \) Solute diffusivity

\( D_T \) Thermal diffusivity

\( \Delta h_f \) Latent heat of fusion per unit volume

\( \Delta x \) Grid spacing

\( \Delta t \) Explicit time step

\( \Delta T_0 \) Freezing range between the liquidus and the solidus temperature

\( \Delta z_{\text{exp}} \) Recoil distance measured in the experiment

\( \Delta z_T \) Total isotherm shift

\( \varepsilon_4 \) Surface tension anisotropy strength

\( F \) Time-dependent flux intensity factor

\( F_\psi \) Noise strength imposed in \( \psi \) field

\( F_{u^0} \) Noise strength imposed in \( U \) field

\( G \) Temperature gradient

\( \gamma \) Surface tension
\( \Gamma \)  Gibbs-Thomson coefficient

\( H \)  Sample thickness

\( \vec{J}_n \)  Noise current

\( k \)  Interface solute partition coefficient

\( \kappa \)  Thermal conductivity

\( \mathcal{K} \)  Local interface curvature

\( k_B \)  Boltzmann constant

\( l_D \)  Diffusion length

\( l_{SB} \)  Length of a sidebranch

\( l_T \)  Thermal length

\( \lambda \)  Spacing

\( \lambda_{coup} \)  Coupling factor

\( m \)  Liquidus slope

\( \mathbf{n} \)  Interface normal vector

\( N_A \)  Avogadro’s number

\( \nu_0 \)  Molar volume of solvent atoms

\( \Omega \)  Solute supersaturation

\( \text{Pe} \)  Péclet number

\( \varphi \)  Phase field

\( \psi \)  Preconditioned phase field

xxx
\( \rho \)  
Dendrite tip radius

\( r_w \)  
Ratio for a wetting condition

\( \sigma \)  
Dendrite tip selection parameter

\( t \)  
Time

\( T \)  
Temperature

\( T_m \)  
Melting temperature of pure solvent

\( \tau_0 \)  
Relaxation time at the temperature \( T_0 \)

\( \tau_d \)  
Delay time

\( \Theta \)  
Grain boundary angle

\( \bar{u} \)  
Dimensionless solute concentration

\( U \)  
Dimensionless solute concentration (different scaling)

\( V \)  
Pulling velocity

\( V_d \)  
drift velocity

\( W \)  
Diffuse interface width
Chapter 1

Introduction

Microstructures inherited from different solidification processes are closely related to mechanical properties of materials [51, 165, 37]. Solidification processes lead to a wide range of different structures: from planar interfaces to cellular arrays (Fig. 1.1a), to complex equiaxed or columnar dendritic grain structures (Fig. 1.1b). From a theoretical standpoint, modeling interfacial pattern formation during solidification is a formidably difficult problem. The dynamics of the solid-liquid interface during this non-equilibrium process is governed by a free-boundary problem involving several different length and time scales, ranging from the nanometer width of the solid-liquid interface to the microscopic scale of the interface pattern,

![Cellular and Dendritic Array Structures](image)

Figure 1.1: Cellular (a) and dendritic (b) array structures from the phase-field simulations using a thin-sample geometry. These microstructures are seen from the side of the sample. We obtained the steady cellular microstructure (a) of a succinonitrile-0.24wt% camphor alloy using the pulling velocity $V = 1 \mu m/s$ and the temperature gradient $G = 13.3$ K/cm. We used $V = 50 \mu m/s$ and $G = 50$ K/cm for the dendritic array (b) of an aluminum-1.4wt% copper alloy. The primary cells and dendrites grow with a primary spacing $\lambda$ at a steady state.
and up to the macroscopic scale of heat and solute transport in bulk phases.

Because of that complexity, numerous open questions remain concerning the selection mechanisms of solidification microstructures [4]. Some of these questions are both of fundamental interest and relevant to industrial processes. For example, on the microstructural scale, what mechanisms control the dynamical selection of the primary cellular or dendritic array spacing $\lambda$ (Fig. 1.1), which has a major effect on the mechanical strength of solidified alloys [51, 37, 128, 36], or the shape of the envelope of dendritic grains (Fig. 1.5)? On a larger grain scale, what mechanisms control the growth competition between dendritic grains of different crystallographic orientations (Fig. 1.4), which dictates the grain texture and also impacts mechanical behavior [150, 154, 153, 142, 143, 141, 50, 49]? 

Recent advances in computational modeling using the phase-field method and more coarse-grained approaches have made it increasingly feasible to solve such complex free-boundary problems and to make predictions on experimentally relevant length and time scales. As a result, computational modeling is being used increasingly to gain fundamental insights into interfacial pattern formation and to assist in the design of new – or optimization of existing – materials and metallurgical processes.

The present research addresses some of the open questions in solidification microstructure selection, using models and simulations optimized for modern massively parallel computational architectures, together with quantitative comparisons with state-of-the-art experiments. Phase-field (PF) simulations are used to investigate the formation of cellular and dendritic array structures during the directional solidification of binary alloys, with a particular focus on the dynamical selection of the array spacing and the growth competition of grains of different crystallographic orientations [31, 150, 154, 142, 143, 141, 50, 49, 12, 148, 124]. In addition, a coarse-grained dendritic-needle-network (DNN) method is used to investigate the competitive growth of dendritic sidebranches that control the envelope shape of dendritic grains [149, 151].
Microstructure evolution and selection in directional solidification

For several decades, directional solidification has been the experimental tool of choice for investigating links between processing conditions and the resulting formation of specific microstructures [156, 70, 11, 15, 2]. As illustrated in Fig. 1.2, this type of experiment involves a partly melted sample inside a furnace where a temperature gradient is imposed. The solid-liquid interface is located between the solidus and liquidus temperature of the alloy. At rest, it stabilizes close to the liquidus. The solid end of the material sample is pulled with an imposed velocity. The resulting setup hence provides control over the alloy concentration ($c_0$), the temperature gradient ($G$), and the growth velocity ($V$) of the microstructure.

When pulling the sample, the initial planar interface moves toward the colder zone until it breaks down to small cells or dendrites [119, 168, 103], if above a certain velocity threshold for planar stability (also related to the alloy and temperature conditions) [146, 119]. Warren and Langer (WL) have developed an approximate analytical model to predict the initial recoil dynamics of the planar interface using a frozen temperature approximation, which assumes a fixed linear temperature gradient [168, 103]. After the morphological instability, the cells compete with neighbors until they reach a stable spacing. Hence, understanding the initial recoil dynamics is important as it provides the initial condition prior to microstructure evolution.

![Figure 1.2: Schematics of the directional solidification experimental setup.](image)

The directional solidification experiments are performed with a furnace where a temperature gradient $G$ due to hot and cold heat sources is imposed. A material sample is located inside this furnace with an alloy concentration $c_0$. With the solid-liquid interface located within the adiabatic zone where the temperature gradient is imposed, the sample is pulled with an imposed velocity $V$. 
Primary spacing selection mechanisms have been thoroughly investigated analytically and experimentally [61, 137, 160, 138, 161, 157, 66, 91, 72]. In classical approaches, primary spacing selection is typically related to three control parameters, namely the freezing range of the alloy, pulling velocity, and temperature gradient [157, 66, 91, 72].

While experimental observations have shown that a similar solidification history leads to similar selected primary spacings [137, 160, 138, 161], it is also well acknowledged that array stability spans a wide range of spacings, which has been further highlighted by recent PF and DNN simulations [64, 43, 149, 147]. Array structures with spacings outside this stable range are unstable with respect to elimination when the primary spacing is too small, and unstable with respect to tip-splitting for cellular arrays or tertiary branching for dendritic arrays when the primary spacing is too large. The ratio between the maximum and minimum spacings was suggested to be close to two in previous theoretical and experimental studies [105, 73]. However, recent numerical simulations show that this ratio may be closer to three or four in the dendritic growth regime [64, 43, 149, 147, 31]. Yet, dynamically selected primary spacings in an extended array appear to be distributed closer to the minimum spacing stability limit [149, 147].

The problem of gravity-induced convection

A major limitation to performing well-controlled solidification experiments with homogeneous processing conditions relates to the presence of gravity volume forces in the liquid phase. Indeed, gradients of temperature and composition, often stemming from different thermophysical properties of solid and liquid phases (e.g. thermal conductivity, component solubility, etc.), result in buoyant convective currents in the liquid under the effect of gravity.

Therefore, the vast majority of previous experimental studies used a confined thin-sample geometry in order to reduce the extent of convection through confinement [61, 137, 160, 138, 161, 157, 66, 91, 72, 105, 73, 43, 149, 147, 31]. Consequently, due to the impossibility to pro-
cess three-dimensional (3D) sample in a homogeneous well-controlled manner in Earth-based experiments, combined with the computational challenges of 3D simulations, dynamical primary spacing selection of extended 3D arrays remains still relatively unexplored.

Recently, a Directional Solidification Insert (DSI) was installed within the DEvice for the study of Critical LIquids and Crystallization (DECLIC) onboard the International Space Station (ISS). This unique setup has enabled our collaborators at Aix-Marseille University (France) and Iowa State University to perform fully 3D directional solidification experiments in very low gravity conditions [12, 129, 11, 148, 116, 118, 124]. These experiments using transparent succinonitrile (SCN)-camphor alloys have produced in situ images of solid-liquid interface dynamics in a wide range of growth conditions, and under very limited fluid convection [12, 129, 11, 116, 124]. As shown in Fig. 1.3, the experimental observations exhibit novel homogeneous 3D microstructures that are growing under a purely diffusive growth condition.

Experimental measurements have revealed that the planar interface relaxes to a stationary position over a finite time after a sudden increase of pulling velocity, more slowly than estimated from WL theoretical approach due to additional thermal effects inherent to the DECLIC-DSI solidification setup. Thus, we introduced more advanced descriptions of ther-

![Figure 1.3: Snapshot image from the observation of the DECLIC-DSI experiment with a SCN-0.24wt% camphor alloy for $V = 2 \mu m/s$ and $G = 19$ K/cm. This 3D cellular microstructure is seen from the front of interface, i.e. with cells appearing brighter growing towards the camera.](image-url)
mal effects in our PF simulations to quantitatively reproduce the recoil dynamics of the planar solid-liquid interface and the subsequent microstructural selection (Sec. 3.1).

We also compared our PF simulations to solidification experiments on Earth, where convection can be reduced but never completely avoided. In order to investigate the spacing selection under the influence of the fluid convection, we used a simplified approach that assumes that solute only diffuses within a region surrounding the solid-liquid interface, within a boundary layer (or a stagnant film) \[54, 55\]. The solute outside of the boundary layer is well mixed at the nominal alloy composition due to strong convection. We introduced this simple approach within the PF model, and compared simulation results with directional solidification experiments of Al-Cu alloys combined with synchrotron X-ray \textit{in situ} radiography performed by collaborators from Los Alamos National Laboratory \[31\] (Sec. 4.3). We also studied the effect of thin-sample thicknesses upon microstructure selection, thus revealing a strong difference between cellular and dendritic growth regimes.

**The influence of grain orientation and polycrystallinity**

When a grain is misoriented with respect to the temperature gradient (red dendrites in Fig. 1.4), the misoriented cells or dendrites drift laterally, and they interact dynamically with surrounding convergent and divergent grain boundaries (GBs). The drift dynamics is related to the local spacing between primary cells/dendrites \[1, 39\]. At a divergent GB (blue dashed line in Fig. 1.4), cells/dendrites are continuously created due to sidebranching, and

![Figure 1.4: Schematics of the grain competition between well-oriented blue and misoriented red grains. The blue grain grows along the direction of the temperature gradient \(G\). The crystalline orientation with respect to \(G\) leads to the lateral movement of the red grain from the divergent grain boundary (GB) to the convergent GB.](image)
the spacing of a new primary branch tends to be larger than the average array spacing \[60, 52, 61, 53, 49, 48\]. At a convergent GB (red dashed line in Fig. 1.4), misoriented cells and dendrites impinge onto one another, as their local spacings decrease until they are eliminated. We investigated the spatiotemporal evolution of primary spacings between GBs within a grain misoriented with respect to the temperature gradient direction, using PF simulations and by developing a simple analytical model (Sec. 4.1).

Furthermore, most columnar microstructures typically consist of polycrystalline structures composed of several grains of different crystal orientations as illustrated in Fig. 1.4. The dynamics of the resulting grain growth competition at GBs is crucial to determine both the microstructure and grain texture.

Polycrystalline microstructure selection mechanisms have been studied experimentally \[49, 50, 48, 2\] and numerically \[150, 97, 141\]. In the classical approach to columnar growth competition \[167\], grains with a higher misorientation are eliminated by a neighbor grain with lower misorientation because the grain with a lower misorientation grows at a lower undercooling, hence ahead of the more misoriented grain. However, recent numerical studies using PF simulations highlighted much more complex mechanisms of GB orientation selection during columnar dendritic growth \[97, 150, 141\], explaining some unexpected grain elimination mechanisms previously observed in experiments \[40, 166, 174\].

Yet, until recently, GB selection mechanisms during dendritic competitive growth (Fig. 1.4) are still too computationally challenging to approach with quantitative simulations in 3D. The combination of orientations for two competing 3D crystals even adds further degrees of freedom to the problem. Thus, focusing at first on a thin sample geometry, we carried out PF simulations to explore the GB orientation selection in a 3D bi-crystalline dendritic array (Sec. 4.4).

We also explored mechanisms of grain growth competition at the convergent GB in bulk 3D samples, based on observations from the microgravity DECLIC-DSI experiments \[124\]. In these experiments, grains with a small misorientation with respect to the temperature
gradient were often observed. Interestingly, groups of cells of a misoriented grain can locally penetrate into the nearby grain at the convergent GB, leading to a complex morphological instability of the GB. In addition, during the penetration of a group of cells, the leader cell can detach itself from its invasion group and continuously move inside the other grain. We reproduced that mechanism using 3D PF simulations, and thus investigated grain boundary instability and the solitary cell dynamics (Sec. 3.2).

**Bridging up to the grain scale**

Despite its great advantages in simulating complex interfaces, the PF method for solidification shows its computational limits when handling concentrated alloys solidifying at a low solute supersaturation. In this regime, the tip radius $\rho$ of a dendritic crystal is several orders of magnitude smaller than the diffusion length $l_D \equiv D/V$ with the dendrite tip growth velocity $V$. Since the PF method requires an accurate morphological description of the tip in order to correctly predict the tip growth dynamics, the computational grid spacing is restricted (at least in the vicinity of the interface) to about one order of magnitude smaller than the dendrite tip radius. Therefore, quantitative PF simulations become computationally challenging in this regime as both $\rho$ and $l_D$ require an accurate spatial representation.

In this low supersaturation regime, we used the newly introduced multiscale DNN model\[149, 151\] to investigate the sidebranching dynamics at the grain scale. As shown in Fig. 1.5, dendritic grains in the DNN model are represented as a network of sharp needle crystals. Needle-like branches are thus modeled as sharp line segments that diffusively interact with each other. Combining a microscopic solvability condition on the dendrite tip scale and a solute mass conservation condition on the dendritic grain scale $95, 6, 8$, one can rigorously predict the growth dynamics of each dendritic branch $149$.

The problem that we studied using DNN simulations is that of the growth competition of secondary sidebranches in a dendritic grain (i.e. vertically growing branches in Fig. 1.5). This competitive growth among sidebranches determines the shape of a dendritic grain, and
Figure 1.5: Schematics of a dendritic grain from a dendritic-needle-network (DNN) simulation. The DNN method uses sharp line segments as branches of a dendritic grain.

the dynamics of its so-called envelope, which ultimately also affects the formation of grain boundaries [165, 158, 70, 71].

In terms of sidebranching onset, analytical studies have demonstrated that thermal noise suffices to trigger sidebranches [125, 5, 94, 23, 24] in quantitative agreement with experimental observations [16, 17, 92]. Further behind the primary dendrite tip, secondary sidebranches continue to grow competitively with only a subset of sidebranches surviving at long times [74, 98, 99, 113, 35]. The tips of those surviving branches form the envelope of the dendritic grain [70, 71, 16, 98, 99, 113, 74].

We used 2D DNN simulations to investigate sidebranches growth competition at a scale much larger than the tip radius, which has so far not been achievable with quantitative PF modeling. From these results, we extracted scaling laws that govern the shape of the envelope of the dendritic grain at different distances from the primary branches (Chapter 5). On this basis, we built and validated an analytical theory for the growth and competition of secondary dendritic sidebranches in 2D.
Chapter 2

Solidification models

2.1 Sharp-interface model

The sharp-interface model is the classical model to describe solidification dynamics assuming that the solid and liquid phases are separated by a sharp boundary. This model consists of three equations which are the diffusion equation, the Stefan condition, and the Gibbs-Thomson relation. First, the diffusion equation shows the time evolution of the solute concentration $c$, which is given by

$$\partial_t c = D \nabla^2 c \quad ,$$

where $D$ is the solute diffusivity.

Second, the Stefan condition describes the solute mass conservation of a moving solid-liquid interface as

$$ (1 - k) c_I v_n = D_s \partial_s c|_i - D_l \partial_l c|_i \quad ,$$

where $k = c_s/c_l$ is the partition coefficient, $c_s$ and $c_l$ are the solute concentration at the interface respectively on the solid and liquid side, $v_n$ is the normal velocity of the solid-liquid interface, and $\partial_{l(s)} c|_i$ is the concentration gradient normal to the interface on the liquid (solid) side. The solute diffusivity in the solid $D_s$ is usually neglected because it is much

10
slower than the diffusivity in the liquid $D_l$. Finally, the interface is assumed to be in local equilibrium at a temperature $T$, determined by the Gibbs-Thomson relation

$$T = T_m - |m|c_l - \Gamma \mathcal{K},$$

(2.3)

where $T_m$ is the melting temperature of the pure solvent, $m$ is the liquidus slope of an alloy, $\Gamma$ is the Gibbs-Thomson coefficient, $c_l$ is the concentration on the liquid side, and $\mathcal{K}$ is the local interface curvature. The Gibbs-Thomson condition follows from the assumption that the interface is in local thermodynamic equilibrium, which is generally valid at a low solidification rate.

### 2.2 Phase-field method

The phase-field (PF) approach is a powerful computational method to simulate complex interface dynamics in various phenomena [28, 18]. In the case of solidification, the PF method introduces an order parameter, or phase field, $\varphi$ that takes a different value in the solid ($\varphi = +1$) and in the liquid ($\varphi = -1$) and has a continuous variation through a solid-liquid interface of a given width. Therefore, challenging free-boundary problems introduced in the sharp-interface model can be solved by tracking the evolution of the phase field. In addition, PF calculations are able to predict the growth of complex anisotropic structures, such as the equiaxed grain illustrated in Fig. 2.1. This is done by constructing a free energy functional that depends on the phase field and solute concentration field and represents the total free-energy of the two-phase solid-liquid system [85, 81, 42].

The PF model for solidification has benefited from numerous developments over the past decades. An analytical asymptotic analysis permits the use of a diffuse interface width much larger than the actual physical width of the interface [85]. Additionally, the introduction of an “anti-trapping” term corrects the numerically introduced solute trapping due to the diffuse interface, and hence allows quantitative predictions [81, 42]. The model has been
recently adapted a previously proposed PF model for directional solidification [42] using a non-linear change of variable (preconditioning) of the phase field $\psi$, i.e. $\varphi \equiv \tanh(\psi/\sqrt{2})$, in order to allow a larger finite difference grid spacing [59]. Finally, we have implemented the PF model on massively parallel GPU (Graphic Processing Unit) architectures, which yield faster calculations.

The evolutions of phase and solute fields were calculated by solving the phase field equations with a thin interface limit [42]. In order to derive the phase field equations, we follow the description in Ref. [42]. The evolution of phase field $\varphi$ given in Eq. (58) of Ref. [42] is

$$
\tau(T) \frac{\partial \varphi}{\partial t} = W^2 \nabla^2 \varphi + \varphi - \varphi^3 - \tilde{\lambda}_c \frac{\tilde{g}'(\varphi)}{1 - k} \left[ e^{\bar{u}} - 1 - \frac{T - T_0}{mc_i^0} \right],
$$

(2.4)

where $\tilde{\lambda}_c$ is a constant related to a phase field diffuse interface width $W$, $\tilde{g}(\varphi)$ is an interpolation function and $\tilde{g}'(\varphi)$ denotes the first derivative of that function. In addition, $c_i^0 = c_\infty/k$ is the equilibrium concentration of the liquid at $T_0$ with the nominal composition $c_\infty$ and the partition coefficient $k$. The dimensionless concentration $\bar{u}$ is defined as

$$
\bar{u} \equiv \ln \left( \frac{2c/c_i^0}{1 + k - (1 - k)\varphi} \right),
$$

(2.5)

When primary branches of an alloy grow along the $x$ direction at an imposed pulling velocity
V, the classical PF model \cite{81, 42} assumes that a temperature profile is frozen within a temperature gradient $G$ as

$$T = T_0 + G(x - Vt) \quad ,$$  

(2.6)

where $T_0$ is the reference (solidus) temperature for $c_\infty$. Then, we can reformulate a temperature-dependent phase-field relaxation time $\tau(T)$ as

$$\tau(T) = \tau_0 \left( 1 + \frac{T - T_0}{mc_0^0} \right)$$

(2.7)

$$= \tau_0 \left[ 1 - (1 - k) \frac{x - Vt}{l_T} \right] \quad ,$$

(2.8)

where $\tau_0$ is the relaxation time at $T_0$, and $l_T = |m|c_0^0(1 - k)/G$ is the thermal length. Additionally, by using Eq. (2.5) and the dimensionless solute field

$$U = \frac{e^\tilde{u} - 1}{1 - k}$$

(2.9)

$$= \frac{1}{1 - k} \left[ \frac{2c/c_0^0}{(1 + k) - (1 - k)\varphi} - 1 \right] \quad ,$$

(2.10)

the last term of Eq. (2.4) becomes

$$-\frac{\tilde{\lambda}_c}{1 - k} \tilde{g}'(\varphi) \left[ e^\tilde{u} - 1 - \frac{T - T_0}{mc_0^0} \right] = -\lambda_{coup} \tilde{g}'(\varphi) \left[ U + \frac{x - Vt}{l_T} \right] \quad ,$$

(2.11)

where $\lambda_{coup} = 15\tilde{\lambda}_c/8$ and the interpolation function

$$g(\varphi) = \frac{8}{15} \tilde{g}(\varphi) = \left( \varphi - \frac{2}{3} \varphi^3 + \frac{1}{5} \varphi^5 \right) \quad .$$

(2.12)

Therefore, Eq. (2.4) becomes

$$\tau_0 F_1(x, t) \frac{\partial \varphi}{\partial t} = W^2 \nabla^2 \varphi + \varphi - \varphi^3 - \lambda_{coup}(1 - \varphi^2)^2 F_2(x, t) \quad (2.13)$$
with two thermal related functions

\[
F_1(x, t) = \left[1 - (1 - k) \frac{x - V t}{l_T}\right], \quad \text{and} \quad (2.14)
\]

\[
F_2(x, t) = \left[U + \frac{x - V t}{l_T}\right]. \quad (2.15)
\]

Then, we expand Eq. (2.13) with an anisotropy function \(a_s(n)\), and reformulate the equation using a non-linear preconditioning of \(\varphi\) [148, 150]. In addition, we transform the equation for \(c\) including an anti-trapping current, i.e. Eq. (53) in Ref. [42], into the one for \(U\) (see Refs. [42, 148, 150] for the details). Then, the evolutions of the phase and solute fields [148, 150] are given by

\[
F_{T_1}(x, t) a_s(n)^2 \frac{\partial \psi}{\partial t} = \nabla \left[a_s(n)^2 \nabla \psi + a_s(n)^2 \left[\nabla^2 \psi - \varphi \sqrt{2} |\nabla \psi|^2\right]\right] + \sum_{m=x,y,z} \left[\partial_m \left( |\nabla \psi|^2 a_s(n) \frac{\partial a_s(n)}{\partial (\partial_m \psi)} \right)\right] + \varphi \sqrt{2} - \lambda (1 - \varphi^2) \sqrt{2} F_{T_2}(x, t), \quad (2.16)
\]

\[
(1 + k - (1 - k) \varphi) \frac{\partial U}{\partial t} = \tilde{D} \nabla \cdot \left[(1 - \varphi) \nabla U\right] + \nabla \cdot \left[(1 + (1 - k) U) \frac{(1 - \varphi^2)}{2} \frac{\partial \psi}{\partial t} \frac{\nabla \psi}{|\nabla \psi|}\right] + \left[1 + (1 - k) U\right] \frac{(1 - \varphi^2)}{\sqrt{2}} \frac{\partial \psi}{\partial t}, \quad (2.17)
\]

with space in the unit of \(W\) and time in the unit of \(\tau_0\) at the temperature \(T_0\) [42]. The coupling factor \(\lambda_{coup}\) is

\[
\lambda_{coup} = a_1 \frac{W}{d_0}. \quad (2.18)
\]

In addition, the dimensionless diffusivity \(\tilde{D}\), velocity \(\tilde{V}\) and thermal length \(\tilde{l}_T\) can be ex-
pressed as

\[ \tilde{D} = \frac{D \tau_0}{W^2} = a_1 a_2 \frac{W}{d_0}, \quad (2.19) \]
\[ \tilde{V} = \frac{V \tau_0}{W} = a_1 a_2 \frac{V d_0}{D} \left( \frac{W}{d_0} \right)^2, \quad (2.20) \]
\[ \tilde{l}_T = \frac{l_T}{W} = \frac{l_T}{d_0} \frac{1}{W/d_0} \quad (2.21) \]

where \( d_0 = \Gamma / [m|c_\infty(1 - 1/k)] \) is the capillarity length with the Gibbs-Thomson coefficient \( \Gamma \), \( a_1 = 5\sqrt{2}/8 \), and \( a_2 = 47/75 \) \[85, 84\]. We use the standard expression of the surface tension for a cubic material, which is

\[ a_s(n) = (1 - 3\varepsilon_4) \left[ 1 + \frac{4\varepsilon_4}{1 - 3\varepsilon_4} (n_x^4 + n_y^4 + n_z^4) \right], \quad (2.22) \]

where the anisotropy strength \( \varepsilon_4 \) \[85, 82, 67\] and the interface normal vector \( n = (n_x, n_y, n_z) \). This anisotropy function is simplified in 2D with an angle \( \theta \) with respect to an interface

\[ a_s(n) = 1 + \varepsilon_4 \cos(4\theta) \quad (2.23) \]

The discrete grid spacing \( \Delta x \) for both fields is measured in the unit of \( W \) \[42\]. Then, Eqs. (2.16) and (2.17) are calculated by using the Euler explicit time scheme with a time step \( \Delta t \). Because of stability condition, the time step \( \Delta t \) for 3D simulations is usually decided by

\[ \Delta t = R_S \frac{(\Delta x)^2}{6D}, \quad (2.24) \]

where the ratio \( 0 < R_S < 1 \) is a constant.

The resulting model is now used to perform quantitative simulations in two (e.g. \[43, 64, 150\]) and three dimensions (e.g. \[12, 57, 148, 31\]) at time and length scales relevant to solidification experiments \[12, 150, 148, 31\]. Thus, we use this model to explore a variety of interface pattern dynamics by considering various influences on the solid-liquid interface.
2.2.1 Noise

The PF model has used a small random noise to consider microscopic fluctuations. In the recently developed PF model \cite{150, 12, 57, 148, 31, 154}, the addition of a noise is achieved by introducing a random perturbation in the preconditioned phase field $\psi$. By using the Euler explicit time scheme, the introduced perturbation is modified as

$$ \psi^{t+\Delta t} = \psi^t + \Delta t\partial_t \psi + F_\psi \sqrt{\Delta t} \zeta , $$

where $F_\psi$ is a noise strength and $\zeta$ is a random number distributed flatly in between -0.5 and 0.5. When we impose a noise, a random number is generated at every time step for every grid point during a simulation.

We could determine microscopic fluctuations quantitatively using the method in Refs. \cite{80, 86, 43}. In the description of Ref. \cite{43}, the noise current $\vec{J}_n$ is introduced on the right-hand side of the diffusion equation Eq. (2.17), which yields

$$ U^{t+\Delta t} = U^t + \Delta t \left( \partial_t U - \vec{\nabla} \cdot \vec{J}_n \right) $$

by using the Euler explicit time scheme. The current $\vec{J}_n$ with a Gaussian variance is

$$ < J^m_s(\vec{r},t)J^n_s(\vec{r}',t') > = D(1-\varphi)F_0^u [1 + (1 - k)U] \delta_{mn} \delta(\vec{r} - \vec{r}') \delta(t - t') , $$

where $F_0^u$ is a noise strength. Then, the discretized noise in 3D becomes

$$ \vec{\nabla} \cdot \vec{J} \approx (J^s_{x,i+1,jk} - J^s_{x,i,jk} + J^s_{y,i,j+1,k} - J^s_{y,i,j,k} + J^s_{z,i,j,k+1} - J^s_{z,i,j,k})/\Delta x . $$

where $J^s_{x,i,j,k}$, $J^s_{y,i,j,k}$, and $J^s_{z,i,j,k}$ are independent Gaussian random numbers with a variance

$$ < J^s_{m,ijk}J^p_{m,i'j'k'} > = D(1-\varphi)[1 + (1 - k)U] \frac{F_0^u}{\Delta x^3 \Delta t} \delta_{ii'}\delta_{jj'}\delta_{kk'}\delta_{pp'} . $$
The superscripts $s$ and $p$ refer to discrete times $t = s\Delta t$ and $t' = p\Delta t$. Additionally, the constant noise magnitude is defined as

$$F^0_u \equiv \frac{k\nu_0}{(1-k)^2N_Ac_\infty} ,$$

with the molar volume of solvent atoms $\nu_0$, the Avogadro’s number $N_A$, and the nominal composition $c_\infty$ \cite{43}. When using the Clausius-Clapeyron relation

$$\frac{|m|}{(1-k)} = \frac{k_B T_0^2}{\Delta h} ,$$

where $\Delta h$ is the latent heat per mole, and $k_B$ is the Boltzmann constant, the amplitude becomes

$$F^0_a = \frac{k}{|m|c_\infty(1-k)} \frac{k_B T_0^2}{L} .$$

While introducing a noise in the $U$ field gives quantitative results, a noise in $\psi$ minimizes the computational cost. Hence, the noise is usually imposed into the $\psi$ field \cite{150, 12, 57, 148, 31}.

### 2.2.2 Wetting conditions

Wetting has to do primarily with the relative surface energies of the solid-wall interface, solid-liquid interface, and liquid-wall interface, not so much the thermal conductivity of the walls that can be larger or smaller than the alloy depending on what wall material is used. In order to account for the wetting condition, we could use a quantitative method using a contact angle between the sample wall and the solid-liquid interface \cite{169}. However, we used a simplified method \cite{57, 31, 154} because we do not have a precise measurement of the contact angle in the experiment. In addition, the triple junction of the solid, the liquid, and the sample wall is typically far from the front of the solid-liquid interface in the performed simulations here, so an accurate description of a contact angle is not crucial.
The simplified approach suggested to impose two boundary conditions \[57\]

\[
\left. \frac{\partial \psi}{\partial z} \right|_{z=0} = - \left. \frac{\partial \psi}{\partial z} \right|_{z=H} = r_w \tag{2.33}
\]

at the bottom \((z = 0)\) and top \((z = H)\) boundaries. The 3D PF simulations using this approach can reproduce the cellular and dendritic dynamics in a thin-sample geometry \[57, 31, 154\]. We typically set the ratio as \(r_w = 1\).

2.2.3 Diffusion boundary-layer approximation

In the experiments on earth, it is difficult to ignore buoyancy-driven fluid convection. While the convective currents could be predicted quantitatively by Navier-Stokes equations using a no-slip condition at the interface \[7\], using this method for the PF model is computationally costly. Thus, we considered a simple one-dimensional (1D) method for the convective effects \[31\]. In this 1D approach, the solute only diffuses from the solid-liquid interface to a boundary layer (or a stagnant film) \[54, 55\]. Then, we assume that, because of strong convective currents, the solute outside of the layer is homogenized, and becomes a given nominal composition \(c_0\). Then, because of the strong convective currents, solute diffuses in the liquid within the range from the interface to a small boundary layer thickness \(\delta\).

We used the nonlinear preconditioning of the phase field variable \(\psi\) to evaluate a boundary-layer thickness \(\delta\). The \(\psi\) linearly decreases with the distance from the solid-liquid interface in the liquid away from the solid-liquid interface. Then, we set \(c = c_0\) beyond a threshold \(\psi = \psi^*\). The details are illustrated in Fig. 2.2.

Fig. 2.2a shows a dendrite array of an aluminum (Al)-1.4wt% copper (Cu) alloy for \(G = 50\) K/cm and \(V = 10\) \(\mu\)m/s \[31\]. We plot the solute composition profile (Fig. 2.2b) and the \(\psi\) field (Fig. 2.2c) as a function of the distance from the tip \(x - x_{\text{tip}}\) along the \((y, z) = (y_{\text{tip}}, z_{\text{tip}})\) line (black dashed line in Fig. 2.2a), where \((x_{\text{tip}}, y_{\text{tip}}, z_{\text{tip}})\) represent the
Figure 2.2: Schematics of the boundary-layer (BL) approach for $G = 50$ K/cm and $V = 10$ $\mu$m/s of an aluminum (Al)-1.4wt% copper (Cu) alloy. The most advanced dendrite is located at $(x_{\text{tip}}, y_{\text{tip}}, z_{\text{tip}})$, and the gray lines in (a) illustrate isovales of $\psi$ around a dendrite array on the $(z = z_{\text{tip}})$ plane for purely diffusive case $(\delta \rightarrow \infty)$. The different colors correspond to the approximate regions between the solid-liquid interface and a length that is equivalent to a boundary thickness $\delta [\mu\text{m}] = 100$ (red), 150 (yellow), 200 (green), 400 (purple), and $\infty$ (blue). (b) and (c) illustrate the concentration profile and preconditioned phase field $\psi$, respectively, along the $(y, z) = (y_{\text{tip}}, z_{\text{tip}})$, i.e. the dashed line in (a). These figures are from Ref. [31] with permission (Fig. C.2).

dendrite tip position. In the preconditioning phase field (Fig. 2.2c), the interface is located at $\psi = 0$, and the $\psi$ (black line) in the liquid ($\psi < 0$) linearly decreases. Using $\psi(x - x_{\text{tip}})$ for $x - x_{\text{tip}} > 0$ from Fig. 2.2c, we can determine the threshold value $\psi = \psi^*$ at a distance $\delta$ from the interface ($\psi = 0$). Then, we set $c = c_0$ for $x - x_{\text{tip}} > \delta$ that corresponds to $\psi < \psi^*$. Fig. 2.2b shows the resulting solute concentration at a steady state in the liquid using different boundary-layer thickness $\delta [\mu\text{m}] = 100$ (red), 150 (yellow), 200 (green), 400 (purple), and $\infty$ (blue). In addition, gray lines in Fig. 2.2a illustrate isovales of $\psi$ on a plane $z = z_{\text{tip}}$ for a purely diffusive case. The colors correspond to the region inside the boundary layer thickness, i.e. $\psi > \psi^*$, which provides a good estimation of the multi-dimensional distance to the interface in the liquid.

We use the dimensionless $U$ field in our PF model. Then, using the thickness $\delta$, the field
is modified by

\[ U = -1 \quad \text{for} \quad \psi(x, y, z) < \psi^* \]  

(2.34)

On the other hand \( \psi(x, y, z) \geq \psi^* \), the \( U \) field is estimated by Eq. (2.17). The corresponding simulations with this simple approximation agree well with the experiments using an Al-Cu alloy [31].

### 2.2.4 Phenomenological thermal drift

Before solidification experiments start, the planar solid-liquid interface is located at the liquidus temperature under a given temperature gradient \( G \). After pulling the sample, the planar interface moves towards the colder zone until it breaks down to small cells [119, 168, 103]. Then, the cells compete with neighbors until they have a stable spacing, and they grow with \( V \) towards a hot zone. Hence, understanding the initial recoil dynamics is important to predict the microstructure selection mechanisms.

The classical Warren-Langer (WL) model is able to predict the initial planar interface dynamics, and solidification experiments with the thin-sample geometry on earth agree with this model [168, 103]. However, in 3D experiments aboard the ISS (International Space Station), the initial planar interface moves from the liquidus temperature further away than the positions predicted by the classical WL model. In a previous study [116], it was shown that the discrepancy between theoretical predictions and experiments originates from a drift of the isotherms and latent heat rejection at the interface. Both effects can be phenomenologically described as [116]

\[ T = T_0 + G(x - Vt) + G \Delta z_T \left( 1 - e^{-t/\tau_d} \right) \]  

(2.35)

where \( \Delta z_T \) is a total isotherm shift, and \( \tau_d \) is a delay time. The total isotherm shift is calculated from \( \Delta z_T = \Delta z_{exp} - \Delta \cdot l_T \), where \( \Delta z_{exp} \) is the recoil distance observed in the experiment. In addition, \( \tau_d \) is adjusted from planar interface positions (i.e. before the
morphological instability) measured in the experiment. The WL model modified by the time dependent thermal drift Eq. (2.35) improves the agreements with the planar interface dynamics in the 3D crucible at different $V$.

We introduced a phenomenological thermal drift into the PF model. As shown in Eq. (2.35), the thermal drift only affects the temperature field. Then, if we use Eq. (2.35) instead of Eq. (2.6), thermal terms Eqsns. (2.8) and (2.11) change to

$$\tau(T) = \tau_0 \left[ 1 - (1 - k) \frac{x - Vt + \Delta z_T (1 - e^{-t/\tau_d})}{l_T} \right],$$

$$- \frac{\tilde{\lambda}_c}{1 - k} g'(\varphi) \left[ e^u - 1 - \frac{T - T_0}{m c_i^0} \right] = -\lambda_{coup} g'(\varphi) \left[ U + \frac{x - Vt + \Delta z_T (1 - e^{-t/\tau_d})}{l_T} \right] .$$

By using the same method to obtain Eq. (2.16), the thermal functions become

$$F_1(x,t) = \left[ 1 - (1 - k) \frac{x - \tilde{V} t + \Delta \tilde{z}_T (1 - e^{-t/\tilde{\tau}_d})}{\tilde{l}_T} \right],$$

$$F_2(x,t) = \left[ U + \frac{x - \tilde{V} t + \Delta \tilde{z}_T (1 - e^{-t/\tilde{\tau}_d})}{\tilde{l}_T} \right],$$

where the terms for the thermal drift (i.e. the total shift $\Delta z_T$ and the delay time $\tau_d$) are scaled as

$$\Delta \tilde{z}_T = \frac{\Delta z_T}{W},$$

$$\tilde{\tau}_d = \frac{\tau_d}{\tau_0} .$$

Hence, the evolution of the $\psi$ fields in Eq. (2.16) uses Eqsns. (2.38) and (2.39) under the influence of the phenomenological thermal drift approximation (TDA). It is important to note that the $U$ field is independent of the thermal effect, so the field evolves with Eq. (2.17).
2.2.5 Coupling with a one-dimensional temperature field

In the PF models [81, 42, 12, 148, 31, 150, 154, 43, 64, 57, 124], the temperature field is assumed to be fixed as in Eq. (2.6) because thermal diffusivity $D_T$ of an alloy is usually much larger than the solutal diffusivity $D$. For the metals and metallic alloys, their $D_T$ are typically five orders of magnitude larger than $D$, and thus this assumption is usually valid. However, it might not be proper to consider for succinonitrile (SCN)-based organic alloys.

As pointed out in Ref. [116], thermal effects, i.e. (i) heat diffusion within an adiabatic zone and (ii) latent heat release at the interface, inside a 3D sample crucible are responsible for a thermal drift of the isotherms in the DECLIC-DSI experiments with a SCN alloy. Even though the PF model uses the phenomenological description as in Sec. 2.2.4, we can quantitatively evaluate the thermal field that is influenced by the thermal effects. While it is possible to introduce a 3D thermal field like the phase and concentration fields, the calculation with the 3D thermal field is computationally challenging because of a time step. For example, the time step of the thermal field for the metals and metallic alloys should be five orders of magnitude smaller than that of the concentration field to calculate the thermal field quantitatively. Hence, we use a 1D thermal field which is coupled with the PF model.

