

The Influence of Hydrodynamic Flow on Microstructure Evolution During Solidification

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Ricardo Siquieri

aus Pres. Prudente - São Paulo - Brasilien

Berichter: Univ.-Prof. Dr.-Ing. Heike Emmerich

Prof. Dr. Michal Benes

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Contents

Abstract	1
Kurzfassung	3
Introduction	5
1 Sharp-interface approach for dendritic growth in presence of forced flow	9
1.1 Sharp interface model equations	12
1.1.1 The dimensionless model equations	15
1.2 Numerical approach	17
1.2.1 Numerical setup and update procedure	19
1.2.2 Time-step control	24
1.2.3 Boundary conditions	25
1.2.4 Discretization scheme	26
1.2.5 Cell flagging	29
1.2.6 Definition of solid interface cells	29
1.3 Numerical validation	33
1.3.1 Stokes flow through an array of cylinders	33

1.3.2	Dendritic tip velocity under the influence of forced flow	35
1.4	Investigation of morphology transition	
	induced by fluid flow	37
1.5	Discussion	42
2	Quantitative phase-field model for binary alloy system in presence of convection	49
2.1	Description of the model	53
2.2	Anisotropic and dimensionless model	57
2.3	Numerical approach	60
2.4	Numerical simulations	63
2.5	Discussion	67
3	Quantitative phase-field modelling of two-phase growth with fluid flow	73
3.1	Phase-field model	74
3.2	Eutectic growth under the influence of convection	78
	3.2.1 Numerical simulations	80
	3.2.2 Discussion	90
3.3	Peritectic growth under the influence of convection	92
	3.3.1 Numerical simulations	96
	3.3.2 Discussion	102
	Summary and Outlook	105
	Acknowledgements	109

Bibliography	120
Curriculum Vitae	121

Abstract

Numerical simulation of solidification and crystal growth has attracted industrial attention as a powerful engineering tool for processes and alloy optimization. In this work we present a detailed study of the influence of flow on the microstructure evolution during solidification. First, we use a classical sharp interface approach combined with an accurate fluid flow solver to simulate dendritic growth under the influence of an imposed flow. Secondly, we include convection effects into an existing quantitative phase-field model [Phys. Rev. E, 70 (2004) 061604] that is meant to simulate dendritic growth of a binary alloy. We apply it to investigate the solidification of a Fe-Mn alloy under external flows conditions. In addition, we present an extension of the quantitative phase-field model of two-phase growth [Phys. Rev. E, (2005) 72 011602] that includes natural and forced convection effects in the melt phase. We use this extension to investigate directional solidification of eutectic lamellae under the influence of convection as well as heterogeneous nucleation and microstructure formation of peritectic growth in the presence of convection.

Kurzfassung

Die numerische Simulation von Kristallwachstum und Erstarrungsprozessen hat in jüngerer Zeit erhöhte Aufmerksamkeit durch die Industrie erhalten, da sie ein starkes Werkzeug für die Entwicklung und Optimierung von Arbeitsprozessen in der Erzeugung von Legierungen darstellt. In dieser Arbeit stellen wir eine detaillierte Studie über den Einfluß von Konvektion auf die Entwicklung der Mikrostruktur während des Erstarrungsprozesses vor. Als erster Schritt wird ein klassischer Sharp Interface-Ansatz in Kombination mit einem Präzisionslösungsverfahren für Flussprobleme verwendet, um dendritisches Wachstum unter dem Einfluß von aussen angelegten Strömungen zu lösen. Des weiteren wurden Konvektionseffekte in ein vorhandenes quantitatives Phasenfeldmodell [Phys. Rev. E, 70 (2004) 061604] eingebaut, welches für die Simulation von dendritischem Wachstum in binären Legierungen entwickelt wurde. Dieses erweiterte Modell wurde verwendet, um die Erstarrung einer Fe-Mn-Legierung unter externen Strömungen zu untersuchen. Darüber hinaus stellen wir eine Erweiterung eines quantitativen Phasenfeldmodells für Zweiphasenwachstum [Phys. Rev. E, (2005) 72 011602] vor, welches natürliche und extern angelegte Konvektionseffekte in der Schmelzphase berücksichtigt. Wir verwenden diese Erweiterung, um gerichtete Erstarrung

von eutektischen Lamellen unter dem Einfluß von Strömung sowie heterogene Nukleation und Mikrostrukturbildung von peritektischem Wachstum unter Berücksichtigung von Strömung zu untersuchen.

Introduction

The investigation of pattern formation in alloy solidification has been the topic of several research studies, see e.g. [45, 83]. The formation of microstructures during solidification plays an important role in determining the properties of nearly all man-made metal products. The simulation of solidification and crystal growth processes has been of growing interest because of its importance in many technological applications. Most theoretical/numerical models on microstructure evolution are based only on diffusive mass transport. The practical relevance of those for real life applications has been questioned by the fact that conditions are only rarely met which permit a direct quantitative comparison with such as theoretical description. Indeed, the description refers to a situation without convection, despite the fact that crystal growth processes almost never occurs in conditions free of convection. Neglecting convection effects is generally motivated by the difficulty of including them in the theory and the argument that the basic prototypes of solidification patterns appear and may be studied without convection. Research under microgravity conditions in the last decades has shown the importance of convection. It has become clear that, even in the best experimental setups used on earth, residual flows can change the microstructure

and thus complicate a detailed quantitative comparison with theoretical predictions which do not take convection into account. The systematic analysis of convective effects and its inclusion in theoretical models is complicated as there are many causes for fluid flow. Melt flow in solidification can be categorized into natural and forced convection. Included as natural convection is convection caused by contraction (or expansion) when the densities of the solid and liquid are different regardless of the presence of the gravitational force. Forced convection is due to externally applied conditions, for instance electromagnetic stirring, rotation, pouring of melt, etc., some of which may be intentionally introduced to cause convection to enhance solute transport from the solid-liquid interface in order to reduce macro- and microsegregation. Natural convection is believed to be responsible for the discrepancies between experimental data under terrestrial conditions and the prediction of diffusion-based theories that ignore convection.

Numerical modeling of crystal growth in the solidification of pure metals and alloys remains a significant challenge in material science and applied physics. Even for the most common growth morphology (i.e. dendritic growth) which has been studied over the past two decades, a full numerical simulation for non-dilute metallic alloys with properties found in real castings still remains challenging even in the absence of convection. The difficulties lie in the widely different length and time scales in the coupled energy and mass transport processes, in the segregation of the solute upon solidification and in the strong dependence of the melting temperature on the liquidus concentration. When convection is included, the problem is further complicated by the coupling of the Navier-Stokes equations in the presence of evolving

solid-liquid interfaces. Melt convection adds new length and time scales to the problem and results in morphologies that are potentially very different from those generated purely by diffusive heat and solute transport.

With the advent of new numerical techniques such problems can be solved with a relatively high order of accuracy and thus it is possible to make predictions which, together with experimental observations, are able to contribute to the understanding of many complicated physical aspects of crystal growth or pattern formation in nature.

The various techniques for the numerical simulation of crystal growth can in principle be divided into two basic groups: explicit interface tracking and the diffuse interface approach. The explicit interface tracking method includes the classical sharp interface approach. The phase-field method together with its variants constitute the diffused-interface approach.

In this work we use the above two different numerical approaches and combine them with a numerical approach for the Navies-Stokes equations to investigate the influence of convection on microstructure evolution during solidification.

We concentrate our investigations on the most frequent types of morphology evolution found during cast processes in metal alloys - namely dendritic growth, eutectic lamellae growth and peritectic growth.