We assume that temperatures at the boundaries of the adiabatic zone are fixed as $T = T_c$ at the low temperature and $T = T_h$ at the high temperature. We obtained these boundary temperatures, i.e. $T_c$ and $T_h$, including a length between the temperatures from the program called CrysVUn, which can reproduce a quantitative 2D axial thermal field [116]. Then, heat within an adiabatic zone (i.e. between $T_c$ and $T_h$) diffuses with a thermal diffusivity $D_T$. $D_T$ in the liquid is assumed to be the same as in the solid because the difference between them is very small and they are much larger than the solute diffusion in the liquid $D_T \gg D$ [165]. In addition, latent heat releases at the solid-liquid interface when the liquid transforms to the solid. This heat rejection would also affect the evolution of the temperature field. Then,
the thermal field along the $x$ direction in a fixed lab frame evolves as

$$
\partial_t T = V \partial_x T + D_T \partial_{xx} T + \frac{\Delta h_f}{c_p} \frac{1}{V} \int \frac{\dot{\phi}}{2} \, dV,
$$

(2.42)

where $V$ is an integrated volume, $\Delta h_f$ is the alloy latent heat of fusion per unit volume, and $c_p$ is its heat capacity.

We solve the above equation using a finite difference implementation of the spatial derivatives with a grid spacing $\Delta x_T$ and an explicit Euler time stepping scheme. We consistently use the same $\Delta t$ as for the other $\psi$ and $U$ fields. Since the numerical stability condition for the 1D temperature field is given by

$$
\Delta t = R_T \frac{(\Delta x_T)^2}{2D_T},
$$

(2.43)

where $R_T$ is the prefactor between 0 and 1, the $\Delta x_T$ for the thermal field becomes

$$
\Delta x_T = \sqrt{\frac{R_S D_T}{R_T 3D}} \Delta x
$$

(2.44)

when it is coupled with Eq. (2.24). $\Delta x_T$ is usually larger than $\Delta x$ because $D_T > D$.

The latent heat rejection, the last term in Eq. (2.42), is numerically integrated over all grid points along $y$ and $z$ within a range of $[x, x + \Delta x_T]$ during a simulation. Then, the volume is given by $V = \Delta x_T \times L_y \times L_z$, where $L_y$ ($L_z$) is the domain size in the $y$ ($z$) direction. Then, the last term on the right-hand-side of Eq. (2.42) corresponding to latent heat diffusion is discretized in the form

$$
\partial_t T = V \partial_x T + D_T \partial_{xx} T + \frac{\Delta h_f}{c_p} \sum_x \frac{\dot{\phi}(x, y, z)}{2} \left( \frac{N_y \times N_z}{(N_y \times N_z)} \right) \frac{\Delta x}{\Delta x_T}.
$$

(2.45)

We modify the PF model to use the 1D temperature field that evolves with the above equation. The $x$ domain for the phase and concentration field is always within a range of

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\[ x_T = 0 \text{ at } T = T_c \text{ and } x_T = L_T \text{ at } T = T_h. \] Hence, we linearly interpolate a temperature corresponding to the \( x \) domain from the temperature field. Thus, for a temperature \( T \), Eqns. (2.8) and (2.11) are

\[
\tau(T) = \tau_0 \left[ 1 - (1-k) \frac{T - T_0}{\Delta T_0} \right], \quad (2.46)
\]

\[
-\frac{\bar{\lambda}_c}{1-k} g'(\varphi) \left[ e^u - 1 - \frac{T - T_0}{m c_0^p} \right] = -\lambda_{coup} g'(\varphi) \left[ U + \frac{T - T_0}{\Delta T_0} \right], \quad (2.47)
\]

where \( \Delta T_0 = |m|c_\infty(1/k - 1) \) is the freezing range. Then, the thermal functions become

\[
F_1(x, t) = \left[ 1 - (1-k) \frac{T(x, t) - T_0}{\Delta T_0} \right], \quad (2.48)
\]

\[
F_2(x, t) = \left[ U + \frac{T(x, t) - T_0}{\Delta T_0} \right]. \quad (2.49)
\]

We use these two functions for \( \psi \) field calculations, i.e. Eq. (2.16). The \( U \) field evolves with time as described in Eq. (2.17).

2.2.6 Crystal orientation

In the experiments, primary branches are seldom perfectly oriented parallel to the temperature gradient or pulling velocity, so we need to consider crystal orientations to explore the dynamics of misoriented cells and dendrites. Thus, we imposed a crystal misorientation into the anisotropy function of the 3D PF model as in the previous studies \[150, 57, 154\].

The standard form of the surface tension anisotropy \[82\] is given by \( \gamma(n) = \bar{\gamma} a_s(n) \), where

\[
a_s(n) = (1 - 3\epsilon_4) \left[ 1 + \frac{4\epsilon_4}{1-3\epsilon_4} \left( n_x^4 + n_y^4 + n_z^4 \right) \right] \quad (2.50)
\]

for a cubic material, \( \bar{\gamma} \) is the average surface tension in a \( \langle 100 \rangle \) plane, \( \epsilon_4 \) is the anisotropy strength, and \( n \) is the unit vector normal to the interface pointing towards the liquid with the Cartesian coordinates \((n_x, n_y, n_z)\) along the \( x \), \( y \), and \( z \) axes, respectively.
Figure 2.3: The rotation of the crystal axes \((x',y',z')\). In order to obtain the crystal axes (red), we rotated the axes in order of a, b, and c. Therefore, the final crystal axes are rotated by imposed angles \((\alpha_0, \beta_0, \gamma_0)\) with respect to the reference Cartesian axes \((x,y,z)\) (black) as illustrated in d.

In order to consider a rotation of a 3D crystal, we imposed crystal angels \(\alpha_0, \beta_0,\) and \(\gamma_0\) into the anisotropy surface tension in Eq. (2.50). Then, crystal axes \((x'',y'',z'')\) are rotated by the angles \((\alpha_0, \beta_0, \gamma_0)\) with respect to a fixed reference set of the Cartesian axes \((x,y,z)\) (Fig. 2.34). We regard the clockwise direction as the positive direction of an angle, then the rotation with respect to the coordinates \((x,y,z)\) can be written in matrix forms:

\[
\begin{bmatrix}
  x' \\
  y' \\
  z'
\end{bmatrix}
= R_1
\begin{bmatrix}
  x \\
  y \\
  z
\end{bmatrix}
= \begin{pmatrix}
  \cos \alpha_0 & \sin \alpha_0 & 0 \\
  -\sin \alpha_0 & \cos \alpha_0 & 0 \\
  0 & 0 & 1
\end{pmatrix}
\begin{bmatrix}
  x \\
  y \\
  z
\end{bmatrix}, \tag{2.51}
\]

\[
\begin{bmatrix}
  x'' \\
  y'' \\
  z''
\end{bmatrix}
= R_2
\begin{bmatrix}
  x' \\
  y' \\
  z'
\end{bmatrix}
= \begin{pmatrix}
  \cos \gamma_0 & 0 & \sin \gamma_0 \\
  0 & 1 & 0 \\
  -\sin \gamma_0 & 0 & \cos \gamma_0
\end{pmatrix}
\begin{bmatrix}
  x' \\
  y' \\
  z'
\end{bmatrix}, \tag{2.52}
\]
and

\[
\begin{pmatrix}
x'''
\end{pmatrix}
= R_3
\begin{pmatrix}
x''
\end{pmatrix}
= \begin{pmatrix}
1 & 0 & 0 \\
0 & \cos \beta_0 & \sin \beta_0 \\
0 & -\sin \beta_0 & \cos \beta_0
\end{pmatrix}
\begin{pmatrix}
x''
\end{pmatrix}.
\]  \hspace{1cm} (2.53)

Thus, the \((x, y, z)\) coordinate rotates with three steps: in order of (i) around the \(z\) axis by \(\alpha_0\) (Fig. 2.3a), (ii) around the \(y'\) axis by \(\gamma_0\) (Fig. 2.3b), and (iii) around the \(x''\) axis by \(\beta_0\) (Fig. 2.3c). It is worth noting that \(\alpha_0\) and \(\gamma_0\) represent a rotation of the crystal growth axis for a primary branch, and \(\beta_0\) is related to growth directions of sidebranches.

We can simplify the rotation matrix as

\[
\begin{pmatrix}
x'''
\end{pmatrix}
= R
\begin{pmatrix}
x
\end{pmatrix} ,
\]  \hspace{1cm} (2.54)

where

\[
R = R_3R_2R_1 = \begin{pmatrix}
r_{11} & r_{12} & r_{13} \\
r_{21} & r_{22} & r_{23} \\
r_{31} & r_{32} & r_{33}
\end{pmatrix}
\]  \hspace{1cm} (2.55)
with

\[
\begin{align*}
    r_{11} &= \cos \alpha_0 \cos \gamma_0 , \\
    r_{12} &= \sin \alpha_0 \cos \gamma_0 , \\
    r_{13} &= \sin \gamma_0 , \\
    r_{21} &= -\sin \alpha_0 \cos \beta_0 - \cos \alpha_0 \sin \beta_0 \sin \gamma_0 , \\
    r_{22} &= \cos \alpha_0 \cos \beta_0 - \sin \alpha_0 \sin \beta_0 \sin \gamma_0 , \\
    r_{23} &= \sin \beta_0 \cos \gamma_0 , \\
    r_{31} &= \sin \alpha_0 \sin \beta_0 - \cos \alpha_0 \cos \beta_0 \sin \gamma_0 , \\
    r_{32} &= -\cos \alpha_0 \sin \beta_0 - \sin \alpha_0 \cos \beta_0 \sin \gamma_0 , \\
    r_{33} &= \cos \beta_0 \cos \gamma_0 .
\end{align*}
\]

Then, the fixed Cartesian coordinates \((x, y, z)\) can be described as

\[
\begin{pmatrix}
    x \\
    y \\
    z
\end{pmatrix} = \mathbf{R}^{-1} \begin{pmatrix}
    x''' \\
    y''' \\
    z'''
\end{pmatrix} = \begin{pmatrix}
    r_{11} & r_{21} & r_{31} \\
    r_{12} & r_{22} & r_{32} \\
    r_{13} & r_{23} & r_{33}
\end{pmatrix} \begin{pmatrix}
    x''' \\
    y''' \\
    z'''
\end{pmatrix} . \quad (2.56)
\]

In order to apply the rotation angles to the crystal anisotropy, we replace the space derivatives of phase field \(\psi\) \([85, 148, 154]\) by its derivatives with respect to its crystal axes \((x''', y''', z''')\). Then, the partial derivatives become

\[
\begin{align*}
    \partial_{x'''} &= \partial_{x'''x} \partial_x + \partial_{x'''y} \partial_y + \partial_{x'''z} \partial_z , \\
    \partial_{y'''} &= \partial_{y'''x} \partial_x + \partial_{y'''y} \partial_y + \partial_{y'''z} \partial_z , \\
    \partial_{z'''} &= \partial_{z'''x} \partial_x + \partial_{z'''y} \partial_y + \partial_{z'''z} \partial_z .
\end{align*}
\]

In order to apply the rotation angles to the crystal anisotropy, we replace the space derivatives of phase field \(\psi\) \([85, 148, 154]\) by its derivatives with respect to its crystal axes \((x''', y''', z''')\). Then, the partial derivatives become

\[
\begin{align*}
    \partial_{x'''} &= \partial_{x'''x} \partial_x + \partial_{x'''y} \partial_y + \partial_{x'''z} \partial_z , \\
    \partial_{y'''} &= \partial_{y'''x} \partial_x + \partial_{y'''y} \partial_y + \partial_{y'''z} \partial_z , \\
    \partial_{z'''} &= \partial_{z'''x} \partial_x + \partial_{z'''y} \partial_y + \partial_{z'''z} \partial_z .
\end{align*}
\]

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or in a matrix form,

\[
\begin{pmatrix}
\partial_{x'''}\psi \\
\partial_{y'''}\psi \\
\partial_{z'''}\psi
\end{pmatrix} =
\begin{pmatrix}
r_{11} & r_{12} & r_{13} \\
r_{21} & r_{22} & r_{23} \\
r_{31} & r_{32} & r_{33}
\end{pmatrix}
\begin{pmatrix}
\partial_x \psi \\
\partial_y \psi \\
\partial_z \psi
\end{pmatrix} . \tag{2.60}
\]

The second derivative of $x'''$ can be calculated as

\[
\partial_{x'''x'''}\psi = r_{11}\partial_x(\partial_{x'''}\psi) + r_{12}\partial_y(\partial_{x'''}\psi) + r_{13}\partial_z(\partial_{x'''}\psi) . \tag{2.61}
\]

The extended forms including the other second derivatives are written below:

\[
\partial_{x'''x'''}\psi = r_{11}^2\partial_{xx}\psi + r_{12}^2\partial_{yy}\psi + r_{13}^2\partial_{zz}\psi + 2(r_{11}r_{12}\partial_{xy}\psi + r_{12}r_{13}\partial_{yz}\psi + r_{11}r_{13}\partial_{zx}\psi) ,
\]

\[
\partial_{y'''y'''}\psi = r_{21}^2\partial_{xx}\psi + r_{22}^2\partial_{yy}\psi + r_{23}^2\partial_{zz}\psi + 2(r_{21}r_{22}\partial_{xy}\psi + r_{22}r_{23}\partial_{yz}\psi + r_{21}r_{23}\partial_{zx}\psi) ,
\]

\[
\partial_{z'''z'''}\psi = r_{31}^2\partial_{xx}\psi + r_{32}^2\partial_{yy}\psi + r_{33}^2\partial_{zz}\psi + 2(r_{31}r_{32}\partial_{xy}\psi + r_{32}r_{33}\partial_{yz}\psi + r_{31}r_{33}\partial_{zx}\psi) ,
\]

\[
\partial_{x'''y'''}\psi = r_{11}(r_{21}\partial_{xx}\psi + r_{22}\partial_{xy}\psi + r_{23}\partial_{xz}\psi) + r_{12}(r_{31}\partial_{xy}\psi + r_{32}\partial_{yx}\psi + r_{33}\partial_{yz}\psi) + r_{13}(r_{21}\partial_{zx}\psi + r_{22}\partial_{zy}\psi + r_{23}\partial_{yz}\psi) ,
\]

\[
\partial_{y'''z'''}\psi = r_{21}(r_{31}\partial_{xx}\psi + r_{32}\partial_{xy}\psi + r_{33}\partial_{xz}\psi) + r_{22}(r_{31}\partial_{xy}\psi + r_{32}\partial_{yx}\psi + r_{33}\partial_{yz}\psi) + r_{23}(r_{31}\partial_{zx}\psi + r_{32}\partial_{zy}\psi + r_{33}\partial_{yz}\psi) ,
\]

and

\[
\partial_{z'''x'''}\psi = r_{31}(r_{11}\partial_{xx}\psi + r_{12}\partial_{xy}\psi + r_{13}\partial_{xz}\psi) + r_{32}(r_{11}\partial_{yx}\psi + r_{12}\partial_{yy}\psi + r_{13}\partial_{yz}\psi) + r_{33}(r_{11}\partial_{zx}\psi + r_{12}\partial_{zy}\psi + r_{13}\partial_{yz}\psi) .
\]

In our PF model, a temperature gradient $G$ is parallel to the $x$ axis, and the crystal growth $x'''$ axis rotates by an angle based on the $x$ axis. In addition, the $\pm y'''$ and $\pm z'''$ directions are related to the growth directions of sidebranches for a four-fold anisotropy. Figs. 2.4
and 2.5 show the schematic figures for different crystal angles in directional solidification.

We used a dendrite of a SCN-0.4wt% acetone alloy growing under a pulling velocity \( V = 25 \, \mu m/s \) and temperature gradient \( G = 30 \, K/cm \). When a dendrite is well-oriented \((\alpha_0, \beta_0, \gamma_0) = (0^\circ, 0^\circ, 0^\circ)\), a primary dendrite grows along the \( x \) axis without a misorientation as illustrated in Fig. 2.4a. The left column figure shows the top view of the dendrite, and its tip is located at the middle of the simulation. On the side view of the dendrite (right column), the dendrite is well-oriented along the temperature gradient that is parallel to the \( x \) axis.

Figs. 2.4b-c show misoriented dendrites at a steady state. In order to see how a dendrite

![Figure 2.4](image-url)

Figure 2.4: Schematic images for a dendrite growth with crystal angles \((\alpha_0, \beta_0, \gamma_0)\) in directional solidification. (a) illustrates a well-oriented dendrite with \((\alpha_0, \beta_0, \gamma_0) = (0^\circ, 0^\circ, 0^\circ)\). (b) and (c) show a stationary dendrite which is rotated by \((\alpha_0, \beta_0, \gamma_0) = (10^\circ, 0^\circ, 0^\circ)\) and \((0^\circ, 0^\circ, 10^\circ)\), respectively.
grows with a crystal angle, simulations used a well-oriented dendrite (Fig. 2.4a) as an initial condition, and suddenly changed its crystal angles to new values. For a dendrite with $\alpha_0 \neq 0^\circ$ ($\gamma_0 \neq 0^\circ$), its crystal $x''''$ axis rotates by $\alpha_0$ ($\gamma_0$) from the $x$ axis towards the $y$ ($z$) axis. Then, the growth direction of the primary dendrite rotates with respect to the fixed Cartesian $x$ axis. Fig. 2.4b and c show a dendrite with $(\alpha_0, \beta_0, \gamma_0) = (10^\circ, 0^\circ, 0^\circ)$ and $(0^\circ, 0^\circ, 10^\circ)$, respectively. Those dendrites are seen from the top of the growth direction (left column), and seen from the side (right column).

The images in Figs. 2.4b-c exhibit that the two angles $\alpha_0$ and $\gamma_0$ affect the growth direction of the primary dendrite. It is important to note that, when a primary branch laterally moves because of a set of $\alpha_0$ and $\gamma_0$, its growth orientation is usually smaller than its crystal orientation [11 39].

The growth directions of sidebranches are related to the $\beta_0$ angle. Dendrites in Fig. 2.5 show how the growth direction of secondary branches rotates as $\beta_0$ increases when $\alpha_0 = \gamma_0 = 0^\circ$. At $\beta_0 = 0^\circ$, each sidebranch grows along the $\pm y$ and $\pm z$ directions (Fig. 2.5a). As $\beta_0$ increases (left to right in Fig. 2.5), the crystal $y'''$ ($z'''$) axis rotates from the $y$ ($z$) direction towards the $z$ ($-y$) direction. Hence, the growth directions of four sidebranches are rotated as shown in Fig. 2.5b-d. Especially, when $\beta_0 = 45^\circ$ (Fig. 2.5d), sidebranches grow along the $[011], [0\bar{1}1], [01\bar{1}], \text{ and } [0\bar{1}\bar{1}]$ directions.

![Figure 2.5: Schematic images for a dendrite shape under the influence of the $\beta_0$ angle. We only vary $\beta_0$ angles, i.e. $\beta_0 = 0^\circ, 15^\circ, 30^\circ, 45^\circ$, and the other angels set as $\alpha_0 = \gamma_0 = 0^\circ$. The images show the morphologies seen from the top of the dendrites.](image)
2.2.7 Grain index

In order to produce grain growth dynamics of two grains by using the PF model, we introduced a grain index \( p \) in the model \([148, 154]\). This index is an integer value with \( p = -1 \) for the first solid grain, \( p = +1 \) for the other solid grain, and \( p = 0 \) for the liquid. We used this grain index to consider the growth of a grain that is misoriented with respect to the temperature gradient.

In the liquid far from the solid liquid interface, the index value is \( p = 0 \). It is updated near the solid, i.e. \((1 - \varphi^2) \geq 0.001\), only when \( p = 0 \). The new index value at a position \((i, j, k)\) is estimated by the neighbor indexes, which is \( p_{(i,j,k)} = +1 \) \((-1)\) if there are more \( p = +1 \) \((-1)\) neighbors near the \( p_{(i,j,k)} \). After it is decided as \( p = \pm 1 \), the value does not change.

In summary, if \( p_{(i,j,k)} = 0 \) and \((1 - \varphi^2_{(i,j,k)}) \geq 0.001\), then the model calculates the sum of the neighbor \( p \) values at a position \((i, j, k)\),

\[
S_{(i,j,k)} = p_{(i+1,j,k)} + p_{(i,j+1,k)} + p_{(i,j,k+1)} + p_{(i-1,j,k)} + p_{(i,j-1,k)} + p_{(i,j,k-1)}
\]

\[+ p_{(i+1,j+1,k)} + p_{(i+1,j-1,k)} + p_{(i-1,j+1,k)} + p_{(i-1,j-1,k)} \]

\[+ p_{(i,j+1,k+1)} + p_{(i,j+1,k-1)} + p_{(i,j-1,k+1)} + p_{(i,j-1,k-1)} \]

\[+ p_{(i+1,j,k+1)} + p_{(i+1,j,k-1)} + p_{(i-1,j,k+1)} + p_{(i-1,j,k-1)} \]

\[+ p_{(i+1,j+1,k+1)} + p_{(i+1,j+1,k-1)} + p_{(i+1,j-1,k+1)} + p_{(i+1,j-1,k-1)} \]

\[+ p_{(i-1,j+1,k+1)} + p_{(i-1,j+1,k-1)} + p_{(i-1,j-1,k+1)} + p_{(i-1,j-1,k-1)} , \quad (2.62)\]

to evaluate the new index as

\[
p_{(i,j,k)} = -1 \quad \text{for} \quad S_{(i,j,k)} < 0 , \quad (2.63)
\]

\[
= +1 \quad \text{for} \quad S_{(i,j,k)} > 0 . \quad (2.64)
\]
2.3 Dendritic-needle-network model

The PF model has been the most successful tool for solidification simulations of a dilute alloy \[12, 148, 31, 150, 154, 43, 64, 57, 124\]; however, it requires a sufficient spatial resolution of dendrite tips. In order to quantitatively predict the tip growth dynamics and describe an accurate dendrite tip morphology, the computational grid space for the model is restricted to about one order of magnitude smaller than a dendrite tip radius \(\rho\). Thus, PF simulations are challenging when dendrites are very sharp and their tip radii are much smaller than a diffusion length \(l_D \equiv D/V\). For this specific regime (i.e. at a low solute supersaturation), the dendritic-needle-network (DNN) model has been recently developed \[149\]. This DNN model is simpler than the PF approach in that it does not seek to represent the details of the complex interface pattern. Instead, each dendritic branch is represented as a sharp needle, and hence each dendritic grain is a network of sharp primary, secondary, and higher order sharp branches.

In the limit of a low Péclet number, i.e. \(Pe \equiv \rho V/(2D) \ll 1\), DNN simulations provide a good agreement with PF simulations, e.g. a relative error of \(\approx 25\%\) on the transient dendrite tip velocity of an equiaxed crystal at \(\Omega = 0.1\) \[149\]. Most importantly, DNN simulations can provide results using a grid space \(\Delta x\) of the order of the steady dendrite tip radius \(\rho_s\) without loss in accuracy, while quantitative PF predictions typically require \(\Delta x \lesssim \rho_s/10\). Therefore, using finite difference and an explicit time scheme, DNN calculations in 2D are about four orders of magnitude faster than PF for a reasonable loss in accuracy.

The DNN model \[149\] uses the dimensionless solute field, defined as

\[
    u \equiv \frac{c^0_l - c}{(1 - k)c^0_l},
\]

where \(c^0_l\) is the concentration on the liquid side of the stationary planar interface. For
isothermal solidification, the model consists of solving the diffusion of $u$ as

$$\partial_t u = D \nabla^2 u$$  \hspace{1cm} (2.66)

which is interacting with a growing needle-like crystal (i.e. a network of sharp line segments) at equilibrium. The growth dynamics of the needle-like dendritic tips is obtained by combining solute balance at two distinct length scales \[149\], as summarized below.

At a low supersaturation, the diffusion length $l_D$ is much larger than the dendritic tip radius. Therefore, one can write a solute balance at an intermediate scale $\gg \rho$ but still $\ll l_D$. At a scale $\gg \rho$, curvature effects can be neglected and a dendritic branch appears like a sharp line segment at a fixed equilibrium concentration $u = 0$. On the other hand, at a scale $\ll l_D$, the solute field relaxes fast enough to assume a Laplacian field $u$ close to the tip. Yet, a Laplacian field exhibits a square-root singularity of its normal gradient in the vicinity of a sharp tip of the form \[38\]

$$\left. \frac{\partial u}{\partial y} \right|_{y=0} = \frac{F}{\sqrt{d_0(x_t - x)}}$$  \hspace{1cm} (2.67)

when the position $x$ tends to the tip position $x_t$, where the time-dependent flux intensity factor $F$ is a measure of the total flux received at the tip, thus defined as

$$F(t) \equiv \lim_{x \to x_t} \sqrt{d_0(x_t - x)} \left. \frac{\partial u}{\partial y} \right|_{y=0}. \hspace{1cm} (2.68)$$

In 2D, the flux intensity factor can be directly calculated with an integral along a contour $\Sigma$ around the tip similar to the J-integral of fracture mechanics \[130\] \[10\] \[149\]

$$F^2 = \frac{d_0}{2\pi} \int_\Sigma \left[ \left( (\partial_x u)^2 - (\partial_y u)^2 \right) n_x + 2 \partial_x u \partial_y u n_y \right] d\Sigma. \hspace{1cm} (2.69)$$

Assuming that further away from the tip the interface position $y_i(t)$ follows the solution of
a 1D diffusion problem. The interface along the $y$ axis is normal to the tip as $dy_i(t)/dt \approx D \partial u/\partial y|_{y=0} = DF/\sqrt{d_0(x_t-x)}$, and that the tip moves in a quasi-steady regime at that scale with the change of variable $x_t - x = Vt$, since $x_t - x \ll D/V$. Then, one can obtain the relation between $\rho$ and $V$ \[149\]

$$\rho V^2 = \frac{2D^2F(t)^2}{d_0}.$$ \hspace{1cm} (2.70)

The second relation, established at the scale of the dendritic tip radius $\rho$, is the solvability condition \[94, 95, 6, 9\],

$$\rho^2 V = \frac{2Dd_0}{\sigma},$$ \hspace{1cm} (2.71)

where $\sigma$ is the tip selection parameter fixed by the interface anisotropy \[6\]. This relation for the existence of a steady growing solution of a parabolic tip has been validated by PF simulations, which have shown that $\sigma$ reaches a constant value as soon as parabolic tips start emerging at the very early stage of dendritic growth \[126\]. Therefore, the relation (2.71) is valid from the early transient regime to the steady state growth of a dendrite.

Hence, combining Eqs. (2.70)-(2.71), one can calculate the tip growth dynamics of each needle tip as

$$\frac{\rho(t)}{d_0} = \left(\frac{2}{\sigma^2 F(t)^2}\right)^{1/3},$$ \hspace{1cm} (2.72)

$$\frac{V(t)d_0}{D} = (2\sigma F(t)^4)^{1/3}.$$ \hspace{1cm} (2.73)

For a supersaturation $\Omega$, the stationary radius $\rho_s$ and velocity $V_s$ of a single free needle tip is \[149\]

$$\frac{\rho_s}{d_0} = \frac{\pi}{\sigma\Omega^2},$$ \hspace{1cm} (2.74)

$$\frac{V_s d_0}{D} = \frac{2\sigma\Omega^4}{\pi^2}.$$ \hspace{1cm} (2.75)
For the DNN calculations, we scale time and space with respect to this sharp needle approximation steady-state tip radius and velocity, such that the dimensionless tip radius $\tilde{\rho} \equiv \rho/\rho_s$ and velocity $\tilde{V} \equiv V/V_s$ evolve with the time $\tilde{t} \equiv tV_s/\rho_s$ as

$$\tilde{\rho} = (2\tilde{D}^2\tilde{F}^2)^{-1/3}, \quad (2.76)$$

$$\tilde{V} = (2\tilde{D}^2\tilde{F}^2)^{2/3}, \quad (2.77)$$

where $\tilde{D} = \pi/(2\Omega^2)$ and $\tilde{F}^2$ is calculated as

$$\tilde{F}^2 = \frac{1}{2\pi} \int_{\Sigma} \left[ \left( (\partial_{\tilde{x}} u)^2 - (\partial_{\tilde{y}} u)^2 \right) n_{\tilde{x}} + 2 \partial_{\tilde{x}} u \partial_{\tilde{y}} u n_{\tilde{y}} \right] d\Sigma \quad . \quad (2.78)$$

Then, Eqs. (2.76)-(2.78) together with the diffusion equation

$$\partial_{\tilde{t}} u = \tilde{D}\nabla^2 u \quad (2.79)$$

constitute the summary of the DNN model for isothermal solidification. In the model, the boundary conditions for the solute field are given by $u = 0$ on each dendrite needle and $u = \Omega$ in the liquid far away from the solid. More details on the DNN model and its implementation appear in Ref. [149]. It is worth noting that this model has been improved and developed for the 3D dendrite dynamics [151].

### 2.3.1 Growth of sidebranches

The DNN model periodically generates a sidebranch at a distance $(N + \zeta) \times \rho$ behind the primary dendrite tip, where $N$ is a preset number and its fluctuation is $\Delta N$, whenever the primary dendrite grows by the same length $(N + \zeta) \times \rho$ [149, 151]. A new random value of $\zeta$ is generated between $-\Delta N/2$ and $+\Delta N/2$ each time when a new branch is created. The values of $N$ and $\Delta N$ are input parameters of the model, and those values are typically set as $5 \leq N \leq 10$ and $\Delta N \approx 10$ from the experimental observations [149, 35]. We have
shown that, as long as sidebranching occurs frequently enough to yield a growth competition among sidebranches, the values of $N$ and $\Delta N$ have little influence on the final resulting microstructure (e.g. in terms of selected primary spacing [149]).

When a new sidebranch is created, its length $l_{SB}$ is initialized to the width of its parent needle at this position, i.e. $l_{SB} = \sqrt{2\rho l_{PS}}$, where $l_{PS}$ is the distance from the primary tip to the root of a new sidebranch.

The early growth of a sidebranch is assumed to occur within a Laplacian field. Using a conformal transformation technique, Hakim has derived the analytical growth law of a needle sidebranch and its parent needle in a Laplacian field as

$$\frac{dl_{SB}}{dt} = \frac{1}{2\eta/2} \frac{l_{SB}^{\eta/2}}{(l_{SB}^2 + l_{PS}^2)^{\eta/4}},$$

$$\frac{dl_{PS}}{dt} = \frac{l_{PS}^{\eta/2}}{(l_{SB}^2 + l_{PS}^2)^{\eta/4}},$$

where $\eta = 4/3$ [65]. We use Eq. (2.80) to describe the early stage growth of a sidebranch, until its length $l_{SB}$ gets large enough to apply the contour integral (2.78) around the tip (i.e. four times the finite difference grid spacing $l_{SB} \geq 4\rho_s$).

### 2.3.2 Estimation of the interface position and mass of a dendritic branch

During dendritic growth, the side of a dendrite also grows due to the supplying of the surrounding solute. In order to calculate the growth of a dendrite width for a time step $\Delta t$, we consider a dendrite located from $(0, j)$ to $(i_t + r, j)$ which is growing along the $x$ direction. The dendrite tip locates at $i_t + r$ ($0 \leq r < 1$) because it is not always located at a grid point $(i_t, j)$ [149]. The added solute on the side of the needle at $(i', j + 1)$, where $0 < i' < i_t$, is given by

$$I(i', j) = -D \frac{u(i', j) - u(i', j + 1)}{\Delta x},$$

(2.82)
where $\Delta x$ is a grid spacing. Then, a dendrite width at $(i', j)$ increases as the amount of $I(i', j) \Delta t \times \Delta x$. In the meantime, the dendrite tip also contributes to the increase of the dendrite area for $\Delta t$ as $I(i_t, j) \Delta t \times \Delta x$, where the trapped solute at $(i_t, j)$ is

$$I(i_t, j) = D \frac{u(i_t + 1, j)}{(1 - r) \Delta x}. \quad (2.83)$$

Thus, we can calculate the total area (i.e. mass) of a 2D dendrite by adding up the volume within $(0, j)$ and $(i_t + r, j)$ from its birth to a time $t$. 
Chapter 3

Phase-field modeling of cellular array patterns in three-dimensional microgravity directional solidification experiments

The following chapter contains material currently being prepared for publication. The results in this chapter reflect my contribution to this work, and all experimental measurements referenced in this chapter are performed by my collaborators, and appropriate credit is given. This work will be published with the following co-authors; Younggil Song\textsuperscript{1}, Damien Tourret\textsuperscript{2,3}, Fatima L. Mota\textsuperscript{4}, Jorge Pereda\textsuperscript{4}, Nathalie Bergeon\textsuperscript{4}, Bernard Billia\textsuperscript{4}, Rohit Trivedi\textsuperscript{5}, Alain Karma\textsuperscript{1}

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3.1 History-dependent pattern selection

3.1.1 Background

Recent directional solidification experiments aboard the ISS (International Space Station) revealed various 3D microstructure dynamics. In the experiments, we observed homogeneous patterns under low gravity conditions [11, 116], and the results provide unique data to validate theoretical and numerical predictions in a purely diffusive regime. Specifically, the oscillatory dynamics in cellular structures observed in the microgravity experiments were reproduced by 3D PF simulations [12, 148, 124]. The PF simulations identified the various characteristics of the oscillations.

Despite this progress, the predicted primary spacing in the classical PF model is smaller than the measured spacing in the experiments. One of the possible reasons for this spacing discrepancy is the thermal condition inside the sample crucible. A recent thorough analysis of interface recoil dynamics [11, 116] reveals that the thermal conditions within the experimental setup could vary while the sample is pulled towards the colder region. The history of the thermal field affects the dynamics of the initial recoil of the planar interface. It could therefore influence the competitive growth of cells or dendrites taking place during the recoil phase, which leads to different primary spacing at a steady state. Thus, in order to quantitatively reproduce the initial solid-liquid interface dynamics, we need to consider the two thermal effects, namely heat diffusion within an adiabatic zone and latent heat rejection when the liquid solidifies. These thermal effects are not considered in the previous PF simulations using a frozen temperature approximation.

The two thermal factors, i.e. heat diffusion and latent heat rejection within an adiabatic zone, are phenomenologically described in Ref. [116]. In addition, we can estimate the thermal factors quantitatively using a 1D thermal field. Therefore, we impose these two thermal representations into the PF model. In the following section, we are going to
show results using the PF model with (i) a classical frozen temperature approximation, (ii) a phenomenological introduction of the thermal drift, and (iii) a quantitative 1D calculation of the thermal field. Then, we compare the initial recoil dynamics and microstructure selection observed in the experiments to the simulation results using different thermal representations.

### 3.1.2 Methods

**Microgravity experiments**

Within the DECLIC (DEvice for the study of Critical LIquids and Crystallization)-DSI (Directional Solidification Insert) experimental setup, a crucible has a cylindrical shape with the inner radius of 5 mm. In the crucible, the solid-liquid interface grows up to 10 cm while the crucible is pulled within a temperature field between hot and cold regions of a Bridgman furnace. The experimental setup is schematically drawn in Fig. 3.1. In the figure, the black square between the hot (red on the right) and cold (blue on the left) heat sources represents the sample crucible. An immersed lens at the top inside the liquid of the sample crucible records an axial imaging of the interface when the light passes through the interface from

![Figure 3.1: (a) schematic figure of the experimental setup. The hot and cold boxes represent the hotter and colder heat sources, and the sample crucible (black box) is located between the heat source. (b) stationary temperature fields within an adiabatic zone predicted by PF simulations at \( V = 4 \, \mu m/s \) with the FTA (blue line), TDA (gray line), and TFC (red line). Black dashed lines in both figures correspond to the initial planar interface position at a liquidus temperature.](image)

\( V \)
the bottom (near the cold heat source) of the crucible. In addition, we are able to observe transverse images through the transparent crucible walls. Thus, we could observe solidifying microstructures from both top-view and side-view images. More details of the experiments are shown in Ref. [124, 11116, 1310712714118]. We focus here on experiments for a temperature gradient $G = 19$ K/cm and pulling velocities in the range of $1 \leq V [\mu m] \leq 8$.

The solid-liquid interface temperature is initially close to the liquidus temperature of the alloy before the sample is pulled, which defines the initial position of the interface inside the temperature gradient. As the sample is pulled towards the colder area, the planar interface slowly grows towards the hotter region, and the interface growth velocity is usually smaller than the pulling velocity. In the meantime, the solute concentration at the interface on the liquid side increases until the planar interface becomes morphologically unstable [146, 119].

As shown in the first left column in Fig. 3.2, wrinkles first form on the interface. Their locations are close to grain boundaries. Then, small bumps near the wrinkles develop into small cells. These cells interact with their neighbors through the solutal diffusion field and the cells that fall behind become screened and are progressively eliminated (the second column in Fig. 3.2). The primary spacing increases towards the stationary value for the microgravity experiments at low velocities $V \leq 1 \mu m/s$; however, for $V \geq 2 \mu m/s$, it exhibits a peak spacing value (the third column in Fig. 3.2) before it slowly decreases towards the stationary spacing (the last column in Fig. 3.2).

**Phase-field modeling**

We recently suggested an appropriate thermal field within the experimental setup based on experimental measurements of the interface position and its time evolution [116]. In this section, we compare different modeling approaches for the thermal field, and discuss their validity in modeling transient interface dynamics and selected microstructures. We compare three different approaches, which we refer to as the standard *Frozen Temperature Approximation* (FTA), a recently proposed *Thermal Drift Approximation* (TDA) [116], and
Figure 3.2: Microstructures seen from the top of the interface of the microgravity experiment at $V = 2 \, \mu m/s$ (a) and $4 \, \mu m/s$ (b) as time elapses $L = Vt$ (left to right).

a time-dependent *Thermal Field Calculation* (TFC), to the experimental measurements.

The FTA assumes a linear temperature profile of the form

$$T = T_0 + Gx,$$  \hspace{1cm} (3.1)

where $T_0$ is a reference temperature. In the TDA, the temperature gradient shifts with time and is given by \[116\]

$$T = T_0 + Gx + G\Delta z_T \left(1 - e^{-t/\tau_d}\right),$$  \hspace{1cm} (3.2)

where $\Delta z_T$ is a total isotherm shift and $\tau_d$ is a delay time. For the TFC, we introduce a one-dimensional (1D) temperature field within an adiabatic zone to quantitatively represent
the thermal diffusion and latent heat rejection at the interface.

\[
\partial_t T = V \partial_x T + D_T \partial_{xx} T + \frac{\Delta h_f}{c_p} \frac{1}{V} \int \frac{\dot{\phi}}{2} dV, 
\]  

(3.3)

where \( V \) is a finite volume to integrate, \( D_T \) is a thermal diffusivity of the alloy, \( \Delta h_f \) is its latent heat of fusion per unit volume, and \( c_p \) is its heat capacity. The detailed descriptions focusing the thermal conditions inside the PF model are given in Sec. 2.2.

**Parameters**

We used similar parameters as in Ref. [148, 124] or in Appendix B.

In the TDA simulations, we calculated \( \Delta z_T \) by using a tip undercooling \( \Delta \) from PF simulations for average \( \lambda \) measured in the corresponding experiment (related to Fig. 3.7a discussed later). Using this \( \Delta z_T \), we predict the planar interface dynamics with a modified Warren-Langer (WL) model [116, 168] at a constant \( k = 0.07 \) [117] by using different \( \tau_d \). We compared the predictions to the experimentally measured interface positions during the transient recoil. Then, we chose the \( \tau_d \) which shows the best agreement with the experimental measurements. The parameters for the thermal drift calculations are summarized in Table 3.1.

The TFC used \( \Delta h_f/c_p = 23 \) K as for pure SCN [165] because the considered alloy is dilute.

**Table 3.1:** Parameters for simulations with the thermal drift approximation. We used a dimensionless tip undercooling \( \Delta \) for a measured average spacing in experiments (Fig. 3.7a) to estimate the total isotherm shift \( \Delta z_T \) when the alloy thermal length is \( l_T = 2290.74 \) \( \mu m \) at \( G = 19 \) K/cm.

<table>
<thead>
<tr>
<th>( V ) [( \mu m/s )]</th>
<th>( \Delta z_T ) [( \mu m )]</th>
<th>( \Delta z_{exp} ) [mm]</th>
<th>( \Delta ) [-]</th>
<th>( \tau_d ) [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>881.81</td>
<td>1.23</td>
<td>0.152</td>
<td>1778</td>
</tr>
<tr>
<td>2</td>
<td>1083.83</td>
<td>1.29</td>
<td>0.090</td>
<td>688</td>
</tr>
<tr>
<td>4</td>
<td>1660.27</td>
<td>1.80</td>
<td>0.061</td>
<td>491</td>
</tr>
<tr>
<td>8</td>
<td>3016.61</td>
<td>3.13</td>
<td>0.050</td>
<td>378</td>
</tr>
</tbody>
</table>
The dilute alloy is filled inside the inner part of the crucible with its radius 5 mm, and the thickness of the quartz wall is 1 mm. The thermal conductivity of the quartz crucible is $\kappa_C = 1.42$ W/m/K, and that of pure SCN is $\kappa_{SCN} = 0.224$ W/m/K [165], which is close to the alloy. Then, the effective thermal conductivity is given by $\kappa_E = \kappa_{SCN} + \kappa_C / 5 = 0.508$ W/m/K, and the thermal diffusivity becomes $D_T = \kappa_E / c_p = 2.54 \times 10^{-7}$ m$^2$/s with $c_p = 2.0 \times 10^6$ J/m$^3$/K, the value for pure SCN [165].