The main goal of this thesis is to gain new insight into the numerical simulation of crystal growth under the influence of a convection field.

This work is divided in four chapters: In the first chapter we present numerical simulations of thermal dendritic growth under the influence of forced convection. We develop a sharp interface approach and couple it with the

Navier-Stokes equations. The validation of the model as well as the comparison of our results with existent results from the literature is also presented. In the last section of this chapter we present a morphology diagram for pattern formation in a pure melt under the influence of forced convection. In the second chapter we present a quantitative phase-field approach for binary alloy systems and extend it to take into account the influence of fluid flow in the melt phase. The validation of the model is presented and we use it to investigate the influence of convection on dendritic growth for the system Fe-Mn. In the third chapter, we use the knowledge of the previous chapters to add the effect of convection to the quantitative phase-field approach by Folch and Plapp. This method is meant to solve eutectic/peritectic growth of binary alloy systems. First, we present the convergence of the model and show that even by coupling the binary phase-field equation with the Navier-Stokes equations we still reproduce quantitative results. Secondly, we present numerical simulations of direction solidification for eutectic growth under the effect of convection and then we show how convection interacts with heterogeneous nucleation and microstructure formation of peritectic alloy systems. Finally we present a summary and an outlook.

Chapter 1

Sharp-interface approach for dendritic growth in presence of forced flow

To simulate fluid flow with free or moving surfaces quite enhanced schemes have been developed in the past decades, see e.g. [71] and references therein. Including a phase change in such problems makes the task more demanding. A further degree of difficulty arises in the context of solidification at the microscale, since in this context special attention has to be paid to the anisotropic physics of the solid-liquid interface. This anisotropy can be of kinetic or of capillary origin and determines to a large extent the morphology evolution of the solidifying crystal microstructure [16]. Thus a challenging task to understand microstructure evolution in solidifying samples is to set up a numerical scheme which accurately takes into account the dynamics of the hydrodynamic field at the moving solid-liquid interface, the phase-change

dynamics as well as the anisotropic effects along the interface.

For the above task the solidification of the dendritic morphology certainly poses a paradigm problem: Dendrites are the basic microstructural form for most crystalline materials. Dendrites may form from the vapour phase, from solution, or by solidification from the melt. In the context of this dissertation we are interested in the investigation of dendrites forming from a hydrodynamically controlled solidification process. Such dendritic structures appear in many material processing systems and have influence on the properties of the final solid products.

The controlled solidification of materials with a desired microstructure in different environments has been the aim of many elaborated research studies. Brener *et al.* [16] have formulated a theory for the fundamental morphologies and the most relevant parameters controlling their appearance. Later on the basic predictions for the fundamental morphologies (dendrites and doublons) [16] were confirmed by Ihle and Müller-Krumbhaar [37] numerically. Ihle and Müller-Krumbhaar carried out a detailed computational study on the advancement of an interface due to diffusive transport. Changes of the growth morphology of dendritic growth were also investigated by Murray *et al.* [57]. They showed computational and experimental results of a competition between two growing dendritic branches and the eventual predominance of one branch. More recently Stalder *et al.* [70] have observed that under a small perturbation one can enforce the morphology transition of the growing crystal from a dendritic to a doublonic morphology.

The evolution of the dendritic microstructure seems to be well understood for experiments with pure materials growing into undercooled melts

under purely diffusive conditions, i.e when fluid flow is absent. Dendritic solidification of pure substances in the absence of hydrodynamic flow has been treated thoroughly. As pointed out above, well accepted analytical results are available for this case [1, 79, 80, 47, 10, 44, 42, 45].

During crystal growth processes, gradients of temperature and solute are always present. In a gravitational field these gradients can give rise to fluid flow in the melt [30]. If the influence of fluid flow is taken into account, the solidification structure alters dramatically [72]. The presence of the flow itself interacts with the morphological instabilities of purely diffusion limited crystal growth. What happens is that convection alters the transport of heat away from the solidifying dendrite, so that the resulting tip velocity and the radius of the curvature of the dendritic tip are modified. Moreover, convection will subsequently lead to changes in the morphology evolution.

In the past few years, quite a lot of numerical investigations involving dendritic solidification with convection have been performed. Beckermann *et al.* [9] and Tong *et al.* [72] investigate the influence of flow on the dendrite tip and the dynamics of dendritic side branching using phase-field method. Tönhard and Amberg [73, 74] also used phase-field method to simulate dendritic growth under externally forced flow influences. They showed that the growth of the side branches was raised on the upstream side and inhibited on the downstream side. More recently, Al-Rawahi and Tryggvason studied dendritic solidification with forced flow using explicit front-tracking methods. In all these simulations equiaxial growth was considered.

Recently, Medvedev *et al.* [56, 55, 54] used a combined phase-field lattice-Boltzmann scheme to simulate dendritic growth subject to an externally

forced flow and thermal convection. Moreover, they report modifications on the kinetic morphology diagram [54], when fluid flow is taken into account.

In order to contribute to the development of this research field it is essential to elaborate a numerical scheme that fulfils the above criteria of accurately taking into account the dynamics of the hydrodynamic field at the moving solid-liquid interface, the phase-change dynamics as well as the anisotropic effects along the interface. The aim of this work is to provide such a scheme as a general mean for systematic investigations of the non-linear dynamics of hydrodynamically influenced microscopic solidification problems in the future. We will explain our scheme in detail in section 1.2 of this work. We will then demonstrate its impact by reporting simulation results on hydrodynamically induced microstructure morphology transitions in dendritic growth. Finally we will conclude with a discussion and an outlook.

1.1 Sharp interface model equations

In the fundamental thermodynamic model of solidification of a pure substance from its melt, growth is controlled by the diffusion of latent heat away from the interface separating the liquid and the solid phase. In this case, the temperature field satisfies the heat diffusion equation

$$\frac{\partial T}{\partial t} = D_S \nabla^2 T, \quad (1.1)$$

in the solid. In the liquid phase, we must take into account the advection of heat by the fluid flow, whose velocity we denote by $\mathbf{u}$. Here, the heat conduction equation for the temperature T can be written in the form

$$\frac{\partial T}{\partial t} + (\mathbf{u} \cdot \vec{\nabla})T = D_L \nabla^2 T, \quad (1.2)$$

with D_L and D_S being the thermal diffusivity of the liquid and solid phase, respectively.

A rough non-faceted interface can be regarded as being in local equilibrium. On the solid-liquid interface the Temperature field T must satisfy the boundary condition corresponding to the Gibbs Thomson equation [49] (in absence of kinetic undercooling)

$$T_I = T_m - T_m \frac{\gamma}{L} \kappa, \quad (1.3)$$

where T_I is the temperature at the interface, T_m is the melting temperature, γ is the surface tension along the interface line, L is the latent heat and κ is the local curvature of the interface. It is important to stress that the Gibbs Thomson relation describes the local thermodynamic equilibrium between the solid-liquid interface. It can be easily seen e.g. in a planar interface, $\kappa = 0$, then $T = T_m$. For the general curved interface, the capillary term $-T_m \frac{\gamma}{L} \kappa$ describes the influence of the atomic surface energy between the crystal structure and the melt on the equilibrium interface.

The condition of heat conservation on the moving interface results in the Stefan condition [49]

$$Lv_n = \left(D_L c_p \vec{\nabla} T \Big|_L - D_S c'_p \vec{\nabla} T \Big|_S \right) \vec{n}, \quad (1.4)$$

with $\vec{n}$ being the normal vector of the interface outward from the solid, v_n is the normal velocity of the interface. c_p and c'_p are the specific heat capacities in the liquid and solid phase, respectively. $\vec{\nabla} T \Big|_L$ and $\vec{\nabla} T \Big|_S$ are

the temperature gradient at the interface in direction to the liquid and solid phase, respectively. Relation (1.4) describes that - when a crystal is growing with velocity v_n - the latent heat produced at the solidifying front needs to be transported away by the heat flow. This relation is valid only locally at the solid-liquid interface. It has to be fulfilled at every time step of the numerical scheme (see section 1.2).

The liquid motion is described by the Navier-Stokes equations and a continuity equation, for a time-dependent incompressible viscous flow given by [27, 35]

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \vec{\nabla})\mathbf{u} = -\frac{1}{\rho}\vec{\nabla}p + \nu\nabla^2\mathbf{u} + \mathbf{g} \quad (1.5)$$

and in the solid it is claimed that

$$\mathbf{u} = 0. \quad (1.6)$$

Here, p is the pressure field, ρ is the density of the fluid, ν is the kinematic viscosity and $\mathbf{g}$ is the gravitational field.

The velocity field $\mathbf{u}$ satisfies the mass conservation relation, i.e.,

$$\vec{\nabla} \cdot \mathbf{u} = 0. \quad (1.7)$$

The boundary conditions for the fluid velocity and the pressure field are given in subsection 1.2.3.

The model equations (1.1)-(1.7) describe, under a mathematic point of view, the sharp-interface model for a microscopic movement of the crystal interface during solidification under the influence of a forced flow field.

1.1.1 The dimensionless model equations

To facilitate the parametrization of equations for numerical investigations, it is common practise to derive dimensionless model equation. Before we start the definitions of the dimensionless equation system relevant in the context of dendritic growth, we make the following assumptions to simplify the model: We will consider diffusion only in the liquid phase i.e $D_S = 0$ (one-side model). We also assume that the crystal and the melt density are equal and that the gravitational field $\mathbf{g} = 0$.

In order to reproduce large scale physical experiments in a scaled-down and more manageable laboratory setting we present here the scaled model system.

The unscaled equations for the one-sided model are:

$$\begin{aligned}\frac{\partial T}{\partial t} + (\mathbf{u} \cdot \vec{\nabla})T &= D_l \nabla^2 T, \\ T_I &= T_m - T_m \frac{\gamma}{L} \kappa, \\ Lv_n &= (D_L c_p \vec{\nabla} T \Big|_L) \vec{n}, \\ \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \vec{\nabla})\mathbf{u} &= -\frac{1}{\rho} \vec{\nabla} p + \nu \nabla^2 \mathbf{u} \\ \vec{\nabla} \cdot \mathbf{u} &= 0.\end{aligned}$$

The dimensionless temperature $\tilde{T}$ is chosen as

$$\tilde{T} = \frac{c_p(T - T_\infty)}{L},$$

where T_∞ is the temperature of the liquid infinitely far from the growing solid. The scaled dimensionless undercooling is given by

$$\Delta = \frac{c_p(T_m - T_\infty)}{L}.$$

The dimensionless undercooling gives the ratio between the latent heat L , which is released per unit volume during the growth process, and the amount of heat $c_p(T_m - T_\infty)$ that is needed to undercool the liquid from the temperature T_∞ to the melt temperature T_m .

Next, we introduce the variable l as the reference length scale. Thus, the operator $\vec{\nabla}$ is scaled as:

$$\vec{\nabla} = \frac{1}{l} \vec{\nabla}^*. \quad (1.8)$$

Hence, the diffusion equation (1.2) in dimensionless form can be written like:

$$\frac{l^2}{D_L} \frac{\partial \tilde{T}}{\partial t} + \frac{l}{D_L} (\mathbf{u} \cdot \vec{\nabla}^*) \tilde{T} = \nabla^{*2} \tilde{T}. \quad (1.9)$$

This equation leads us to define other two reference scales: The dimensionless time t^* is given by

$$t^* = \frac{D_L}{l^2} t, \quad (1.10)$$

whereas the dimensionless velocity field $\bar{\mathbf{u}}$ reads

$$\bar{\mathbf{u}} = \frac{l}{D_L} \mathbf{u}. \quad (1.11)$$

Thus, by using the defined variables above we can write equations (1.2)-(1.7) in dimensionless form as follows:

Heat conduction:

$$\frac{\partial \tilde{T}}{\partial t^*} + (\bar{\mathbf{u}} \cdot \vec{\nabla}) \tilde{T} = \nabla^2 \tilde{T}, \quad (1.12)$$

Gibbs Thomson relation:

$$\tilde{T}_I = \Delta - d_0^* \kappa^*, \quad (1.13)$$

with κ^* being the dimensionless local curvature and d_0^* is the anisotropic capillary length given by [80, 47]

$$d_0^*(\theta) = d_0(1 - \epsilon_m \cos(m\theta)), \quad (1.14)$$

where m determines the number of axis of symmetry for the dendrite, ϵ_m the anisotropy strength and θ denotes the angle between the global growth direction and the local normal direction at the respective point along the interface¹, where d_0 is given by

$$d_0 = \frac{c_p T_m}{L^2} \gamma.$$

Stefan condition:

$$v_n^* = -\vec{\nabla} \tilde{T}_I \vec{n}, \quad (1.15)$$

with v_n^* being the dimensionless solid-liquid interface growth velocity

Navier-Stokes equations:

$$\frac{\partial \bar{\mathbf{u}}}{\partial t} + (\bar{\mathbf{u}} \cdot \vec{\nabla}) \bar{\mathbf{u}} = -\vec{\nabla} p + Pr \nabla^2 \bar{\mathbf{u}}, \quad (1.16)$$

$$\nabla \cdot \bar{\mathbf{u}} = 0, \quad (1.17)$$

where $Pr = \frac{\nu}{D}$ is the Prandtl number.

In Table (1.1) we give a summary of all the scaled variables in the model.

1.2 Numerical approach

In this chapter we describe our computational approach to microstructure solidification taking into account hydrodynamic convection in the liquid

¹In this work all the simulations were carried out using four fold symmetry i.e $m = 4$

Variable	Unscaled	Scaled
Temperature	T	$\tilde{T} = \frac{c_p(T - T_\infty)}{L}$
Time	t	$t^* = \frac{D_L}{l^2}t$
Space	x	$x^* = \frac{x}{l}$
Velocity	$\mathbf{u}$	$\bar{\mathbf{u}} = \frac{l}{D_L}\mathbf{u}$
Capillary length	$d_0 = \frac{c_p T_m}{\delta x L^2} \gamma$	$d_0^* = \frac{c_p T_m}{L^2 l} \gamma$
Pressure	p	$\bar{p} = \frac{l^2}{D_L^2 \rho} p$

Table 1.1: Summary of the scaled system used in the model.

phase - which we call ROTSMAC (Rotational-Simplified-Marker-And-Cell approach) - in detail. The aim of this approach is to resolve the anisotropic effects along the microstructure's solid-liquid interface in such detail that also the so-called doublonic microstructure (see section 1.4), whose rise is known to depend crucially on anisotropic effects, can be investigated with respect to its evolution under the influence of hydrodynamic convection in the liquid phase.