We assumed that the initial temperature field within heat sources forms at rest (i.e. $V = 0$ $\mu$m/s) and that the boundary temperatures of the adiabatic zone remain fixed during the solidification process. Thus, we estimated the hot ($T_h$) and cold ($T_c$) boundary temperatures from axisymmetric thermal simulations (called CrysVUn) of the experimental setup [116]. In our considered TFC simulations, the boundary temperatures are $T_h = 347.75$ K and $T_c = 308.43$ K over an adiabatic zone length of 2.07 cm, which are independent of the pulling velocity. The temperature linearly increases from $T_c$ to $T_h$ before a simulation starts, and thus the thermal field is initialized with $G = 19$ K/cm.

We considered four different pulling velocities $V [\mu$m/s$] = 1, 2, 4, \text{ and } 8$ for PF simulations with three different thermal representations. Accordingly, diffuse interface widths are $W/d_0 = 198.0$ for $V = 1$ $\mu$m/s, 140.0 for $V = 2$ and 4 $\mu$m/s, and 98.0 for $V = 8$ $\mu$m/s, which respectively correspond to a grid spacing $\Delta x [\mu$m$] = 3.54, 2.50, \text{ and } 1.75$, and to an explicit time step $\Delta t [s] \simeq 0.0069, 0.0035, \text{ and } 0.0015$. The simulations used symmetric boundaries at the $x$ axis and periodic boundary conditions along $y$ and $z$ boundaries. In order to reproduce thermal fluctuations, a noise has been imposed into the $\psi$ field with a strength $F = 0.02$ [12, 148, 124, 57]. We mostly considered a large system size, i.e. $L_x \times L_y \times L_z [\mu$m$^3$] = 3444.4 $\times$ 700.2 $\times$ 700.2 for $V = 1$ $\mu$m/s, 1495.3 $\times$ 495.1 $\times$ 495.1 for $V = 2$ $\mu$m/s, 1115.2 $\times$ 495.1 $\times$ 495.1 for $V = 4$ $\mu$m/s, and 696.6 $\times$ 500.6 $\times$ 500.6 for $V = 8$ $\mu$m/s.

We additionally performed simulations to construct stable spacing ranges of a hexagonal array using the method in Ref. [12, 148, 124]. We initially found one-quarter of a cell at a stationary state, and then we progressively expanded the simulation size of one-quarter of
a cell by one grid spacing $\Delta x$ until its sidebranch became a primary branch. We bilinearly interpolated the stationary $\psi$ and $U$ fields from a previous simulation to restart a simulation with expanding or reducing the domain size (additional or fewer grid points in the $y$ and $z$ axis) while other simulation parameters were not changed. We also achieved simulations with 1.5 cells of a hexagonal array to test the stability limit with respect to elimination. For the TFC simulations, the thermal field for the new simulation was initialized with a stationary thermal field from the previous simulation.

3.1.3 Results and discussions

Transient interface dynamics

At the beginning of each experiment, the planar solid-liquid interface temperature is $T = 330.85$ K, which corresponds to the liquidus temperature of the alloy. When the sample is moved towards the colder temperature with a pulling velocity $V$, the interface recoils within a temperature gradient $G$. In the meantime, the solute concentration on the liquid side of the interface builds up. When the solute concentration is high enough (or the concentration gradient in front of the interface on the liquid side exceeds a critical value), the planar front becomes unstable [146, 119]. After the front breaks down, the small cells compete with neighboring cells. Many of them are eliminated during the competition, and the surviving primary branches grow with a stable spacing.

In the experimental measurements, the initial planar interface starts to move from its initial position $x_i = 0$ right after the sample is pulled, as illustrated in Figs. 3.3a-d (black squares). These measurements are compared to the positions predicted by PF simulations with three different thermal descriptions, i.e. the FTA (blue solid lines), the TDA (gray solid lines), and the TFC (red solid lines).

In the experiments and the simulations, the solid-liquid interface grows while the sample moves with $V$. The planar interface moves towards the colder temperature ($x_i < 0$) because
its growth velocity $V_i$ is smaller than $V$. After the morphological instability, small cells that emerge from the interface grow very fast, and then $V_i$ for the surviving cells approach the imposed pulling velocity $V$. Thus, in Fig. 3.3, the local maximum of $x_i(L)$ between the initial recoil and the stationary growth are related to the instability.

In the FTA simulations (blue lines in Fig. 3.3), the initial planar interface moves relatively faster than the other simulations and experiments. Accordingly, the planar front is destabilized earlier than in the experimental measurements (red shaded areas in Fig. 3.3). At the final stationary state, cell tips are located much closer to the liquidus temperature ($x_i = 0$) than the experimental observations.
At a lower velocity $V = 1 \, \mu m/s$ (Fig. 3.3a), the onset of the instability and the final stationary positions in the simulations show a discrepancy from the experiments. This can be caused by convection [118], and the effects are expected to be more significant at lower $V \leq 1 \, \mu m/s$. Therefore, we focus on the simulations at $V \geq 2 \, \mu m/s$ in the following analysis. When $V \geq 2 \, \mu m/s$ (Figs. 3.3b-d), the results (initial planar interface dynamics, the time for morphological instability, and the final stationary tip positions) in PF simulations with both the TDA and FTA agree better with the experimental observations than the FTA simulation results. It is worth noting that the TFC provides better interface dynamics observed in the experiment than the TDA without any additional adjustable parameter as in Fig. 3.3b at $V = 2 \, \mu m/s$.

In order to assess the influence of the latent heat rejection on the initial recoil, we additionally performed a PF simulation at $V = 2 \, \mu m/s$ with the TFC method without the last term in Eq. (3.3), which corresponds to the red dashed line in Fig. 3.3b. Even though the result improves the initial recoil dynamics or time for morphological instability compared to the FTA, it underestimates the interface positions at a stationary state. Therefore, we need to consider the latent heat rejection to properly describe the interface dynamics as pointed out in Ref. [116].

**Onset of planar instability**

After the planar interface breaks down to small cells, most cells are progressively eliminated and some selected cells find a stable spacing during coarsening dynamics. Thus, the interface evolves dramatically as illustrated in Fig. 3.4. For the figure, we use the TFC simulation at $V = 4 \, \mu m/s$, and snapshots correspond to green plus symbols in Fig. 3.3c and in corresponding plots of Fig. 3.5.

Small bumps, which are related to an initial wavelength $\Lambda_0$, are formed right after the planar solid-liquid interface becomes morphologically unstable (Fig. 3.4a). Then, as tips of these bumps accelerate, they grow into small cells (Fig. 3.4b). These cells compete with
Figure 3.4: Microstructures in the TFC at $V = 4 \, \mu m/s$ during coarsening dynamics after the morphological instability. These images are taken from the top (top row) and the side (bottom row) as time passes (left to right).

other neighboring cells while they are growing, and many of them are progressively eliminated (Fig. 3.4c-e). When this initial coarsening dynamics (or progressive elimination process) is finished, a primary spacing is selected (Fig. 3.4e). This selected spacing seldom changes afterward.

We measure the interface concentration $c_l$ (a, top row), velocity $V_i$ (b, center row), and the overall selected spacing $\Lambda$ (c, bottom row) during the FTA (blue lines) and TFC (red lines) as shown in Fig. 3.5. The predicted evolutions of $c_l$, $V_i$, and $\Lambda$ at different $V \, [\mu m/s] = 2$ (left column), 4 (center column), and 8 (right column) with $G = 19 \, K/cm$ are compared to each other.

As the sample is pulled towards the colder temperature, the solute concentration at the interface on the liquid side $c_l$ builds up (Fig. 3.5a). In the FTA simulations (blue solid lines), $c_l$ increases with the planar front, and the morphological instability occurs at $L \approx 0.53 \, mm$ where $c_l$ is approximately maximal. Then, the small cells accelerate (Fig. 3.5b) while $c_l$ at the advanced cell tip decreases towards a stationary state. The interface velocities (Fig. 3.5b)
Figure 3.5: The evolution of the interface concentration $c_l$ (a), velocity $V_i$ (b), and the average spacing (c) as a function of the solidification length $L$ at $V = 2$ (first column), 4 (center column), and 8 $\mu$m/s (last column). The blue and red lines correspond to the FTA and TFC results, and the black squares indicate experimental measurements. The red shaded areas are related to the time ranges of the morphological instability in the microgravity experiments. Green plus symbols at $V = 4$ $\mu$m/s show time for morphologies in Fig. 3.4 (from left to right as time increases). We calculated critical velocities $V_c$ for the morphological instability using Eq. (3.4) \cite{146119} (black dashed line) and a time dependent $\Delta c_i(t) = c_i(t)(1 - k)$ from simulations (colored dashed lines).

Also decreases towards the imposed pulling velocity after its peak. In the meantime, the interface also approaches a stationary position.

In the TFC simulations (red solid lines), $c_l$ and $V_i$ increase slowly compared to the FTA simulations, and thus the time for the instability improves the agreement with the experiments (red shaded area). At the instability, the peak of $c_l$ ($V_i$) is higher (lower) than the
FTA. The lower peak \( V_i \) provides a first indication for the different primary spacing at a steady state (Fig. 3.5c).

The interface velocity \( V_i = V + dz_i/dt \) of the planar interface increases slowly as the sample is pulled. In the classical theory, a planar interface can break down to small cells when \( V_i \) exceeds a critical velocity \( V_c \), predicted using the constitutional undercooling criterion \[ V_c \] 

\[
V_c = \frac{GD}{m|\Delta c_i|}, \quad (3.4)
\]

where \( m \) is the liquidus slope, and \( \Delta c_i \) is the concentration gap at the interface. In the classical theory, the gap is calculated at the alloy solidus temperature, i.e. \( \Delta c_i = c_0(1/k - 1) \), and thus the critical velocity is \( V_c^0 = 0.118 \ \mu \text{m/s} \) for the experiments. The black dashed lines in Fig. 3.5b indicate this constant \( V_c^0 \). In all simulations, \( V_i \) crosses \( V_c^0 \) very early after the interface moves, and much earlier than the morphological instability.

The classical approach Eq. (3.4) is modified by using the instantaneous interface concentration \( c_l(t) \) or \( \Delta c_i(t) = (1 - k)c_l(t) \). We additionally performed both FTA and TFC simulations with a reduced size instead of using \( c_l \) from a large system in Fig. 3.5a. In the simulations, the interface remains planar until the end of the simulation, so we could continuously trace \( c_l(t) \) variations of the planar front. Then, we use the results of the planar interface to calculate \( V_c(t) \). In addition, we assume \( G \) remains the nominal value because we find \( G = 18.4 \ \text{K/cm} \) for \( V = 2 \) and \( 4 \ \mu \text{m/s} \) and \( 18.2 \ \text{K/cm} \) for \( V = 8 \ \mu \text{m/s} \) at the morphological instability. Thus, the calculated \( V_c(t) \) for the TFC (FTA), i.e. the red (blue) dashed line in Fig. 3.5b, illustrates an instantaneous critical velocity, and approaches \( V_c^0 \) as the interface moves towards the solidus temperature. The modified \( V_c(t) \) with the FTA is smaller than with the TFC because of the relatively slow increase of \( c_l \) in the TFC (Fig. 3.5a). Thus, the lower \( V_i(t) \) and the higher \( V_c(t) \) could lead to the later planar destabilization in the TFC.

In all simulations in Fig. 3.5b, the time \( t = t_i \) for the morphology instability (when \( V_i \) surges) is significantly later than the time \( t = t_0 \) when \( V_i(t) \) intersects \( V_c(t) \). This is because it takes time for an initial wavelength to be amplified, and the amplification is related to
Figure 3.6: Initial spacings and critical times as a function of $V$.

(a) shows initially measured average spacing in the experiments (black squares), the FTA (blue diamonds), and the TFC (red circles). We calculated critical spacing $\Lambda_c$ at a critical time $t_c$ using simulation data from the analytical approach in Ref. [26]. As shown in (b), at this critical time $t_c$, the amplification rate and its derivative are $\omega(k_n) \approx 0$ and $d\omega(k_n)/dk_n \approx 0$ at $k_n = k_c$. Thus, we calculated the critical wavelength at $k_c$ using the data in the FTA (blue dashed line in a) and in the TFC (red solid line in a). (c) illustrates that the critical time $t_c$ is close to $t_0$ (up triangles) at which $V_i(t)$ crosses $V_c(t)$ rather than $t_1$ (down triangles) for the morphological instability.

thermal fluctuations [168]. Fig. 3.6a shows the initially measured spacing $\Lambda_0$ in the FTA (blue diamonds), the TFC (red circles), and the experiments (black square dots) including minimum and maximum spacings (error bars). In all cases, this $\Lambda_0$ decreases as $V$ increases.

In the classical theories [119, 168, 26], a critical initial spacing $\Lambda_c$ at the instability was predicted using a dispersion relation $\omega(k_n)$, where $\omega$ is an amplification rate and $k_n$ is a wave number, at a given solute concentration at the interface and an interface velocity.

More specifically, for $\Lambda_c$ estimations using PF simulation data, we solved the dispersion equation Eq. (32) in Ref. [26], i.e.

$$\omega \left[ 1 - \frac{1 - k}{r} \xi \right] - k(1 + \dot{\xi})g_c(t) - \frac{\dot{\xi}}{r} = \left[ q + (1 + \dot{\xi})(k - 1) \right] \left[ -g_c(t) - \frac{1}{r} - \frac{d_0}{l_D}k_n^2 \right], \quad (3.5)$$

where $\xi = \xi(t)$ is the instantaneous interface position within the solidus and liquidus temperatures, and $r = l_T/l_D$ is the ratio between the thermal and diffusion length. We modify
the ratio by introducing an instantaneous thermal length \( l_T(t) = |m \Delta c_i(t)|/G \), which yields \( r(t) = l_T(t)/l_D = V/V_c(t) \). The solute gradient at the interface on the liquid side \( g_c(t) \) is given by

\[
g_c(t) = -(1 + \dot{\xi})\left[1 - \frac{\xi}{r}(1 - k)\right], \tag{3.6}
\]

and the inverse decay length \( q \) is given by

\[
q = \frac{1 + \dot{\xi}}{2} + \left[\frac{(1 + \dot{\xi})^2}{4} + \omega + k_n^2\right]^{1/2} \tag{3.7}
\]

from the diffusion equation. In order to solve the dispersion relation Eq. (3.5) using \( V_i \) and \( c_l \) at time \( t \) from our simulation data, we assume \( \omega \ll k_n^2 \). This assumption is reasonable because the amplification rate becomes \( \omega(k_c) = 0 \) at the critical wave number \( k_n = k_c \). Then, for the evaluations of \( \xi \) and its time derivative \( \dot{\xi} = d\xi/dt \), we use the local equilibrium condition

\[
u_l = 1 - \xi/r \tag{3.8}
\]

that is equivalent to the dimensionless solute concentration at the interface \( u_l = (c_l - c_0)/[c_0(1/k - 1)] \) and the interface velocity

\[
V_i = V(1 + \dot{\xi}) \tag{3.9}
\]

Thus, we could read the time dependent \( V_i \) and \( c_l \) directly from Fig. 3.5a-b to solve Eq. (3.5). For the evaluations, we assume the temperature gradient is fixed as the initial \( G = 19 \) K/cm because the variance of \( G \) is less than 1 K/cm (i.e. \( G = 18.4 \) K/cm for \( V = 2 \) and 4 \( \mu m/s \) and 18.2 K/cm for \( V = 8 \) \( \mu m/s \)) at morphological instability in the simulations.

Fig. 3.6b shows the \( \omega(k_n) \) at \( V = 2 \) \( \mu m/s \). Using the simulation data at \( t = t_0 \) (green line), the amplification rate does not exceed 0. Some time later at \( t = t_c \) (purple line), the maximum \( \omega(k_n) \), i.e. \( d\omega(k_n = k_c)/dk_n \approx 0 \), becomes \( \omega(k_n) = 0 \). Thus, we used this critical wave number \( k_n = k_c \) to calculate the critical spacing \( \Lambda_c \). After the critical time
\( t_m = 0.5(t_0 + t_1) > t_c \) (dark blue line), \( \omega(k_n) \) becomes larger than 0 at a small \( k_n \) and its maximum is larger than 0. At the time \( t_1 \) at the onset of the morphological instability (red line), the gap between small and large \( k_n \) for \( \omega(k_n) = 0 \) is much larger than at \( t_m \). The maximal \( \omega(k_n) \) is also larger than the previous time.

We evaluate \( k_c \) at \( t_c \) using PF simulations at different velocities (Fig. 3.5), and calculate the critical spacing with

\[
\Lambda_c = \frac{2\pi l_D}{k_c}.
\]

(3.10)

In Fig. 3.6a, the calculated \( \Lambda_c \) from both FTA (blue dashed line) and TFC (red solid line) are close to both simulations (hollow dots) and experiments (square dots).

Fig. 3.6c compares the critical time \( t_c \) (circles) with \( t_0 \) (△) and \( t_1 \) (▽) in both FTA (blue) and TFC (red). In all considered simulations, these \( t_0 \), \( t_c \), and \( t_1 \) decrease as \( V \) increases, and \( t_c \) is closer to \( t_0 \) than \( t_1 \). The closeness of \( t_c \) to \( t_0 \) could tell us that the initial perturbation takes a long time to arise from the planar interface. Interestingly, we observe that the time interval \( \Delta t = t_1 - t_0 \) decreases as a power law of \( V \), i.e. \( \Delta t \sim V^{-a} \), where \( a \) is a positive constant. In our simulations, the exponent is \( a = 0.9 \) for the FTA and 1.5 for the TFC. Thus, we could deduce that the amplification of the interface perturbation tends to be delayed under the influence of the thermal diffusion and the latent heat release. It is important to note that the strong thermal fluctuation leads to fast morphological instability. Therefore, a different noise strength rather than \( F = 0.02 \) in all simulations could possibly affect \( t_1 \) and \( a \).

**Stationary spacing selection**

The selected primary spacings in a thin-sample geometry have been studied analytically and experimentally \[61, 137, 160, 138, 161, 157, 66, 91, 72\]. In the experiments, a similar solidification process leads to a similar spacing selection \[137, 160, 138, 161\]. The analytical studies show that the spacing selection mechanisms are controlled by three main parameters, i.e. the freezing range of an alloy, pulling velocity, and temperature gradient \[157, 66, 91, 72\].
In the recent numerical studies using FTA with spatially extended systems, selected spacings are close to the lower limit of the stability range \[43, 149, 148, 31\] even though a cell/dendrite can select a primary spacing in a wide stable range \[43\].

Fig. 3.7a shows the stability ranges for \(G = 19\ \text{K/cm}\) and \(V = 1, 2, 4,\) and, \(8\ \mu\text{m/s}\) predicted by PF simulations. In the figure, solid lines indicate the stability ranges with the FTA (filled circle dots) and the TFC (cross dots). The dots represent tip undercooling of a quarter of a cell in a hexagonal array at a steady state from the simulations. For \(V = 1\ \mu\text{m/s}\), the minimum \(\lambda_{\text{min}}\) and maximum \(\lambda_{\text{max}}\) spacing limits are the same in the FTA and TFC. For the other \(V \geq 2\ \mu\text{m/s}\), \(\lambda_{\text{min}}\) (\(\lambda_{\text{max}}\)) is smaller (larger) in the TFC than in the FTA, and thus the stability range in the TFC has been widened slightly.

Boxes in Fig. 3.7b correspond to the stable spacing ranges for FTA, which are very close to the TFC as illustrated in Fig. 3.7a. The measured average spacings (black square dots)
and their standard deviations (error bars) in the microgravity experiments are inside this predicted stability ranges. In addition, the average Λ decreases with a power law of V as described in the analytical approach Λ ∼ V^{−1/4} [157, 66, 91, 72].

The selected spacings in the FTA (blue diamonds) and the TFC (red circles) are smaller than the experimental measurements; however, the TFC improves the agreement. The larger spacing selection in the TFC could be linked to the lower peak V_i and the slower increase of c_i after the morphological instability as illustrated in Fig. 3.6a-b.

Fig. 3.5 shows Λ in the experiment overshoots before it slowly decreases towards a Λ at a steady state; however, simulations do not exhibit the overshoot of a spacing. The experiments exhibit that grains are misoriented with respect to the temperature gradient, and grain boundaries are systemically formed between the misoriented grains. The misorientation and the existence of a grain boundary could affect the initial evolutions of a primary spacing. The remaining discrepancy could be caused by additional uncertainties on exact alloy or processing parameters. The quantized cells in an extended system of the simulations could also affect the spacing selection. For example, in the TFC simulations at V = 2 µm/s, about seven cells in total were present inside the domain. Additionally, because of this quantization effect, Λ between two simulations using a different random number seed was sometimes different from a stationary state.

Table 3.2: Steady state tip undercooling from the TFC (∆_{PF}), and the analytical predictions of the Bower-Brody-Flemings model [22] (∆_{BBF}), and the Karma-Pelcé model [83] (∆_{KP}).

<table>
<thead>
<tr>
<th>V [µm/s]</th>
<th>∆_{PF}</th>
<th>∆_{BBF}</th>
<th>∆_{KP}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.150</td>
<td>0.118</td>
<td>0.138</td>
</tr>
<tr>
<td>2</td>
<td>0.0878</td>
<td>0.0589</td>
<td>0.0804</td>
</tr>
<tr>
<td>4</td>
<td>0.0595</td>
<td>0.0295</td>
<td>0.0516</td>
</tr>
<tr>
<td>8</td>
<td>0.0492</td>
<td>0.0147</td>
<td>0.0372</td>
</tr>
</tbody>
</table>
Tip undercooling at a stationary state

We could predict a tip undercooling of a stationary microstructure using the previous analytical approaches \[22, 83\]. First, Bower, Brody, and Flemings \[22\] proposed

\[ \Delta_{BBF} = \frac{D}{V_{LT}} . \]  \hspace{1cm} (3.11)

Recently, Karma and Pelc´e \[83\] modified the previous approach using a partition coefficient \(k\) and a solid fraction \(f_s\) in a region behind the tip, which was given by

\[ \Delta_{KP} = \frac{f_s k + (1-f_s) \frac{D}{V_{LT}}}{1-f_s(1-k)} . \]  \hspace{1cm} (3.12)

We measured the temperature of the most advanced tip in the FTC simulations, and calculated a corresponding tip undercooling. For the expression of a Saffman-Taylor finger \[133, 109, 32, 162\], the finger width (or a cell width) is close to half of a channel width when surface tension anisotropy is negligible. Thus, we used this ratio to estimate the solid fraction \(f_s = 1/4\) for a 3D structure, which was used for \(\Delta_{KP}\) calculations.

Table 3.2 summarized the calculated \(\Delta_{BBF}, \Delta_{KP}, \) and \(\Delta_{PF}\) from the FTC. The initial approach \(\Delta_{BBF}\) underestimates the \(\Delta_{PF}\), and \(\Delta_{KP}\) improves agreements with the TFC results that are close to the experiments.

3.1.4 Summary

In this section, we discussed the initial transient recoil dynamics of the planar interface and the spacing selection observed in the microgravity experiments. We performed PF simulations with different thermal representations to explore the influence of the thermal field on the microstructure dynamics. The simulation results were compared to the experimental measurements.

We considered three different representations of the thermal field, namely
• FTA: the classical *Frozen Temperature Approximation*,

• TDA: the phenomenological *Thermal Drift Approximation* [116], and

• TFC: a one-dimensional *Thermal Field Calculation* coupled with PF simulations,

to reproduce solidification dynamics observed in the experiments. These representations individually imposed into the quantitative 3D PF simulations as explained in Sec. 2.2.4 for the TDA and Sec. 2.2.5 for the TFC.

In Fig. 3.3, the TDA or TFC simulations significantly improve the agreement with the measured interface dynamics compared to the FTA results. In the FTA, the initial solid-liquid interface moves fast, and reaches a stationary position relatively earlier than in the experiments. In addition, its final stationary position is too close to the liquidus temperature. On the other hand, the interface in either TDA or TFC moves similarly to the measurements from the initial state to the final stationary positions. Moreover, the morphological instability in the TDA and TFC occurs close to the experimental observations.

The solute $c_l$ at the interface on the liquid side builds up while the planar interface moves towards the colder area. In the meantime, the interface velocity $V_i$ also increases. In the TFC under the influence of thermal diffusion and latent heat rejection at the interface, $c_l$ and $V_i$ increase relatively slower than in the FTA (Fig. 3.5a-b), which leads to the later occurrence of the destabilization of the planar interface.

The morphological instability occurs when the interface velocity exceeds the critical velocity $V_c$. In our considered simulations, $V_i$ becomes larger than $V_c^0$ from the constitutional undercooling critical velocity [119, 168] at the early stage of the transient recoil (Fig. 3.5b). In order to improve the prediction of the morphological instability, we modify Eq. (3.4) using the time-dependent solute concentration gap at the interface. With this modified $V_c(t)$, the time $t_0$ when $V_i(t)$ intersects $V_c$ in the TFC simulations is much later than $t_0$ in the FTA simulations. In addition, the modified prediction using the TFC improves an agreement with the onset of the instability observed in the experiments. It is worth noting that an
acceleration of the tips occurs later than the predicted $t_0$ because it takes time to amplify the initial wavelength $\Lambda_0$.

We are also able to predict the initial spacings $\Lambda_0$ measured in the experiments and the simulations. The dispersion relation in Ref. [26] is modified by accounting for the time dependent $V_c(t)$. The modified relation was solved using simulation data (Fig. 3.5a-b) at the critical time $t_c$ (which is later than $t_0$) to calculate the critical initial spacing $\Lambda_c$. The predicted $\Lambda_c$ shows a good agreement with the experimental measurements.

The selected spacings of stationary microstructures are within the stability ranges for both the FTA and the TFC. The stability ranges under both thermal representations are similar to each other; however, the selected stationary spacings in the TFC are higher than in the FTA. After morphological instability, the interface acceleration is slower and the peak velocity is lower with the TFC than in the FTA (Fig. 3.5b). Thus, both effects could lead to higher spacings in the TFC rather than the initially selected spacing. Interestingly, initial spacings in both simulations are similar to one another.

Even though the TFC simulations cannot predict the spacing overshoot and slow decrease towards a final stationary $\Lambda$ observed in the microgravity experiments at $V \geq 2 \mu m/s$, the selected primary spacings in the TFC improve agreements with experimentally measured $\Lambda$.

### 3.2 Grain boundary instability and solitary cell dynamics

#### 3.2.1 Background

In the solidification experiments using the DECLIC-DSI unit aboard the ISS [11, 124, 116, 107, 108, 118], columnar microstructures typically formed several grains with small misorientations with respect to a temperature gradient $G$ [124]. Accordingly, grain boundaries were formed between the misoriented grains. The grain boundary (GB) dynamics
of the 3D microstructure observed in the microgravity experiment was more complex than the dynamics in a thin-sample geometry [154] because misoriented cells can penetrate into the other grain [69, 143]. Especially, the observations from the microgravity experiments revealed that a localized group of cells of a misoriented grain penetrated into a nearby grain. This penetration process leads to the instability of a grain boundary at the convergent GB. Remarkably, during the invasion process, the leader cell of the invasion group can detach itself from its own invasion group. This cell can survive and continue to move as a misoriented solitary cell inside a nearby grain with another crystallography.

We used the 3D PF model to reproduce this novel phenomenon in the 3D microstructure during DECLIC-DSI solidification experiments. In the DECLIC-DSI facility, a succinonitrile (SCN)-0.24% camphor alloy was solidified under various conditions. Here, we focus on one condition, namely a pulling velocity \(V = 1.5 \mu m/s\) and a temperature gradient \(G = 19 K/cm\). The experiments with these conditions show interesting microstructure dynamics at the convergent GB, i.e. the GB instability and the dynamics of a solitary cell. The material parameters for this SCN-0.24% camphor alloy can be found in Appendix B or elsewhere [12, 148, 116, 118, 124].

For the numerical parameters, the 3D PF simulations use the diffuse interface thickness as \(W = 179d_0\) with a discrete grid spacing \(\Delta x = 1.2 W \approx 3.2 \mu m\). Accordingly, the explicit time step is given by \(\Delta t \approx 0.00567 \text{ s}\). We use a large simulation size \(L_x \times L_y \times L_z = 2295 \times 1272 \times 633 \mu m^3\) where \(L_x, L_y,\) and \(L_z\) correspond to the domains of the \(x, y,\) and \(z\) axes, respectively. We used the periodic conditions along the \(z\) boundaries, and symmetric conditions for the other boundaries. For the thermal fluctuations, a noise was imposed onto the \(\psi\) field with its strength \(F_\psi = 0.01\) [12, 148, 124, 57].

We use a steady microstructure of two well-oriented grains as the initial condition for the new simulation, as shown in Fig. 3.9a. For the new simulations, we impose crystal angles. Since our interest here is the convergent GB dynamics, one grain (or both grains) is moved towards the other grain when the simulation starts.
3.2.2 Experimental observation of a three-dimensional array

In a thin-sample array, as illustrated in Fig. 3.8a, the crystal orientation of a grain (i.e. a group of cells which have the same crystallographic orientation) is simply expressed with a polar angle \( \theta \) (black arrow), which is oriented with respect to the temperature gradient \( G \) (purple arrow). For the 3D array, however, we need to introduce another angle \( \phi \) to trace the growth direction of a misoriented grain. We could define this angle using the GB (black dashed line in Fig. 3.8b). The GB is formed between two misoriented grains, and we assume the GB is a straight line. If we consider a normal to the GB (colored dashed lines in Fig. 3.8b), the angle \( \phi \) is oriented with respect to the normal direction. As illustrated in Fig. 3.8b, we define \( \phi_A \) for the left grain \( A \) and \( \phi_B \) for the right grain \( B \). Then, due to the geometrical relation, the angle \( \phi_A = 0^\circ \) is equivalent to \( \phi_B = 180^\circ \). The positive angle \( \phi_A \) (\( \phi_B \)) corresponds to a downward (upward) direction with respect to the normal (colored dashed lines) in Fig. 3.8b (or other figures in this section).

Fig. 3.8c shows the microstructure from the DECLIC-DSI experiment at \( V = 1.5 \, \mu m/s \) and \( G = 19 \, K/cm \). We could find two misoriented grains in the microstructure. The left and right grains grew towards each other, resulting in the formation of the convergent grain boundary (red line) between them. As illustrated in the arrows at the top of Fig. 3.8c, both grains move towards the grain boundary (red line) with an angle \( \phi \). The angles are \( \phi_B = -56^\circ \) for the left grain and \( \phi_A = 84^\circ \) for the right grain.

The polar angle \( \theta \), which is the crystal orientation of a grain with respect to the temperature gradient (Fig. 3.8a), can be calculated using the drift velocity of the grain. The cells in the left grain move with \( V_d \approx 0.09 \, \mu m/s \), and the cells in the right grain move with \( 0.04 \, \mu m/s \). Accordingly, the drift angles using the geometrical relation \( V_d = V \tan \theta_d \), are \( \theta_d = 3.3^\circ \) and \( 1.5^\circ \), respectively. The previous experimental observations discovered that \( \theta_d \) is related to the local spacing in a thin-sample geometry [1, 39]. This relationship is given
Figure 3.8: Schematics of the drift angles. In a 3D array, a grain consists of a group of cells which have the same crystallographic orientation. When two misoriented grains grow towards each other, the grain boundary forms between the two grains. The orientation (or crystal angles) of a misoriented grain can be described with a polar angle $\theta$ (a) and an azimuthal angle $\phi$ (b). The polar angle $\theta$ (a) of the misoriented grain is oriented with respect to the temperature gradient $G$. For the estimation of $\phi$ (b), we assume the GB is a straight line. Then, we can evaluate the grain growth direction with respect to the normal to the grain boundary (black dashed line in b). As illustrated in b, we define the angle $\phi_A$ and $\phi_B$ for both grains. The snapshot of the microstructure in (c) is seen from the top of the sample from the experiment with $V = 1.5 \, \mu m/s$ and $G = 19 \, K/cm$ for a SCN-0.24wt% alloy. The red line represents the grain boundary between the grains. The blue and red arrows at the top are related to the growth directions of the left ($\phi_B = -56^\circ$) and right ($\phi_A = 84^\circ$) grains, respectively.

by

$$\frac{\theta_d}{\theta} = 1 - \frac{1}{1 + f\lambda^g} \quad .$$

(3.13)

It describes the drift dynamics of a misoriented cell/dendrite better than using $\text{Pe} = \lambda/l_D$, which is the ratio of the spacing to the diffusion length $l_D = V/D$ [139]. In a 3D array, the misoriented cells/dendrites follow this relation as well (the details are discussed later in this section). Hence, we could estimate the crystal angle of the grains at the average spacing $\Lambda \approx 260 \, \mu m$, which yields $\theta \approx 6.2^\circ$ and $2.8^\circ$ respectively for the left and right grain in Fig. 3.8:
3.2.3 Grain boundary morphologies in PF simulations

The microstructure in Fig. 3.8c shows that the convergent grain boundary (red line) is not straight. In a thin-sample geometry, the convergent GB typically remains at an initial position as mentioned in Refs. [150, 154, 153]. However, the convergent GB in the 3D array fluctuates as a group of misoriented cells penetrates into the nearby grain. Thus, as illustrated in Fig. 3.8c, the GB is twisted rather than being uniform.

In order to investigate the dynamics of a convergent GB with the 3D PF simulations, we initially obtained a 3D bi-crystallography microstructure as shown in Fig. 3.9a. In this stationary microstructure, both the red (A) and blue (B) grains are well-oriented. We used this microstructure as the initial condition, and introduced a crystal angle $\theta_A$ at $\phi_A = 0^\circ$ for the red grain. Then, in the new simulation, the red cells start to drift towards the other blue grain. In contrast, the blue grain remains well-oriented with $\theta_B = 0^\circ$. We considered four different angles, namely $\theta_A = 5^\circ, 10^\circ, 15^\circ$, and $20^\circ$ for $\phi_A = 0^\circ$. Then, within 3 h, the convergent GB between the grains evolved as cells in the misoriented grain drift.

Figs. 3.9b-e show the microstructures 3 h after the red grain starts to drift towards the

![Microstructures for different angles](image_url)

Figure 3.9: Dynamics of the convergent grain boundary under the influence of $\theta$. From the initial microstructure in (a), the convergent GB varies after 3 h under the influence of $\theta_A = 5^\circ$ (b), $10^\circ$ (c), $15^\circ$ (d), and $20^\circ$ (e) at $\phi_A = 0^\circ$. The other blue grain is always well oriented with $\theta_B = \phi_B = 0^\circ$. 

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blue grain from the initial microstructure shown in Fig. 3.9a. For $\theta_B = 5^\circ$ (Fig. 3.9b), the misoriented red cells push the well-oriented blue cells, and the convergent GB slowly move towards the blue grain. For $\theta_B = 10^\circ$, the red cells penetrate into the blue grain. Thus, the convergent GB in Fig. 3.9c is not uniform as in the initial structure, but it is twisted as in the experimental observation (Fig. 3.8c). The convergent GB remains in a stationary position at $\theta_B = 15^\circ$ (Fig. 3.9d). Interestingly, the red cells with $\theta_B = 20^\circ$ are eliminated when they try to move towards the blue grain. During the elimination process, the blue cells near the convergent GB drift towards the red grain. As a result, the GB moves towards the red grain as shown in Fig. 3.9e. We expect that the convergent GB between a well-oriented grain and a misoriented grain with $\theta_B > 20^\circ$ moves towards the misoriented grain.

The misoriented grains are not always directly oriented towards the convergent GB. In the experimental observations, the grain growth direction makes an angle with the convergent GB as illustrated in Fig. 3.8. The two grains in Fig. 3.8 are oriented with $(\theta_A, \phi_A) \approx (2.8^\circ, 84^\circ)$ for the right grain (red arrow) and $(\theta_B, \phi_B) \approx (6.2^\circ, -56^\circ)$ for the left grain (blue arrow). To study this, we perform a simulation with crystal angles similar to that in the experiment (Fig. 3.8c).

For the simulation with two misoriented grains in a 3D array, we use the initial mi-

![Figure 3.10: Dynamics of the convergent grain boundary under the influence of $\theta$ and $\phi$. We imposed crystal angles $(\theta_B, \phi_B) = (6.2^\circ, 56^\circ)$ for the blue grain and $(\theta_A, \phi_A) = (2.8^\circ, -84^\circ)$ for the red grain. This configuration is equivalent to the experimental observation (Fig. 3.8c). The convergent GB evolves as time elapses (left to right). We observed that a solitary cell (yellow circle in b) was created during the simulation. This solitary cell was eliminated when it reached the right boundary; therefore we cannot find it in (c). The domain sizes in the figure are 1272 $\mu$m laterally and 633 $\mu$m vertically.](image-url)
crostructure shown in Fig. [3.10a]. In this microstructure, the convergent GB is located approximately at the center of the lateral simulation domain. We impose crystal angles \((\theta_A, \phi_A) = (2.8^\circ, -84^\circ)\) for the red grain and \((\theta_B, \phi_B) = (6.2^\circ, 56^\circ)\) for the blue grain. Thus, even though the cells in the simulation move upward in the figure, their \((\theta, \phi)\) are equivalent to the experimental observations, because of the symmetry.

When the simulation starts, both the grains grow towards each other. The cells in the blue grain drift faster than in the red grain, because \(\theta_A > \theta_B\). Consequently, the convergent GB moves towards the red grain as time elapses (left to right in Fig. 3.10). During the evolution of the GB, the boundary morphology becomes a twisted shape as in the experiment.

We carry out additional simulations to investigate the details of convergent GB mor-

![Figure 3.11](image_url)

**Figure 3.11:** Grain boundary morphologies after 3 h in simulations when \(\phi_A > 0^\circ\) and \(0^\circ \leq \phi_B \leq 75^\circ\). The crystalline orientation of the red grain is rotated from the left direction \(\phi_A = 0^\circ\) to the downward direction of the figure as \(\phi_A\) increases. The crystal angle \(\phi_B\) of the blue grain is rotated from the right \((\phi_B = 0^\circ)\) to the upward direction of the figure. The angle \(\theta \approx 5^\circ\) is fixed for both the left blue and the right red grains. The white dashed lines represent the initial GB location.
Figure 3.12: Grain boundary morphologies after 3 h in simulations when $\phi_A < 0^\circ$ and $15^\circ \leq \phi_B \leq 75^\circ$. When $\phi_B = 0^\circ$, the crystal orientation of the blue grain is pointing the right direction of the figure. As $\phi_B$ increases, the crystal orientation is rotated from the right toward the upward direction of the figure. The crystalline orientation of the red grain is rotated from the left direction $\phi_A = 0^\circ$ to the upward direction of the figure as $\phi_A$ decreases. The other crystal angle is fixed as $\theta \approx 5^\circ$ for the both grains. The white dashed lines show the initial GB location.

For the blue grain, we use $0^\circ \leq \phi_B \leq 75^\circ$. Hence, the grain at $\phi_B > 0^\circ$ moves relatively upward in the figure. When $\phi_B = 0^\circ$, the grain moves right. We considered various $\phi_A$ ranges, i.e. $-90^\circ \leq \phi_A \leq 90^\circ$, for the red grain. If the grain has $\phi_A = 0^\circ$, it moves towards the left. The grain with a positive or negative $\phi_B$ moves upward ($\phi_B > 0^\circ$, Fig. 3.11) or downward ($\phi_B > 0^\circ$, Fig. 3.11), respectively. Thus, depending on the angle configurations, the GB is initially located at the center of the domain.
Figure 3.13: The maps for penetrations of a grain and solitary cell observed in the PF simulations (Fig. 3.11 and Fig. 3.12). Blue and red triangles designate the penetration of blue and red grain, respectively. When both the grains have a higher $\phi$, the grain boundary between them remains a monotonous shape (black squares). Blue (red) circles represent the observations of a solitary cell of a blue (red) grain in the simulations, which are related to yellow circles in Fig. 3.11 and Fig. 3.12. In the DECLIC-DSI microgravity experiments, the solitary cell is also observed (black circles) when $V = 1.5$ and $2 \mu m/s$ for $G = 19 K/cm$.

of $(\phi_A, \phi_B)$, the GB morphology evolves as illustrated in Fig. 3.11 and 3.12.

We first focus on one $\phi_B = 0^\circ$ at different $\phi_A$ (left column in Fig. 3.11), the blue grain with a low $\phi$ angle always penetrates into the red grain. However, the penetration of the red grain is related to its angle $\phi_A$. Red cells with higher $\phi_A \geq 75^\circ$ do not move inside the blue grain; however, the cells with the lower angle can penetrate into the blue grain.

When $|\phi_B| \geq 75^\circ$ for the blue grain (right column in Fig. 3.11 and 3.12) and $|\phi_A| \geq 75^\circ$
for the red grain (bottom two rows in Fig. 3.11 and 3.12), the grain with a higher $|\phi|$ does not penetrate into the other grain in most cases. Thus, the convergent GB remains near the initial location with a linear shape when two grains have higher $|\phi|$ (bottom right in Fig. 3.11 and 3.12). Otherwise, we observe the penetration process of a grain frequently.

We summarize the penetration process in Fig. 3.13. If more than one cell penetrated into the other grain in Figs. 3.11 and 3.12 we consider that penetration has occurred. Blue and red triangles in the figure correspond to the penetration of the left blue and right red grain, respectively. The penetration processes are frequently observed except for the higher $|\phi|$. In most simulations, the grain with a higher $|\phi| \geq 75^\circ$ does not move inside the other grain. Hence, when both grains have higher $|\phi|$, the GB remains a linear shape.

### 3.2.4 Observation of a solitary cell

One interesting observation in Figs. 3.10, 3.11, and 3.12 is the existence of a solitary cell (yellow circles). As illustrated in Fig. 3.10, the blue solitary cell continuously moves inside the other red grain until it is eliminated at the right boundary of the simulation. We could observe frequently the isolated solitary cell in Fig. 3.11 and 3.12. This novel phenomenon is also observed in the microgravity experiment, as illustrated in Fig. 3.14.

In the microgravity experiment at $V = 1.5 \mu$m/s and $G = 19$ K/cm, an invasion group of cells penetrates into the other grain at the convergent boundary. The leader cell of the invasion group is typically eliminated by the other grain. However, the leader cell can detach itself from its invasion group (second image of Fig. 3.14), and then this cell will be surrounded by cells in the other grain, which has another crystal orientation. The experimental observation reveals that this cell can survive and move inside the other grain for a long time, as shown in Fig. 3.14.

The simulations show the solitary cell could form frequently in an extended array system (yellow circles in Fig. 3.11 and 3.12). When we observe the solitary cell during the simulations, we draw circle dots in Fig. 3.13. Colors correspond to the red and blue solitary cell.
In this figure, we could find the formation of a solitary cell in many configurations. The only limit we found here is $\phi_A + \phi_B = 90^\circ$ (gray dashed line). In the simulations, the solitary cell was not created at $\phi_A + \phi_B > 90^\circ$. Moreover, all the observations of the solitary cell including the microgravity experiments (black circles) are within $\phi_A + \phi_B < 90^\circ$ in Fig. 3.13. Therefore, we expect that the solitary cell could be created only when $\phi_A + \phi_B < 90^\circ$.

Then, how does a solitary cell move inside the other grain once it is created? In order to investigate the dynamics of a solitary cell in a disordered array with the PF model, we prepared two initial microstructures as shown in the first column figures in Fig. 3.15. The microstructure at $t = 0$ h in Fig. 3.15c is different from the other cases. For the simulations, we used periodic boundary conditions along the lateral $y$ axis and the vertical $z$ axis, and the other numerical parameters were the same as those used in the previous simulations, including the simulation size (1272 $\mu$m laterally and 633 $\mu$m vertically), as shown in Fig. 3.15.

We first considered the experimental configuration. In Fig. 3.15a, the red solitary cell has $(\theta_A, \phi_A) = (6.2^\circ, 236^\circ)$ (equivalent to the blue grain in Fig. 3.10), and the surrounding blue cells grow with $(\theta_B, \phi_B) = (2.8^\circ, 96^\circ)$ (equivalent to the red grain in Fig. 3.10). Thus, both red and blue cells in Fig. 3.15a move upward as considered previously in Fig. 3.10. This simulation shows that the solitary cell moves continuously with the other blue cells as time elapses (left to right).

In Fig. 3.15b, the solitary cell with $(\theta_A, \phi_A) = (5^\circ, 0^\circ)$ is isolated inside the well-oriented blue grain. The initial location of the solitary cell is the same as in Fig. 3.15a. For this angle,
(a) a solitary cell with $(\theta_A, \phi_A) = (6.2^\circ, 236^\circ)$
\[ t = 0 \text{ h} \quad t = 3.0 \text{ h} \quad t = 6.0 \text{ h} \]

(b) a solitary cell with $\theta_A = 5^\circ$
\[ t = 0 \text{ h} \quad t = 3.0 \text{ h} \quad t = 6.0 \text{ h} \]

(c) a solitary cell with $\theta_A = 5^\circ$
\[ t = 0 \text{ h} \quad t = 2.0 \text{ h} \quad t = 3.0 \text{ h} \]

(d) a solitary cell with $\theta_A = 10^\circ$
\[ t = 0 \text{ h} \quad t = 1.3 \text{ h} \quad t = 3.0 \text{ h} \]

Figure 3.15: Dynamics of a solitary cell. We considered four different solitary cell with $(\theta_A, \phi_A) = (6.2^\circ, 236^\circ)$ (a), $(5^\circ, 0^\circ)$ (b) - (c), and $(10^\circ, 0^\circ)$. This red solitary cell was isolated inside the blue grains with $(\theta_B, \phi_B) = (2.8^\circ, 96^\circ)$ (a), and $(0^\circ, 0^\circ)$ (b) - (d).

The solitary cell also survives, at least, until 6 h. In addition, we expect that the solitary cell in Fig. 3.15a-b would survive longer than 6 h.

The solitary cell, however, does not survive all the time. When we used a different location for the solitary cell surrounded by $\theta_B = 0^\circ$ grain (Fig. 3.15c), the solitary cell with $(\theta_A, \phi_A) = (5^\circ, 0^\circ)$ was eliminated soon. For a higher $\theta_A = 10^\circ$ at $\phi_A = 0^\circ$ (Fig. 3.15d), the solitary cell was also eliminated after it moved a short distance.

The observations from the experiment and simulations revealed that a solitary cell can
Figure 3.16: Dynamics of a misoriented cell. We considered hexagonal (a) and FCC (b) arrays including a thin-sample geometry (c). Using the drift velocity \( V_d = V \tan \theta \) of a cell, we calculated the drift angle \( \theta_d \). For the hexagonal array (d), we considered three different angles \( \theta = 5^\circ \) (red square), \( 10^\circ \) (green square), and \( 15^\circ \) (blue square). We fit Eq. (3.13) to the hexagonal array (black line in d-e), which yielded \( f = 0.00032 \) and \( g = 1.47 \). The fit line agrees with the results for the hexagonal array, FCC array (purple circle), and thin-sample geometry (brown diamond). For the solitary cells from the simulation in Fig. 3.15a (gray cross) and the experiment in Fig. 3.14 (black plus), we used the average spacing of a disordered array. Their drift angle \( \theta_d \) was typically smaller than those for the other regular arrays.

survive inside a grain with different crystal angles. This solitary cell can survive for a long time under specific growth conditions that may be linked to the crystal angle and/or the number of cells surrounding the solitary cell. In addition, the primary spacing or a polar angle \( \theta \) can also affect the continuous growth of a solitary cell.

### 3.2.5 Dynamics of a misoriented cell

The dynamics of a misoriented cell in a thin-sample geometry is related to \( \text{Pe} = \lambda / l_D \) \[1\] \[39\]. Recent numerical simulations have confirmed this relationship \( \theta_d(\text{Pe}) \) \[97\] \[57\] \[150\]. The description \( \theta_d(\lambda) \) in Eq. (3.13) can also describe the misoriented cell dynamics without the modification of \( \lambda \) using the diffusion length \( l_D \). This equation using \( \lambda \) improves the agreement with the experimental results than that of using \( \text{Pe} \) \[139\].

In order to investigate the dynamics of misoriented cells in a 3D array, we considered a
hexagonal (Fig. 3.16a) and a face-centered-cubic (FCC) (Fig. 3.16b) array as well as a thin-sample geometry (Fig. 3.16c). For the estimation of $\theta(\lambda)$, we first produced well-oriented array structures, as shown in Fig. 3.16a-c. We used stationary microstructures, as shown in Fig. 3.16a-c, as the initial condition, and performed new simulations with a crystal angle $\theta$ at $\phi = 0^\circ$. For the boundaries, the simulations used periodic conditions for the $y$ axis, so that the cells could move continuously during the simulation ($t = 2$ h). For the hexagonal and FCC array structures, the $z$ boundaries have a periodic condition. The thin-sample geometry had a thickness $H \approx 200 \mu$m, and the symmetric and wetting conditions with a slope $r_w = 1$ were accounted for by the $z$ boundaries. The symmetric $x$ boundaries were imposed for all simulations.

The SCN-0.24wt% camphor alloy typically forms cellular structures at $V = 1.5 \mu$m/s and $G = 19$ K/cm. Hence, we initially considered a hexagonal array. As shown in Fig. 3.16, we considered three different angles, i.e. $\theta = 5^\circ$ (red square), $10^\circ$ (green square), and $15^\circ$ (blue square) at $\phi = 0^\circ$. The cells moved laterally towards the right of Fig. 3.16a-c during the simulation. We estimated the movements of the cells to calculate the drift angle $\theta_d$ using the geometrical relation $V_d = V \tan \theta_d$. As shown in Fig. 3.16d, the scaled drift angles $\theta_d/\theta$ as a function of $\lambda$ at different $\theta$ exhibits similar relations. Hence, we used the results at $\theta = 10^\circ$ to estimate the two constants $f$ and $g$ in Eq. (3.13). The fitting line with $f = 0.00032$ and $g = 1.47$ (black line in Fig. 3.16d-e) agrees with the dynamics of the misoriented cells in the hexagonal arrays.

We also considered FCC arrays and a thin-sample geometry with thickness $H \approx 200 \mu$m. For these array structures, we only considered one $\theta = 10^\circ$. As shown in Fig. 3.16e, the dynamics of the misoriented cells in a thin-sample geometry (purple circle) and an FCC array (brown diamond) agree with the results of the hexagonal array. This result indicates that the empirical law in Eq. (3.13) can describe the dynamics of a misoriented cell even if the array structure is different. Thus, using two fitting parameters $f = 0.00032$ and $g = 1.47$, Eq. (3.13) can be used to estimate the dynamics of the misoriented microstructure shown
Then, using the average spacing $\Lambda = 260 \, \mu m$ of the microstructure, we calculated $\theta \approx 6.2^\circ$ for the left grain, and $2.8^\circ$ for the right grain.

Another factor that needs to be considered here is the solitary cell dynamics. In the experimental observation, the solitary cell initially moves slowly right after it detached itself from its invasion group. As it moves inside the other grain, its velocity increases. For the plot, we used the average $\theta_d$ (black plus) at the $\Lambda = 260 \, \mu m$. The measured drift angle is always smaller than $\theta_d$ for regular array structures.

Fig. 3.16e also shows the values of $\theta_d$ for the solitary cells from Fig. 3.15a (gray cross). We used the average spacing $\Lambda \approx 186 \, \mu m$ for the simulation result. The result agrees well with the average $\theta_d$ in the experiment.

### 3.2.6 Summary

During the solidification of a SCN-0.24wt%camphor alloy with $V = 1.5 \, \mu m/s$ and $G = 19 \, K/cm$ in the DECLIC-DSI facility aboard the ISS, we observed interesting dynamics of misoriented grains near the convergent grain boundary. Experimental observations revealed that a group of misoriented cells near the convergent GB was able to penetrate into the nearby grain. Therefore, the GB between misoriented grains moves actively in contrast to the orientation of a convergent GB within $5^\circ$ in a thin-sample geometry [154].

In order to reproduce the convergent GB dynamics in a 3D array, we used 3D PF simulations. We first considered the influence of $\theta$, which is oriented with respect to the temperature gradient. Simulations showed that the GB was stable when the misoriented grain at $\theta = 15^\circ$ moved towards the well-oriented grain. If $\theta < 15^\circ$, the cells in a misoriented grain can penetrate into the other grain, which leads to an active movement of the GB as in the experimental observation. On the other hand, for $\theta > 15^\circ$, the convergent GB moves towards the misoriented grain due to cell eliminations. In addition, we also studied the influence of $\phi$, which is the angle of a grain with respect to the normal of the GB, for $\theta \approx 5^\circ$. The simulation results show that penetration occurs frequently. The GB remains stable only when both the
grains are $\theta \geq 75^\circ$.

One remarkable observation is the existence of a solitary cell in both the experiment and simulation. During the penetration process, the leader cell of an invasion group can detach itself from the group and remain inside the other grain with a different crystallography. Interestingly, this cell can survive and move continuously as a misoriented solitary cell inside the other grain. The PF simulations show that the number of cells around the solitary cell and the misoriented angle $\theta$ can have an influence on the survival of the cell.

Finally, we explored the dynamics of misoriented primary cells/dendrites in a 3D array. In the three array structures that were considered, namely hexagonal array, FCC array, and thin-sample geometry, the drift dynamics of a misoriented cell is related to its spacing as in the experimental [1, 39] and numerical [150, 97, 57] observations. For a solitary cell, its drift angle $\theta_d$ is typically lower than that for a regular array.

It is worth noting that the PF simulations for the GB dynamics were performed only once for each configuration; therefore, these results provide one realization of the dynamics. Especially, the GB dynamics in a 3D array could be affected by the array structure or the angle configurations, including the $\theta$ angle.
Chapter 4

Phase-field modeling of cellular and dendritic array patterns in thin-sample directional solidification experiments

4.1 Influence of crystal orientation

The following section contains material currently being prepared for publication. The results in this chapter reflect my contribution to this work, and all experimental measurements referenced in this chapter are performed by my collaborators, and appropriate credit is given. This work will be published with the following co-authors: Younggil Song\(^1\), Silvère Akamatsu\(^2\), Sabine Bottin-Rousseau\(^2\), Gabriel Faivre\(^2\), Alain Karma\(^1\)

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4.1.1 Background

Strong gravity on earth hinders formation of homogeneous three-dimensional (3D) microstructures. The force of gravity causes solutal and thermal convective currents in front of the solidification front, which yields inhomogeneous microstructures [112, 77]. Therefore, solidification experiments on earth use a thin-sample geometry to reduce convective currents [61, 137, 160, 66, 52, 56].

During directional solidification processes, cells and dendrites in columnar microstructures of binary alloys select a stable spacing [137, 160, 138, 161]. For primary spacing selection mechanisms, previous studies [157, 66, 91, 72] have suggested three important parameters, namely a freezing range $\Delta T_0$ of a nominal alloy composition $c_0$, a pulling velocity $V$, and a temperature gradient $G$.

If columnar microstructures are well aligned with a given temperature gradient, the variation of a selected primary spacing is very small. However, columnar grains are usually misoriented with respect to the temperature gradient $G$ as illustrated in Fig. 4.1. At the divergent grain boundary (right edge in the figure), a new created primary branch due to sidebranching has a spacing larger than the initially selected one [66, 52, 61, 53, 49, 48].

Fig. 4.1 shows a single grain seen from the side of a thin sample in the experiment (a) and

![Figure 4.1](image-url)

Figure 4.1: Schematic microstructures in a thin-sample geometry in an experiment (a) and in a simulation (b). The single grain inside the sample is misoriented with respect to the temperature gradient (parallel to the x axis). The misorientation of the grain leads to the lateral movements of primary branches from the divergent grain boundary (source) to the convergent grain boundary (sink). The crystal angle $\alpha_0$ is usually larger than the drift angle $\alpha$, which is related to a primary spacing $\lambda$ [1, 39].
in the simulation (b). This grain is misoriented with respect to the temperature gradient $G$ (parallel to the $x$ axis), and this misorientation leads to the lateral movements of primary branches from the divergent grain boundary (right edge in the figure) to the convergent grain boundary (left edge in the figure).

When the primary branches drift, its drift angle $\alpha$ (see Fig. 4.1b) calculated by the geometrical relation $V_d = V \tan \alpha$ is usually smaller than its crystal angle $\alpha_0$ [1, 39]. In the previous experiments [1, 39] and simulations [150, 97, 57], the drift angle is related to a primary spacing $\lambda$ or Péclet number $Pe = \lambda/l_D$, which is the ratio of the spacing to the diffusion length $l_D = V/D$.

It is worth noting that the $\alpha_0$ and $\alpha$ are related to $\theta$ and $\theta_d$, respectively, in the previous section. In a 3D array, we need to calculate a polar angle of a crystalline axis $\theta$ using the combination between $\alpha_0$ and $\gamma_0$ inside the PF model (Sec. 2.2.6). However, we set $\gamma_0 = 0^\circ$ in a thin-sample geometry, and the angle $\alpha_0$ represent the angle only in the $x$-$y$ plane as illustrated in Fig. 4.1. In addition, the positive (negative) $\alpha_0$ represent the rotation from the positive $x$ axis to the positive (negative) $y$ axis. Therefore, we use $\alpha_0$ rather than $\theta$ for simulations using a thin-sample geometry.

As primary branches move, grain boundaries (GB) are systematically formed at the edges of the grain. In Fig. 4.1a-b, the divergent GB was formed on the right edge. Primary branches move away from this GB, so the distance between them becomes larger. When the distance is large enough, a sidebranch becomes a new primary branch with its primary spacing larger than the initially selected spacing after morphological instability [66, 52, 61, 53, 49, 48]. Thus, this GB behaves like a source of primary branches. On the other hand, as the primary branches approach the other convergent GB (left edge in Fig. 4.1a-b), their primary spacings become smaller, and they are finally eliminated. Hence, this boundary acts as a sink of the primary branches.

In this section, we investigate the global evolution of the primary spacing between the convergent and the divergent grain boundaries. We perform simulations and experiments
with a misoriented grain in a thin sample. We observe that primary branches are continuously
created at the source (i.e. divergent GB) by sidebranching \[66, 52, 61, 53, 49, 48\] and
eliminated at the sink (i.e. convergent GB). Thus, we initially determine the relation between
the primary spacing and its drift velocity as in Ref. [1, 39]. Then, using the drift velocity,
we suggest a geometrical model to predict the evolution of the primary spacing between
the boundaries. We additionally propose a velocity for spacing propagation estimated from
the conservation of spacing density in a finite region. The predictions using the suggested
models are compared to the PF simulations.

4.1.2 The growth of misoriented primary branches

We used a succinonitrile (SCN)-0.24wt% camphor alloy to investigate the misoriented
grain growth under the influence of \(V\) and \(\alpha_0\) in a thin-sample geometry. We can find the
alloy parameters in Refs. [12, 145, 102, 155, 148] or in Appendix B. For the simulations, we
set a temperature gradient \(G = 12\ \text{K/cm}\) and varied \(\alpha_0 = -5^\circ, -10^\circ, -15^\circ,\) and \(-20^\circ\) for
\(V = 4\ \mu\text{m/s}\). In order to explore the \(V\) influence, we performed simulations with \(V [\mu\text{m/s}] = 4, 12,\) and \(20\) at \(\alpha_0 = -15^\circ\). Here, the positive crystal angle \(\alpha_0\) corresponds to a clockwise
direction with respect to the \(x\) axis (or \(G\) axis). In the simulations, the angle is \(\alpha_0 < 0\) that
leads to the drift of a primary branch from right to left along the \(y\) axis.

As \(V\) increases, the primary tip radius becomes smaller [94, 95, 6, 9]. Hence, in order
to quantitatively reproduce the primary branch dynamics, we need to use smaller interface
thickness \(W\) at a higher \(V\). We used three different \(V [\mu\text{m/s}] = 4, 12,\) and \(20\), which yields
\(W \approx 47.56, 28.26,\) and \(17.23\ \text{d}_0\), where \(d_0\) is the capillary length. The ratio between \(W\) and
a grid spacing \(\Delta x\) is fixed as \(W/\Delta x = 1.2\), so the grid spacing \(\Delta x\) and the explicit time step
\(\Delta t\) decreases accordingly as \(V\) increases, namely \((\Delta x [\mu\text{m}], \Delta t [\text{s}]) \approx (3.00, 5.00 \times 10^{-3}),\)
\((1.78, 1.75 \times 10^{-3}),\) and \((1.09, 6.55 \times 10^{-4}).\)

We also used different extended domains \(L_x \times L_y \times L_z\), where \(L_x, L_y,\) and \(L_z\) are the
domain length respectively for \(x, y,\) and \(z\) directions. The domain size depends on \(V,\) which
are $L_x \times L_y \times L_z \approx 1290 \times 2490 \times 114 \, \mu m^3$ for $V = 4 \, \mu m/s$, $709 \times 2563 \times 82 \, \mu m^3$ for $V = 12 \, \mu m/s$, and $485 \times 1998 \times 50 \, \mu m^3$ for $V = 20 \, \mu m/s$. Within these extended systems, we could observe a single array structure including more than ten primary branches at a stationary state. We considered a thin-sample geometry, so $z$ boundaries have symmetric and wetting conditions with a slope $r_w = 1$ in Eq. (2.33) [57, 154, 31]. For the other boundaries, we used symmetric conditions. In addition, we imposed a random noise onto the $\psi$ field with strength $F_\psi = 0.01$, which showed quantitative comparison with experiments with a SCN alloy [57, 150, 12, 148].

The simulations with an extended system start with a planar interface with small random perturbations, and the solute builds up on the liquid side of the solid-liquid interface as the sample is pulled. The interface is destabilized when the solute builds up large enough [146, 119, 168]. After the morphological instability, small primary branches arise from the solid-liquid interface. These branches solutally interact with one another, and some cells and dendrites are eliminated during the interactions. Since the eliminations could affect the misoriented grain growth dynamics, we used microstructures from $t_0$ after the elimination during the initial transient growth regime. Microstructures in simulations grow until $t_{\text{max}} = 20000 \, s$ for $V = 4 \, \mu m/s$, and 2000 s for the other velocities.

Primary branches are well-aligned with a single row approximately after $t = t_0$ for a time when the initial coarsening is stopped. In this time range, primary tips locate at the middle of the sample thickness $z = H/2$. This time $t_0$ is related to $V$ and $\alpha_0$ in simulations, so we use different $t_0$ for the analysis. When $V = 4 \, \mu m/s$, $t_0 \approx 4043 \, s$ for $\alpha_0 = -5^\circ$, and 2043 s for the other $\alpha_0$. In addition, at $\alpha_0 = -15^\circ$, $t_0 \approx 896 \, s$ for $V = 12 \, \mu m/s$, and 218 s for $V = 20 \, \mu m/s$.

Fig. 4.2 shows the solid-liquid interfaces at $z = H/2$ (black lines) for $V = 4 \, \mu m/s$ and $\alpha_0 = -15^\circ$. In the figure, the array structure grows from the bottom to the top in each column, and the column length corresponds to the interface growth $V t$ of 12 mm. In addition, the interfaces on the left column occur earlier than the right ones. Thus, the
Figure 4.2: Solid-liquid interfaces of the cross section at the middle of the sample when \( \alpha_0 = -15^\circ \). This figure shows the interfaces approximately every 63 s from \( t_0 = 2043 \) s (bottom left) to the end of the simulation \( t_{\text{max}} = 20000 \) s (top right). The interface grows from bottom to top, and interfaces on a left column happened earlier than the right ones. We used these interfaces to measure the primary tip positions.

structure grows from bottom to top and from left to right. As illustrated in the figure, the elimination within an array was not observed from \( t_0 = 2043 \) s (bottom first interface of the left most column) to the end of the simulation \( t_{\text{max}} = 20000 \) s (top first interface of the right most column). In addition, we could observe that the primary branches move from right boundary to the left boundary because of a negative crystal angle \( \alpha_0 < 0^\circ \).

Using the interfaces (Fig. 4.2), we estimated primary tip positions and corresponding spacings. The primary tips during the lateral movements locate at \( x > 0.95 \ L_{\text{sol}} \), where \( L_{\text{sol}} \) is the solid length in the simulation. The tips at \( x \leq 0.95 \ L_{\text{sol}} \) were eliminated near the sink, so we ignored them for the estimation. We used different solid lengths related to \( V \),

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\( L_{sol} = 500 \, \mu m \) for \( V = 4 \, \mu m/s \), \( 400 \, \mu m \) for \( V = 12 \, \mu m/s \), and \( 240 \, \mu m \) for \( V = 20 \, \mu m/s \). Accordingly, the time steps for the \( z = H/2 \) interface outputs were also adjusted to 63 s, 8 s, and 3 s respectively for \( V [\mu m/s] = 4, 12, \) and 20. Then, we used C/C++ program to measure all primary tip positions within the time range of \( t_0 \leq t \leq t_{max} \). Using the positions, we calculated a spacing \( \lambda \) between one primary tip and the previous one and a drift velocity \( V_d \) of a primary branch.

### 4.1.3 Results and discussion

The large spacing selected at the source propagates slowly towards the inter-grain region, and the primary spacing at the sink becomes smaller due to the elimination processes. Accordingly, the global spacing profile between the boundaries evolves slowly. In most simulations, the spacing profiles reach a stationary state at the end of the simulation. Before looking directly into the evolutions of a primary spacing profile, we study the dynamics of a single primary branch. Then, in order to investigate the propagative dynamics of a primary spacing profile, we propose an analytical model. The model prediction is compared to the simulation results for different \( \alpha_0 \) and \( V \).

#### Dynamics of a single primary branch

The experimental observations reveal that a drift angle \( \alpha \) of one misoriented primary branch from the drift velocity \( V_d = V \tan \alpha \) is related to its spacing \( \lambda \) or Péclet number \( Pe = \lambda V/D \) [1, 39], which yields

\[
\frac{\alpha}{\alpha_0} = 1 - \frac{1}{1 + f \lambda^g},
\]

(4.1)

where \( f \) and \( g \) are constants. In the recent experimental observations, the above relation shows better agreement with the \( \alpha(\lambda) \) than that of using \( Pe \) [139]. In the PF simulations with a 2D or a confined 3D array, this relation is also observed [97, 57, 150]. Even though this
Figure 4.3: The drift angle $\alpha$ as a function of $\lambda$. We considered four different $\alpha_0 = -5^\circ$ (a), $-10^\circ$ (b), $-15^\circ$ (c), and $-20^\circ$ (d) for $V = 4 \, \mu m/s$. We also performed simulations with different $V = 12 \, \mu m/s$ (e) and $20 \, \mu m/s$ (f) for $\alpha_0 = -15^\circ$. The drift angles $\alpha$ (red square dots) from simulations with a single cell in a perfect array are usually lower than $\alpha_0$ (green dashed lines). These results agree with the primary branches in an extended disordered array (blue circle dots).

relation $\alpha(\lambda)$ in Eq. (4.1) describes the local dynamics of a misoriented cells or dendrites, we use the simulations with one single cell/dendrite in a perfect ordered array for the following analysis. We find that the simulation results show better agreement with the primary branch dynamics in an extended array.

We consider a perfect array with $\lambda$ to reproduce dynamics of a misoriented primary branch. For a thin-sample geometry, we use symmetric and wetting boundary conditions at the $z$ boundaries. The domain size along the $z$ axis is related to a sample thickness, i.e. $L_z = H$. The $y$ domain has periodic boundaries with its size $L_y = \lambda$ to consider a perfect array. In addition, the $x$ boundaries are symmetric. Then, we initially find one single primary cell for $\alpha_0 = 0^\circ$ at a spacing $\lambda$ equal to its thickness $H$, i.e. $\lambda = H = 114 \, \mu m$ for $V = 4 \, \mu m/s$,
82 \mu m for V = 12 \mu m/s, and 50 \mu m for V = 20 \mu m/s. For the next simulation which has
one more or less grid spacing \Delta x than the previous simulation along the y axis, we bilinearly
interpolate the initial stationary \psi and U fields. The interpolated fields were used as the
initial fields for the next simulation, and the new simulation is performed till it reaches a
steady state. Similarly, we restart simulations continuously by adding or subtracting \Delta x
along the y axis from the previous one within a spacing range of \lambda_{\text{min}} < \lambda < \lambda_{\text{max}}. The
higher spacing limit \lambda_{\text{max}} is related to sidebranching dynamics. One sidebranch of a primary
branch at \lambda > \lambda_{\text{max}} is able to become a new primary branch [43]. On the other hand, the
primary branch at \lambda < \lambda_{\text{min}} shows a flat interface along the y domain. In simulations within
the stable spacing region \lambda_{\text{min}} < \lambda < \lambda_{\text{max}}, we trace tip positions at a stationary state to
calculate its drift velocity \mathbf{V}_d and drift angle \alpha = \arctan(\mathbf{V}_d/V).

We consider different \alpha_0 and V to estimate the relation \alpha(\lambda) for a misoriented primary
branch. Fig. 4.3 shows the simulation results with a single cell (red dots) in a perfect array
at different \alpha_0 = -5^\circ (a), -10^\circ (b), -15^\circ (c) and -20^\circ (d) for V = 4 \mu m/s. We also consider
different V = 12 \mu m/s (e) and 20 \mu m/s (f) for \alpha_0 = -15^\circ. In each plot, the left-most red
dots are related to \lambda_{\text{min}} = 22.5, 16.9, and 10.3 \mu m for V = 4, 12, and 20 \mu m/s, respectively.
This lower limit \lambda_{\text{min}} decreases as V increases. The right-most red dots link to the higher
limit \lambda_{\text{max}}. This limit decreases as V increases, i.e. \lambda_{\text{max}} = 322.5 \mu m for V = 4 \mu m/s,
220.2 \mu m for V = 12 \mu m/s, and 190.8 \mu m for V = 20 \mu m/s. In Fig. 4.3a-d, we observe
that \lambda_{\text{max}} is also affected by \alpha_0. The \lambda_{\text{max}} for V = 4 \mu m/s increases as |\alpha_0| increases:
\lambda_{\text{max}} [\mu m] = 301.5, 313.5, 322.5 and 337.5 in order of increasing |\alpha_0|. This could be because
the sidebranch growth of a primary branch is compressed by the adjacent primary branch
at a large |\alpha_0| in a thin-sample geometry.

The blue dots in Fig. 4.3 correspond to the calculated \alpha in an extended system. In order
to avoid the initial coarsening dynamics, we use the data within a time range of \mathbf{t}_0 < \mathbf{t} < \mathbf{t}_{\text{max}}.
The left convergent or right divergent boundaries can influence the dynamics of a misoriented
cell, so we do not include the data near the boundaries in the figure as well. The dispersion of
blue dots come from the disordered array structure in an extended system. In all considered cases, the single misoriented cell dynamics agrees with the results observed in a perfectly ordered array.

**Predictive models for the spacing dynamics**

When primary branches move from the divergent (source) boundary to the convergent (sink) boundary as illustrated in Fig. 4.2, the spacing within an array also evolves. In order to predict this spacing evolution, we propose two models for (i) the global spatiotemporal evolution of a primary spacing profile within boundaries and (ii) the propagation of a spacing.

For the prediction of a global spacing profile between the source and the sink, we use the drift velocity $V_d$ that is related to $\lambda$ as in the previous section. We assume that one primary branch moves with $V_d$, i.e.

$$\frac{dy_t}{dt} = V_d,$$

(4.2)

where $y_t$ is a primary tip position. Then, we can calculate the tip position after a small time step $\Delta t$ using the Euler explicit time stepping scheme. We measure the spacing $\lambda$ from one primary tip to the previous one (see Fig. 4.1), and linearly interpolate the corresponding $V_d$ from simulation results with a perfectly ordered array (red dots in Fig. 4.3).

This simple geometrical model Eq. (4.2) uses the spacing profile of a simulation at time $t_0$ as an initial condition. For the cell eliminations and creations, we need to set boundary conditions for the model. We assume a new primary branch appears when the last primary tip moves away from the divergent boundary ($y = L_y$) more than $\lambda_M$. The spacing for the new primary branch is the same as the higher limit $\lambda_M$. For the eliminations, we consider the first cell is eliminated when the distance between the cell tip and the convergent boundary ($y = 0$) is smaller than the lower limit $\lambda_e$. Both $\lambda_M$ and $\lambda_e$ values are related to $V$ and $\alpha_0$, which are summarized in Table 4.1. Then, using a small time step $\Delta t = 0.1$ s, the model calculates all tip positions within the array from $t_0$ to $t_{max}$.

In our considered cases, the drift velocity $V_d$ is usually much faster than a phase diffusion.
of the alloy. Thus, the contribution of a phase diffusion is negligible. However, if a microstructure has a small $V_d$ due to a small $\alpha_0$ or a low $V$, we need to introduce the diffusion effect for the spacing profile predictions as in a eutectic array structure [76, 93].

The geometrical model may predict the global spacing profiles of a quasi-2D array; however, it could not describe the spacing dynamics. A spacing itself may not move with the corresponding drift velocity $V_d$, so we consider the conservation of spacing density, defined as $n \equiv 1/\lambda$, within a finite region.

Fig. 4.4 illustrates misoriented primary branches in a quasi-2D array. The primary branches move from the right to the left, and their drift velocities $V_d$ are related to $\lambda$. When we consider a finite region (vertical black lines), a primary branch comes inside the region through the right boundary, and goes out through the left boundary. Thus, we assume

Table 4.1: The elimination ($\lambda_e$) and creation ($\lambda_M$) limit spacings for the geometrical model, and the approximate median spacing $\lambda_p$ for the spacing propagation. The velocity for $\lambda_p$ is closer to $V_\lambda$ in Eq. (4.8) rather than to $V_d$.

| $V$ [µm/s] | $\alpha_0$ [$^\circ$] | $\lambda_e$ [µm] | $\lambda_p$ [µm] | $\lambda_M$ [µm] | $|V_d|$ [µm/s] | $|V_\lambda|$ [µm/s] |
|------------|-----------------|-----------------|-----------------|-----------------|-------------|-------------|
| 4          | -5              | 54              | 145             | 180             | 0.2388      | 0.0980      |
|            | -10             | 54              | 145             | 192             | 0.4735      | 0.1488      |
|            | -15             | 54              | 165             | 201             | 0.7602      | 0.3005      |
|            | -20             | 54              | 165             | 211             | 0.9955      | 0.3410      |
| 12         | -15             | 27              | 105             | 140             | 2.6684      | 1.6612      |
| 20         | -15             | 19              | 85              | 117             | 4.8690      | 3.7327      |
that spacing density within this finite region is conserved as

\[ \partial_t n + \partial_y [V_d \cdot n] = 0 \] \hspace{1cm} (4.3)

Using the definition of \( n \) and the relation \( V_d \sim \lambda \), we obtain

\[ \partial_t n = -\frac{1}{\lambda^2} \partial_t \lambda \] \hspace{1cm} (4.4)

and

\[ \partial_y [V_d \cdot n] = V_d \partial_y n + n \partial_y V_d \] \hspace{1cm} (4.5)

\[ = V_d \left( -\frac{1}{\lambda^2} \right) \partial_y \lambda + n \frac{\partial V_d}{\partial \lambda} \frac{\partial \lambda}{\partial y} , \] \hspace{1cm} (4.6)

which yields

\[ \partial_t \lambda + \left[ V_d - \lambda \frac{dV_d}{d\lambda} \right] \partial_y \lambda = 0 \] \hspace{1cm} (4.7)

because \( V_d \) is only a function of \( \lambda \) at a given \( \alpha_0 \) and \( V \). Then, the velocity

\[ V_\lambda \equiv V_d - \lambda \frac{\partial V_d}{\partial \lambda} \] \hspace{1cm} (4.8)

could correspond to a spacing propagation.

**Influences of crystal orientations and pulling velocities**

We first look at the spacing profile evolutions at different crystal orientations \( \alpha_0 = -5^\circ, -10^\circ, -15^\circ, \) and \( -20^\circ \) for \( V = 4 \mu m/s \). In order to avoid the initial coarsening growth regime after the morphological instability, we use the profiles after the initial coarsening dynamics, i.e. from \( t_0 \approx 4043 s \) for \( \alpha_0 = -5^\circ \) and \( 2043 s \) for the other angles to \( t_{\text{max}} = 20000 s \). The microstructure forms a single row array, and the primary tips are located at the middle of
Figure 4.5: Evolution of spacing profiles (a) and the dynamics of the spacing (b). Figures on the left column (a) show the primary tip positions and spacings along the $y$ direction measured in simulations (filled circle dots) at different $\alpha_0$ for $V = 4 \mu m/s$. We predict the spacing profiles (solid lines) at different time steps (colors). The hollow dots indicate the predicted tip positions with the corresponding spacing. The median spacing $\lambda_p$ (black arrow) between the low plateau of initial $\lambda$ and high plateau of steady $\lambda$ propagates as spacing profile evolves. Figures on the right column (b) show that the $\lambda_p$ propagations (black circles) agree with $V_\lambda$ (red solid lines) rather than $V_d$ (blue dashed lines).

We measure spacing profiles $\lambda(y)$ at different time steps (corresponding colors as noted in Fig. 4.5a). After the initial transient growth, the selected spacings at $t_0$ (red filled dots) in the inter-grain region are similar to each other except for the boundaries. On the right

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divergent GB, the selected spacing due to sidebranching is consistently close to $\lambda_M$. As the primary branches run into the other convergent GB, their spacings decrease because of elimination processes.

As time elapses, the spacing profiles evolve from the initially selected spacing towards the stationary state at the end of the simulation (dark green dots in Fig. 4.5a). At the stationary state, the primary spacings are uniform as $\lambda_M$ until they drop abruptly near the sink. As the primary branches have a higher $|\alpha_0|$, the profiles reach a stationary state faster. The primary branches drift slowly at a lower $\alpha_0$, so the profile for $\alpha_0 = -5^\circ$ still evolves at $t_{max}$. However, we expect that it would reach a steady state sometime after $t_{max}$ like the other simulations.

For the spacing profile predictions with Eq. (4.2), we use $\lambda(y)$ at $t_0$, i.e. the red filled dots in Fig. 4.5a, as an initial condition. As we discussed earlier, the model considered two boundary limits that are $\lambda_e$ for the elimination of primary branches near the sink ($y = 0$) and $\lambda_M$ for the creation near the source ($y = L_y$). These limits are listed in Table 4.1 and correspond to the shaded area in Fig. 4.5a. We use the $V_d(\lambda)$ from a single cell simulation in a perfectly ordered array, i.e. using red dots in Fig. 4.3. Then, the geometrical model calculates primary tip positions and corresponding $\lambda$ with a time step $\Delta t = 0.1$ s from $t_0$ to $t_{max}$.

The solid lines in Fig. 4.5a correspond to spacing profiles at different time steps (colors) predicted by the geometrical model. The hollow dots indicate the predicted primary tip positions and spacings. The model predicts precisely the spacing profiles and corresponding tip positions in most cases.

For the predictions at $\alpha_0 = -5^\circ$, the predictions show small deviations from the simulation results near the lower $\lambda$ plateau region. It could be caused by a phase diffusion of the array because the drift velocity at this lower $\alpha$ is small. At the higher $\alpha_0 = -20^\circ$, the discrepancies between predictions and simulations occur near the higher plateau region ($\lambda \sim \lambda_M$). We presume that a faster primary branch could push its previous neighbor, which leads to the
faster $\lambda_M$ propagations.

As illustrated in black arrows in Fig. 4.5a, we measure the positions of a spacing $\lambda_p$ at different time steps from $t_0$ to investigate the propagation of a spacing. The $\lambda_p$ is decided by an approximate median value of the initially selected lower plateau $\lambda$ and final higher plateau $\lambda = \lambda_M$, which are summarized in Table 4.1. Fig. 4.5b shows the measured positions $y_p$ at different time steps from its initial position $y_0$ at $t_0$ as a function of time, which corresponds to black dots. In the measurements, the distance from the initial position $Y = |y_p - y_0|$ of $\lambda_p$ exhibits approximately a linear increase as time increases. Thus, in order to predict the $\lambda_p$ propagation, we use two velocities: (i) $V_d$ from Fig. 4.3 and (ii) $V_\lambda$ in Eq. (4.8) (see Table 4.1 for the estimated values). In Fig. 4.5b, the blue dashed lines correspond to the trajectories of $\lambda_p$ with $V_d$. These lines always overestimate the measured $\lambda_p$ positions. However, using $V_\lambda$ (red solid lines) improves the agreements.

We also considered the array structure dynamics at a higher $V = 12$ and 20 $\mu$m/s for $\alpha_0 = -15^\circ$. The corresponding spacing profiles from $t_0$ are plotted as filled circle dots in Fig. 4.6. The large spacing $\lambda_M$ propagates from the source, and primary spacings at a steady state are $\lambda = \lambda_M$ from the source until it decreases near the sink due to eliminations.