To do so we introduce on the one hand an additional, grid-independent polygon line to represent the solid-liquid interface. This polygon has independent point resolution, this means that this polygon has the freedom to move in between the diffusion grid. Another important issue of this approach is that we impose the no-slip condition exactly at the solid-liquid interface. It is done by employing linear/bilinear interpolation of the velocity field direct at the points on the solid-liquid interface. The flow field is computed by employing all necessary elements from an extension of the GESMAC method given in [71]. Since the whole physical problem is very sensitive to all kind of anisotropy, in the resulting algorithm, we average calculations for four interfaces rotated with respect to each other, to additionally average out numerical anisotropies from the underlying Eulerian grid. Doing so, we follow again the approach discussed in [37] for microstructure solidification without hydrodynamics in the molten phase.

This combination of methods and the resulting highly accurate resolution of the anisotropic energetics along the solid-liquid interface allows us to simulate the doublonic structure under the influence of flow as described in section 1.4. It is exactly this highly precise treatment of the anisotropic physics along the solid-liquid interface in which this approach differs from previous approaches for microstructure solidification taking into account the effect of flow as given e.g. in [72, 9, 2, 54]

1.2.1 Numerical setup and update procedure

Before we describe our new numerical approach we define our computational domain. The computational domain consists of a channel formed by

two rigid sidewalls, a frame far away from the interface and a frame which gives the moving solid-liquid interface. An inflow region is located on top and an outflow region on bottom of the investigated domain (see Fig. 1.1).

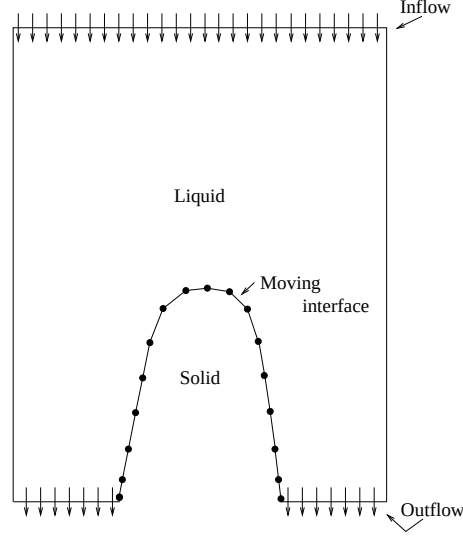


Figure 1.1: Description of the physical problem.

In the context of studies of this chapter we consider the growth of a crystal from its melt (pure substance) in a way similar to the freezing of ice in a sample of pure water. The growth process is controlled by the diffusion of latent heat. The liquid phase is modelled as an incompressible viscous fluid, so that for a given time t_0 the velocity field $\bar{\mathbf{u}}(\mathbf{x}, t_0)$ and the boundary conditions for the velocity and pressure are known.

The initial diffusion field $\tilde{T}(\mathbf{x}, t_0)$ is given based on the Ivantsov solution for a parabolic needle crystal [38].

$$\tilde{T}(\mathbf{x}, t_0) = 2e^{Pe} \sqrt{Pe} \int_{\sqrt{Pe}}^{\infty} e^{-x^2} dx \quad (1.18)$$

where $Pe = \frac{\rho_{tip}\eta}{2D}$ is the Péclet number, with ρ_{tip} being the tip radius and η

the growth velocity. When treating the above free boundary problem arising in convection-influenced solidification at the microscale it is extremely important to reduce the numerical anisotropy sufficiently, so that it does not override the physical, i.e. capillary, anisotropies along the solid-liquid interface, which strongly influence the morphology evolution at the microscale. Therefore, to suppress the numerical anisotropy sufficiently, we employ a scheme proposed by Ihle and Müller-Krumbhaar in [37] which is combined with an enhanced scheme for hydrodynamic flow in moving domains based on the GENSMAC method [71]. The scheme proposed in [37] employs two or more computational grids which are rotated with respect to each other.

In this work we make use of four grids rotated by a fixed angle of $\pi/8$ against another (see Fig. 1.2).

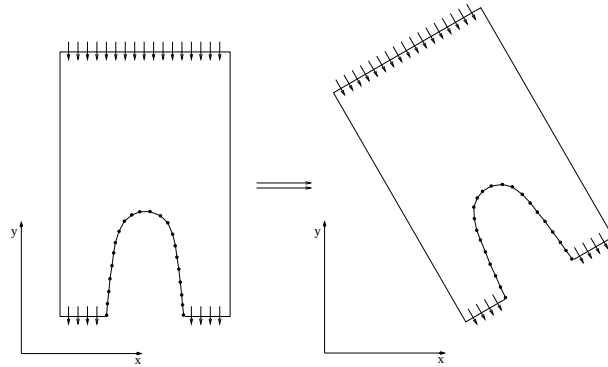


Figure 1.2: Example of the rotated grid.

After defining the computational domain, consistent initial conditions have to be applied to start the calculations.

As a part of the procedure to suppress numerical anisotropy the following scheme is computed independently on all four grids and respective interfaces.

1. Initialize the velocity, pressure and diffusion field for all the grids.

The updated growth velocity at the time $t_{n+1} = t_n + \delta t$ is calculated following:

- (a) Flag the domain using the procedure described in subsection 1.2.5.
- (b) Apply the correct boundary conditions for the fluid velocity components, the pressure field and the diffusion field.
- (c) With the initial diffusion field, calculate the local curvature and the Gibbs-Thomson relation (1.13) at each interface point.
- (d) Calculate the intermediate velocity field $\tilde{\mathbf{u}}$ as

$$\frac{\partial \tilde{\mathbf{u}}}{\partial t} = -(\tilde{\mathbf{u}} \cdot \vec{\nabla})\tilde{\mathbf{u}} - \vec{\nabla}\tilde{p} + Pr\nabla^2\tilde{\mathbf{u}} \quad (1.19)$$

with $\tilde{\mathbf{u}}(\mathbf{x}, t_0) = \bar{\mathbf{u}}(\mathbf{x}, t_0)$ using the correct boundary conditions for $\bar{\mathbf{u}}(\mathbf{x}, t_0)$ and $\bar{p} = \tilde{p}$ the intermediate pressure. It can be shown [71] that $\tilde{\mathbf{u}}(\mathbf{x}, t)$ has the correct vorticity at time t . However, $\tilde{\mathbf{u}}(\mathbf{x}, t)$ does not satisfy (1.7).

Thus, there is a scalar function $\psi(\mathbf{x}, t)$, so that

$$\bar{\mathbf{u}}(\mathbf{x}, t) = \tilde{\mathbf{u}}(\mathbf{x}, t) - \nabla\psi(\mathbf{x}, t) \quad (1.20)$$

with

$$\nabla^2\psi(\mathbf{x}, t) = \vec{\nabla} \cdot \tilde{\mathbf{u}}(\mathbf{x}, t). \quad (1.21)$$

Now it is easy to see, that $\bar{\mathbf{u}}(\mathbf{x}, t)$ satisfies (1.7) and the vorticity remains unchanged.

We compute the system of equation (1.21) using the method of Conjugated Gradient Solver [6] to find the values of $\psi(\mathbf{x}, t)$, then

we recover to the equation (1.20) to calculate the updated velocity field $\bar{\mathbf{u}}(\mathbf{x}, t)$.

- (e) Moreover, we have to compute the updated pressure field using

$$p(\mathbf{x}, t) = \tilde{p}(\mathbf{x}, t) + \frac{\psi(\mathbf{x}, t)}{\delta t}. \quad (1.22)$$

- (f) Calculate the diffusion field in the liquid phase using (1.12)

- (g) Finally we calculate the interface velocity v_n using the relation (1.15)

To calculate the normal velocity, a second order approximation method was used. Since the points of the solid-liquid interface do not coincide with the diffusion grid, there is a need to use a special six-point interpolation which is symmetrized and insensitive to changes of the normal direction. For further improvement, this scheme is combined with a boundary element method [37] to calculate the normal velocity².