We use the geometrical model Eq. (4.2) to predict the spacing profiles at different time steps from $t_0$ (red filled dots in Fig. 4.6a). The gray shaded areas on the left and the right of Fig. 4.6a are related respectively to the elimination $\lambda_e$ and creation $\lambda_M$ limits that are summarized in Table 4.1. We also use the time step $\Delta t = 0.1$ s for the model predictions. The predicted $\lambda(y)$ are marked as hollow dots and the solid lines between them. As illustrated in Fig. 4.6a, the model predictions also agree with the spacing profiles observed in the simulations.

We also measure the $\lambda_p$ positions at different time steps as the black arrows in Fig. 4.6a designate. We choose $\lambda_p$ (given in Table 4.1) as the median of the lower and higher plateau $\lambda$. Black dots in Fig. 4.6b represent the estimated $Y$ for $\lambda_p$ positions from the initial $y_0$ and $t_0$ as a function of time. As we observe in the previous simulations, the trajectory of $\lambda_p$
Figure 4.6: Influence of $V$ at $\alpha_0 = -15^\circ$. Even if we increase $V$, the geometrical model (solid lines with hollow dots in a) can predict spacing profiles in simulations (filled dots in a) at different time steps (colors). Using $V_\lambda$ (red line in b) describes the propagation of $\lambda_p$ (black arrow in a and black circle dots in b) better than using $V_d$ (blue dashed line in b).

Using $V_\lambda$ (red solid line) agrees better with the simulation measurements than using $V_d$ (blue dashed line). The detailed values for $V_\lambda$ and $V_d$ are given in Table 4.1.

We observe one interesting thing for the $\alpha_0 = -15^\circ$ simulations. The $V_\lambda$ approaches the $V_d$ as $V$ increases. Hence, we plot the ratio $R_V = V_\lambda/V_d$ as a function of $V$ as in Fig. 4.7. This plot clearly shows that the ratio (square dots) increases as $V$ increases, and we presume the ratio $R_V = V_\lambda/V_d$ is close to 1 at a higher $V$. This assumption $R_V \to 1$ is reasonable when we look Fig. 4.3. Fig. 4.3 shows $\alpha$ approaches $\alpha_0$ faster when $V$ is large, and, once $\alpha \approx \alpha_0$, the variation $d\alpha/d\lambda$ is very small. Thus, as $V$ increases, the derivative part in Eq. (4.8) becomes smaller, which leads to $V_\lambda \to V_d$ or $R_V \to 1$.

Figure 4.7: $V_\lambda$ approaches $V_d$ as $V$ increases, which yields $R \to 1$. The square dots are from the simulations, and the solid line indicates a guide line.
Beyond the fluctuation of a spacing profile

The spacing profile of a misoriented grain barely changes after the array reaches a stationary state with a uniform $\lambda$ distribution. However, the stationary state could fluctuate due to sidebranching near the divergent GB. We observe this complex behavior in our simulation.

In Fig. 4.6a, the spacing profile at $V = 20 \mu m/s$ and $\alpha_0 = -15^\circ$ shows a stationary profile at $t = 698$ s (yellow filled dots). After this stationary state, a spacing for the new sidebranch at the source gradually increases (but remains close to $\lambda_M$), and the spacing between the last primary tip to the divergent GB becomes large enough to generate two primary branches sometime after after 698 s. We captured this moment in the PF simulation as illustrated in Fig. 4.8. The microstructures in the figure are seen from the side of the sample approximately every 12 s from $t = 1238$ s (bottom) to 1298 s (top). At $t = 1238$ s, the last primary branch is far away from the right divergent GB; however, a new sidebranch has not been created yet. The spacing between the primary tip and the GB is relatively large, so two sidebranches simultaneously grow and become two primary branches when we see the above image at the next time step $t = 1250$ s. These new primary branches move towards the inter-grain region without an elimination (red dashed lines for the guides).

When two primary branches are created simultaneously, their spacings are smaller than $\lambda_M = 117 \mu m$, which is the most commonly observed spacing at the source. Hence, this
complex behavior leads to the fluctuation of the stationary spacing profile. For the microstructure at $t = 1298$ s (purple box in Fig. 4.8), its spacing profile (purple filled dots) is fluctuated as shown in Fig. 4.8a.

We measure the spacing profile from $t = 1298$ s to explore the evolution of a primary spacing beyond the fluctuation. In the simulation (filled dots in Fig. 4.9a), the smaller spacings after the complex behavior propagate away from the source; meanwhile, they relax towards the $\lambda_M$. Hence, the profile reaches a stationary state again (blue filled dots), which is similar to the previous stationary state (see corresponding figures in Fig. 4.6a).

We test our geometrical model to capture spacing profile dynamics after this complex behavior. Hence, we use the $\lambda(y)$ at $t = 1298$ s (purple filled dots in Fig. 4.9a) as an initial condition for the model. We consistently use same spacing limits and $V_d(\lambda)$ as the previous prediction used for Fig. 4.6a. The hollow dots (including the solid lines between them) in Fig. 4.9a correspond to the model predictions at different time steps (colors). These predicted primary tip positions and their spacings show a good agreement with the simulations.

We also examine the propagation of a spacing $\lambda_p$. At this time, we manually select a spacing $\lambda_p = 105$ $\mu$m. This spacing is smaller than $\lambda_M$, but, larger than the smallest spacing

Figure 4.9: Spacing profiles (a) and $\lambda_p$ propagation (b) after the simultaneous creation of two primary branches. Even after this complex behavior, the model prediction (solid lines with hollow dots) agrees with the simulation results (filled dots). $V_d$ (blue dashed line in b) overestimates the $\lambda_p = 105$ $\mu$m (black arrow in a and black circle dots in b), and $V_\lambda$ (red solid line in b) improves the agreements.
after the fluctuation. Then, we measure the positions of $\lambda_p$ from $t_1 = 1358$ s to $t = 1598$ s as the black arrow in Fig. 4.9a shows. The calculated distances from the initial position at $t_1$ as a function of time correspond to black dots in Fig. 4.9b. In this figure, we also observe that the $\lambda_p$ positions move with $V_\lambda = 3.9957$ µm/s (red solid line) rather than $V_d = 5.0832$ µm/s (blue dotted line).

### 4.1.4 Summary

We have shown the evolution of a primary spacing profile when a grain in a thin-sample geometry is misoriented with respect to the temperature gradient $G$ axis. In the misoriented grain, primary branches move laterally, and thus the convergent and divergent grain boundaries are systematically formed at the edges of the $y$ domain in the PF simulations. As the primary branches run into the convergent grain boundary (GB), they are continuously eliminated near this GB. On the other hand, as the branches go away from the divergent GB, new primary branches are created by sidebranching dynamics [52, 61, 53, 49, 48, 66]. In the inter-grain region (i.e. away from the boundaries), primary branches drift from the divergent GB to the convergent GB with a drift velocity $V_d = V \tan \alpha$. The drift angle $\alpha$ is usually smaller than its crystal angle $\alpha_0$, and it is related to its spacing $\lambda$ [1, 39].

We initially perform simulations to construct the relation $\alpha(\lambda)$ for our considered alloy and solidification conditions. We use one single primary branch with a perfectly ordered array. The primary branch misoriented with respect to the $G$ axis moves laterally, and its drift angle $\alpha$ from its drift velocity $V_d$ links to its spacing $\lambda$ as previous studies discovered [1, 39]. Primary branches in the extended disordered array also show similar dynamics as shown in the perfectly ordered array system (Fig. 4.3).

We use these measured $V_d$ for the simple geometrical model, i.e. Eq. (4.2), to estimate the spacing profiles. We assume that primary tips drift with an instantaneous $V_d$ at a small time step, and the model calculates the movements of all primary branches in a quasi-2D array. Then, from the initial spacing profile at a time $t_0$ after the initial coarsening dynamics, we
predict the following spacing profiles. The predictions show quantitative agreements with the simulations at different $\alpha_0$ (Fig. 4.5) and $V$ (Fig. 4.6).

When we focus on the propagation of one spacing when the spacing profile evolves, the drift velocity $V_d$ for a spacing $\lambda_p$ overestimates the $\lambda_p$ propagation. Thus, we derive a velocity $V_\lambda$ from the conservation law of spacing density within a finite region. The trajectories of $\lambda_p$ using $V_\lambda$ improve the agreement with the simulations in all considered simulations (Fig. 4.5 and Fig. 4.6). In addition, we observed that $V_\lambda$ approaches $V_d$ as $V$ increases (Fig. 4.7). Therefore, we expect that $V_\lambda$ would become $V_d$ at a higher $V$, or possibly in the more dendritic growth regime with sharper primary tips.

4.2 Influence of spatial confinement

4.2.1 Background

A planar solid-liquid interface is formed near the liquidus temperature of an alloy under a given temperature gradient before conducting solidification experiments. Then, the interface grows towards the hotter area, as the solute concentration at the interface on the liquid side builds up while the sample is pulled towards the colder area. If the solute build-up is sufficiently large, the planar interface breaks into small cells. These small cells compete with neighbors, leading to cell eliminations. The primary cells and dendrites that survive during the competition find a stable spacing within a wide stability range [138, 161, 91, 137, 47, 66, 73, 105, 168]. However, similar spacings could be selected from similar solidification processes [66, 170].

The primary spacing selection mechanisms have been studied analytically and experimentally with a thin-sample geometry [61, 160, 52, 72, 91]. The analytical approach suggested that the primary spacing is determined by three control parameters: the alloy composition that fixes the freezing range $\Delta T_0$, pulling velocity $V$, and temperature gradient $G$ [160, 72, 91].
In this section, we investigate the microstructure selection in a thin-sample geometry. The use of the thin samples for solidification experiments could limit the convective currents; however, the sample thickness $H$ could influence microstructure selection [137]. Therefore, we performed PF simulations to explore the primary spacing selection under the influence of $H$ in cellular and dendritic growth regimes. This investigation is important to relate the results of thin-sample experiments on earth and microgravity experiments using spatially extended 3D samples aboard the ISS.

4.2.2 Cellular growth regime

The oscillations in a local region constitute a generic secondary instability in interface patterns that form in systems out of thermodynamic equilibrium, which has been observed in the previous experiments of a cellular growth regime [56, 12, 148]. This oscillation dynamics could stay longer at a specific spacing range [148, 124]; however, it is usually terminated by the elimination of an oscillating cell. Then, the neighboring cells obtain a bigger spacing by occupying the area of the eliminated cells [56, 148]. Experiments reveal that, in a thin-sample geometry, elimination of a cell during oscillation causes the surviving neighbor cells to form doublets or multiplets [56, 89]. These multiplets have a bigger spacing than a symmetric cell, and they are usually expected to be more stable [89, 104].

In order to investigate the spacing selection mechanisms depending on the sample thickness of a cellular growth regime, we used a transparent succinonitrile (SCN)-0.25 wt% camphor alloy for the phase-field (PF) simulations. The PF simulation results were compared to the experimental results starting from the initial planar interface dynamics to the final selected spacings. In addition, we studied the oscillation dynamics and the formation of multiplets observed in the PF simulations.
Initial planar interface dynamics

The spacing selection mechanisms are related to the history of interface growth dynamics [137, 160, 138, 161], and therefore, different initial planar interface dynamics could lead to different microstructures at a steady state as pointed out in the previous chapter and recent studies [116, 171]. In the experiments which were performed with a SCN-0.25wt% camphor alloy, the interface temperatures were measured while the sample with thickness $H = 200 \mu m$ was pulled at $V = 1 \mu m/s$ under $G = 13.3 \text{ K/cm}$. We measured the interface temperature until the planar front was destabilized, and in order to validate the simulations, the measurements were compared to the simulations as illustrated in Fig. 4.10.

We first performed PF simulations with an extended array (bigger sample size) using no-flux boundaries along all the axes and wetting boundaries at the contact surfaces of the sample, i.e. at the minimum of $z = 0$ and the maximum of $z = H$ on the $z$ axis. The stationary temperature field in the thin-sample experimental setup was measured by thermocouples, which were located outside of the sample, and the field overlapped an imposed linear temperature profile [171]. Thus, we used a frozen temperature approximation in the PF simulations. In order to investigate the thickness effects, we used different sample sizes: $H \text{[} \mu m\text{]} = 100, 125, 150, 175$, and $200$ for a sample length of $L = 2 \text{ mm}$, and $H \text{[} \mu m\text{]} = 100$, $150$, and $200$ for $L = 4 \text{ mm}$. These simulations started with a planar interface having a small spatiotemporal noise in the range of $[-0.5, 0.5] \Delta x$. The simulations continued until $t = 5 \text{ h}$ and $10 \text{ h}$ for $L = 2 \text{ mm}$ and $4 \text{ mm}$, respectively. For the comparison with measured initial interface temperatures, we used the selected simulation data, i.e. $H = 100 \mu m$, $150 \mu m$, and $200 \mu m$ with a sample width of $L_y = 4 \text{ mm}$.

Fig. 4.10 shows the temperature of the initial planar interface as a function of time. The experiment measured the temperatures of the planar interface, which are marked as gray dots. Its first measured temperature, immediately after pulling the sample, was $57.2^\circ \text{C}$; therefore, we considered this temperature as the liquidus temperature of the alloy in the simulation, i.e. $T_L = 57.2^\circ \text{C}$. The red solid, green dashed, and blue dotted lines indicate the
simulation results for $H = 100 \, \mu m$, 150 $\mu m$, and 200 $\mu m$, respectively, at the same sample length ($L_y = 4 \, mm$). The PF simulations measure the tip undercooling $\Delta$, which is the normalized distance from the liquidus, of the most advanced tip, and hence we estimate the interface temperatures $T$ from

$$T = T_L - \Delta \cdot |m|c_{\infty}(1/k - 1) \ ,$$

where $m$ is the liquidus slope, $c_{\infty}$ is a nominal composition, and $k$ is an alloy partition coefficient.

In Fig. 4.10, it can be seen that the initial planar interface positions from the simulations (lines) are similar to each other, and these results agree with the experimental measurements (dots). In addition, the morphological instability occurs at similar times in the simulations and the experiment. The dots in the figure are only for the planar interface, and the morphological instability occurs at a time that is close to the last point $t \sim 2000 \, s$. In the simulations, the interface temperature increased suddenly after the morphological instability near the last experimental point. This increase was caused by the advanced tips, which grew faster after the instability. These results show that $H$ does not influence the initial planar interface dynamics. Thus, the thermal history of the performed simulations is similar.
to that observed in the experiment at a fixed linear temperature field.

It is worth noting that the temperature field can evolve under the influence of thermal effects (heat transfer between heat sources and the latent heat rejection at the interface) as we discussed in Sec. 3.1 The thermal conductivity depends on an alloy, a material of the sample crucible, and the sample geometry. In addition, the influence of latent heat rejection becomes stronger when \( V \) is higher. Therefore, these conditions lead to the evolution of a temperature field, and thus the recoil dynamics of the planar interface can be different from the results using a frozen temperature field approximation.

**Sample thickness and average cell spacing**

Microstructures select a spacing after the morphological instability and initial coarsening dynamics. The primary spacing is known to be determined by the freezing range of the alloy \( \Delta T_0 \), the pulling velocity \( V \), and the temperature gradient \( G \) \([160, 72, 91]\). However, the simulations show that the selected \( \Lambda \) depends on \( H \) as mentioned in previous observations \([137]\).

Fig. 4.11 shows the microstructures in a stationary state at the end of the PF simulations, i.e. \( t = 10 \) h for \( H = 100 \) \( \mu \)m (a-b) and 200 \( \mu \)m (c-d). These simulations have the same sample lengths (\( L_y = 4 \) mm), and the other solidification conditions remain the same. Two different view points are shown: as seen from the top (a and c) and as seen from the side (b and d). These figures show that the microstructure with \( H = 100 \) \( \mu \)m has a bigger \( \lambda \) than that with \( H = 200 \) \( \mu \)m.

The selected spacings for the other values of \( H \) are plotted in Fig. 4.12. We did not consider simulations when \( H < 100 \) \( \mu \)m, because when the value of \( H \) is small, the cells are continuously split or eliminated. This figure shows the average spacing \( \Lambda \) measured from simulations at \( t = 5 \) and 10 h for \( L = 2 \) mm (pentagon dots) and 4 mm (triangle dots), respectively.

The simulations with \( L_y = 2 \) mm (brown pentagon dots) show that \( \Lambda \) decreases with an increase in the sample thickness \( H \). The values of \( \Lambda \) for \( L_y = 2 \) mm follows the brown
Figure 4.11: Dynamically selected microstructures of a SCN-0.25wt% camphor alloy in thin-sample simulations using $G = 13.3$ K/cm and $V = 1 \mu$m/s. The morphologies at $t = 10$ h are taken from the top (a and c) and the side (b and d) of the sample at different sample thicknesses $H = 100$ and 200 µm for the sample width $L_y = 4$ mm.

dashed line, which is a linear guide line $\Lambda \sim -H$. Even though the decreasing rate $d\Lambda/dH$ for $L_y = 4$ mm is smaller than that for $L_y = 2$ mm, $\Lambda$ for $L_y = 4$ mm (purple triangle dots) also becomes smaller as $H$ increases. The experimentally measured spacing at $H = 200$ µm (black diamond dots) is close to this guide line.

As shown in Fig. 4.12, the selected spacings in an extended array or in the experiment (dots) are within the stable spacing ranges (error bars). The red, green, and blue error bars represent stable spacing ranges for $H [\mu$m] = 100, 150, and 200, respectively. These lines correspond to Fig. 4.13a, and these ranges will be discussed in detail in the next section (see Fig. 4.13).

An interesting observation at a small value of $H$ is the cells oscillating with their neighbors. In the simulations, this oscillation leads to cell elimination. When a cell is eliminated during
The cellular or dendritic arrays can grow in steady-state over a wide range of stable spacings \[138, 161, 91, 137, 47, 66, 73, 105, 168\]. Recently, PF simulations constructed the entire stable spacing range for a set of solidification conditions \[148, 43, 64, 124, 31, 12\]. Those 3D simulations considered the symmetric conditions of a cell/dendrite to find a relation between the tip undercooling \(\Delta\) and \(\lambda\) for a stability range \[148, 64, 124, 31, 12\]. In our quasi-2D simulations, asymmetrical multiplets were widely observed as shown in the microstructures in Fig. 4.11. Therefore, we used one entire cell (see Fig. 4.13) to construct stable spacing ranges at different sample thicknesses \(H = 100 \mu m, 150 \mu m,\) and \(200 \mu m\).

In order to obtain a full stable cell shape, we first performed simulations with a quarter of a cell with \(N_y/\Delta x = N_z/\Delta x = 10, 15,\) and \(20\) respectively for \(H = 100 \mu m, 150 \mu m,\) and
200 µm at \( G = 10 \) K/cm. We increased the spacing by one \( \Delta x \) until \( \lambda/2 \approx 90 \) µm, and made half cells for the three different values of \( H \) by using symmetric boundary conditions. Then, by using a cell with \( \lambda \approx 180 \) µm, we gradually changed the temperature gradient from \( G = 10 \) to 13.3 K/cm in 2 h. Finally, we produced one full cell from the stable half cell at \( G = 13.3 \) K/cm by using symmetry conditions. For this stable full cell, we used no-flux (symmetric) boundary conditions in all directions, and wetting conditions were imposed at the sample walls. Then, using this cell as an initial condition for the next simulation, we increased or decreased its spacing by one \( \Delta x \). When the spacing was too small, the cell shape changed from a full cell to a half cell. On the other hand, the cell tip was split when its spacing was too large.

At a larger spacing, we also observed isolated spacing ranges, which were away from the continuous spacing range, as shown in Fig. 4.13a. In order to reach this spacing region, we used a half cell with \( \lambda/2 = 130 \) µm for \( H = 150 \) µm and 140 µm for \( H = 200 \) µm at \( G = 10 \) K/cm as an initial condition for the simulations. We increased the value of \( G \) of this half cell from 10 K/cm to 13.3 K/cm. Then, we constructed one full cell by using symmetry conditions. From this cell with the no-flux and wetting boundaries, we changed one \( \Delta x \) until their minimum or maximum spacings for this isolated region were reached.

To obtain the minimum stable spacing \( \lambda_{\text{min}} \), we used a cell with its spacing \( \lambda \) as an initial condition for different values of \( H \). In these simulations, two cells with the same \( \lambda \) were facing each other, and grew together until \( t = 60000 \) s. When the two neighboring cells have \( \lambda < \lambda_{\text{min}} \), one cell is eliminated, and the other cell grows with a spacing \( 2\lambda \). Otherwise, the cells grow together.

Fig. 4.13a shows the stability ranges and some examples of cell shapes at different values of \( H \). When a cell has a symmetric shape at small values of \( H \) and \( \lambda \), its tip is located at the center of a cell \( (H/2 \text{ and } \lambda/2) \). One example of a symmetric cell when \( \lambda = 150 \) µm and \( H = 100 \) µm is shown in Fig. 4.13b. The red and blue lines represent \( y = \lambda/2 \) and \( z = H/2 \), respectively. The black circle indicates the region near the cell tip \( (x_{\text{tip}}, y_{\text{tip}}, z_{\text{tip}}) \).
Figure 4.13: Tip undercooling $\Delta$ as a function of cell spacing $\lambda$ (a) with the shapes of representative symmetric cell (b), doublet (c), and quadruplet (d) for $V = 1 \, \mu m/s$ and $G = 13.3 \, K/cm$ of a SCN-0.25wt% camphor alloy. In (a), the symbols indicate symmetry cells (squares), doublets (triangles), and quadruplets (circles), and the solid lines correspond to a stable spacing. Three different views are shown for the shape as seen from the front of the tip (left) and as seen from different sides (right) in (b)-(d). The black circle indicates the region near the cell tip, and the lines represent the centered lines where $y = \lambda/2$ (red line) and $z = H/2$ (blue line). In (b), the cell with $H = 100 \, \mu m$ and $\lambda = 150 \, \mu m$ is symmetric. (c) and (d) show a doublet with $H \times \lambda = 150 \, \mu m \times 200 \, \mu m$ and a quadruplet with $H \times \lambda = 200 \, \mu m \times 200 \, \mu m$, respectively.

view of the cell (top left of Fig. 4.13b), it can be seen that the red and blue lines cross each other at the center of the black circle. This means that the cell tip is located at the center of the circle. The figures on the right-hand side of Fig. 4.13b show the cell shapes as seen from its sides. These figures show that top positions of the grooves (i.e. the end of blue and red lines) located in the middle of the cell. Thus, a quarter of a cell could represent its whole shape.
In Fig. 4.13a, the symmetric cells are marked as square dots. Symmetric cells are stable when $H = 100 \, \mu m$ and $150 \, \mu m$ in a short range of $\lambda_{\text{min}} < \lambda < \lambda_{\text{max}}^s$, where the limit of a symmetric cell $\lambda_{\text{max}}^s = 172.5 \, \mu m$ for $H = 100 \, \mu m$ and $167.5 \, \mu m$ for $H = 150 \, \mu m$. $\lambda_{\text{min}}$ is related to a lower limit of the stable spacing range due to cell eliminations. If two cells grow together with $\lambda < \lambda_{\text{min}}$, then one cell is eliminated. These minimum spacings are close to $\lambda_{\text{min}} \approx 50 \, \mu m$ for each $H$, which corresponds to the lower limits of the stability ranges in Fig. 4.12.

We observed that cells can exist when $\lambda > \lambda_{\text{max}}^s$. These cells show a doublet shape. The spacing of a doublet can increase until the maximum limit of a doublet $\lambda_{\text{max}}^d = 257.5 \, \mu m$ for $H = 100 \, \mu m$ and $262.5 \, \mu m$ for $H = 150 \, \mu m$, which are marked as triangle dots in Fig. 4.13a. If a doublet has bigger spacing than the limit $\lambda_{\text{max}}^d$, it is unstable due to tip splitting or sidebranching. Then, two symmetric cells grow together.

Fig. 4.13c shows a doublet shape when $\lambda = 200 \, \mu m$ and $H = 150 \, \mu m$. The black circle indicates the vicinity of the cell tip, and the red and blue lines represent the centered lines with $y = \lambda/2$ and $z = H/2$, respectively. From the top view (top left of the figure), it can be seen that the cell tip is not at the center. The cell shapes in the right column show that it is symmetric with respect to the blue $z = H/2$ line (top right); however, the symmetry is broken around the red $y = \lambda/2$ line (bottom right). Therefore, its groove shape is asymmetric along $y = \lambda/2$.

Unlike the other thicknesses, we cannot find a stable symmetric cell when $H = 200 \, \mu m$. Cells at this thickness become doublets even with a small $\lambda$. These doublets are symmetric with respect to $y = \lambda/2$, and the symmetry of the cells is already broken along $z = H/2$. The blue triangles in Fig. 4.13a represent the stable doublets with $H = 200 \, \mu m$. The maximum spacing for the doublet is $\lambda_{\text{max}}^d = 167.5 \, \mu m$, which is close to $\lambda_{\text{max}}^s$ for the symmetric cells with other values of thicknesses.

The simulation results for the doublets may indicate that the surface tension along one direction only sustains a symmetry with respect to the corresponding direction until a limit
spacing $\lambda_l$, and therefore, the tension along the other direction does not affect the shape in the other direction. Our simulations show that the symmetry of a cell along an axis is broken when $\lambda$ or $H$ is larger than $\lambda_l$. Hence, the cells with $H = 100 \mu m$ and $150 \mu m$ have become doublets when $\lambda > \lambda_l$. The cells with $H = 200 \mu m$ cells have already shown doublet shapes because $H > \lambda_l$. Thus, $H < \lambda_l$ or $\lambda < \lambda_l$ is necessary for a cell to retain its symmetry on one side. The limit $\lambda_l$ could be variable due to the anisotropy of an alloy. For the alloy under consideration, the limit is $\lambda_l \simeq 170 \mu m$.

When both $H$ and $\lambda$ are bigger than $\lambda_l$, a doublet becomes a quadruplet as shown in Fig. 4.13d. Fig. 4.13d shows an example of the shape of a quadruplet with $H = \lambda = 200 \mu m$ as seen from different sides. The black circle indicates the region around the tip, and both the centered lines (red line for $y = \lambda/2$ and blue line for $z = H/2$) do not cross the tip. In addition, the grooves are asymmetric along $z = H/2$ (top right) and $y = \lambda/2$ (bottom left).

The quadruplets are marked as circle dots in Fig. 4.13a. This figure shows that the steady state spacing range for quadruplets is in the range of $\lambda_d^{\text{max}} < \lambda < \lambda_d^{\text{max}} = 252.5 \mu m$. If the spacing is larger than the maximum spacing for a quadruplet, i.e. $\lambda > \lambda_d^{\text{max}}$, a new doublet is created.

In the simulations for $H = 150 \mu m$ and $200 \mu m$, we observed additional isolated stable ranges. As in Fig. 4.13a, symmetric cells are observed in the range of $257.5 < \lambda [\mu m] < 287.5$ for symmetric cells with $H = 150 \mu m$ and $237.5 < \lambda [\mu m] < 307.5$ for doublets with $H = 200 \mu m$. One interesting result is that the doublets and quadruplets with $H = 200 \mu m$ could exist together at a bigger $\lambda$. The higher limits of the stability ranges in Fig. 4.12 correspond to the maximum spacing of the stability ranges, including the isolated region.

It is worth noting that the maximum spacings $\lambda_{\text{max}}$ of the continuously increasing spacing regions (without the isolated ranges) for different values of $H$ are also similar to each other. These continuous stable ranges increase until $\lambda_{\text{max}} = 257.5 \mu m$ for $H = 100 \mu m$ and $262.5 \mu m$ for the other values of $H$. 

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Oscillations in a thin-sample geometry

Solidification experiments with a thin-sample geometry showed oscillation dynamics in a cellular regime [56]. More recently, microgravity experiments revealed that the cells in a 3D hexagonal array oscillate with their neighbors within a local region when the pulling velocity is small, and the corresponding 3D PF simulations agree with the experimentally measured oscillations [12, 148, 124]. Here, we used similar solidification conditions as in the microgravity experiments [12, 148, 124, 116], and the simulations show oscillation dynamics.

Using PF simulations, we measured the period $\tau_d$ of the oscillating cells for each $H$ in the range $100 \leq H [\mu m] \leq 200$ for $L = 2$ mm.

Fig. 4.14a shows the final morphology of the simulation with $H = 125 \mu m$ and $L = 2$ mm when $t = 5$ h. In the morphology, the cells are well aligned in this thin-sample geometry. We observed that many cells including the colored ones oscillate around a stationary state.
We considered the cell oscillation as a function $A(t) = a + bt + c \sin\left[2\pi(t - t_i)/\tau_d\right]$ with the fitting parameters $a, b, c,$ and $\tau_d \ [12, 138, 124]$. The area of a cell $A(t)$ is scaled with respect to an average area $\bar{A} = \int_{t_i}^{t_f} A(t) \ dt/(t_f - t_i)$ within the times $t_i$ and $t_f$. Then, the normalized area of a cell is given by

$$\frac{A(t)}{\int_{t_i}^{t_f} A(t) \ dt/(t_f - t_i)} \quad (4.10)$$

We fit the measurements in the simulation to the above function $A(t)$ to find the constants. Usually, the simulation results between $t_i = 2.5$ h and $t_f = 5$ h are used.

The two cells (marked as the blue circle and the red square in Fig. 4.14a) oscillate during the simulation, as shown in Fig. 4.14b. The measured area of the blue (red) cell in Fig. 4.14a corresponds to the blue circle (red square) dots in Fig. 4.14b. The dashed lines represent the oscillations with the fitting $A(t)$ curve. The phase shift between the two oscillating cells is close to $\pi$. We assume that the sample walls forced to make the cells formed an aligned array, and hence the diffusive interactions between the nearest neighbors led to this oscillation with a phase shift of $\pi$. It is important to note that, in the simulation, the elimination of a cell during oscillation could lead to the creation of a doublet. The doublets show oscillations with a very small amplitude as observed in the experiment [56].

In addition, as shown in Fig. 4.14c, we calculated the periods $\tau_d$ for different values of $H$. The red circle dots indicate the average $\tau_d$ among the oscillating cells, and the blue triangles indicate the minimum (up triangles) and maximum (down triangles) at the corresponding $H$. The results show that $\tau_d$ decreases as $H$ increases within a range of $112.5 < H [\mu m] < 175$. In addition, the periods are stabilized at $H \geq 175$ $\mu m$. At $H \leq 112.5$ $\mu m$, $\tau_d$ decreases, because the cells are continuously eliminated by oscillation and created by tip splitting.

In a 3D hexagonal array, the oscillation period is linked to the spacing between cells [148, 124]. In a confined thin-sample geometry, $\Lambda$ could also be an important factor in deciding $\tau_d$ for cell oscillations. As $\Lambda$ decreases (equivalent to $H$ increases), the diffusive interactions
between neighboring cells become stronger, which leads to a shorter $\tau_d$. In addition, when $\Lambda$ becomes smaller than $H$, the measured $\tau_d$ is similar to that of the 3D array. In Fig. 4.14c, the oscillatory mode with a period $\tau_d$ is stabilized when the average spacing becomes smaller than the thickness $H \geq 175 \mu m$. The stabilized period $\tau_d \simeq 30$ min is close to $\tau_d \simeq 29$ min from the previous 3D simulation results [48].

4.2.3 Dendrite growth regime

In a cellular growth regime, the sample thickness could influence the selection of the primary spacing. Dendrites, however, are less influenced by the sample thickness; the thickness effects may be negligible for the spacing selection in a dendritic growth regime.

For the investigation of spacing selection in a dendritic growth regime, we performed PF simulations in a thin-sample geometry. As illustrated in Ref. [31], solidifying an Al-1.4wt% Cu alloy forms dendrites under the solidification conditions of a pulling velocity $V = 10 \mu m/s$ for $G = 50 K/cm$. Therefore, these solidification conditions were used for the PF simulations to demonstrate the stable spacing ranges and selected spacings in an extended system with different sample thicknesses $H = 52, 100, 200, 300, \text{and } 400 \mu m$. The material parameters are given in Ref. [31] or in Appendix B.

Stable spacing ranges

We first investigated the stable spacing ranges in a dendrite growth regime depending on the sample thickness.

For the stability tests, we used a similar method as in Ref. [12, 148, 124, 31]. Using the PF simulation, we initially constructed a stable dendrite with $L_y \times L_z = \lambda/2 \times H$. Then, we used bilinearly interpolated $\psi$ and $U$ fields of the stable dendrites as the initial condition for the new simulation, which has larger/smaller domain size along the $y$ axis than the previous stationary fields. The new simulations were performed until the dendrite reached a stationary state. Then, we continuously restarted the simulations by increasing the size of
\[
H \text{ [\(\mu m\)]} \quad \lambda = \lambda_{\text{min}} \quad \lambda_{\text{min}} < \lambda < \lambda_{\text{max}} \quad \lambda = \lambda_{\text{max}}
\]

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Figure 4.15: Dendrite shapes of an Al-1.4wt% Cu alloy for different thickness \(H = 100\) (first row), 200 (second row), and 400 \(\mu m\) (third row) for the solidification conditions of \(V = 10 \mu m/s\) and \(G = 50\) K/cm. The microstructures illustrate the stationary dendrites as seen from the side and the top with minimum spacing (left column), maximum spacing (right column), and \(\lambda = 503\) \(\mu m\) (center column).

The \(y\) domain in steps of a discrete grid spacing \(\Delta x\) at a fixed \(L_z = H\) until the dendrite is unstable due to the sidebranching at maximum spacing \(\lambda_{\text{max}}\). We also reduced the spacing of a dendrite to \(\lambda \approx 200\) \(\mu m\) in order to test the stability with respect to cell eliminations. For the evaluation of stable spacing at a low \(\lambda\), we put two halves of stable dendrites facing each other. If the spacing is smaller than the minimum limit, i.e. \(\lambda < \lambda_{\text{min}}\), one of them is eliminated.

Fig. 4.15 illustrates selected stationary dendrites in a purely diffusive regime, for different values of the sample thickness \(H \text{ [\(\mu m\)]} = 100, 200,\) and 400. For each \(H\), the dendrites are shown for the lower and upper limits of the stable spacings, i.e. \(\lambda \approx \lambda_{\text{min}}\) (left column)
The tip undercooling \( \Delta \) in a dendritic growth regime is shown in Fig. 4.16a. This figure illustrates stable spacing ranges (solid lines with square dots) and unstable regimes (dashed lines) due to cell eliminations for \( H = 52, 100, 200, 300, \) and 400 \( \mu \text{m} \). One noticeable
observation here is that the dendrite tip for a higher value of $H$ is located near the liquidus temperature, which yields a smaller $\Delta$, compared to that obtained for a lower value of $H$. Dendrites at a higher $H$ have a bigger tip radius along the $z$ axis (see Fig. 4.15), and this bigger radius could lead to a smaller $\Delta$.

The upper ($\lambda_{\text{max}}$) and lower spacing ($\lambda_{\text{min}}$) before spacing limits are related to $H$. The solid lines with square dots in Fig. 4.16a correspond to the stable spacing ranges. The black error bars in Fig. 4.16b also indicate the stable spacing ranges within $\lambda_{\text{min}}$ and $\lambda_{\text{max}}$ for different $H$. These simulations show that both $\lambda_{\text{min}}$ and $\lambda_{\text{max}}$ decrease as $H$ increases. In addition, the ranges $\lambda_{\text{max}} - \lambda_{\text{min}}$ also show an approximately linear decrease. These relations are different from those of the cellular growth regime. In the cellular growth regime, $\lambda_{\text{min}}$ is independent of $H$, and $\lambda_{\text{max}}$ including the range $\lambda_{\text{max}} - \lambda_{\text{min}}$ decreases with an increase in $H$, as discussed in the previous section.

**Selected spacings in an extended array**

We also studied the naturally selected spacings in a dendritic growth regime. We used the same alloy and solidification process parameters to carry out PF simulations with an extended system $L_y \approx 2$ mm for different values of $H$. In the simulations, the microstructures select spacings after the initial coarsening dynamics in a purely diffusive regime.

Fig. 4.16b shows the dynamically selected average spacings $\Lambda$ (green circles) within the spatially extended array. The microstructures form a one-row array in most simulations except for the highest value of $H$. At this $H = 400$ $\mu$m, we observed a heterogeneous microstructure with one-row and two-row dendrite arrays, which was still evolving towards a one-row structure after 20 minutes. However, as discussed in Ref. [31], the average spacing in the one-row growth region for the highest $H$ can represent the final steady state spacings, which are plotted in Fig. 4.16b.

The selected microstructures show dendrite shape transition from flat dendrites at the smallest $H = 52$ $\mu$m to four-fold symmetric tips at the larger $H$. In the meantime, the total
number of primary dendrites only changes by one, namely from five at $H = 50 \ \mu m$ to six at $H = 300 \ \mu m$. Hence, the variation of the selected spacings is small, as illustrated by the green shaded vertical region that spans $350 \pm 45 \ \mu m$. The variation was mostly caused by the quantization effect due to the limited total number of spacings in the spatially extended simulations.

The selected spacings, including the variation, are within the stability limits between $\lambda_{min}$ and $\lambda_{max}$ (black error bars). Interestingly, the dynamically selected spacings are always within the variation region $\Lambda = 350 \pm 45 \ \mu m$, and $\Lambda$ selection looks independent of $H$. This is different from the selection mechanisms in the cellular growth regime, in which the selected $\Lambda$ decreases linearly as $H$ increases. The dendrites do not show an additional dynamics, such as an oscillatory dynamics in the cellular growth regime, that leads to an increase of the primary spacing. Thus, the primary spacing selection in the dendritic growth regime is only history-dependent, and the selected primary spacings are close to the lower limit of the stability range as observed in the previous simulations [149, 147]. In addition, the sample size $L_y$ could be related to the spacing selection in a dendritic growth regime because maximum six dendrites were present in the simulations with an Al-1.4wt% Cu alloy.

### 4.2.4 Summary

In this section, we have investigated microstructure selection mechanisms under the influence of sample thickness. We performed phase-field simulations to examine the influence of spatial confinement.

Before directly looking at the microstructure selection under the influence of a sample thickness $H$, we observed the initial recoil dynamics of a planar interface when $G = 13.3 \ \text{K/cm}$ and $V = 1 \ \mu m/s$. This is because different initial planar interface dynamics could lead to different microstructures at a steady state [116, 171]. The initial recoil dynamics of the simulations agree well with the experimental measurements, and $H$ does not affect the initial dynamics.
We observed that the average spacing $\Lambda$ depends on the sample thickness $H$, as previously observed $^{[137]}$. In the simulations, the selected $\Lambda$ in an extended system decreased linearly as $H$ increased. One of the reasons for this increase in the selected $\Lambda$ is the oscillation dynamics, which leads to cell elimination. If a cell is eliminated during oscillation, its neighbors take up that space. They sometimes formed multiplets that were more stable than a symmetric cell. The formation of multiplets results in a bigger average spacing in a thin sample.

We also explored stable spacing ranges for three different values of $H \, [\mu m] = 100$, 150, and 200. The maximum stable spacing increases as $H$ increases, while the minimum stable spacing $\lambda_{\text{min}}$ is independent of $H$. The similar $\lambda_{\text{min}}$ indicates that the direct solutal interactions between cells strongly affect the $\lambda_{\text{min}}$ decision.

One interesting observation in the stability ranges is that, for each $H$, the cells change from symmetric cells to doublets, or from doublets to quadruplets as $\lambda$ increases. The shape conversion from a symmetric cell (doublet) to a doublet (quadruplet) occurred approximately at similar spacings. We assume that this is due to the symmetry of a cell. The symmetry on one side is broken when the spacing in a cell is larger than the spacing limit, i.e. $\lambda > \lambda_l$ (or its sample thickness $H > \lambda_l$), and the cell attains the form of a doublet (when $\lambda$ or $H > \lambda_l$) or a quadruplet (when both $\lambda$ and $H > \lambda_l$). In the solidification conditions that we considered, the limit was $\lambda_l \simeq 170 \, \mu m$.

Some cells oscillate with their neighbors during their growth. We observed that when $100 < H \, [\mu m] < 175$, the oscillation period $\tau_d$ decreases as $H$ increases (or $\lambda$ decreases). In the simulations, $\tau_d$ was stabilized when $H \geq 175 \, \mu m$. The stabilized period $\tau_d \simeq 30 \text{ min}$ is similar to the period measured in the 3D studies $^{[12]}$ $^{[148]}$ $^{[124]}$. On the other hand, at a small $H$, the cell oscillation leads to tip splitting or elimination, and therefore, for $H = 125 \, \mu m$, the period is smaller than $\tau_d$.