- (h) Calculate the new interface position [37]

²At this point must be clear that the interpolation method used to compute the normal velocity produce a systematic numerical error and this error generate numerical noise in the whole system. The influence of this noise in the growth of the dendritic structure was investigated in the references [41]. In these investigations they have shown that the noise, from one side contribute to the growth of side branches in the dendritic structure and from the other side, there is a critical noise value in which it makes the dendritic tip unstable [37, 41]. This critical noise is dependent of the anisotropy ϵ_m and they have shown that only for very small value of the anisotropy it can be reached(achieved). This means that only in the case of very small anisotropy value we have to take care about the influence of numerical noise in the system.

(i) Update the time

After the interface velocity has been calculated for all 4 grids, we determine the average over all these interfaces. This average interface is then redistributed to the different grids by rotation and translation.

To be able to investigate the long-time behavior of the dendritic tip, we implement the above scheme in a moving frame, which means that if the most advanced solid line reaches a marked height the bottom line of the grid point is moved out of the domain and a new top line is added.

1.2.2 Time-step control

In this work we solve the Navier-Stokes equations and the heat equation using an explicit scheme. In order to maintain numerical stability, the time-step has to be selected as follows:

From the heat equation we obtain the condition

$$\delta t_1 < \frac{1}{2D_L} \left(\frac{1}{\delta x^2} + \frac{1}{\delta y^2} \right)^{-1}. \quad (1.23)$$

Moreover, the second stability restriction requires for the viscosity [78]:

$$\delta t_2 < \frac{1}{2\nu} \left(\frac{1}{\delta x^2} + \frac{1}{\delta y^2} \right)^{-1}. \quad (1.24)$$

The third and last restriction states that a virtual particle should cross no more than one grid spacing in each time-step. This criteria is known as CFL (Courant, Friedrichs and Lewy) condition [35]:

$$\delta t_3 < \min \left(\frac{\delta x}{|\bar{u}|_{\max}} + \frac{\delta y}{|\bar{v}|_{\max}} \right), \quad (1.25)$$

where $\bar{u}$ and $\bar{v}$ are the main system velocities. Thus, the stability-limiting time-step used in our implementation follows as:

$$\delta t = \min(\delta t_1, \delta t_2, \delta t_3). \quad (1.26)$$

1.2.3 Boundary conditions

In this work we use the following boundary conditions:

Velocity field:

- **Moving interface:** At the moving interface we apply the no-slip condition

$$\bar{\mathbf{u}} = 0. \quad (1.27)$$

The procedure to apply this boundary condition directly at the solid-liquid interface is described in section (1.2.6).

- **Rigid contour:** At the rigid contour we apply the symmetry boundary condition

$$\frac{\partial \bar{u}_t}{\partial n} = 0 \quad \text{and} \quad \bar{u}_n = 0, \quad (1.28)$$

where n means the normal direction, u_n is the normal velocity and u_t is the tangential velocity.

- **Inflow:** The basic condition for flow injection reads

$$\bar{\mathbf{u}}_n = U_{inf} \quad \text{and} \quad \bar{u}_t = 0, \quad (1.29)$$

where U_{inf} is the prescribed inflow velocity.

Enforcing this condition on the different rotated grids leads to the following definitions:

$$\bar{\mathbf{u}} = R_\theta U_{inf}, \quad (1.30)$$

where R_θ is the rotation matrix

$$R_\theta = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix}.$$

- **Outflow:** The condition for flow ejection reads

$$\frac{\partial \bar{u}_t}{\partial n} = 0 \quad \text{and} \quad \bar{u}_n = \bar{u}_{out}, \quad (1.31)$$

where $\bar{u}_{out}$ is the outflow velocity.

Diffusion field:

- **Rigid contour:** At the rigid contour we apply reflecting boundary conditions for the diffusion field, i.e.

$$\frac{\partial \tilde{T}}{\partial n} = 0, \quad (1.32)$$

- **Moving interface:** The diffusion field $\tilde{T}$ at each interface point is given by the Gibbs-Thomson relation (1.13), with the curvature being computed locally at each interface point.

1.2.4 Discretization scheme

Following the underlying ideas of the SMAC [5] and GENSMAC [71] methods, the above equations (1.12)-(1.17) are discretized employing a finite

difference approach on a staggered grid [35]. Fig. 1.3 shows an example of the computational cell configuration and the respective locations of the physical field variables. Note that the velocities are calculated on the face of the cell and operations for pressure, diffusion and the divergences are evaluated at the center of each cell. The choice of a “staggered grid” as a computational cell is directly connected to the discretization of the Poisson equation [27].

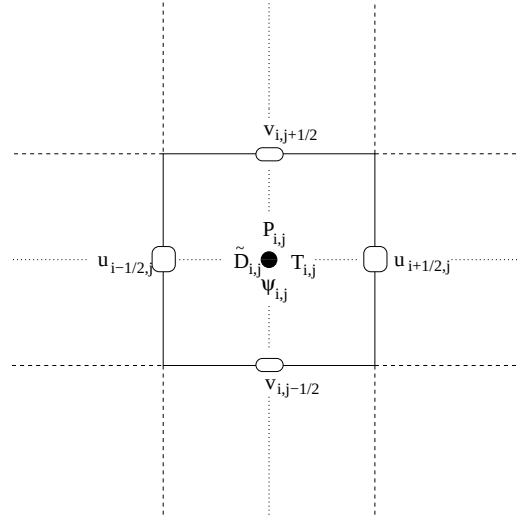


Figure 1.3: Staggered grid, where u is the x -component of velocity and v is the y -component of velocity.

For simplicity we show the discretization only for the x -component, consider $\bar{\mathbf{u}} = (\bar{u}, \bar{v})$.

The x -component of the momentum equation (1.16) is discretized by finite differences at the point $(i + 1/2, j)$ using a first order approximation for the time derivative and second order approximation for the viscous term

$$\begin{aligned}
\tilde{u}_{i+\frac{1}{2},j}^{n+1} = & \bar{u}_{i+\frac{1}{2},j}^n - \delta t \left[\text{conv}(\bar{u})_{i+\frac{1}{2},j} + \left(\frac{\tilde{p}_{i+1,j} - \tilde{p}_{i,j}}{\delta x} \right) \right. \\
& - Pr \left(\frac{\bar{u}_{i-\frac{1}{2},j} - 2\bar{u}_{i+\frac{1}{2},j} + \bar{u}_{i+\frac{3}{2},j}}{\delta x^2} \right. \\
& \left. \left. + \frac{\bar{u}_{i+\frac{1}{2},j-1} - 2\bar{u}_{i+\frac{1}{2},j} + \bar{u}_{i+\frac{1}{2},j+1}}{\delta y^2} \right) \right]. \quad (1.33)
\end{aligned}$$

The convective term $\text{conv}(\bar{u})_{i+\frac{1}{2},j}$ is discretized using a first order upwind scheme [35].

In a similar manner the scheme for the y -component can be derived.

The Poisson equation (1.21) is discretized using a second order approximation for the Laplace term and the divergent term

$$\frac{\psi_{i-1,j} - 2\psi_{i,j} + \psi_{i+1,j}}{\delta x^2} + \frac{\psi_{i,j-1} - 2\psi_{i,j} + \psi_{i,j+1}}{\delta y^2} = \tilde{D}_{i,j}, \quad (1.34)$$

where

$$\tilde{D}_{i,j} = \frac{\tilde{u}_{i+\frac{1}{2},j} - \tilde{u}_{i-\frac{1}{2},j}}{\delta x} + \frac{\tilde{v}_{i,j+\frac{1}{2}} - \tilde{v}_{i,j-\frac{1}{2}}}{\delta y}. \quad (1.35)$$

The energy equation is discretized using a second order approximation,

$$\begin{aligned}
\tilde{T}_{i,j}^{n+1} = & \tilde{T}_{i,j}^n - \delta t \left[\text{conv}(\bar{u}\tilde{T})_{i,j} \right. \\
& \left. - \left(\frac{\tilde{T}_{i-1,j} - 2\tilde{T}_{i,j} + \tilde{T}_{i+1,j}}{\delta x^2} + \frac{\tilde{T}_{i,j-1} - 2\tilde{T}_{i,j} + \tilde{T}_{i,j+1}}{\delta y^2} \right) \right], \quad (1.36)
\end{aligned}$$

where $\text{conv}(\bar{u}\tilde{T})_{i,j}$ is the convective term discretized using a first order upwind scheme [35].

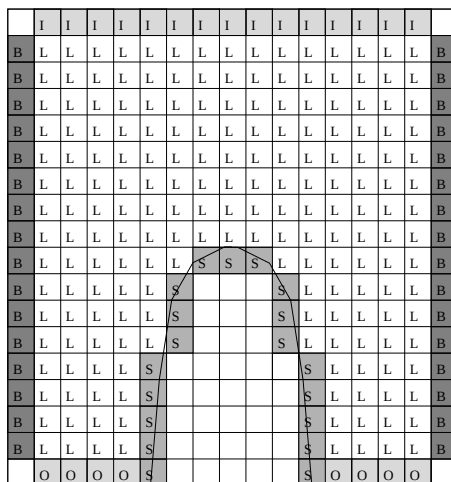
1.2.5 Cell flagging

The domain region is flagged to identify the region where we have to apply boundary conditions and solve the above equations (see Fig. 1.4). Moreover, the mesh is flagged as:

1. **Boundary cells (B):** These are the cells which describe the position of the rigid contour.
2. **Liquid cells (L):** These are the cells which describe the position of the liquid.
3. **Inflow cells (I):** These are the cells which describe the position of the injector.
4. **Outflow cells (O):** These are the cells which describe the position of the ejector.
5. **Solid cells (S):** These are the cells which describe the position of the solid.

1.2.6 Definition of solid interface cells

If the boundary coincides with the mesh grid, we have no problems when the above finite difference equations are applied. However, in our implementation the moving interface is an independent polygon which does not need to coincide with the mesh points. This is necessary to model the physical anisotropies along the solid-liquid interface with high accuracy (see section 1.1)



To solve this problem we took advantage of the method GENSMAC to treat problems where all the boundaries are arbitrarily shaped and the mesh points do not coincide with the boundary points.

The moving interface is defined as a polygon where the space between two polygon points is not bigger than the mesh space δx (see [37]). This polygon train is implemented in a vector structure where we can easily access the polygon points. For each interface point (polygon point) we have to check the coordinate of the forward and the backward interface point and analyze the segment which connects these points (see Fig. 1.5).

The basic idea underlying the classification procedure is to identify where the computational cells are intercepted. Accordingly, these cells are flagged

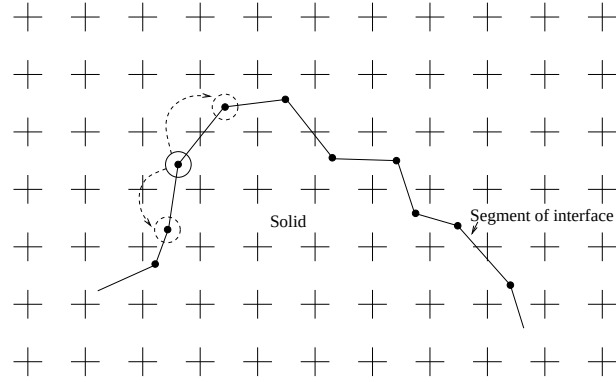


Figure 1.5: Segment of the moving interface.

as S cells or not. First we assume that the interface polygon train cuts a computational cell at two of its edges.

For this scenario we consider eight regular cases which are divided into two groups: The first group are the cells where the curved boundary cuts two adjacent side edges. The second group are the cells where the curved boundary cuts two opposite edges.

To flag the cells, we assume that a cell is divided in four quadrants. If three or more quadrants of a cell are occupied by solid regions we say that this cell is a solid cell (S), otherwise we consider it to be a liquid cell (L).

In the case that an edge cell is cut twice by an interface segment (see Fig. 1.6), we assume that this cell is a liquid cell and the next inner cell is assumed to be a solid cell.

Now the cells are flagged, so that we can impose the no-slip condition directly on the solidifying front. Therefore, the velocities $\bar{\mathbf{u}}$ from the liquid (L) cells which are adjacents to the Solid\Boundary (S\B) cells are interpolated. As described in [71], standard linear (bilinear) interpolation techniques are

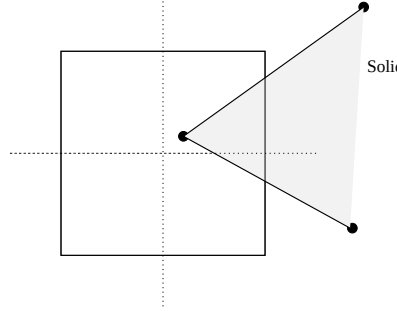


Figure 1.6: Example of a computational cell.

employed. If an S cell has one open side, the $\bar{u}$ values are computed using linear interpolation (see the figure 1.7).

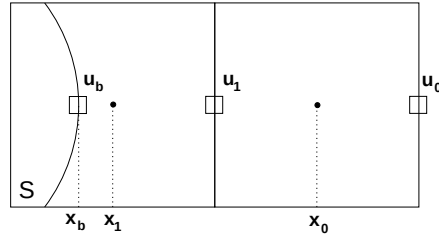


Figure 1.7: S cell with one side open to the liquid.

Then, using linear Lagrangian interpolation to compute u_1 we have

$$u_1 = \frac{x_1 - x_0}{x_0 - x_b} u_0 + \frac{x_1 - x_0}{x_b - x_0} u_b, \quad (1.37)$$

and applying the no-slip condition, $u_b = 0$. We then have

$$u_1 = \frac{x_1 - x_0}{x_0 - x_b} u_0, \quad (1.38)$$

where u_0 is the internal value and x_0, x_1 are points of the diffusion grid.

If an S cell has two sides open to the interior cell (L), then we apply bilinear interpolations, like in [71].

1.3 Numerical validation

To validate and check the implementation of the above equations (1.12)-(1.17) we have performed a number of tests. The flow solver is validated through a comparison with analytical solutions for the Stokes flow through a square array of infinity cylinders.

We also test the convergence of the method by grid refinement studies. The effect of fluid flow on dendritic growth is tested by comparing the results of our numerical implementation with the results found in the literature for dendritic tip velocity.

To conduct the tests, in this section we consider the domain as a square with a circular seed in the center. The crystal axis are aligned with the x - y coordinate axis. We introduce an inlet flow on the top of the domain and an outlet flow on the bottom. We apply symmetrical boundary conditions on the sidewalls of the domain. We set the same temperature in the liquid phase and in the inlet. The flow field is set to the value of U_{inf} in the whole liquid phase. The flow field is relaxed until the steady flow around the seed is achieved.

1.3.1 Stokes flow through an array of cylinders

We start our studies by testing the accuracy of the flow solver and the ability of the flow to pass a curved interface. The fluid flow problem was numerical simulated over a square array of parallel cylinders for different volume fractions. The results were compared to the analytical solution of Drummond and Tahir [23] and Sangani and Acrivos [63]. They derived an

analytical expression for the drag force on the cylinders as a function of the solid fractions.