For the dendritic growth regime, we performed simulations with a dilute Al-Cu alloy to explore the microstructure selection mechanisms in thin-sample experiments. The PF simulations show that the selected spacings are not strongly related to the sample thickness
$H$, while the stability limits, i.e. $\lambda_{\text{max}}$ and $\lambda_{\text{min}}$, and the range $\lambda_{\text{max}} - \lambda_{\text{min}}$ decrease as $H$ increases. The dendrites form under a relatively short diffusion length due to a higher $V$; therefore, naturally selected spacings are less affected by $H$.

4.3 Influence of convection

This section (including Sec. 2.2.3) contains material that has been published in Ref. [31]. I contributed as a co-author in this article, and have used some material from Ref. [31] with the permission from the publisher, as shown in Fig. C.2. The results in this section reflect my contributions to this work, and all the experimental measurements referenced in this section was performed by my collaborators, to whom appropriate credit is given.

4.3.1 Background

The strong gravity on earth affects heat and mass transport in liquid alloys, and accordingly leads to heterogeneous microstructures [163, 114, 33, 121, 77, 135, 58]. Especially, convective currents are known to play an important role in selecting the microstructure of aluminum-copper (Al-Cu) alloys [114, 60, 41, 159, 140], even in a thin-sample geometry [20, 19, 122].

In this section, we investigate the primary spacing selection mechanisms in thin-sample directional solidification under convective currents. For the investigation, we modified the PF model with a diffusion boundary-layer approximation [54, 55]. The simulation results were compared to the synchrotron X-ray in situ observations from dilute Al-Cu alloy solidification [31]. In addition, we studied the selected primary tip radii in a thin-sample geometry.
4.3.2 Method

In the solidification experiments, an Al-0.6at.% Cu alloy (i.e. 1.4wt% Cu) was solidified at a constant pulling velocity $V$ and an imposed temperature gradient $G$ within a sample size $L_w \times H \approx 10 \text{ mm} \times 200 \mu\text{m}$. The $G$ and $V$ ranges explored in the experiments were $50 \lesssim G \,[\text{K/cm}] \lesssim 85$ and $1 \lesssim V \,[\text{K/cm}] \lesssim 65$, respectively, as illustrated in Fig. 4.19. The other parameters of this alloy are summarized in Appendix B and the detailed experimental procedures are described in Ref. [31].

We selected a dilute alloy (Al-1.4wt% Cu, i.e. Al-0.6at.% Cu) for the reasonable comparison between X-ray images and quantitative 3D PF calculations. The X-ray imaging contrast is directly related to the local density of the solute concentration density; therefore, we can obtain sharper images with a more concentrated Al-Cu alloy [30, 152]. However, it is challenging to model sharper dendritic microstructures of more concentrated alloys, because they need a small grid spacing to quantitatively describe the tip radius morphology. Moreover, in order to explore the morphological transitions between planar and cellular microstructures, using dilute alloys helps model the transitions easily.

We introduced the boundary layer (BL) thickness $\delta$ to produce the limited solute diffusion due to the convection effects, as explained in Sec. 2.2.3 in detail. We used different values of BL thickness ($\delta = 100, 150, 200, \text{ and } 400 \mu\text{m}$ including fully diffusive conditions that correspond to $\delta \rightarrow \infty$).

For an extended system, the sample size in PF simulations is typically set as $L_y \times H \approx 2 \text{ mm} \times 200 \mu\text{m}$. Then, the boundary conditions are symmetric along the $x$ boundaries, periodic along the $y$ boundaries, and symmetric including wetting conditions along the $z$ boundaries.

In terms of the processing parameters for numerical simulations of the Al-Cu alloy, we explored various pulling velocities from $V = 5$ to $50 \mu\text{m/s}$ at one temperature gradient $G = 50 \text{ K/cm}$. We set the finite grid spacing ratio $\Delta x/W = 1.2$ for different $V$. However,
as $V$ increased, the smaller diffuse interface width $W/d_0$ was used, which also yielded the smaller grid spacing $\Delta x$ and explicit time step $\Delta t$, as summarized in Table 4.2. We also set different positions for the most advanced primary tip $x_{\text{tip}}$, and the corresponding length of the dendrite $L_{\text{sol}}$ is listed in Table 4.2. For the fully diffusive regime (i.e. $\delta \to \infty$), we used $L_{\text{liq}}$, which is the length from the interface front to the end of the $x$ domain. These values are also listed in the table.

We observed that the slope $\partial \psi / \partial x$ in the liquid depends on $V$. Therefore, in order to determine the threshold $\psi^*$ for $\delta$, we performed a preliminary simulation with a quarter dendrite at $\delta \to \infty$. Using the slope of the simulation at a stationary state (see Fig. 2.2), we estimated $\psi^*$. Then, simulations with a finite $\delta$ were performed with the liquid length as $L_{\text{liq}} \approx \delta + 100 \ \mu m$.

### 4.3.3 Results and discussions

#### Overall microstructure selection

In the experiments and simulations, we observed transitions from planar to cellular and cellular to dendritic microstructures. The microstructures shown in Fig. 4.17 are X-ray radiographs obtained from the solidification experiments at various $V$, with $G = 50 \ \text{K/cm}$. In the images, the contrast corresponds to the solid-liquid interface that grows in an upward

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<td>1206</td>
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<td>20</td>
<td>229.7</td>
<td>2.56</td>
<td>$0.41 \times 10^{-3}$</td>
<td>600</td>
<td>1036</td>
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<tr>
<td>35</td>
<td>190.6</td>
<td>2.13</td>
<td>$0.28 \times 10^{-3}$</td>
<td>500</td>
<td>772</td>
</tr>
<tr>
<td>50</td>
<td>162.9</td>
<td>1.82</td>
<td>$0.21 \times 10^{-3}$</td>
<td>400</td>
<td>644</td>
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direction. At a smaller $V$ (the top image), the microstructures were stable with a planar interface. As $V$ increases (from top to bottom), the planar solid-liquid interface became unstable, and cellular and dendritic microstructures were formed.

The PF simulations were performed for a fixed $G = 50$ K/cm with different $V$ in the range of $5 \leq V \text{ [\mu m/s]} \leq 50$ and $\delta$ between $\delta = 100 \text{ \mu m}$ and $\delta \to \infty$. Some selected microstructures in a steady state are illustrated in Fig. 4.18. Since we assumed that the strong convective currents lead to smaller value of $\delta$, the convective currents tend to be stronger as $\delta$ decreases (i.e. left to right in Fig. 4.18).

As shown in Fig. 4.18, the boundary layer (BL) thickness $\delta$ significantly affects microstructure selection. The transition of the selected microstructure occurs progressively in the vicinity of $\delta \approx D/V$ (thick light blue line). When $\delta < D/V$, the average spacing in the figure decreases as $\delta$ decreases. When the solute convective current is very strong (top right of
\[ \delta = 200 \, \mu m \quad \delta = 100 \, \mu m \]

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<th>( V [\mu m/s] )</th>
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<th>( \delta = 200 , \mu m )</th>
<th>( \delta = 100 , \mu m )</th>
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<td>50</td>
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Figure 4.18: Selected microstructures in the PF simulations within a sample width \( L_y \approx 2 \, mm \). The figure shows microstructure selection under the influence of three different boundary layer thicknesses, i.e. full diffusion \((\delta \to \infty\), left column\), \( \delta = 200 \) (center column), and \( 100 \, \mu m \) (right column) at various \( V \) (rows) for \( G = 50 \, K/cm \). The thick light blue line illustrates the boundary \( l_D \sim \delta \) between the diffusion length \( l_D = D/V \) and \( \delta \).

Fig. 4.18, the microstructure forms a two-row array of primary branches (red marks) rather than a one-row array of dendrites (blue marks).

For \( \delta = 100 \, \mu m \) and \( V = 15 \) or \( 50 \, \mu m/s \), we could observe that the microstructure forms one-row arrays in one region and two-row arrays in the other parts within a sample. However,
when we continued the simulations, the one-row array region slowly widened, as cells in the two-row array were eliminated [31]. Hence, the one-row array would be dominant after a considerable amount of time.

As illustrated in Fig 4.18, the microstructures appear to be strongly influenced by the BL thickness $\delta$, which is directly related to the solute convective currents in the liquid. In the following subsections, we compare the simulation results to the experimental measurements.

Morphological selection

In the experiments, we observed three different microstructures for different values of $G$ and $V$. As illustrated in Fig. 4.19 we observed planar (blue diamonds), cellular (green circles), and dendritic (red triangles) growth regimes at different values of $G$ and $V$. Hence, the colored lines in Fig. 4.19 approximately represent the two morphological transitions: (i) between planar and cellular growth (green solid line), and (ii) between cellular and dendritic growth (red dashed line). We considered primary branches as dendrites when secondary sidebranches grow from the primary stem.

One interesting observation here is that the planar-to-cellular transition (green solid line in Fig. 4.19) occurred at a higher $V$ than the expected $V_c$ (gray solid line), which was obtained from the classical approach using the constitutional undercooling criterion [146, 119]. In

Figure 4.19: Microstructural selection from the Al-Cu experiments. The thick gray line corresponds to the critical velocity for the morphological instability in a purely diffusive regime, i.e. Eq. (4.14). The symbols represent planar ($\diamond$), cellular ($\circ$), or dendritic ($\triangle$) microstructure. There were two interface growth directions that are from the bottom upward (open symbols) and from the top downward (full symbols). The green solid and red dashed lines show the approximate transient limits between different growth regimes in the bottom-up experiments.
front of the planar interface, the concentration field in the liquid is a one-dimensional (1D) profile. Thus, the solute concentration in the liquid is given by

$$c_l(x_i) = c_\infty \left( \frac{1}{k} - 1 \right) e^{-\frac{V}{D} x_i} + c_\infty ,$$  \hspace{0.5cm} (4.11)

where $x_i$ is the distance from the solid/liquid interface ($x_i = 0$), $c_\infty$ is the nominal composition of the alloy, $k$ is the partition coefficient, and $D$ is the solute diffusivity in the liquid. Then, the planar-to-cellular transition occurs when the liquid is constitutionally supercooled \[146, 119\], which is predicted by

$$\left. \frac{dc_l}{dx_i} \right|_{x_i=0} = \left. \frac{dT}{dx_i} \right|_{x_i=0} ,$$  \hspace{0.5cm} (4.12)

where $T$ is the temperature, or

$$c_\infty \left( \frac{1}{k} - 1 \right) \frac{V}{D} = \frac{G}{|m|} ,$$  \hspace{0.5cm} (4.13)

with $m < 0$ being the liquidus slope. Thus, the constitutional supercooling onset velocity $V_c$ is

$$V_c = \frac{GDk}{|m|c_\infty(1-k)} .$$  \hspace{0.5cm} (4.14)

Using this equation, the critical velocity for the alloy under consideration at $G = 50$ K/cm is $V_c \approx 0.465 \mu m/s$. However, the transition in the experiments at this $G$ happened at $V \approx 3.0 \mu m/s$. At the other $G$, we also observed that the planar-to-cellular transition shifted towards a higher $V$ from the $V_c$ estimated using Eq. (4.14). Accordingly, the velocities for the cell-to-dendrite transitions (red dashed line in Fig. 4.19) were observed to be approximately four times higher than that for $V$ of the planar-to-cellular transitions in the experiments.

We expect that the convective solute current in the liquid could lead to a shift in the planar-to-cellular transition, as pointed out in earlier studies \[60, 20, 19, 122\]. Thus, the liquid convection could lead to a higher $V_c$ in the experimental observations. In addition, the
experimental results for different growth directions of the interface are another evidence for the existence of convective currents. As the copper solute is heavier than the average liquid, the top to downward direction for solidification leads to stronger convection \[108\,58\,20\,19\]. In consequence, experiments with top to downward solidification direction reveal that the planar-to-cellular transition occurs at a higher \( V \) than in the down to upward solidification direction under similar solidification conditions. Indeed, the transitions in our experiments were further shifted towards the higher velocity with the top to downward direction (full dots in Fig. 4.19).

Using our assumption on \( \delta \), we could reevaluate the solute concentration in the liquid \( c_l(x_i) \) and the critical velocity for the planar-to-cellular transition \( V_c \). When we introduce a \( \delta \) ahead of the interface, the impurities in the liquid only diffuse within this boundary layer, i.e. \( x_i < \delta \). However, we assumed that the liquid has been well-mixed at the nominal composition \( c_\infty \) at \( x_i \geq \delta \) due to convection. Then, the solute diffusion in the liquid is given by

\[
c_l(x_i) = Ae^{-\frac{V}{D}x_i} + B ,
\]

where \( A \) and \( B \) are constants. In our assumption, the boundary conditions for \( c_l(x_i) \) are \( c_l(x_i = 0) = c^0_l \) at the interface and \( c_l(x_i = \delta) = c_\infty \) at the end of the BL. In addition, the solute mass conservation gives

\[
V(1-k)c^0_l = -D \frac{\partial c}{\partial x_i} \bigg|_{x_i=0} \quad (4.16)
\]

at the interface \( x_i = 0 \). Using Eqns. (4.15) and (4.16), we estimate \( A \) as

\[
A = c^0_l(1-k) .
\]

(4.17)
We use the condition $c_l(x_i = \delta) = c_\infty$ to identify $B$ as

$$c_l(x_i = \delta) = c_\infty = c_l^0(1 - k)e^{-\delta/l_D} + B,$$

$$B = c_\infty - c_l^0(1 - k)e^{-\delta/l_D},$$

where $l_D = D/V$ is the diffusion length. Then, using Eq. (4.15) at the interface ($x_i = 0$) yields

$$c_l(x_i = 0) = c_l^0 = A + B,$$

$$= c_l^0(1 - k) + c_\infty - c_l^0(1 - k)e^{-\delta/l_D},$$

The relation between $c_l^0$ and $c_\infty$ is

$$c_l^0(k + (1 - k)e^{-\delta/l_D}) = c_\infty,$$

$$c_l^0 = \frac{c_\infty}{k + (1 - k)e^{-\delta/l_D}}.$$

Finally, the solute diffusion equation with a boundary layer thickness is given by

$$c_l(x_i) = c_l^0(1 - k)e^{-x_i/l_D} + c_\infty - c_l^0(1 - k)e^{-\delta/l_D}$$

$$= \frac{c_\infty(1 - k)}{k + (1 - k)e^{-\delta/l_D}}e^{-x_i/l_D} + c_\infty - \frac{c_\infty(1 - k)}{k + (1 - k)e^{-\delta/l_D}}e^{-\delta/l_D}.$$

This equation reduces to Eq. (4.11) in a purely diffusive regime, i.e. $\delta \to \infty$.

We also calculated the constitutional supercooling onset velocity using Eq. (4.25). From the relation Eq. (4.12),

$$\frac{dc_l}{dx_i}|_{x_i=0} = \frac{dc_l}{dT}|_{x_i=0} ,$$

$$= \frac{c_\infty(1 - k)}{k + (1 - k)e^{-\delta/l_D}} \frac{V}{D} = \frac{G}{m},$$

where $G = m$. 

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which yields,

\[ V_c = -\frac{DG}{mc_\infty (\frac{1}{k} - 1)} \left( 1 + \frac{1}{k} e^{-\frac{V_c}{D} \delta} \right) . \]

(4.27)

We can reformulate this equation as

\[ \delta = -\frac{D}{V_c} \ln \left( \frac{k}{k - 1} - \frac{mc_\infty}{DG V_c} \right) . \]

(4.28)

For a purely diffusive regime \( \delta \to \infty \), the modified \( V_c \) with \( \delta \) becomes the classical expression in Eq. (4.14). Additionally, this modified relation indicates that a lower \( \delta \) from a stronger convection leads to a higher \( V_c \). Thus, the planar-to-cellular transition occurs at a higher \( V \) under a strong convection, as we expected.

In order to validate our \( \delta(V_c) \) relation given by Eq. (4.28), we compared the PF simulations with different \( \delta \) to the prediction of \( \delta(V_c) \). The PF simulations used symmetric boundary conditions in all directions, and their domain sizes are \( L_y = L_z = 200 \) \( \mu \)m along the \( y \) and \( z \) axes. We initially imposed a small random perturbation on the solid-liquid interface. Then, the interface moved away from the liquidus temperature. Since the planar interface can be destabilized slowly, the simulations were performed for a long time \( 50000 \) s. We measured the gap between the maximum and minimum interface positions along the growth \( x \) axis \( \Delta x_i = x_{\text{tip}} - x_{\text{groove}} \) during the simulations with different \( \delta \). The gap tends to \( \Delta x_i = 0 \) at \( t \to \infty \) when the planar interface is stable; otherwise, \( \Delta x_i \) has a non-zero value.

Using Eq. (4.27) at \( G = 50 \) K/cm, we calculated \( V_c = 3.14, 2.99, 2.86, 2.74, 2.54, \) and \( 2.39 \) \( \mu \)m/s for \( \delta = 50, 100, 150, 200, 300, \) and \( 400 \) \( \mu \)m, respectively. Then, we carried out PF simulations with different \( V = V_c \pm 0.05 \) \( \mu \)m/s as in Fig. 4.20 to test the stability of the planar interface front.

In Fig. 4.20, the red line illustrates the analytical prediction of the planar-to-cellular transition \( V_c \) in Eq. (4.27). The PF simulation results agree well with this law; therefore, the planar interface is stable for \( V < V_c(\delta) \) (up triangles) and unstable for \( V > V_c(\delta) \) (down triangles).
In addition, we could estimate the strength of convection in the experiments with these results. The experimental observations show that the transition occurs at $V_c \approx 3 \mu m/s$ (green dashed line in Fig. 4.20). This observed value is close to the onset velocity at $\delta \approx 100 \mu m$. Therefore, we conclude that strong convective currents existed during the experiments.

**Selection of primary spacing**

We measured the spacings from the experiments, as shown in Fig. 4.21. This figure shows the average spacing (symbols) with the measured minimum ($\Lambda_{low}$) and maximum ($\Lambda_{high}$) spacings (error bars). We did not show the experiments for $V < 5 \mu m/s$, because the measurements showed a large deviation near the planar-to-cellular transition.

Interestingly, the larger $V$ leads to larger spacings, as shown in Fig. 4.21a. In the classical approaches, the primary spacing decreases with a power law of $V$, i.e. $\Lambda \sim V^\alpha$, and the typical ratio is $\alpha = -0.25$ in a dendritic growth regime. However, the ratio in our measurements was close to $\alpha \geq 0.5$ for all values of $G$ that were considered, as shown by the $\Lambda \sim V^{1/2}$ guide line in Fig. 4.21.

We carried out PF simulations using a spatially extended system with $L_y \approx 2 mm$ and $H = 200 \mu m$ under the influence of BL thicknesses: $\delta = 100, 150, 200, 400 \mu m$, and $\infty$. We used symmetric (no-flux) $x$ boundaries, periodic $y$ boundaries, and symmetric $z$ boundaries.
Figure 4.21: Average primary spacings in experiments (a) and simulations (b). (a) shows the average spacings (symbols) including the minimum and maximum spacings (error bars) for the experiments at different $G$. The dots in (b) correspond to the measured average spacings in the simulations with $G = 50$ K/cm at different $\delta$. Simulations usually show one-row arrays (hollow dots); however, microstructures sometimes form two-row arrays (filled dots). The shaded areas in (b) represent the measured spacing ranges between $\Lambda_{\text{low}}$ and $\Lambda_{\text{high}}$ in an extended array system. The gray dotted lines in both plots are the guide lines for $\Lambda \sim V^a$, where $a = 1/2$ in (a) and $-1/2$ in (b).

After the simulations started, the planar interface initially located at the liquidus temperature moved towards the colder zone.

The average spacing (dots) within the selected spacing ranges of the minimum $\Lambda_{\text{low}}$ and maximum $\Lambda_{\text{high}}$ (shaded regions) are shown in Fig. 4.21b. In the simulations, most of the microstructures reached a stationary state with narrow spacing ranges.

The stronger convection ($\delta = 100 \, \mu m$) at lower velocities leads to a lower spacing because the reduced $\delta$ from convection prevents diffusive interactions between dendrites. As a result, the microstructures for $\delta = 100 \, \mu m$ at $V \leq 10 \, \mu m/s$ form stable two-row array microstructures (filled dots in Fig. 4.21b). As $V$ increases, the diffusion length $l_D = D/V$ is comparable to $\delta = 100 \, \mu m$, which yields a mixed inhomogeneous microstructure. The simulations at higher velocities, i.e. $V = 15$ or $50 \, \mu m/s$, show a mixed inhomogeneous microstructure with one-row (hollow dots) and two-row (filled dots) growth regions. As illustrated in Fig. 4.21b, the spacings in the two regions are different. We expect that the microstructures would
finally select a spacing in the one-row region at very long time \([31]\).

As \(\delta\) increases and \(V\) increases (i.e. less influence of convection), the selected spacing approaches that of \(\delta \to \infty\) simulations. Hence, in the fully diffusive growth regime, \(\Lambda\) follows \(\Lambda \sim V^{-1/2}\) (gray dotted line in Fig. 4.2b).

In our observations, the power law \(a\) for the spacing selection \(\Lambda \sim V^{a}\) is positive under the influence of convection, and becomes negative as \(\delta \to \infty\). The transition from \(a > 0\) to \(a < 0\) occurs at \(l_D \approx \delta\). The selected \(\Lambda\) at different \(\delta\) shows the maximum value near the transition region. Interestingly, the transient \(V\) at different \(\delta\) in our simulations is close to the cell-to-dendrite transition at \(V \approx V_c(1 + k)/k\) in the classical theory \([114, 60]\). The values, for example, are \(V_c(1 + k)/k \approx 19, 22,\) and \(24\) \(\mu m/s\) respectively for \(\delta = 400, 200,\) and \(100\) \(\mu m\), using Eq \((4.28)\) for \(V_c(\delta)\).

With \(\delta = 100\) and \(150\) \(\mu m\), the experimental measurements (black crosses in Fig. 4.21b) are in between those of the simulations. Including the previous comparison for the onset velocity, the best agreements between the experiments and simulations are for \(\delta \sim 100\) \(\mu m\). These results indicate that strong liquid convection occurred during solidification in the Al-Cu alloy experiments.

Even though there are some quantitative differences between the experimental and simulation results due to inaccurate knowledge of the alloy parameters or the limited image contrast in the experiments, the simulation results indicate that, in the experiments, the alloy solidified under strong convection. Therefore, the selected spacings increase as \(V\) increases.

**Stable spacing ranges with a boundary layer thickness**

We also examined the stability spacing ranges for different BL thickness \(\delta = 100, 150, 200\) \(\mu m\), and for the full diffusive case, i.e. \(\delta \to \infty\). The imposed boundary conditions were symmetric along the \(x\) and \(y\) boundaries. For the \(z\) boundaries, we used the symmetric (along with the wetting) conditions as in the spatially extended simulations. For the calculations,
(a) Minimum limits

\[ \Lambda_{\text{min}} \text{ [\(\mu\text{m}\)]} = 100 \quad 150 \quad 200 \quad \infty \]

\[ \text{Velocity [\(\mu\text{m}/s\)]} \]

Experiments

\[ \Lambda \sim V^{-1/2} \]

Figure 4.22: Minimum \( \Lambda_{\text{min}} \) (a) and maximum \( \Lambda_{\text{max}} \) (a) spacing limits for stability ranges as a function of \( V \) for \( G = 50 \text{ K/cm} \). We considered different \( \delta \text{ [\(\mu\text{m}\)]} = 100 \) (red), 150 (orange), 200 (green), and \( \infty \) (blue). The results were compared to the experimental measurements (×). The \( \Lambda \sim V^{-1/2} \) guide lines (gray lines) were fit to \( \Lambda_{\text{min}} \) and \( \Lambda_{\text{max}} \) with \( \delta \to \infty \).

In Fig. 4.22, the measured lower \( \Lambda_{\text{min}} \) (a) and higher \( \Lambda_{\text{max}} \) (b) spacing limits are plotted.

Figure 4.22: Minimum \( \Lambda_{\text{min}} \) (a) and maximum \( \Lambda_{\text{max}} \) (a) spacing limits for stability ranges as a function of \( V \) for \( G = 50 \text{ K/cm} \). We considered different \( \delta \text{ [\(\mu\text{m}\)]} = 100 \) (red), 150 (orange), 200 (green), and \( \infty \) (blue). The results were compared to the experimental measurements (×). The \( \Lambda \sim V^{-1/2} \) guide lines (gray lines) were fit to \( \Lambda_{\text{min}} \) and \( \Lambda_{\text{max}} \) with \( \delta \to \infty \).

From one-half of a stable primary branch, we used bilinearly interpolated fields of \( U \) and \( \psi \) as the initial fields for the next simulations with larger or smaller domain size along the \( y \) domain. Then, at the upper limit \( \Lambda_{\text{max}} \), the primary branch becomes unstable due to sidebranching. We used a dendrite on a stable primary branch having a small spacing to test cell elimination. We performed simulations with the initial fields for two halves of a cell facing each other, using a stable cell with a small \( \Lambda \), to examine the spacing stability with respect to cell elimination for the lower limit of spacing stability \( \Lambda_{\text{min}} \).

The simulations with one-half cell were carried out until \( t = 1500, 600, 400, 400, \) and 180 s, respectively for \( V = 5, 10, 15, 20, \) and 50 \( \mu\text{m}/s \). For the cell elimination tests with two halves of a cell facing each other, we used a longer simulation time up to \( t = 12000 \) s for \( V = 5 \mu\text{m}/s \), since the elimination can occur very slowly.

In Fig. 4.22, the measured lower \( \Lambda_{\text{min}} \) (a) and higher \( \Lambda_{\text{max}} \) (b) spacing limits are plotted
as a function of $V$ for different $\delta$. The experimental measurements ($\times$) are also shown in the figure.

The spacing limits $\Lambda_{\text{min}}$ and $\Lambda_{\text{max}}$ change in a similar manner, as in the spatially extended simulations (see Fig. 4.22). For a fixed $V$, both the limits in Fig. 4.22 increase as $\delta$ increases. At a fixed $\delta$, the limits exhibit an increase with $V$ at a lower $V$; however, they approach the $\Lambda \sim V^{-1/2}$ (gray lines in Fig. 4.22) at a higher $V$ as $\delta \to \infty$. This power law agrees well with the limits from simulations in a fully diffusive regime as in the simulations with an extended domain.

For the simulations with strong convection at $V < 10 \mu m/s$ for $\delta = 100 \mu m$, a cell is not stable with a one-row array. However, the experimental measurements at $G = 50 \text{ K/cm}$ are mostly within the stability ranges for simulations at $V \geq 10 \mu m/s$ for $\delta = 100 \mu m$ or $150 \mu m$. These results also emphasize that the influence of convective currents on the microstructure selection in the experiments is not negligible.

**Primary tip radius**

In previous studies, it was observed that the tip selection parameter $\sigma \sim 1/(\rho^2V)$ is a constant for an alloy [21, 79, 100, 78, 106, 110, 111, 101]. Therefore, we expect that our experiments and simulations could show a similar relation $\rho \sim V^{-1/2}$, even if convective currents in the liquid affect the microstructure selection.

Using *in situ* X-ray images, we measured the radii of the primary tip (symbols in Fig. 4.23) including their distribution ranges (error bars). We assumed that this wide distribution is caused by the contrast in the images and the convection effects. We could identify the interface shapes in the X-ray images; however, the contrast of the images is not enough to assess the precise solid-liquid interface positions as seen in Fig. 4.17. In addition, due to the convection effects, it is also difficult to measure the primary tip radii of inhomogeneous microstructures.

Interestingly, the average primary tip radii follow the classical power law $\rho \sim V^{-1/2}$ despite
the large distributions of radii. In Fig. 4.23, the measured radii at $G = 50$ and $65$ K/cm show reasonable agreements with the power law from solvability theory (gray line) [94, 95, 6, 9].

We also measured the primary dendrite tip radii in the PF simulations for $G = 50$ K/cm [31]. For the measurements, we used the cross-sections of the solid-liquid interface at the planes $y = y_{\text{tip}}$ and $z = z_{\text{tip}}$ for each tip. We fit the interface shape to a parabola, i.e. $x = x_{\text{tip}} - (y - y_{\text{tip}})^2/(2\rho_y)$ within the $z = z_{\text{tip}}$ plane and $x = x_{\text{tip}} - (z - z_{\text{tip}})^2/(2\rho_z)$ within the $y = y_{\text{tip}}$ plane. The distance from the primary tip might affect the fitted tip radii; therefore, we used a distance of one radius behind the tip location, as used in the experimental measurements. We searched for different distance ranges to fit the radius, and selected the one where the fitting distance was closest to the fitted radius. Then, we obtained $\rho_y$ and $\rho_z$ for each primary tip, and calculated the mean radius $\rho$ using $1/\rho = (1/\rho_y + 1/\rho_z)/2$ in the extended array system (symbols in Fig. 4.23b).

The simulation results in Fig. 4.23b also follow the classical theory [21] as in the experiments. We only show the average $\rho$ in the figure because the distribution of $\rho$ is narrow. The mean radii in the one-row growth regime (open symbols) were independent of the influence

![Figure 4.23: Average primary tip radius (symbols) and its distribution ranges (error bars). In both experiments under different $G$ (a) and simulations with different $\delta$ (b), primary tip radii agree with the power law decrease $\rho \sim V^{-1/2}$ (gray dotted line). The cross symbols in (b) represent the experimental measurements for $G = 50$ K/cm.](image-url)
of convection, and the radii decreased with $V$ as $\rho \sim V^{-1/2}$ (gray dotted line). In addition, the selected radii in the simulations are close to the experimental measurements (cross dots).

In the two-row growth regime, under strong convection ($\delta = 100 \, \mu\text{m}$) at a low $V$, the dendrite tip radii (full symbols) also follow the power law. The smaller tip radii in the two-row growth regime agree with the results of experiments; therefore, the experimental microstructures could form two rows of dendrites at a low velocity.

The simulation results in Fig. 4.23b indicate that the curvature-induced diffusive fluxes around the primary dendrite tip influence the tip radius selection rather than the solutal diffusive interactions. The solutal diffusive interactions are affected by the boundary layer thickness $\delta$ that is related to the convective currents. Thus, when $\delta$ is comparable to (or smaller than) the diffusion length $D/V$, the microstructure selects a smaller spacing than in the purely diffusive regime. On the other hand, $\delta$ is always larger than $\rho$; therefore, the convection effects on the tip radius could be small.

### 4.3.4 Summary

In this section, we have investigated the microstructure selection mechanisms under the influence of the convection effect. In order to introduce the influence of liquid convection, we suggested a simple model with a one-dimensional diffusive boundary layer (BL) model. This model assumes that diffusive transport is limited inside a finite boundary layer of thickness $\delta$ ahead of the interface, and that the liquid is well-mixed with a nominal composition outside of the boundary layer.

We analytically described that the convection effects shift the critical velocity $V_c$ for morphological instability of a planar interface towards a higher velocity than that obtained from the constitutional undercooling criterion [146, 119]. Relatively, the cellular-dendritic transition also occurs at higher velocities. The PF simulations modified with $\delta$ validate this analytical prediction. In the experiments with Al-Cu alloy, the planar-cellular transitions occurred at $V_c \approx 3 \, \mu\text{m/s}$ for $G = 50 \, \text{K/cm}$, which is larger than $V_c \approx 0.465 \, \mu\text{m/s}$ from
the classical prediction for a purely diffusive regime. This indicated that the liquid solidified under strong convective currents during the experiments.

We observed that, due to the convection effects, the relation between $\Lambda$ and $V$ in the experiment is positive ($\partial \Lambda / \partial V > 0$), which is opposite to the relation ($\partial \Lambda / \partial V < 0$) obtained from the classical theory for diffusive regime \[91, 72\]. In PF simulations, convection lowers the stable spacing limits and selected spacings at low velocities. This could be because the convection limits the diffusive interactions between dendrites when $l_D > \delta$. Thus, at a higher velocity (linked to a smaller diffusive length), the convection weakly affects the microstructure selection.

In both the experiments and simulations with liquid convection, the measured average primary tip radius follows the classical relation $\rho \sim V^{-1/2}$ from microscopic solvability theory \[79, 100, 78, 106, 101, 110, 111\]. We assume that since the tip radius is selected at a smaller scale $\rho < \delta$, the convection effects on the radius selection is weak.

In summary, the comparison of phase-field simulations and experiments demonstrates that convection strongly influences the selection of the primary spacing. Importantly, this conclusion is independent of the diffusive boundary-layer approximation used to model convection since the phase-field simulations show a decrease of spacing with increasing velocity in a purely diffusive regime, while the experiments show an initial increase of spacing with increasing velocity. The boundary-layer approximation only provides an approximate treatment of convection. While this approximation suffices to reproduce the increase of spacing with velocity, a more quantitative model of convection remains to be developed.

### 4.4 Grain growth competition

This section contains material that has been published in Ref. \[154\]. I contributed as a co-author in this article, and have used some material from Ref. \[154\] with the permission
from the publisher, as shown in Fig. C.1. The results in this section reflect my contribution to this work.

4.4.1 Background

The dynamics of a grain boundary (GB) between dendritic grains that are misoriented with respect to the temperature gradient determines the grain texture [49, 48, 40, 166, 174]. In the early description by Walton and Chalmers [167], the grain that has the highest misorientation with respect to the temperature gradient, referred to as the misoriented grain or unfavorably-oriented grain, is always eliminated due to its undercooling of the grain

![Phase-field simulation of the grain competition in a thin-sample geometry of a SCN-0.4wt% acetone alloy at $G = 30$ K/cm and $V = 25$ $\mu$m/s. The figure shows the competition between well-oriented blue grain with $\alpha = \beta = 0^\circ$ and the red grain misoriented with $(\alpha, \beta) = (-30^\circ, 45^\circ)$. The competition leads to the formation of divergent and convergent GBs (green lines) at an angle ($\Theta_C$ for the convergent GB and $\Theta_D$ for the divergent GB) with respect to the temperature gradient, which is parallel to the $x$ axis in the figure.]

Figure 4.24: Phase-field simulation of the grain competition in a thin-sample geometry of a SCN-0.4wt% acetone alloy at $G = 30$ K/cm and $V = 25$ $\mu$m/s. The figure shows the competition between well-oriented blue grain with $\alpha = \beta = 0^\circ$ and the red grain misoriented with $(\alpha, \beta) = (-30^\circ, 45^\circ)$. The competition leads to the formation of divergent and convergent GBs (green lines) at an angle ($\Theta_C$ for the convergent GB and $\Theta_D$ for the divergent GB) with respect to the temperature gradient, which is parallel to the $x$ axis in the figure.
being lower than that of favorably-oriented dendrites. However, recent experimental observations \[40, 166, 174\] and numerical studies \[97, 150, 142\] show that the favorably-oriented dendrites can be eliminated at the convergent GB.

Recently, a number of computational studies have investigated the mechanisms of polycrystalline grain growth competition \[97, 142, 150, 154, 141, 45, 46, 44, 63\]. Many PF simulations use 2D arrays \[97, 150, 154, 63\] to investigate the GB orientation selection in a thin-sample geometry, however the 2D simulations have limitations in that they do not model realistic 3D microstructures. The significant difference between solute redistribution profile in 2D and 3D thus typically leads to much larger macrostructural features, such as spacings, in 2D. For the two competing 3D dendritic arrays, we also need to consider additional degrees of freedom for the 3D orientations of the two grains with respect to the temperature gradient. Sidebranches of 2D dendrites always grow directly towards the neighboring dendrites. Their growth directions could be variable as shown in Fig. 2.5 of Sec. 2.2.6. The sidebranching dynamics at the GBs could be influential in determining the GB orientation \(\Theta_C\) for the convergent GB and \(\Theta_D\) for the divergent GB. As illustrated in Fig. 4.24, the red misoriented dendrites could be eliminated by the blue well-oriented dendrites when the sidebranches of the red dendrites grow towards the sample wall due to the 3D orientation for the crystal. This 3D sidebranching dynamics could lead to a larger \(\Theta_D\), or perhaps a larger \(\Theta_C\) as well, than the 2D simulation results \[150, 154\].

In this section, we explore the grain growth dynamics in a thin-sample geometry with the 3D PF model. In the 3D, one crystalline angle \(\alpha\) is oriented with respect to the direction of the temperature gradient as illustrated in Fig. 4.25. The other \(\beta\) angle of the crystal orientation is related to the orientation of the orthogonal planes containing secondary branches. Thus, using the angle configurations of \(\alpha\) and \(\beta\), we try to find (i) whether 2D simulations are capable of representing 3D simulations at \(\beta = 0^\circ\), and (ii) whether the \(\beta\) angles for the growth direction of a sidebranch affects the grain growth competition. 3D PF calculations take a longer time than 2D simulations; therefore, we perform 3D simulations to explore
only some grain orientations that are inherently 3D.

4.4.2 Method

For the 3D simulations, we used a succinonitrile (SCN)-0.4wt% acetone (ace) alloy at a fixed temperature gradient $G = 30 \text{ K/cm}$ and a pulling velocity $V = 25 \mu\text{m/s}$. The results were compared to the 2D simulations $^{150, 154}$. The detailed material parameters are provided in Ref. $^{150, 154}$ and in Appendix B.

The simulations were performed with a thin-sample geometry $L_x \times L_y = 1002 \times 1515 \mu\text{m}^2$, where $L_x$ ($L_y$) is the domain size along the $x$ ($y$) direction, within a sample thickness $L_z = H = 120 \mu\text{m}$ over 640 s. We used symmetric conditions for the $x$ boundaries, periodic conditions for the $y$ boundaries, and symmetric (including wetting conditions with the ratio $r_w = 1$ $^{57}$) for the $z$ boundaries to investigate the grain growth competition in a thin sample. We added a random noise with an amplitude $F_\psi = 0.01$ to the $\psi$ field for thermal fluctuations $^{150, 86, 57}$. For the 3D simulations, we used same diffuse interface width $W = 169.3d_0$ with a finite grid spacing $\Delta x = 1.4W \approx 1.4 \mu\text{m}$. Accordingly, the Euler explicit time step was $\Delta t = 0.9\Delta x^2/(6D) \approx 0.00023$ s.

The simulations start with a planar front of two grains that have different crystal angles, i.e. $\alpha$ and $\beta$ as illustrated in Fig. 4.25 (see Fig. 2.4 and Fig. 2.5 for further details). We use $A$ and $B$ to distinguish the two grains. The fraction along the $y$ direction between the two grains is usually selected as 25 to 75% for one grain. In the simulations, the planar front is destabilized approximately when the front advanced by 600 $\mu\text{m}$. At the early stage of the dendritic growth (i.e. immediately after the morphological instability), a misoriented grain could be eliminated relatively fast by the other grain. In order to prevent this early elimination, we enforce no-flux boundary conditions between the two grains until the microstructure front advanced by 1.8 mm. This length of 1.8 mm is long enough for the microstructures to reach a stationary undercooling with the imposed fraction between the grains $^{154}$.

In the following sections, we use the GB angle $\Theta$ between grains $A$ (red) and $B$ (blue), as
illustrated in Fig. 4.25. This angle Θ can represent both the convergent and divergent grain boundary angles. We used the counterclockwise direction with respect to the +x direction in the (x, y) plane as the positive direction. Accordingly, in Fig. 4.25, αB for grain B (blue) is a positive angle, and αA for grain A (red) is a negative angle. In addition, the GB angle Θ is negative.

4.4.3 Selection of grain boundary orientation in 2D

Using the 2D PF simulations, we investigated grain competition and GB orientation selection for two grains, mapping the entire [−45°, 45°] orientation range for the two grains [150, 154]. The simulation results reveal that the 2D GB typically follows the growth direction of the grain with lower α; however, there are three exceptional cases:

- (i) When two grains are oriented in the same direction, i.e. αA × αB > 0, the convergent GB progressively approaches Θ → 0° at high misorientation, i.e. as Θ → 45°, due to a transition from a dendritic to a degenerate growth regime.

- (ii) When both grains are oriented in opposite direction, i.e. αA × αB < 0, their divergent GBs remain close to Θ ≈ 0°.