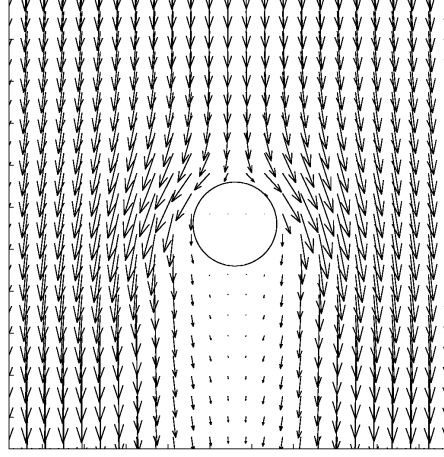


Figure 1.8: Numerical simulation of Stokes flow through an array of cylinders, solid fraction equal to 0.2235.

The simulations were done for a large range of solid fraction. In Fig. 1.8 we show an example of the flow field around a cylinder, with $200d_0 \times 200d_0$ grid points and solid fraction equal to 0.2235.

In figure 1.9 we plot the mean flow velocity versus the solid fraction. We show the comparison of our numerical solution with the analytical expression of Drummond and Tahir [23] and Sangani and Acrivos [63]. As you can see from the picture 1.9 we obtain a very good agreement with the analytical solution, for the case of small solid fraction. In the case of large solid fraction the numerical results deviates from the analytical curve, but this is expected, since the analytical solution breaks down in this regime [23].

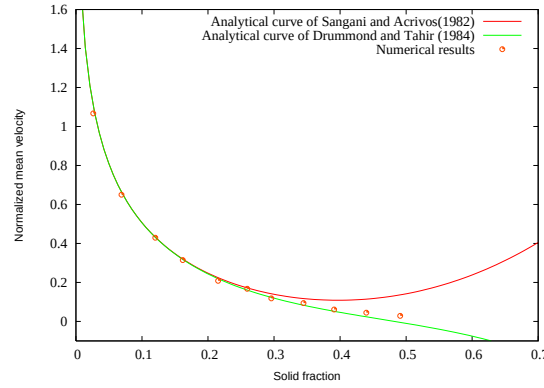


Figure 1.9: Comparison of the analytical solution for the flow passing through an array of cylinders [23, 63] with the numerical solution.

1.3.2 Dendritic tip velocity under the influence of forced flow

In order to validate the simulation of our model for dendritic growth under the influence of a flow field we compare our numerical simulations to the results found in the literature.

In the past few years many authors [42, 56] have used the numerical results of Beckermann et. al. [72] for the tip velocity of a dendritic to test and calibrate their numerical models.

In this section we compare our numerical simulations with the result from Beckermann for the tip velocity of a dendritic growing under the influence of forced convection.

To do so, we select the same input parameters as used in Beckermann simulations, $Pr = 23.1$, $\Delta = 0.55$, $\epsilon_4 = 0.05$ and $U_{inf} = 0.135$. In figure 1.10 we plot the tip velocity of the dendritic versus the dimensionless time.

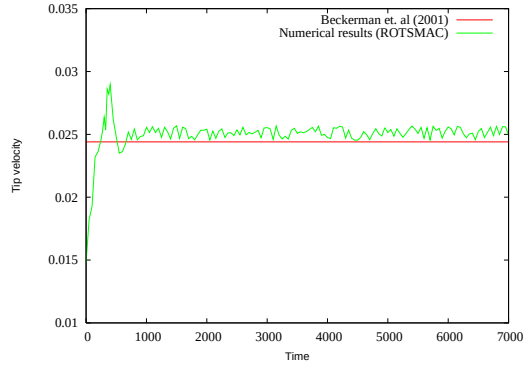


Figure 1.10: Comparison of the dendritic tip velocity under forced flow.

Moreover, we show the comparison of the tip velocity computed using our method with the value of the tip velocity given in the reference [72]. In fact, we observe a very good agreement between our simulations and the results from Beckermann. The converged tip velocity from our method was found to be 0.0252 while Beckermann et al. [72] shows the upstream converged tip velocity equal to 0.0244.

We also compare the tip radius from our simulations to the one from Beckermann method. We obtain the tip radius value equal to 6.1 while from Beckermann et al. [72] the tip radius was found to be equal to 6.88. Within the limits of numerical accuracy this still accounts to an excellent agreement as well as an excellent validation of our numerical approach.

1.4 Investigation of morphology transition induced by fluid flow

Dendritic growth is the best known solidification structure with complex pattern formation at conditions far from equilibrium. Brener *et al.* [16] have analytically formulated a morphology diagram for dendritic growth, which predicts the morphology evolution for different processing parameters. The original morphology diagram is formulated for the case of purely diffusion limited crystal growth, i.e when fluid flow is absent (see Fig. 1.11). Such a morphology diagram tells us for a given material which morphologies and morphology transitions can be expected depending on the two process parameters, surface tension anisotropy and undercooling.

To conduct our investigation on the crystal growth with forced convection we used the kinetic morphology diagram from Brener (Fig. 1.11) as the starting point.

We chose different points of this morphology diagram and used our numerical method to simulate the growth of dendrites, with and without an imposed flow field. In the case of simulations without forced flow i.e. $U_{inf} = 0$, our model can reproduce the predictions of the kinetic morphology diagram of Brener *et al.* [16], see e.g. figure 1.12.

In the case where we include the forced convection in the melt phase, a different scenario was found. We observe that under a certain parameter regime forced flow change the selected tip radius and growth velocity resulting in morphology changes. This has interesting implications for predictions theories of crystal growth under an imposed flow. In such parameter regime

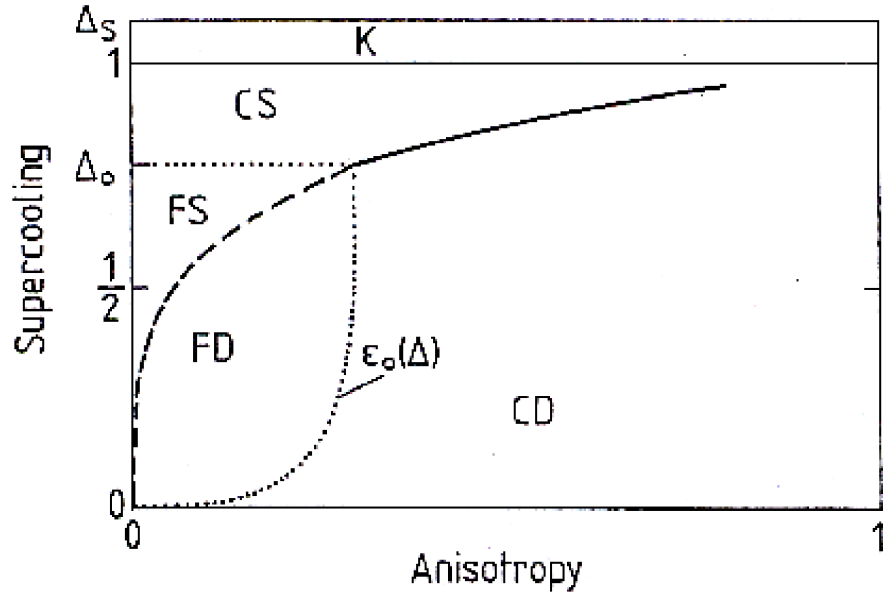


Figure 1.11: Kinetic morphology diagram of pure diffusive crystal growth. It describes the growth morphology in dependence of anisotropy ϵ_4 and the dimensionless undercooling Δ . The possible morphologies are (CD) compact dendrites, (FD) fractal dendrite, (ES) fractal doublon, (CS) compact doublon. The picture was taken from [16].

we find metastable transition from a doublonic to a dendritic morphology. The figure 1.13 illustrates this observation.