- (iii) For αA × αB < 0, the convergent GB changes from the growth direction of one grain to the direction of the other grain within a narrow range |αA + αB| ≤ 5°.
We suggest a simple analytical law for GB orientations using the 2D simulations results and the symmetry condition \( \Theta(\alpha_A, \alpha_B) = -\Theta(-\alpha_B, -\alpha_A) \) \cite{154} \cite{153}, which is given by

\[
\Theta_{2D} = \begin{cases} 
0^\circ & \text{if } \alpha_B > 0^\circ \text{ and } \alpha_A < 0^\circ; \\
\max \{\bar{\alpha}_B, -\bar{\alpha}_A\} \frac{\bar{\alpha}_A + \bar{\alpha}_B}{\delta} & \text{if } |\alpha_A + \alpha_B| < \delta \text{ and } \alpha_A \times \alpha_B < 0; \\
\frac{\bar{\alpha}_A}{\varepsilon}(\alpha_B + 45^\circ) & \text{if } \alpha_A < 0^\circ \text{ and } -45^\circ \leq \alpha_B < -45^\circ + \varepsilon; \\
\frac{\bar{\alpha}_B}{\varepsilon}(45^\circ - \alpha_A) & \text{if } \alpha_B > 0^\circ \text{ and } 45^\circ \geq \alpha_A > 45^\circ - \varepsilon; \\
\bar{\Theta}(\alpha_A, \alpha_B) & \text{otherwise.}
\end{cases}
\]

(4.4)

We obtain the constants \( \varepsilon = 7^\circ \) and \( \delta = 5^\circ \) from the 2D simulations \cite{154}. We use the notation \( \bar{\alpha} \) for the drift angle of a grain, which is usually smaller than its crystal angle \( \alpha \) \cite{1,39}. For the estimation of the drift angle, we use the empirical law \cite{1,39}

\[
\frac{\bar{\alpha}}{\alpha} = 1 - \frac{1}{1 + f \text{Pe}^g},
\]

(4.5)

where \( \text{Pe} = \Lambda V / D \). In addition, we also use the scaling law \cite{52,150}

\[
\Lambda = \Lambda_{\bar{\alpha}} / \cos \alpha,
\]

(4.6)

\[
\Lambda_{\bar{\alpha}} = \Lambda_0 \left\{ 1 + d \left[ (\cos \alpha)^{-e} - 1 \right] \right\},
\]

(4.7)

from experiments \cite{52} for the selection of primary spacing \( \Lambda \) at a crystal angle \( \alpha \). We use \( f = 0.2, g = 1.7 \), and \( \Lambda_0 = 273.8 \mu m \) for previous simulations of the same SCN-ace alloy \cite{150}, and \( d = 0.15 \) and \( e = 8 \) from experimental measurements \cite{52}, which were found in good agreement with simulations.

In Fig. 4.26, we compare the prediction for GB orientation using Eq. (4.4) to the 2D PF simulations, showing the GB orientation as a function of grain \( B \) angle \( \Theta_{2D}(\alpha_B) \) for two values of \( \alpha_A = -25^\circ \) (Fig. 4.26a) and 20° (Fig. 4.26b). In this figure, circles correspond to the simulation results and the solid lines represent Eq. (4.4). In most configurations,
Figure 4.26: Comparisons between the prediction for GB orientation Eq. (4.4) (colored solid line) and the 2D PF simulations (circles) in Ref. [154]. For the prediction, we used two constants $\gamma = 7^\circ$ and $\delta = 5^\circ$. We compared two representative configurations of $\alpha_A = -25^\circ$ (a) and $20^\circ$ (b). The yellow dashed line represents the $\ddot{\alpha}_A$ curve.

the $\Theta_{2D}$ follows the orientation of the favorably-oriented grain growth, i.e. $\Theta_{2D} = \ddot{\alpha}_A$ for $\alpha_A < \alpha_B$. This GB orientation selection corresponds to the last relation in Eq. (4.4). As illustrated in the first relation in Eq. (4.4), the divergent GB for the case (ii) ($\alpha_B > 0^\circ$ in Fig. 4.26a) remains close to $\Theta_{2D} \approx 0^\circ$. The blue colored region in Fig. 4.26a corresponds to the third relation in Eq. (4.4). In this region that is related to the case (i), the grain $A$ has a degenerate structure, and thus the convergent GB progressively approaches $0^\circ$ when $\alpha_B \to -45^\circ$. The red colored area in Fig. 4.26b contains the region of transition of the GB orientation from the orientation of the one grain to that of the other grain, within a range $|\alpha_A + \alpha_B| < \delta$, i.e. case (iii) and the second relation in Eq. (4.4). Fig. 4.26 shows that the prediction for GB orientation agrees well with the simulations within an error range of $5^\circ$ [154].

It is worth noting that the GB orientation exhibits significant fluctuations around the three exceptional cases mentioned above. Furthermore, our suggested law only describes the grain competition for a well-developed dendritic growth regime. For the cellular growth regime, the selection mechanisms of the GB orientations could be significantly different [141].
4.4.4 Selection of GB orientation in 3D

Using 3D PF simulations, we explored the influence of the azimuthal angle $\beta$ (Fig. 4.25 and Fig. 2.5) on the GB selection. For a given configuration $(\alpha_A, \alpha_B, \beta_A, \beta_B)$ of the grain A and B, we typically performed one simulation, because 3D simulations take much longer time than 2D. For the same reason, we considered some selective simulations for our purpose. Thus, the results illustrate particular realizations of GB selection dynamics rather than statistical averages as in 2D simulations [150, 154].

Comparison to 2D results

We first considered the 3D simulations resembling the 2D array configurations, i.e. $\beta_A = \beta_B = 0^\circ$. As illustrated in Fig. 4.27a, the sidebranches of the 2D dendrites always grow towards the neighbors. This configuration corresponds to $\beta_A = \beta_B = 0^\circ$ in the 3D simulations. Then, we changed the other angles $\alpha_A$ and $\alpha_B$ to compare the results with those of the 2D simulations. As shown in Fig. 4.27a-b, with $(\alpha_A, \alpha_B) = (10^\circ, -10^\circ)$, the 3D simulation (b) can be directly compared to the corresponding 2D simulations (a).

The GB selection in the 3D simulations with $\beta_A = \beta_B = 0^\circ$ (Fig. 4.27b-d) shows similar behavior as that in the 2D simulations. For $\alpha_A \times \alpha_B = 0$ (Fig. 4.27e), the variation of the GB angle $\Theta$ is small. For $\alpha_A \times \alpha_B \geq 0$ (Fig. 4.27f), the angle $\Theta$ follows the drift angle of a grain with a smaller $\alpha$. In the case of $\alpha_A \times \alpha_B < 0$ (Fig. 4.27b), $\Theta$ is close to $\alpha_A = 10^\circ$ rather than $\alpha_B = 20^\circ$. When $\alpha_A \times \alpha_B < 0$ (Fig. 4.27b), the GB fluctuates strongly, especially for $\alpha_A = -\alpha_B$, as shown in the 2D simulations (Fig. 4.27a). These three dynamical behaviors are the main features observed in 2D that could be reproduced by the 3D simulations [154].

It is worth noting that we only show the simulations in 2D and 3D using $(\alpha_A, \alpha_B) = (10^\circ, -10^\circ)$ (Figs. 4.27a-b) for the comparison because the GB is fluctuated when $|\alpha_A| = |\alpha_B|$ and $\alpha_A = -\alpha_B$. In the other configurations, the GB dynamics in 3D simulations with $|\beta_A| = |\beta_B|$ is similar to the GB behavior observed in 2D [154]. The comparison shows that
Figure 4.27: 3D simulations at $\beta_A = \beta_B = 0^\circ$ in a thin-sample geometry. For $(\alpha_A, \alpha_B) = (+10^\circ, -10^\circ)$, we directly compared the 2D simulation results (a) to the 3D simulation results (b). The microstructures in (c)-(d) represent the 3D simulations at $\alpha_A \times \alpha_B = 0$ (c) and $\alpha_A \times \alpha_B > 0$ (d).

the difference between average GB angles in 2D and in 3D with $|\beta_A| = |\beta_B|$ remains smaller than $5^\circ$.

**Sidebranching at divergent GBs**

As the azimuthal angle $\beta$ of a dendrite grain increases from $0^\circ$ to $45^\circ$, the secondary branches grow towards the sample walls. Consequently, for $\beta = 45^\circ$, the branches quickly run into the sample walls, and thus their growth is suppressed. Since secondary branches for two different grains compete with each other near the divergent GB [150, 52], their competition could affect the divergent GB orientation [150, 52].

In order to explore the influence of secondary branches on the GB selection, we used two specific grain growth configurations: $(\alpha_A, \alpha_B) = (30^\circ, 0^\circ)$ and $(\alpha_A, \alpha_B) = (30^\circ, -30^\circ)$. For
each configuration, we set $\beta_B = 0^\circ$ and changed $\beta_A$ from $0^\circ$ to $45^\circ$ with steps of $5^\circ$. Fig. 4.28 shows the selected orientation of divergent (a) and convergent (b) GBs as a function of $\beta_A$.

We observe that there was a significant increase in $\Theta$ at the divergent GB (Fig. 4.28a). The GB orientation $\Theta$ in a 2D or quasi-2D (i.e. 3D simulations in a thin sample) simulation is close to $\Theta_{2D} = 0^\circ$ (black dotted line). When $\beta_A$ is lower, 3D simulations also follow this orientation $\Theta \approx \Theta_{2D}$. For the range $15^\circ \leq \beta_A \leq 40^\circ$ at $\beta_B = 0^\circ$, the GB orientation progressively increases towards the growth direction $\bar{\alpha}_A$ (gray dashed line) of the A grain. The divergent GB tends to follow the growth direction of the highest $|\beta|$ grain. This indicates that the growth of sidebranches in this grain is inhibited at the divergent GB.

In contrast, the effect of sidebranching competition on the convergent GB orientation selection is not significant, as illustrated in Fig. 4.28b. Two grains grow towards each other at this GB, and thus the grain growth competition between the grains is more influential than sidebranching competition. Therefore, the relative $\Theta$ stays close to $\Theta_{2D} = 0^\circ$ within a range of $4^\circ$.

Fig. 4.29 shows some selective microstructures of $(\alpha_A, \alpha_B)$ configurations. As observed in Fig. 4.28, both convergent and divergent GBs remain close to $\Theta_{2D}$, i.e. similar to the

![Figure 4.28](image-url)

Figure 4.28: GB orientation selection at the divergent GB (a) and the convergent GB (b) as a function of $\beta_A$ when $\beta_B$ remains $0^\circ$. The gray dashed line in a represents the drift angle $|\bar{\alpha}| \approx 26.3^\circ$ of the misoriented grain with $|\alpha| = 30^\circ$. The black dotted lines are for $\Theta = 0^\circ$. 

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temperature gradient parallel to the $x$ axis, when $\beta_A$ for the misoriented red grain is low (Fig. 4.29a1 and b1). For $\beta_A \geq 30^\circ$ (Fig. 4.29a2 and b2), the orientation of the divergent GB approaches $\bar{\alpha}_A$. Since the sidebranches of the red grain are still growing, the angle $\Theta$ does not reach $\bar{\alpha}_A$. As shown in the front-view snapshots (Fig. 4.29a3 and b3), we could observe that the primary dendrite of grain A at the GB emits frequently secondary and tertiary branches. However, for a high $\beta_A$ (bottom), the growth of sidebranches are limited, because they quickly run into the sample walls. Accordingly, the other grain $B$ actively creates sidebranches.

(a) $\alpha_A = +30^\circ, \alpha_B = 0^\circ, \beta_B = 0^\circ$

(b) $\alpha_A = +30^\circ, \alpha_B = -30^\circ, \beta_B = 0^\circ$

Figure 4.29: Evolutions of microstructures under the influence of $\beta_A$ for two configurations with $(\alpha_A, \alpha_B, \beta_B) = (30^\circ, 0^\circ, 0^\circ)$ (a), and $(\alpha_A, \alpha_B) = (30^\circ, -30^\circ, 0^\circ)$ (b). The larger $\beta_A$ leads to faster elimination of $A$ grain with a larger $\Theta$ at the divergent GB. (a3) and (b3) show microstructures with a misoriented grain (red grain) of $\beta_A > 0^\circ$.  

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**Combined effect of azimuthal angles \((\beta_A, \beta_B)\)**

In the previous section, we showed that a misoriented grain with a higher \(|\beta|\) is eliminated by the other grain with a lower \(|\beta|\) at the divergent grain boundary. We now explore the \(\Theta\) selection at different configurations of \(\beta_A \neq 0\) and \(\beta_B \neq 0\). As done previously, we focus on two representative cases: \((\alpha_A, \alpha_B) = (0^\circ, 30^\circ)\) (Fig. 4.30a) and \((\alpha_A, \alpha_B) = (-30^\circ, 30^\circ)\) (Fig. 4.30b).

**Figure 4.30:** GB orientation \(\Theta\) in 3D PF simulations with \((\alpha_A, \alpha_B) = (30^\circ, 0^\circ)\) (a) and \((\alpha_A, \alpha_B) = (30^\circ, -30^\circ)\) (b). We considered different configurations of the azimuthal angle \(\beta\). The GB orientation of \(\Theta \geq 0^\circ\) \((\Theta < 0^\circ)\) is related to the elimination of the \(B\) \((A)\) grain at the convergent GB and of the \(A\) \((B)\) grain at the divergent GB.
For the growth of \((\alpha_A, \alpha_B) = (30^\circ, 0^\circ)\) in Fig. 4.30a, the bottom border in (a2) is related to the progressive increase of the divergent GB discussed earlier (Fig. 4.28). In this configuration, the convergent GB shows small variations, which are relevant to the left border in (a1). Additionally, \(\Theta\) at the convergent GBs in Fig. 4.30a1 is always close to 0\(^\circ\) (gray); therefore, the influence of \(\beta\) at this GB appears limited. For the divergent GBs in Fig. 4.30a2, a higher \(\beta_A\) causes a higher GB orientation with the elimination of the grain \(A\). In turn, the divergent GB orientations decrease as \(\beta_B\) approaches \(\beta_A\). Hence, for the three cases of \((\beta_A, \beta_B) = (0^\circ, 0^\circ), (0^\circ, 45^\circ), (45^\circ, 45^\circ)\), \(\Theta\) for the divergent GB is low.

In the other configurations with \(\alpha_A \times \alpha_B \geq 0^\circ\), the orientation of the divergent GB could be higher than the relative 2D prediction \(\Theta_{2D}\) \cite{154}. As we have observed, the deviation from \(\Theta_{2D}\) at the divergent GB only occurs when \(|\beta|\) of the more misoriented grain is high. Hence, for the grains with \(\alpha_A \times \alpha_B \geq 0^\circ\) in a thin-sample geometry, a high \(|\beta|\) of the highly misoriented grain can accelerate its elimination.

The results of \((\alpha_A, \alpha_B) = (-30^\circ, 30^\circ)\) in Fig. 4.30b represent the GB orientation for \(\alpha_A \times \alpha_B < 0\). Similar to the behavior of \(\alpha_A \times \alpha_B \geq 0^\circ\) in Fig. 4.30a, the convergent GB remains close to \(\Theta \approx 0^\circ\). However, for the divergent GB, the orientation tends to tilt towards the grain with the higher \(|\beta|\). Thus, grain 1 is rapidly eliminated at \((\beta_A, \beta_B) = (45^\circ, 0^\circ)\), and vice versa. In the other configurations for \(\alpha_A \times \alpha_B < 0\) \cite{154}, \(\Theta\) at the divergent GBs approaches the growth direction of the grain with a higher \(|\beta|\) grain, which leads to a higher \(|\Theta|\).

### 4.4.5 Summary

In this section, we investigated a variety of grain boundary dynamics in a thin-sample geometry using the 3D PF model.

We used a thin-sample geometry to explore the dynamical selection of GB orientations under the influence of azimuthal angles of the grains. We initially considered 3D simulations with \(\beta_A = \beta_B = 0^\circ\), and similar \(\alpha_A\) and \(\alpha_B\) angles as in the 2D configurations. These
simulations showed a good agreement with the 2D results [150,154].

3D simulations revealed that sidebranching dynamics could significantly affect the divergent GB orientation. For the case of $\alpha_A \times \alpha_B \geq 0$, the divergent GB angle increases when a highly misoriented grain has a $|\beta|$ higher than the other grain. For $\alpha_A \times \alpha_B < 0$, the $\Theta$ for the divergent GB tends to be tilted towards the grain with a higher $|\beta|$. In the 3D simulations, the variation of the convergent GB was limited within $5^\circ$. 
Chapter 5

Dendritic-needle-network modeling of sidebranch competition in isothermal dendritic solidification

The following chapter contains material currently being prepared for publication. The results in this chapter reflect my contribution to this work. This work will be published with the following co-authors: Younggil Song\textsuperscript{1}, Damien Tourret\textsuperscript{2}, Alain Karma\textsuperscript{1}.

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5.1 Background

In the DECLIC-DSI experiment for $V = 30\ \mu\text{m/s}$ and $G = 12\ \text{K/cm}$, the microstructure forms a dendritic array as seen in Fig. 5.1. One noticeable difference between a dendritic array and a cellular array is the existence of sidebranches \cite{137, 157, 160, 161}. The sidebranch growth of dendrites leads to a spatial organization in an FCC (face-centered-cubic) structure.
rather than a hexagonal array structure in a cellular growth regime. In such a spatially ordered array, the dynamics of sidebranches along a dendrite is strongly correlated with the sidebranches of its neighboring dendrites.

PF simulations qualitatively reproduce the 3D microstructure dynamics observed in the microgravity experiments [12, 138, 118]. However, it is challenging to explore dendritic microstructures as the one shown in Fig. 5.1 with 3D PF calculations because a smaller grid spacing is required to demonstrate small sidebranches quantitatively. Hence, before directly looking at the dendritic microstructures of directional solidification in Fig. 5.1, we investigated the dynamics of 2D sidebranches under an isothermal condition. The dendrite growth of an isothermal condition is also important because it is frequently observed after the columnar-to-equiaxed transition [90].

Secondary sidebranches appear away from the primary tip, and they grow from the primary stem. If we focus on one sidebranch, it competes with neighboring sidebranches from its birth to grow longer than the others. If it survives continuously, then it can grow without any interference. For the life of this surviving sidebranch, we propose an analytical growth scenario from its birth until it becomes a free dendrite. As shown in Fig. 5.2, this scenario has three steps that are briefly explained below.

• **Step I:** at an early stage of sidebranches, they grow very close to each other and each dendrite finds itself confined between its neighbors that screen the solute flux. Then, the neighbors act as symmetric boundaries (or walls) with respect to solute diffusion.
Therefore, a sidebranch may be represented as growing in a narrow channel of width equal to the secondary dendritic spacing $\Lambda$ (Fig. 5.2a).

- **Step II**: later on, the diffusive interactions (i.e. the competition for solute concentration) among dendrites lead to progressive eliminations of sidebranches. Then, the average spacing $\Lambda$ between surviving sidebranches increases as the length $L$ of a dendrite increases (Fig. 5.2b).

- **Step III**: as the average secondary dendrite arm spacing increases, the solutal interactions among sidebranches get weaker. Some selected dendrites finally grow as a free dendrite (Fig. 5.2c).

The detailed analytical approach is in Sec. 5.2. This simple analytical theory has been compared to various simulation results using both PF and DNN (dendritic-needle-network) models.

![Figure 5.2: Schematics of the three steps of dendritic sidebranches growth. A dendrite from the DNN simulation at $\Omega = 0.25$ is drawn on the bottom side with black lines representing branches. Three growth steps for secondary sidebranches are described on the upper side.](image-url)
5.2 Theory for sidebranch growth

As shown in Fig. 5.2, we propose a theory for the growth and competition of sidebranches involving three steps. In this section, we are going to present a more detailed explanation for the analytical approach.

5.2.1 Step I: Confined dendrite

Fig. 5.2a describes the early growth of a sidebranch. Its growth at this stage is similar to confined growth inside a channel of width $\Lambda$. At this scale $\Lambda \ll l_D = D/V$, with solute diffusivity $D$ and tip growth velocity $V$, we can consider that the solute field around a needle tip is Laplacian. The contour integral around the tip

$$
F^2 = \frac{d_0}{2\pi} \int_{\Sigma} \left[ (\partial_x u)^2 - (\partial_y u)^2 \right] n_x + 2 \partial_x u \partial_y u n_y \right] d\Sigma
$$

in a channel width $\Lambda$ yields that the flux intensity factor $F$, which is related to the solute gradient in front of the tip in the needle growth direction $x$ as (see Ref. [149] or Sec. 2.3 for the details)

$$
F(t)^2 = \frac{\Lambda d_0}{2\pi} \left( \frac{\partial u}{\partial x} \right)^2.
$$

At a diffusive length scale ($\sim l_D$), the needle in a narrow channel could act as a planar interface, so the diffusion in the channel is similar to the one-dimensional (1D) approximation suggested by Zener [173],

$$
\frac{\partial u}{\partial x} \approx \frac{\Omega}{\sqrt{\pi D t}}.
$$

Using this result in Eq. (5.1) about $F(t)$, the velocity of the needle tip from Eq. (2.73) is

$$
V(t) = \frac{dL}{dt} = \left( \frac{\sigma \Lambda^2 D}{2\pi^4 d_0 \Omega^4} \right)^{1/3} t^{-2/3},
$$
which by integration yields

\[ L(t) = 3 \left( \frac{\sigma \Lambda^2 D}{2\pi^4 d_0 \Omega^4} \right)^{1/3} t^{1/3}. \]  

(5.4)

5.2.2 Step II: Growth competition

Sidebranches diffusively interact with their neighbors, which leads to the progressive elimination. Because of this elimination process, the effective spacing \( \Lambda \) becomes larger as the distance from the primary branch \( \Lambda \) increases, as illustrated in Fig. 5.2b. This eliminating phenomenon was also observed in the previous quasi-2D experiments [88, 35], which show that fewer sidebranches can survive as they grow from the primary stem. The theoretical approach proposed that this progressive elimination of sidebranches yields \( \Lambda \sim L \) [27, 87, 24], which agrees with experimental [88] and numerical [134, 131] results. Thus, we used this linear relationship to develop the second step growth for sidebranches as

\[ \Lambda = bL. \]  

(5.5)

where \( b \) is a constant. Then, using Eq. (5.3), the velocity of a dendrite in this step is

\[ V(t) = \frac{dL}{dt} = \left( \frac{\sigma b^2 D}{2\pi^4 d_0 \Omega^4} \right)^{1/3} \left( \frac{L}{t} \right)^{2/3}, \]  

(5.6)

and its length is given by

\[ L(t) = \sigma \frac{D}{d_0} \frac{b^2}{2\pi^4} \Omega^4 t. \]  

(5.7)

Therefore, we can simplify the equation for the velocity of surviving sidebranches by using the steady state velocity \( V_s \) in Eq. (2.75), which yields

\[ V = \frac{\sigma D}{d_0} \frac{b^2}{2\pi^4} \Omega^4 = \frac{b^2}{4\pi^2} V_s. \]  

(5.8)
This equation shows that a Step II dendrite grows with a velocity that is proportional to (i.e. $b^2/(4\pi^2)$ times) the free dendrite velocity.

### 5.2.3 Step III: Free dendrite

The last step Step III is for a free dendrite. If a sidebranch continuously grows, then its spacing becomes larger than the diffusion length $l_D$. Then, this branch leaves Step II growth and goes into Step III growth. Finally, the Step III dendrite escapes diffusive interactions between neighbors and grows as a free dendrite with $V_s$.

### 5.2.4 Model summary and scaling

We use the tip radius $\rho_s$ in Eq. (2.74) and velocity $V_s$ in Eq. (2.75) for a sharp dendrite at a steady state to scale the equations for our suggested dynamics. Then, the scaled values become $\tilde{V} \equiv V/V_s$, $\tilde{L} \equiv L/\rho_s$, $\tilde{\Lambda} \equiv \Lambda/\rho_s$ and $\tilde{t} \equiv tV_s/\rho_s$. This scaling method yields

\begin{align}
\tilde{L} &= 3 \left( \frac{\tilde{\Lambda}}{2\pi} \right)^{2/3} \tilde{t}^{1/3} , \\
\tilde{V} &= \left( \frac{\tilde{\Lambda}}{2\pi} \right)^{2/3} \tilde{t}^{-2/3}
\end{align}

(5.9)(5.10)

for the Step I growth, which is a sidebranch growth at the early stage. Then, in the Step II, longer sidebranches grow with a constant velocity

\[
\tilde{V} = \frac{b^2}{4\pi^2} 
\]

(5.11)

during the competition between neighbors. Then, the surviving dendrite passes a transient growth regime and its growth rate approaches

\[
\tilde{V} \to 1 
\]

(5.12)
which is the velocity of a free dendrite.

### 5.3 Results and discussions

#### 5.3.1 Numerical parameters

We use PF and DNN simulations to validate the proposed three steps for a growing sidebranch described in the previous section. The simulations always use the same $k = 0.15$, $\varepsilon_4 = 0.03$, and $\sigma = 0.22$ even if other external conditions are changed. For the DNN simulation, we used values $N$ and $\Delta N$ that are related to the birth location of a new sidebranch as explained in Sec. 2.3 or in Ref. [149, 151]. Those numerical parameters are listed in Table 5.1.

Simulations mostly use the same techniques for initial and boundary conditions. Initially, the solute field $U$ for PF simulations is $U = 0$ on a seed and $U = -\Omega$ for the rest. The solid seed is always located at the left bottom corner of the domain and its shape is one-quarter of a circle. Symmetric (i.e. no-flux) boundary conditions are applied on all boundaries of the domain. In DNN simulations, the initial $u = \Omega$ except for $u = 0$ on a needle. Most DNN simulations use no-flux boundary conditions; however, periodic boundary conditions at the boundary points on the $y$ axis are used for the dendrite array growth dynamics.

<table>
<thead>
<tr>
<th>Symbols</th>
<th>PF parameters</th>
<th>DNN parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Omega$</td>
<td>0.05, 0.2</td>
<td>0.05, 0.1, 0.15, 0.2, 0.25</td>
</tr>
<tr>
<td>$k$</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_4$</td>
<td>0.03</td>
<td>0.22</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>$\Delta x$</td>
<td>1 [W]=30, 400 [d_0]</td>
<td>1, 2 [$\rho_s$]</td>
</tr>
<tr>
<td>$N$</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>$\Delta N$</td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>
5.3.2 Step I growth

Sidebranches are close to each other at the early stage of their growth. This short distance between branches yields screening the solute diffusion of a sidebranch as drawn in Fig. 5.2a. Thus, we assume that an initial growth of a sidebranch is like the growth of a dendrite in a narrow channel as described in Eq. (5.3). This analytical approach shows that a dendrite in a narrow channel grows with a power law $V \sim t^{-2/3}$. We performed PF and DNN simulations to examine our approach for a dendrite growth in a narrow channel.

The performed simulations used a low solute supersaturation $\Omega = 0.05$. PF simulations had a grid spacing $\Delta x = W = 0.07 \rho_s$ with $W/d_0 = 400$. Since a dendrite grew in the middle of the narrow channel, the simulations used a half of the channel width $\Lambda/\rho_s$ using the symmetric condition. We considered different channel widths $\Lambda/\rho_s = 4.2, 10.9, \text{ and } 44.5$ with the same channel length of $2801.0 \rho_s$. Initially, a quarter of a seed with a radius $100 d_0 \simeq 0.0175 \rho_s$ was located at the left corner of the simulation, and it grew during $tV_s/\rho_s \simeq 100$. In corresponding DNN simulations, two needles with $3 \rho_s$ at the bottom left corner grew within a half of the channel width $\Lambda/\rho_s = 44.5$ and the length $8000 \rho_s$ until $\tilde{t} = 1100$. One needle grew along the $x$ axis, and the other moves along the $y$ axis.

We traced the growth velocity of a dendrite in a channel with $\tilde{\Lambda} = 44.5$ during both PF and DNN simulations. The simulation results (solid lines in Fig. 5.3a) were compared to the analytical prediction Eq. (5.10) (dotted purple line in Fig. 5.3a). In both simulations (blue solid line for the DNN and red solid line for the PF), the dendrite growths follow the analytical line $V \sim t^{-2/3}$ soon after the simulation starts.

Fig. 5.3b and c, respectively for the DNN and for the PF, show the interface shapes at different time steps $\tilde{t} = 0.01, 0.1, 1, 10, \text{ and } 100$. The interfaces in Fig. 5.3c were calculated by using the accumulating solute flux on the needle. The actual needle size during the simulation is always sharp compared to the channel width as the analytical model assumed. The interface thickness in the DNN does not influence needle growth or solute flux. Therefore,
the dendrite velocity in the DNN goes to the predicted growth faster than in the PF, and
the DNN result agrees better than the PF simulation (Fig. 5.3a).

Effects of a dendrite volume

In order to investigate the influence of a dendrite volume, we carried out more PF simula-
tions at a smaller $\tilde{\Lambda} = 10.9$ and 4.2. For the comparison, we used the same initial and growth
conditions as in the previous simulation (Fig. 5.3c). We assumed that a smaller dendrite
volume leads to a faster velocity of a dendrite in a narrow channel. Thus, a dendrite in a
narrower channel may grow faster than in a larger channel.

We reformulate Eq. (5.10) because the velocity is related to the channel width and de-
creases as the power law, which yields

$$\tilde{V} \tilde{\Lambda}^{-2/3} = \left(\frac{2\pi \tilde{t}}{2}\right)^{-2/3}.$$  \hspace{1cm} (5.13)

Figure 5.3: Calculated growth ve-
locity of a dendrite within a nar-
row channel of width $\tilde{\Lambda} = 44.5$
at a dimensionless solute super-
saturation $\Omega = 0.05$ compared
to the analytical prediction $\tilde{V} =
[\tilde{\Lambda}/(2\pi)]^{3/2} \tilde{t}^{-2/3}$ (a), and snap-
shots of the interface shape at $\tilde{t} =
0.01, 0.1, 1, 10, \text{ and } 100$ predicted
by dendritic-needle-network cal-
culation with $\Delta x = \rho_s$ (b) and PF
calculation with $W = 400d_0$ (c).
Thus, when simulation results are scaled with respect to $\tilde{\Lambda}^{2/3}$, one analytical prediction is valid for all results at different $\Lambda$ as shown in Fig. 5.4a. In this figure, the analytical prediction (blue dotted line) is valid for simulations at different channel widths $\tilde{\Lambda} = 44.5$ (red solid line), 10.9 (gray dashed line), and 4.2 (black dotted line).

These simulations show that the velocity of a dendrite within a larger $\tilde{\Lambda}$ is closer to the analytical prediction than within the larger channel width. As we assumed previously, the dendrite volume leads to this deviation from the analytical model. Three dendrite interfaces are drawn in Fig. 5.4b-d at $\tilde{\tau} = 0.01, 0.1, 1, 10$, and 100 after scaling with respect to $\Lambda$. The dendrite width in Fig. 5.4b is still small compared to $\Lambda$, so it grows with the power law $t^{-2/3}$. On the other hand, the dendrite at $\tilde{\Lambda} = 4.2$ (Fig. 5.4d) occupies the channel faster than the other $\Lambda$, which yields the deviation from Eq. (5.10).

Even though a dendrite velocity at $\tilde{\Lambda} = 4.2$ decreases with time, the power law for the velocity seems larger than the prediction $-2/3$ in Eq. (5.10). Then, what could be the final value of this velocity? Our assumption is that the final dendrite velocity in a narrower channel would reach $V \sim t^{-1/2}$ for the planar front growth, as pointed out in Ref. 123.

Our analytical model shows that a dendrite in a narrow channel slows down as time passes. In the meantime, its radius increases, as shown in Fig. 5.4b-d and as described by the solvability condition 94, 95, 6, 9. The solvability condition shows that $\rho^2V$ is a

![Figure 5.4](image)

Figure 5.4: Growth velocity of a dendrite at $\Omega = 0.05$ at a narrow channel of different width $\tilde{\Lambda} = 44.5, 10.9, \text{ and } 4.2$ compared to the analytical law $\tilde{V} \sim \tilde{t}^{-2/3}$ (a), and snapshots of the interface shape at $\tilde{t} = 0.01, 0.1, 1, 10, 100$ for $\tilde{\Lambda} = 44.5$ (b), 10.9 (c), and 4.2 (d).
constant, so a decrease of $V$ leads to an increase of a dendrite tip radius in a narrow channel. Then, while a dendrite slows down in a channel, its interface fills the channel, and its front becomes planar. The planar front growth is the 1D problem solved by Zener, $V \sim t^{-1/2}$ \cite{173}. Therefore, we can deduce that the growth rate of a dendrite in a narrow channel changes from $V \sim t^{-2/3}$ to $V \sim t^{-1/2}$. Hence, the interface shape in our PF simulations could be in the middle of changing their shapes and their dynamics.

It is worth noting that a dendrite is a line segment in the DNN simulation, so the size of a dendrite is always sharp compared to the channel width. Thus, the DNN simulations agree with our suggested model.

**Limit of a power law growth**

A dendrite in a narrow channel grows with the power law prediction in our simulations. On the other hand, when a channel width is large enough, a dendrite in a channel grows like a free dendrite and thus its velocity becomes $\tilde{V} = 1$. Thus, we can deduce that there exists a crossover width that determines a growth in a narrow channel or a free dendrite growth. We assume that the crossover is related to $\tilde{l}_D = \pi/(2\Omega^2)$ for a free dendrite, so simulations used a higher supersaturation to decrease the relative diffusion length.

In order to search for a crossover channel width $\Lambda_c$, we performed both PF and DNN simulations at a higher supersaturation $\Omega = 0.2$. PF simulations used $\Delta x = W = 30 \ d_0$. In the corresponding simulations, a quarter seed with its radius $100 \ d_0 \approx 0.28 \ \rho_s$ was located at the bottom left corner, and the crystal grew over $\tilde{t} = 200$. In the DNN simulations, one single needle with its length $3 \ \rho_s$ was located in the middle of a channel width. The needle grew predominantly in the $x$ direction during $\tilde{t} = 25000$. The considered channel sizes were $\tilde{\Lambda} = 13.1, 26.6, 53.4, 107.2, \text{ and } 214.8$ for the channel length $1075.46 \ \rho_s$ for the PF simulations. The DNN simulations were performed with $\tilde{\Lambda} = 29, 61, 125, 157, 213, 253, 509, \text{ and } 4093$ at the channel length $9021 \ \rho_s$ for the two smallest channel widths and $27069 \ \rho_s$ for the rest.

Dendrite velocities as a function of time are plotted in Fig. 5.5 for PF simulations (a)
Figure 5.5: Growth velocity of a dendrite at $\Omega = 0.2$ within channels of different width $\tilde{\Lambda}$ predicted by PF calculations (a), and by dendritic-needle-network calculations (b). The crossover between the analytical law $\tilde{V} \sim \tilde{t}^{-2/3}$ at narrow width and $V \to V_s$ at larger width appears when the channel width $\Lambda$ gets larger than $\approx 5$ times the diffusion length $l_D = D/V$.

and for DNN simulations (b). Both simulation results show a power law growth at this $\Omega$. Additionally, dendrite growth approaches a stationary velocity $\tilde{V} \to 1$ for a larger $\Lambda$.

PF results in Fig. 5.5a show that a dendrite within $\tilde{\Lambda} \leq 53.4$ exhibits the power law growth. When $\Lambda \leq 53.4$, a dendrite within a wider width takes longer time to reach $\tilde{V} \sim \tilde{t}^{-2/3}$. For $\tilde{\Lambda} = 107.2$ (purple dotted line), a dendrite velocity is still decreasing at the end of the simulation. Hence, we assume it would follow the power law if it continuously grows after this simulation. On the other hand, the velocity of a dendrite in $\tilde{\Lambda} = 214.8$ approaches a constant velocity at the end of the simulation (cyan line). Thus, we assume that the crossover spacing is located between $107.2 < \tilde{\Lambda}_c < 214.8$.

DNN simulations also show two different growth dynamics as described in Fig. 5.5b. While dendrite velocities at $\tilde{\Lambda} = 29, 61, 125$ and 157 (respectively corresponding to red, green, blue, purple line) decreases as time elapses, the remaining dendrites at $\tilde{\Lambda} \geq 213$ grow with a steady state velocity. Even though a steady state $\tilde{V}$ at $\tilde{\Lambda} = 213$ (cyan line) is smaller than the results at the largest $\tilde{\Lambda} = 4093$, its $V$ becomes a constant. Hence, $\tilde{\Lambda}_c$ is located between $\tilde{\Lambda} = 157$ and 213.
In Fig. 5.5b, the stationary velocities at a wider $\Lambda$ are not same. Stationary velocities when $\tilde{\Lambda} = 213$ and 253 are smaller than the results at $\tilde{\Lambda} \geq 509$. This slower velocity could be caused by diffusive interactions between channel walls and a dendrite. The width $213 \leq \tilde{\Lambda} < 509$ is wide enough for a dendrite to reach a steady state velocity. However, because a dendrite in this spacing range could still diffusively interact with the channel wall, its velocity is slightly smaller than a dendrite at a wider width $\tilde{\Lambda} \geq 509$.

The solute flux could be one important factor to affect dendrite growth, so using a relative diffusion length is reasonable to determine $\Lambda_c$. In the simulations at $\Omega = 0.2$, the corresponding diffusion length for a free dendrite is $l_D \approx 39.3 \rho_s$. Then, using this $l_D$, the crossover in Fig. 5.5 happens at $2.7 \lesssim \Lambda_c/l_D \lesssim 5.5$ for PF simulations and $4.0 \lesssim \Lambda_c/l_D \lesssim 5.4$ for DNN simulations. Overall, dendrites show the growth in Eq. (5.10) when $\Lambda < 4.0l_D$ and they grow like a free dendrite at $\Lambda > 5.4 l_D$. Hence, the crossover width would be $\Lambda_c \approx 5.0 l_D$.

### 5.3.3 Dendritic array growth and competition

While many sidebranches are eliminated in the first growth stage, other surviving branches keep growing and enter *Step II* growth. In this growth stage, we expect progressive eliminations of sidebranches which yields a linear relationship between the average spacing $\Lambda$ and the distance from the primary stem $L$ as the previous studies [24, 27, 87] suggested. In addition, this linear relationship leads to a constant velocity for the surviving sidebranches as predicted by Eq. (5.11).

Instead of directly exploring sidebranch growth from a primary branch, we consider one DNN simulation with a dendrite array with the simulation size $N_x \times N_y = 14976 \times 8032 \rho_s^2$, where $N_x$ and $N_y$ are the domain sizes along the $x$ and $y$ axes. We used the grid spacing $\Delta x = \rho_s$. Then, 803 needles are located at the bottom of the $x$ domain with their lengths $(3 \pm \delta l_i) \rho_s$ with the fixed spacings $10 \rho_s$ between them. The small perturbation of the $i$ needle $\delta l_i$ is a uniformly distributed random number between $[-0.5; 0.5] \times 10^{-10} \rho_s$. During the simulation, those needles grew together at $\Omega = 0.2$. Boundary conditions were no-flux...
Figure 5.6: The growth competition of 803 evenly spaced needles at $\Omega = 0.2$. Snapshots of the needles and the solute field $u(x, y)$ in (a) through (d) show the progressive elimination of dendritic branches by diffusive interactions. The time evolution of the length of 14 needles appears in log-log scale in (e) and in linear scale in (f), following the theory described in Sec. 5.2 as: Step I with $L \sim t^{1/3}$ (black dashed line in e); Step II with $V = V_s/(2\pi)^2$ (black dashed line in f); and Step III with $V \to V_s$.

for $x$ boundaries and periodic for $y$ boundaries.

The results are shown in Fig. 5.6. Figs. 5.6a-d illustrate dendrites (gray shapes) with iso-$u$ lines at $\tilde{t} = 2291.09$ (a), 7995.23 (b), 13786.2 (c), and 20000 (d).

As the needle dendrites grow, a larger dendrite absorbs more solute than the smaller ones, and hence the bigger ones grow more than the smaller ones even at the early stage as shown
in Fig. 5.6a. In this figure, the interface globally looks like a planar interface; however, larger dendrites grew more than their neighbors when we took a close look near the interface.

As time goes on, the larger needles grow more and more by competing with their neighbors (Fig. 5.6b-c). During the competition, small needles are eliminated and the surviving ones are able to grow further. Hence, we expect the spacing between the surviving needles is related to the length of a dendrite, which leads to a constant velocity of a surviving needle (Sec. 5.2).

The competition between neighboring branches end when a dendrite has a large enough spacing, allowing each surviving dendrite to grow like a free dendrite. In Fig. 5.6d, the four longest dendrites become free dendrites, growing with $\tilde{V} \approx 1$.

We traced the lengths of the dendrites during the simulation, and the lengths of the selected dendrites are plotted in Fig. 5.6e-f. In these figures, three colors represent each growth step, i.e. blue for Step I, red for Step II, and green for Step III.

Dendrites in the array agree with our suggested dynamics. We suggested that the dendrite velocity slows down with the power law Eq. (5.10), and the length of a dendrite grows with Eq. (5.9). The small plot in Fig. 5.6e shows the early stage of dendrite growth in the simulation with the suggested growth law with the channel width $10 \rho_s$ (black dashed line) in a log-log scale. The dendrites show the suggested growth $L \sim t^{1/3}$. Thus, our assumption for the Step I growth is valid for dendrites in an array.

During the Step II growth, because of the progressive elimination, the average spacing is assumed to be linearly increasing with the distance from the primary stem as $\Lambda = bL$ [24, 27, 87, 131, 134]. Thus, we first measure the relation between $\Lambda$ and $L$ to quantify the linear relation with a constant $b$.

During the simulation, dendrites stayed at their final lengths when they stop growing. Hence, we measured all dendrite lengths at the end of the simulation, and evaluated the average spacing $\langle \tilde{\Lambda} \rangle$ as a function of the length $\tilde{L}$. We counted the number of the surviving needles at a length $N(L)$, so the average spacing is $\langle \tilde{\Lambda} \rangle = L_y/N(L)$, where $L_y$ is the simulation
domain width. We assume that the linear relationship holds up to \( L \simeq 5l_D \) which is related to the limit of the width of a narrow channel \( \Lambda_c \).

The assumption Eq. (5.5) needs to be corrected for the dendrite array simulation because initial \( L \) and \( \Lambda \) were not 0 and \( u \) field is not stabilized initially. The spacing was set as \( \tilde{\Lambda}_0 = 10 \), and the length of the smallest dendrite is \( \tilde{L}_0 = 44.824 \) at the end of the simulation. We assume that the elimination starts where \( L > L_0 \) with the initial spacing \( \tilde{\Lambda}_0 \). Thus, the corrected relation is

\[
\langle \tilde{\Lambda} \rangle = b(\tilde{L} - \tilde{L}_0) + \tilde{\Lambda}_0.
\]  

(5.14)

We use \( b = 1 \) to compare the simulation results with the prediction of Eq. (5.14), which corresponds to the red solid line in Fig. 5.7.

In Fig. 5.7, simulation results (blue cross dots) show the linear relationship \( \Lambda(L) \) before the length \( L \) reaches the expected limit \( L = 5l_D \), where \( l_D = 39.3 \rho_s \simeq 196.5 \rho_s \) at \( \Omega = 0.2 \).

Interestingly, this linear relationship continues even for \( L > 5l_D \). We guess that solutal interactions between neighboring dendrites continue even after the limit \( L > 5l_D \), which leads to continuing eliminations. Thus, the relation continues approximately until \( L \sim 800 \rho_s \) in the simulation.

The simulation results show that the ratio \( \langle \Lambda \rangle/L \) is \( b \simeq 1 \), so we use this value for Eq. (5.11). Then, the Step II growth becomes \( \tilde{V} = 1/(2\pi)^2 \). We used this growth rate for
the slope of the black dashed line in the small plot of Fig. 5.6f. This small plot shows that
dendrites in this step (red lines) follow the suggested linear growth even in a short time.

If a dendrite continuously survives, then it reaches the final *Step III* growth of a free
dendrite. In the considered simulation, four dendrites become free dendrites as shown in
Fig. 5.6f. The average spacing between these dendrites is 2007.5ρs that is about 50 times
larger than $\tilde{l}_D$, so we expect no solutal interactions between them. One notable thing is that
the transition time from *Step II* to *III* is much longer than the time for *Step I* and *II*.

### 5.3.4 Growth competition of secondary sidebranches

When a sidebranch appears from the side of its primary dendrite, its length is usually
smaller than its neighbors. In addition, the new sidebranch is under the influence of the
primary tip. Thus, the sidebranch dynamics could be different from the one in a dendritic
array as we discussed earlier.

In order to investigate the growth dynamics of sidebranches, we performed DNN simula-
tions. We used DNN simulations to investigate the growth dynamics of secondary branches at
Ω = 0.2. Initially, one needle is located at the bottom left corner with its length 8 ρs = 4 ∆x.
This needle grows in the x direction by generating secondary branches which grow along the
y axis. For the creation of the sidebranches, sidebranches appear at $(N \pm \Delta N)\rho$ behind
the primary tip with the imposed $N = 10$ and $\Delta N = 5$. The simulations continue until
$\tilde{t} = 100000$ in the domain $N_x \times N_y = 24000 \times 20000 \rho_s^2$. We used no-flux boundary condi-
tions for all axes. During the simulation, the primary tip stays at a fixed position after the
tip reaches the position, 80% of $N_x$ in our simulations.

The DNN simulation starts with the initial needle located at the bottom left corner.
When the simulation starts, this dendrite grows towards the right (+x direction) by creating
secondary branches. At the early stage, some sidebranches grow much faster than its neigh-
bors before the u-field is stabilized with the primary branch growth. These longer branches
block the growth of other secondary branches. This initial sidebranch growth is not realistic,
so we ignored the simulation data until the unrealistic secondary branches moved out of the simulation domain.

A stationary dendrite shape for $\Omega = 0.2$ at $\tilde{t} = 100000$ is drawn with $u$-field in Fig. 5.8. The colored lines illustrate isovalue $u$-field, and the black thick line and gray lines represent the primary stem and sidebranches, respectively. At this stationary state, the secondary branches seem to compete after their birth, and several sidebranches become free dendrites far away from the primary tip.

Fig. 5.9a-b show the growths of the ten selected sidebranches from their birth at time $\tilde{t}_i^0$, where $i$ is the index of a sidebranch, in linear scale (a) and in log-log scale (b). The primary branch grows linearly with a constant velocity $V_s$ (yellow lines). Four gray lines indicate secondary branches which are stopped during competition. During the simulation, six sidebranches become free dendrites (black lines in Fig. 5.9), and their growth velocities $V$ approach $V_s$ like the primary dendrite growth.

The Step I is the power law growth. In a dendrite array, the proposed growth is $L \sim t^{1/3}$, which is confirmed by the numerical calculations in the previous sections. For the sidebranch growth, the power law is different from the array growth. As the blue line in Fig. 5.9b illustrates, the power law value is about $3/5$ as the analytical approach described in Ref. [23]. The analytical approach considered a sidebranch growth of a 3D dendrite with a cubic
Figure 5.9: The sidebranch growth for $\Omega = 0.2$ in Fig. 5.8. The time evolution of the length of the primary branch (yellow line) and of ten secondary sidebranches appears in linear scale in (a) and log-log scale in (b), exhibiting three growth steps: Step I with Brener’s approach $\tilde{L} = (5\tilde{t}/3)^{3/5}$ (blue line) [23]; Step II with $V \approx V_s/\pi^2$ (red line); and Step III with $V \to V_s$.

symmetry by using 2D approximations [75, 3], which is given by

$$\tilde{L} = \left(\frac{5\tilde{z}}{3}\right)^{3/5} \left(\frac{\sigma_{SB}}{\sigma}\right)^{1/5}, \quad (5.15)$$

where $\tilde{z} = (\tilde{x}_t - \tilde{x})$ is the distance from the primary tip $\tilde{x}_t$ and $\sigma_{SB}$ is the tip selection parameter for a sidebranch which is the same as $\sigma$ in our consideration.

Eq. (5.15) is derived based on a analogy between 2D time-dependent growth and 3D steady-state growth [23]. The 2D time-dependent growth problem considers an equiaxed grain with four competing primary dendrite arms. This geometry is very different from the present 2D geometry where secondary branches forming behind a primary dendrite branch compete in a tilted array structure. It is possible that the $t^{3/5}$ power law derived for an equiaxed grain geometry still holds some validity to describe sidebranch competition during Step I in a tilted array geometry. The comparison to the DNN simulations in Fig. 5.9b indicates that a $t^{3/5}$ power law indeed approximately describes the growth competition of sidebranches in Step I. This agreement, however, may be coincidental since the equiaxed
geometry assumed to rigorously derive the $t^{3/5}$ power law \cite{3} is very different than the tilted array geometry. Aside from the physical origin of the $t^{3/5}$ law, one clear conclusion is that different power laws describe the Step I coarsening regime of a uniform array of dendrites that have equal initial lengths, which is described by our theoretically derived 1/3 power law (Fig. 5.6a), and a tilted array forming behind a primary branch, which we empirically find to be well fitted by a 3/5 power law (Fig. 5.9b).

In the simulation, the distance from the primary tip corresponds to the velocity of the primary tip, i.e. $\tilde{z} = \tilde{V} \tilde{t}$ with $\tilde{V} = 1$, so Eq. (5.15) can be reformulated as

$$\tilde{L} = \left( \frac{5\tilde{t}}{3} \right)^{3/5}.$$  \hspace{1cm} (5.16)

This relation (blue line in Fig. 5.9b) agrees with the initial growth of sidebranches observed in the simulation.

Secondary branches show the Step II growth after the first power law growth. In a dendrite array, a dendrite in the second step grows with its constant velocity $V/V_s = 1/(2\pi)^2$. Sidebranches also show a constant growth rate after the initial step; however, the velocity is four times faster than a Step II dendrite, i.e. $V/V_s = 1/\pi^2$. The guide red line in Fig. 5.9a-b indicates $L = (V_s/\pi^2) t$, which agrees well with the simulation results.

The first two growth steps of a sidebranch are different from our proposed analytical prediction. We guess two main factors lead to the differences. The first reason is the existence of the primary dendrite. Newly generated sidebranches are close to the primary dendrite tip, and they interact with each other diffusively. Additionally, the lengths of sidebranches are not uniform as in a dendrite array. Our prediction did not consider the influence of the primary tip or non-uniform branch length. Hence, even though sidebranches show the first and second step growths, their dynamics is different from our approaches.

A sidebranch approaches the final Step III growth after it passed through the Step II. As shown in Fig. 5.9a-b, it takes a long time to reach the Step III after the Step II. This
transition time is longer than the duration of the initial two steps. After the long transition, the velocity of the sidebranch at the last step is close to \( V \) like a free dendrite.

The previous experimental study \cite{35} uses a local lateral diffusion length, which is

\[
\bar{l}_{SD} \approx 2\sqrt{2}D(\rho^2
\end{equation}

\[
\bar{t}^1/2 e^{\frac{1}{4} - \frac{1}{4}} V^{-\frac{1}{4} - \frac{1}{4}} t \frac{1}{2} \rho \frac{1}{2}.
\end{equation}

(5.17)

to describe the spacing between free secondary branches \( \Lambda_E \) using an escape time \( t_e \), which is the time to deviate from the Step II growth, the velocity of a primary tip \( V \) and the tip radius \( \rho \). Then, the spacing measured from the experiment is \( \Lambda_E \approx (0.18 \pm 0.03)\bar{l}_{SD} \) \cite{35}. We scaled the \( l_{SD}^S \) with respect to \( \rho_s \) and \( V_s \) for our simulations. Then, the diffusion length can be rewritten as

\[
\bar{l}_{SD} \approx 2\sqrt{2}\bar{D}(\bar{\rho}\bar{V})^{-1/2} \bar{t}^{1/2}.
\end{equation}

(5.18)

In the simulation results in Fig. 5.9a, the escape time is approximately in a range \( 6000 < \bar{t}_e < 9000 \). Because the primary branch has \( \bar{\rho} = 1 \) and \( \bar{V} = 1 \), the local lateral diffusion length becomes \( 8603.61 < \bar{l}_{SD}^S < 10537.22 \). We calculated the average spacing \( \langle \bar{\Lambda} \rangle = 1640.13 \) using 16 sidebranches in the Step III that are longer than \( 10000\rho_s \). In the unit of \( \bar{l}_{SD}^S \), this average spacing is in a range of \( 0.16 \bar{l}_{SD}^S \) and \( 0.19 \bar{l}_{SD}^S \), which shows excellent agreement with the experimental observation.

### 5.3.5 Dendrite envelopes

When we draw a line from the primary dendrite tip to secondary sidebranches that are longer than previous sidebranches (envelope branches), the connected line makes an envelope shape. Previous experimental studies \cite{98,99,113} explored dendrite envelopes by using pure succinonitrile (SCN) or SCN-acetone alloys. Using our simulations, we are also able to draw this dendrite envelope.

For a dendrite envelope, we additionally performed DNN simulations at different \( \Omega = 0.1, 0.15, \) and \( 0.25 \) to investigate 2D dendrite envelopes. We used the same numerical conditions
Figure 5.10: Stationary dendrite envelopes at different supersaturation $\Omega = 0.1, 0.15, 0.2, \text{ and } 0.25$. For four different supersaturations, the length $L$ of the secondary envelope sidebranches as a function of a distance from the primary tip $z$. The envelopes show the transition from *Step I* (blue solid line) to *Step II* (red dashed line) (a), and from *Step II* to *Step III* (green solid line) (b). The transition between *Step II* and *Step III* occurs approximately at $L \approx 7.5 l_D$ (gray dotted line in b and c). (c) shows the dendrite envelope near the transition between *Step II* and *Step III*.

used in the previous $\Omega = 0.2$ simulation. Then, the primary dendrite initially located at the bottom left corner grows along the $+x$ direction during $\tilde{t} = 100000$. We used the dendrites at the end of the simulations to analyze the relation between the lengths $L$ of envelope branches and the distance from the primary tip $z$. For the following analysis, we use three growth steps as shown in Fig. 5.10a-b.

Fig. 5.10a shows lengths $L$ of envelope dendrites as a function of the distance $z$ behind the primary tip in log-log scale. Open symbols indicate the envelope branches at different $\Omega = 0.1$ (brown down triangles), 0.15 (yellow squares), 0.2 (purple circles), and 0.25 (green up triangles). We expect that the branch length increases with the *Step I* power law, and then grows with the linear growth for *Step II*. In the figure, the blue solid line indicates the first step growth $L \sim (5z/3)^{3/5}$, and the red dashed line indicates the second step $L = z/\pi^2$. The simulation results for all considered $\Omega$ agree with these two steps. The results also show
that transitions from Step I to II occurs at the same place $\tilde{z} \approx 660$.

In the experimental observations of 3D dendrites [98, 99, 113], the envelope shows the power law growth with $\tilde{L} \sim \tilde{z}^{0.85}$, which is independent of $\Omega$. Because a dendrite is 3D in experiments, the power law could be larger than our 2D simulations.

The second transition from Step II to III is drawn in a linear plot Fig. 5.10b. At this time, we scaled $L$ and $z$ with respect to $l_D$. The Step I growth regime is difficult to find in the plot because the Step II is much longer than Step I. In all considered $\Omega$, envelope branches (open symbols) agree with the red dashed line for the Step II, i.e. $L = z/\pi^2$. Then, the second transition occurs approximately at $L = 7.5\ l_D$, which is marked as a gray dotted line (see Fig. 5.10c). After this transition, the longer branches become free dendrites, and hence their growths are close to $dL/dz = 1$ (green solid line).

It is important to note that sidebranches also show the relation $L = \Lambda$ as the simulation with a dendrite array showed in Fig. 5.7. The limit of this relation for sidebranching simulations is $L \approx 7.5\ l_D$. This limit from the simulation reasonably agrees with the experimental observation with an NH$_4$Cl alloy [88]. After this limit, sidebranches approach Step III growth.

We use the Step II and III to draw the dendrite envelope shape. The Step I is negligible because it appears in a very short region compared to the region for Step II as shown in Fig. 5.10. Then, the envelope linearly increases with $L = V_s t/\pi^2$, where $V_s t$ is equivalent to $z$, before $L = 7.5\ l_D$ from the primary dendrite tip. After this limit, it grows with $dL/dz = 1$. We compared the simulation results to the shapes drawn with the simple suggested law.

Fig. 5.11 shows the dendrites taken from the end of simulations at $\Omega = 0.1$ (a), 0.15 (b), and 0.2 (c). The gray lines represent the sidebranches including the primary branch, and the red solid lines correspond to the actual dendrite envelopes from simulation results. We suggested that envelopes can be fit by two straight lines, i.e. $dL/dz = 1/\pi^2$ for $L \leq 7.5l_D$ and $dL/dz = 1$ afterward (blue dotted lines). In Fig. 5.11, the simple predictions are closely aligned with the dendrite grains from the simulations.
5.3.6 2D dendrite area

In the DNN model, a 2D dendrite area can be calculated by estimating incoming solute flux towards a needle branch. Calculating the whole dendrite area at a small $\Omega$ and a large domain during a simulation is computationally challenging, so we considered a domain size $\tilde{L}_x \times \tilde{L}_y \approx 12000 \times 9984$ with no-flux boundaries and time $\tilde{t} = 52000$ for a dendrite growth at $\Omega = 0.25$. Other numerical parameters are the same as previous simulations for Fig. 5.11. The DNN model used a small domain size and shorter time; however, secondary branches can reach the Step III growth during the simulation.

The gray shape in Fig. 5.12a represents a stationary dendrite at the end of the simulation $\tilde{t} = 52000$. We measured the dendrite area $\tilde{A}$, i.e. gray area in Fig. 5.12a, from the primary tip $\tilde{z} = 0$ of a dendrite in (a). The log-log plot in Fig. 5.12b corresponds to the measured area (red dots) as a function of $\tilde{z}$.

We observed two power law growths of $A$, i.e. $\tilde{A} \sim \tilde{z}^\gamma$, in Fig. 5.12b. The dendrite area initially increases with $\gamma = 3/2$ (black dashed line). This value could come from a parabola equation $y = \sqrt{2\rho z}$ with radius $\rho$. Integrating the equation leads to the equation for an area.
\[ A = \sqrt{8\rho/\rho_s^3/2} \]. Because the primary tip has its radius \( \rho/\rho_s \approx 1 \) at a stationary state, the area scaling respect to \( \rho_s \) becomes

\[ \tilde{A} = \sqrt{8/9} \tilde{z}^{3/2} \],

which corresponds to black dashed line in Fig. 5.12(b). This prediction agrees with simulation results.

The power law growth of a dendrite area behind the primary tip was observed in the previous experimental studies [34, 98, 99, 113]. The quasi-2D dendrite of ammonium bromide dendrites [34] shows its area growth follows the power law \( \gamma = 1.5 \). In the other studies [98, 99, 113], the projected area of 3D dendrites shows \( \gamma = 1.72 \) for pure succinonitrile (SCN) dendrites [99] and \( \gamma = 1.77 \) for SCN-acetone alloys [113]. Those experimental observations are close to the simulation \( \gamma = 1.5 \).
In Fig. 5.12b, the power law growth in Eq. (5.19) continues until $\tilde{z} \approx 2700$. The transition occurs approximately 50% later than the second growth transition $\tilde{z} = 7.5\pi^2 \tilde{l}_D = 1860.38$, where $\tilde{l}_D = 25.13$ at $\Omega = 0.25$. This could be because the selected sidebranches take some time to reach the Step III growth after the Step II growth. After this transition at $\tilde{z} \approx 2700$, the area increases with $\tilde{A} \sim \tilde{z}^3$ (black solid line in Fig. 5.12b). We guess, as sidebranches become free dendrites, the power law has been doubled, i.e. $\gamma = 3$. Hence, this $\gamma$ would be fixed after the transition limit as our simulation shows (Fig. 5.12b).

5.4 Summary

We have presented three growth steps for 2D sidebranching dynamics with analytical and numerical approaches. A sidebranch at the early stage (Step I) is confined between its neighbors, hence it grows like a dendrite in a narrow channel; its growth depends on $\Lambda$ and shows a power law growth. If a sidebranch grows longer, then it exhibits the Step II growth. Diffusive interactions between sidebranches in this step lead to a stationary velocity by assuming that the average spacing as a function of a sidebranch length linearly increases, i.e. $\Lambda \sim L$ [24, 88, 27, 87, 131, 134]. The stationary velocity at this growth step is smaller than $V_s$ for the free dendrite. Finally, in Step III, as the solutal interaction between sidebranches is reduced (or negligible), sidebranches grow like free dendrite, In order to examine our suggested growth scenarios for a sidebranch, we performed PF and DNN simulations.

The growth for a Step I sidebranch resembles a dendrite growth in a narrow channel. Thus, we considered a dendrite growth in a channel with the PF and DNN models for the Step I. The analytical approach in Eq. (5.10) predicts that a dendrite velocity decreases with time with a power law $V \sim t^{-2/3}$, which agrees well with the PF and DNN simulations.

When a dendrite is located in a wide channel, it is not influenced by the channel, and grows like a free dendrite as shown in the previous studies [123, 132]. Thus, we expected that a dendrite in a wide channel, i.e. $\Lambda > \Lambda_c$, grows like a free dendrite. In order to determine
where the crossover regime $\Lambda_c$ is located, the PF and DNN simulations were carried out with different $\Lambda$. In both simulations, the crossover occurred at $\Lambda_c \approx 5.0 \, l_D$. Hence, a dendrite in a channel $\Lambda < \Lambda_c$ shows the power law growth, otherwise its growth velocity is close to $V_s$ for a free dendrite.

The first step growth is also observed in other simulations with different conditions, i.e. the growth of a dendrite array and a sidebranch. At the early stage of the array growth, lengths of dendrites increase with time with the power law, i.e. $L \sim t^{1/3}$ like Eq. (5.9). Additionally, a new sidebranch created from its primary branch shows a power law growth. For the sidebranch, the power law is $3/5$ like the previous analytical approach $L \sim t^{3/5}$ [23]. Because of the influence of the primary branch and a non-uniform sidebranch array, the power law $3/5$ is different from Eq. (5.9).

After the Step I, sidebranches diffusively interact with their neighbors, which leads to their progressive elimination. For the second step growth, we assume that the spacing between sidebranches increases linearly as the length of a dendrite increases $\Lambda \sim L$ [24, 88, 27, 87, 131, 134]. In the simulation with a dendrite array, this linear relationship was observed.

Using $\Lambda \simeq L$, we deduced Eq. (5.11) for the constant growth rate of a Step II sidebranch. In a dendrite array, the velocities of Step II dendrites are about $V_s/(4\pi^2)$ as we expected in Eq. (5.11). The Step II sidebranches also show a constant velocity $V_s/\pi^2$ before they become free dendrites. The difference between the Step II growth velocity of a dendrite in an array and for a sidebranch is likely caused by the influence of the primary branch and a non-uniform sidebranch array.

If a dendrite in an array or a sidebranch survives the second growth step, it approaches Step III. After a slow transition from Step II to III, the surviving branch increases with $V_s$. The surviving Step II dendrites reach the Step III growth regime in the corresponding DNN simulations.

We measure the average spacing between the Step III free sidebranches when $\Omega = 0.2$. In the previous experimental observations [35], the spacing between free dendrites
is \((0.18 \pm 0.03)l_D^S\), where \(l_D^S\) is the local lateral diffusion length. The simulation shows the average spacing is in between \(0.16l_D^S\) and \(0.19l_D^S\), which shows excellent agreements with the experimental measurements.

If we draw a line between the longer sidebranches (or envelope sidebranches) and the primary tip, we find the envelope shape for a dendrite. We analyze this envelope with the three growth steps. Simulations show the envelope sidebranches in Step I increase with \(\tilde{L} = (5\tilde{z}/3)^{3/5}\) like the previous analytical approach \[23\]. This growth rate continues until the transition from Step I to II at \(z \approx 660\rho_s\). In Step II, the envelope sidebranches grow with the constant velocity \(L = V_s/\pi^2\) before the second transition \(L \approx 7.5l_D\). Then, the branches away from the primary tip longer than \(7.5l_D\) approach the Step III for a free dendrite growth.

Based on our sidebranch growth scenarios, we can predict the dendrite envelope morphology. The first growth step is negligible because the Step II growth regime is much shorter than the Step II. Then, the prediction \(L(z)\) consists of two straight lines: (i) \(L = z/\pi^2\) from the primary tip to \(L = 7.5 l_D\) and (ii) \(L \sim z\) for \(L > 7.5 l_D\). The simulation results are in accordance with these simple analytic envelopes.

In previous experimental studies \[98, 99, 113, 74\], projected areas of 3D dendrites increased by the distance from the primary tip with a power law, \(A \sim z^\gamma\). These experimental measurements can be comparable to a 2D dendrite area. In our DNN simulation at \(\Omega = 0.25\), a 2D dendrite area initially increases with a power law \(A \sim z^{3/2}\) like a parabola shape. This power law \(\gamma = 3/2\) is the same as the experiment of a quasi-2D dendrite \[34\], and similar to the projection areas for 3D dendrites \[98, 99, 113\]. After \(\tilde{z} \approx 2700\), the power law for a dendrite area changes to \(\gamma = 3\), as sidebranches grow independently, i.e. Step III growth. This area growth transition occurs about 50 % later than the second transition for a sidebranch because Step III sidebranches take time to get their own volume.
Chapter 6

Conclusions

In this thesis, we use state-of-the-art PF models to investigate microstructural pattern formation during directional solidification of binary alloys. These investigations focus on the dynamical selection of the primary spacing of cellular and dendritic arrays and grain growth competition. PF simulations in a purely diffusive regime are conducted in spatially extended bulk samples to interpret unique observations of 3D cellular/dendritic array evolution in a microgravity environment where convection is suppressed as well as in thin samples where convection is eliminated on earth in transparent organic materials. However, spatial confinement by the sample walls affects microstructure selection. For this reason, we investigate the influence of the sample thickness in order to relate the results of earth-based thin-sample and microgravity bulk-sample experiments. We also investigate spacing selection in metallic Al-Cu alloys that exhibit a significant amount of convection even in a thin-sample geometry [20, 19, 122]. In addition to PF simulations, we also carry out DNN simulations to investigate fundamental aspects of the growth competition of secondary branches and deduce from those simulations scaling laws describing this competition.

Our PF modeling of microgravity observations in the DECLIC-DSI experiments [118] allows us to model interface pattern stability and primary spacing selection quantitatively for the first time in 3D on experimentally relevant length and time scales, thereby allowing us to carry out detailed quantitative comparisons in a purely diffusive regime (Sec. 3.1).
results show that the initial recoil of the planar interface is strongly influenced by thermal effects that include thermal diffusion and latent heat rejection. Those effects delay the build-up of the solutal boundary-layer ahead of the interface during the recoil phase and hence delay the onset of morphological instability. The predicted solidification length corresponding to the onset of morphological instability and the initial unstable wavelength are both in good quantitative agreement with experiments when PF simulations include thermal effects, but not when simulations use the standard frozen-temperature-approximation, which neglects latent heat rejection and assumes that the temperature field relaxes instantaneously to a linear profile. Furthermore, simulations show that the inclusion of thermal effects increases the dynamically selected steady-state primary spacing, away from the minimum stable spacing towards the maximum stable spacing, in a way that improves the agreement between PF modeling predictions and experiments. The increase in primary spacing increases with pulling velocity and is undoubtedly linked to latent heat rejection. We can conjecture that this increase appears linked to a reduction of peak interface velocity during the acceleration phase following morphological instability. However, further work is needed to elucidate the precise cause of the spacing increase induced by thermal effects.

We also compare our PF simulations to solidification experiments using a thin sample on Earth, where convection could be reduced but never completely avoided.

We explore the primary spacing selection at different sample thicknesses (Sec. 4.2). In a cellular growth regime, a local oscillatory dynamics may lead to a larger spacing induced by primary cell elimination. We frequently observe oscillatory dynamics at a smaller sample thickness $H$, and thus the selected primary spacing in a thin sample decreases as the sample thickness $H$ increases in a cellular growth regime. However, in a dendritic growth regime, the dendrites reach a stable spacing after initial coarsening dynamics. This selected spacing is independent of the sample thickness $H$.

We investigate spacing selection under the influence of convective currents in the liquid phase (Sec. 4.3). These currents can be quantitatively predicted by Navier-Stokes equations
using a no-slip condition at the interface [7]. However, PF calculations using this method are currently very costly computationally. Therefore, we use a simplified approach, which assumes that the solute diffuses within a finite boundary layer (or a stagnant film) surrounding the solid-liquid interface [54, 55]. The solute outside of the boundary layer is well mixed at the nominal alloy composition due to strong fluid convection. The PF simulations with this approach show that strong convection (i.e., small boundary layer thickness) leads to smaller spacings, particularly at low growth velocities.

In addition, we investigate the evolution of a primary spacing profile in a grain that is misoriented with respect to the temperature gradient (Sec. 4.1). In a thin-sample geometry, primary spacings generated at the divergent grain boundary (GB) are shown to be larger than the initially selected array spacing [66, 52, 61, 53, 49, 48]. The larger spacing originating at the divergent GB propagates towards the inner grain region as cells/dendrites drift laterally with a velocity related to the grain orientation and to the local spacing [1, 39]. At the convergent GB, spacing decreases until cell (or dendrite) elimination. We propose a simple geometrical model for these creation, drift, and elimination events between GBs, which predict the spatiotemporal evolution of a primary spacing profile in a misoriented grain, and agree with PF simulation results at different $V$ and crystal angles.

While the aforementioned model can predict the pattern drift of a single array within a thin sample geometry, spacing propagation dynamics and the overall pattern behavior are expected to be different in 3D microstructures. The array pattern in a 3D microstructure can take the form of a hexagonal array, a face-centered-cubic array, or a globally disordered array with a high density of tiling defects. Furthermore, sidebranching mechanisms also differ significantly when primary and higher order branches in a 3D array are not well aligned as in a confined array. Therefore, we also investigate grain selection mechanisms during the grain growth competition at GBs in 3D, and considering the 3D orientations of grains, crucial to determine the grain texture in columnar microstructures.

We examine the selection of GB orientation using the 3D PF model in a thin-sample
geometry (Sec. 4.4). When grains are close to a 2D configuration (i.e. when the azimuthal angle of a crystal $\beta = 0^\circ$), the GB orientations of 3D simulations agree with that of the 2D PF simulations [154, 153]. As the azimuthal angle $|\beta|$ increases, sidebranches of the corresponding primary dendrites grow towards the sample walls, leading to an increasingly fast elimination of a misoriented grain with a higher $|\beta|$ at the divergent GB. Interestingly, the convergent GB in a thin-sample geometry remains stable within $5^\circ$.

In addition, we explore the morphological instability of the convergent GB observed in 3D microstructures (Sec. 3.2).

DECLIC-DSI observations aboard the ISS reveal the existence of a morphological instability of GBs characterized by inter-penetration of two misoriented grains and a novel unexpected phenomenon of solitary cell dynamics. The PF simulations reproduce both of those phenomena and yield a good quantitative agreement with experiments for the drift velocity of solitary cells. Furthermore, the simulations shed light on the role of GB bi-crystallography and array structure. We find that GB instability only occurs for low misorientation with respect to the temperature gradient axis because classic grain elimination is favored when the misorientation exceeds a threshold of about 15 degrees. However, when both grains have a low misorientation with respect to the temperature gradient, so that grain elimination does not occur, GB instability occurs over a very large range of relative drift directions of the two grains, where the drift direction is determined by the projection of the primary dendrite growth axis in the plane perpendicular to the temperature gradient axis. From this standpoint, GB instability is a very general phenomenon that should be widely observable in directional solidification where the misorientation with respect to the temperature gradient is typically low. Our simulations also demonstrate that the survival rate of a solitary cell depends on its number of nearest neighbors, with five neighbors facilitating the drift motion of the solitary cell within the array, and seven neighbors caging the solitary cell and leading to its elimination. Given the fact that cellular arrays are typically disordered, solitary cell dynamics and elimination is inherently a stochastic process.
In the last Chapter, we consider secondary sidebranching dynamics of an isothermal dendrite using the DNN model. We develop an analytical model for the growth of sidebranches. In the first growth step, a sidebranch is confined between its neighboring branches, thus following a power law growth rate. Then, the dendrite goes through a stage of progressive elimination of sidebranches. In this stage, a sidebranch grows with a constant velocity that is smaller than that of a free dendrite. The DNN simulations confirm these two initial stages of sidebranch growth. Additionally, we propose an analytical formula for the grain envelope shape (formed by the main primary tip and longer secondary tips), which describes well the envelope of a stationary dendrite grain in DNN simulations.

Several future avenues of investigations appear worthwhile pursuing in the light of the computational studies presented in this thesis.

With regards to the primary array spacing selection in a purely diffusive regime, several studies are warranted. First, PF simulations of the DECLIC-DSI observations have so far failed to reproduce the spacing overshoot prior to the establishment of a steady-state spacing. This discrepancy is potentially due to the assumption that the temperature diffuses instantaneously in the radial direction (i.e. the direction parallel to the solidification front), which was used to reduce the thermal field calculation to one dimension. Relaxing this assumption by a full three-dimensional calculation of the temperature field may allow PF simulations to capture the overshoot of the spacing observed experimentally. Second, our single GPU 3D simulations have so far been limited to system sizes smaller than the experimental sample diameter. Multi-GPU simulations should be able to model significantly larger system sizes and to explore the role of convergent and divergent grain boundaries on spacing selection in spatially extended arrays. Third, detailed quantitative comparisons of PF simulations in thin-samples and earth-based experimental observations in transparent organic systems where convection is suppressed remain to be performed.

With regards to microstructural pattern selection in the presence of fluid convection, our PF simulations have used a very crude boundary-layer approximation. The simulations
are able to reproduce the main effects of convection, namely a dramatic reduction of the primary spacing and the change of slope of the spacing-velocity relationship. However, more quantitative modeling of fluid flow and solidification remains needed to establish more reliable comparisons with experimental observations and to make predictions that are free of adjustable parameters such as the boundary-layer thickness.

With regards to grain growth competition, our 3D PF simulations in a fully dendritic regime have been restricted to thin samples. Additional simulation studies are needed to explore the dendritic regime of polycrystalline solidification in 3D and, in particular, the newly discovered phenomena of GB instability and solitary cell dynamics. There is experimental evidence that GB instability is also present in 3D in a dendrite growth regime \[68, 172\].

Finally, with respect to dendrite growth competition, the origin of different scaling exponents describing the first stage of sidebranch competition for uniform and tilted dendritic arrays in 2D remains to be elucidated. While we have developed an analytical understanding of the scaling regime of uniform arrays, the case of tilted arrays relevant for dendritic grains is more complex and warrants further theoretical work. Moreover, DNN simulation studies remain needed to better understand the extension of those scaling laws to 3D dendrites.
Appendix

A Validation tests of crystal anisotropy

The theoretical shape of an equilibrium crystal in Cartesian coordinates \((x,y,z)\) is described as \[\text{[25, 164, 85]}\]

\[
x = R_0 \left[ f(\theta, \phi) \sin \theta \cos \phi + \partial_\theta f(\theta, \phi) \cos \theta \cos \phi - \partial_\phi f(\theta, \phi) \sin \phi / \sin \theta \right], \quad (A.1)
\]

\[
y = R_0 \left[ f(\theta, \phi) \sin \theta \sin \phi + \partial_\theta f(\theta, \phi) \cos \theta \sin \phi + \partial_\phi f(\theta, \phi) \cos \phi / \sin \theta \right], \quad (A.2)
\]

\[
z = R_0 \left[ f(\theta, \phi) \cos \theta - \partial_\theta f(\theta, \phi) \sin \theta \right], \quad (A.3)
\]

where

\[
f(\theta, \phi) = 1 + \frac{4\varepsilon_4}{1 - 3\varepsilon_e} \left[ \cos^4 \theta + \sin^4 \theta (1 - 2 \sin^2 \phi \cos^2 \phi) \right]. \quad (A.4)
\]

The angles \(\theta\) and \(\phi\) are the standard polar and azimuthal angles, respectively, that the normal to the solid-liquid interface pointing in the outside of the solid. This theoretical description can be reformulated in a matrix form,

\[
\begin{pmatrix}
  x \\
  y \\
  z
\end{pmatrix} = R_0 \begin{pmatrix}
  \sin \theta \cos \phi & \cos \theta \cos \phi & -\sin \phi / \sin \theta \\
  \sin \theta \sin \phi & \cos \theta \sin \phi & \cos \phi / \sin \theta \\
  \cos \theta & -\sin \theta & 0
\end{pmatrix} \begin{pmatrix}
  f(\theta, \phi) \\
  \partial_\theta f(\theta, \phi) \\
  \partial_\phi f(\theta, \phi)
\end{pmatrix}, \quad (A.5)
\]
Figure A.1: Comparison between an equilibrium shape of the PF model and the theory. The PF model simulated a 3D equilibrium shape when its anisotropy $\varepsilon_4 = 0.05$ with crystal angles $(\alpha_0, \beta_0, \gamma_0) = (13^\circ, 35^\circ, 7^\circ)$ (a). We match the interface of (a) to the analytical shape (red lines) at the interface of $z = 7$ (b), 0 (c), and $-3$ (d) (black dots).

or

$$
\begin{pmatrix}
  x \\
  y \\
  z
\end{pmatrix} = \frac{R_0}{1 - 3\varepsilon_4} \begin{pmatrix}
  \sin \theta \cos \phi & \cos \theta \cos \phi & -\sin \phi \\
  \sin \theta \sin \phi & \cos \theta \sin \phi & \cos \phi \\
  \cos \theta & -\sin \theta & 0
\end{pmatrix} F
$$

(A.6)

with

$$
F = \begin{pmatrix}
  1 - 3\varepsilon_4 + 4\varepsilon_4 & \cos^4 \theta + \sin^4 \theta(1 - 2\sin^2 \phi \cos^2 \phi) \\
  -8\varepsilon_4 \sin(2\theta) & \cos^2 \theta - \sin^2 \theta(1 - 2\sin^2 \phi \cos^2 \phi) \\
  8\varepsilon_4 \sin^3 \theta \sin(2\phi) & \sin^2 \phi - \cos^2 \phi
\end{pmatrix}.
$$

(A.7)

As explained in Sec. 2.2.6, the crystal angles in the PF model rotate from the cartesian $(x, y, z)$ coordinate in sequence of (i) by $\alpha_0$ around the $z$ axis, (ii) by $\gamma_0$ around $y'$ axis, and (iii) by $\beta_0$ around $x''$ axis. Thus, we found an equilibrium shape of a crystal with crystal angles $\alpha_0, \beta_0,$ and $\gamma_0$ using the PF model. This steady crystal shape is compared to the theoretical approach.

Fig. A.1a shows the equilibrium shape at $\alpha_0 = 13^\circ,$ $\beta_0 = 35^\circ,$ and $\gamma_0 = 7^\circ$ from the PF simulation. From this equilibrium shape, we find the interface positions at $z = c$ (black lines) where $c = 7,$ $c = 0,$ and $c = -3.$ Black diamonds in Fig. A.1b-d correspond to the interpolated solid-liquid interfaces from (a). The red lines in Fig. A.1 indicate analytical equilibrium interface positions at $z = c$ from Eq. (A.5). These figures show that interfaces
from the equilibrium shape of the PF model are in a good agreement with the theoretical
descriptions.

B Material parameters

We used a succinonitrile (SCN) alloy and an aluminum alloy to investigate solidification
processes under different conditions.

The material parameters of a succinonitrile (SCN)-0.24wt% camphor alloy were widely
studied \[145, 102, 155, 148, 137, 138, 117\], and are summarized in Table B.1. It is worth
noting that this alloy has an anisotropy $\varepsilon_4 = 0.011$ higher than a previous estimation $\varepsilon_4 = 0.007 \[155, 57, 148\]$. The partition coefficient $k = 0.21$ was used in Chapter 4.2; however,

Table B.1: Material parameters for the succinonitrile (SCN)-camphor, aluminum (Al)-
copper (Cu), and SCN-acetone (ace) alloys. These parameters were used for the PF simula-
tions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>Alloy composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solute concentration</td>
<td>$c_\infty$</td>
<td>0.24, 0.25</td>
<td>wt%</td>
<td>SCN-camphor</td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td>$D$</td>
<td>270</td>
<td>$\mu m^2/s$</td>
<td></td>
</tr>
<tr>
<td>Liquidus slope</td>
<td>$m$</td>
<td>-1.365</td>
<td>K/wt%</td>
<td></td>
</tr>
<tr>
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$k = 0.07$ has been measured in the recent experiments \[117\].

We used an aluminum (Al)-1.4wt% copper (Cu) alloy in Sec. 4.2 and Sec. 4.3. The corresponding parameters are listed in Table B.1. For this alloy, $k$ and $\Gamma$ are known from Ref. \[165, 144, 120, 62\]. When simulations use the diffusion coefficient $D \approx 2.4 \times 10^3 \ \mu m^2/s \ [96]$, the results show best agreement with the experiments. The anisotropy strength $\varepsilon_4 = 0.012$ was measured using molecular dynamics simulations \[115\]. We used $m = -3.0 \ \text{K/wt\% Cu}$, which is an intermediate value between $m \approx -2.6 \ \text{K/wt\% Cu} \ [165]$ and $-3.4 \ \text{K/wt\% Cu} \ [144, 120]$.

For a SCN-acetone alloy, most material parameters are from Ref. \[29, 136, 137, 50\] as summarized in Table B.1.

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