This regime was mainly found for dendrites with comparatively high surface tension anisotropy. In the beginning of the simulation the shape of the crystal is a parabola. Then the tip region widens and tip splitting starts. At this time the microstructure undergoes a transition from a doublon to a dendritic morphology. This transition scenario looks similar to the transition from a dendritic to a doublonic morphology found by Stalder *et al.* [70]

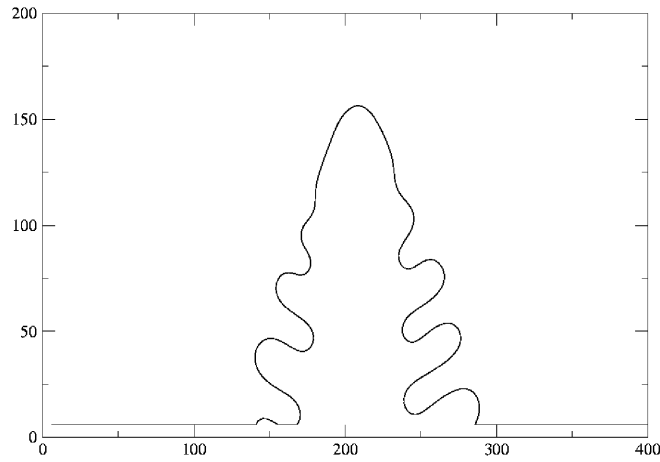


Figure 1.12: Dendritic growth in pure diffusion with $400d_0 \times 400d_0$ lattice size, $d_0^* = 0.2$, $\Delta = 0.5$ and $\epsilon_4 = 0.3$.

(see Fig. 1.14), during experiments with pure melt of a supercooled Xenon. Note, however that in their case the transition was triggered by perturbing the system locally in the experiment. Here no perturbation was carried out. Rather the additional nonlinearities due to the hydrodynamic transport field obviously destabilize the system in a manner that similar dynamic transition scenarios can be triggered. To ensure that this effect is not a simple numerical artifact we carried out simulations with different resolutions which all converged to the displayed scenario.

We could also find stable doublon morphology see Fig. 1.15. In this regime simulations starting from a parabolic shape result in a splitting of the front tip where two fingers grow and remain stable throughout the simulation.

The investigations above allow us to report changes on the morphology diagram of Brener *et al.* [16] when convection effects is taken into account. The new morphology diagram is depicted in Fig. 1.16. The thin line in-

indicates the transition between the dendritic and doublon morphologies for the purely diffusive limited growth case ($U_{inf} = 0$). As you can take from Fig. 1.16 in our simulations with opposed flow this transition has moved in the direction of higher anisotropies. The gray dots indicate fractal dendritic or doublonic morphologies, whereas black squares indicate compact dendritic microstructures. Moreover, similar results were also reported by Medvedev *et al.* [54], although, in their case, the reported shift in the transition line seems not to be only due to flow effects but also due to an artifact of the phase-field approach. Note, however that the morphology diagram should be displayed in three dimensions, as it is calculated using the parameters ϵ_4 , Δ and U_{inf} . Here we choose to show only a plane of this 3D morphology diagram corresponding to the flow velocity $U_{inf} = 0.1$. The three dimensional representation of the morphology diagram (Fig. 1.16) can be seen elsewhere in [68].

A second investigation we carried out concerns the extraction of an improved scaling relation for the microstructure tip velocities we calculated with ROTSMAC. Universal scaling relations of the growth velocities have proved to be a useful tool to summarize the parameter dependence of the nonlinear dynamics at the microscale. In diffusion limited crystal growth these scaling relations only depend on the surface tension anisotropy, the kinetic anisotropy and the strength of the undercooling [1]. They are the link to a second area of interest in crystal growth as well, namely the goal of also improving application-oriented macroscopic solidification simulations. As in the more recent analysis of other multi-phase systems, in this context solidification is starting to be modeled using rigorously derived continuum equations

[10]. In this regard, the incorporation of proper constitutive relations describing the interface topology and the phase interaction on a microscopic scale continues to be the main challenge. A unified model providing a framework for such an incorporation has been recently developed by Wang and Beckermann based on a multi-phase approach and volume averaging [76]. Within their approach the microscale dynamics are incorporated into the macroscopic continuum equations by exchange terms which account for the transfer of mass, momentum, energy and solute across the dendritic interface. Since the momentum exchange term is a function of the dendritic tip velocity, the model depends on a scaling relation for this velocity as discussed above. This implies that the accuracy of the unified model is limited by the accuracy of this scaling relation. Thus, precise scaling relations fit to the respective applied crystal growth conditions are indispensable for quantitative predictions of solidification. In that sense our new approach is a valuable tool for providing more systematic studies of the nonlinear dynamics of hydrodynamically influenced microstructure evolution in solidifying samples. Within this scope, we can extract results for the macroscopic engineering approaches towards solidification via volume averaging [76].

Analytically solving the problem of dendritic growth opposed to a forced flow is an intriguing problem. Even in the case of a forced flow with asymptotically constant velocity used only for the problem of a needle crystal without surface tension, i.e. essentially the analogon of the Ivantsov solution, an exact solution can not be found. Only for the two special cases of an Oseen flow and a potential flow could it be proven rigorously that the exact analytical solution is still an Ivantsov parabola [38], but with a different relation be-

tween undercooling and growth velocity, which is now also a function of the Peclet number of flow [20, 64, 4, 15].

Approaches to solve the above problem taking into account the effects of surfaces tension are based on scaling arguments on one hand [11], as well as on a singular perturbation theory on the other [14]. These theories disagree with respect to the existence of stationary dendritic solutions for the case of an opposed flow. Following Ben Amar and Pomeau [11] a stationary dendritic crystal should exist for arbitrary velocities of the forced flow field, whereas according to Bouissou and Pelce [14] such stationary solutions can not exist beyond a certain velocity of the imposed flow.

From our simulations we get no indication of any stationary needle crystal, up to a certain imposed flow strength. Moreover, just as Bouissou and Pelce [14] we find that for large values of the inflow velocity U_{inf} , oscillations of the tip velocity arise which fully destroy the dendritic growth. For smaller values of U_{inf} , however, we find that V_{tip} (tip velocity) scales with U_{inf} as $V_{tip} \sim U_{inf}^{0.4}$. For the parameter regime we used the cross-over between both scaling regimes which occurs at $U_{inf} = 0.95$ (see Fig. 1.17).

1.5 Discussion

To conclude, here we have presented a new numerical scheme which accurately takes into account the dynamics of the hydrodynamic field at the moving solid-liquid interface, the phase-change dynamics as well as the anisotropic effects along the interface based on a **Sharp interface formulation**. We have applied this scheme successfully to demonstrate the impact

of hydrodynamic flow on a dendritic sample, where it can induce morphology transitions quite different from the ones observed in diffusion limited dendritic growth. Moreover, we have obtained a new relation between the strength of a forced flow U_{inf} and the dendritic tip velocity for the case of small U_{inf} . In that sense our new approach is a valuable tool to provide more systematic studies of the nonlinear dynamics of hydrodynamically influenced microstructure evolution in solidifying samples with the scope to extract these results for macroscopic engineering approaches towards solidification via volume averaging, as well.

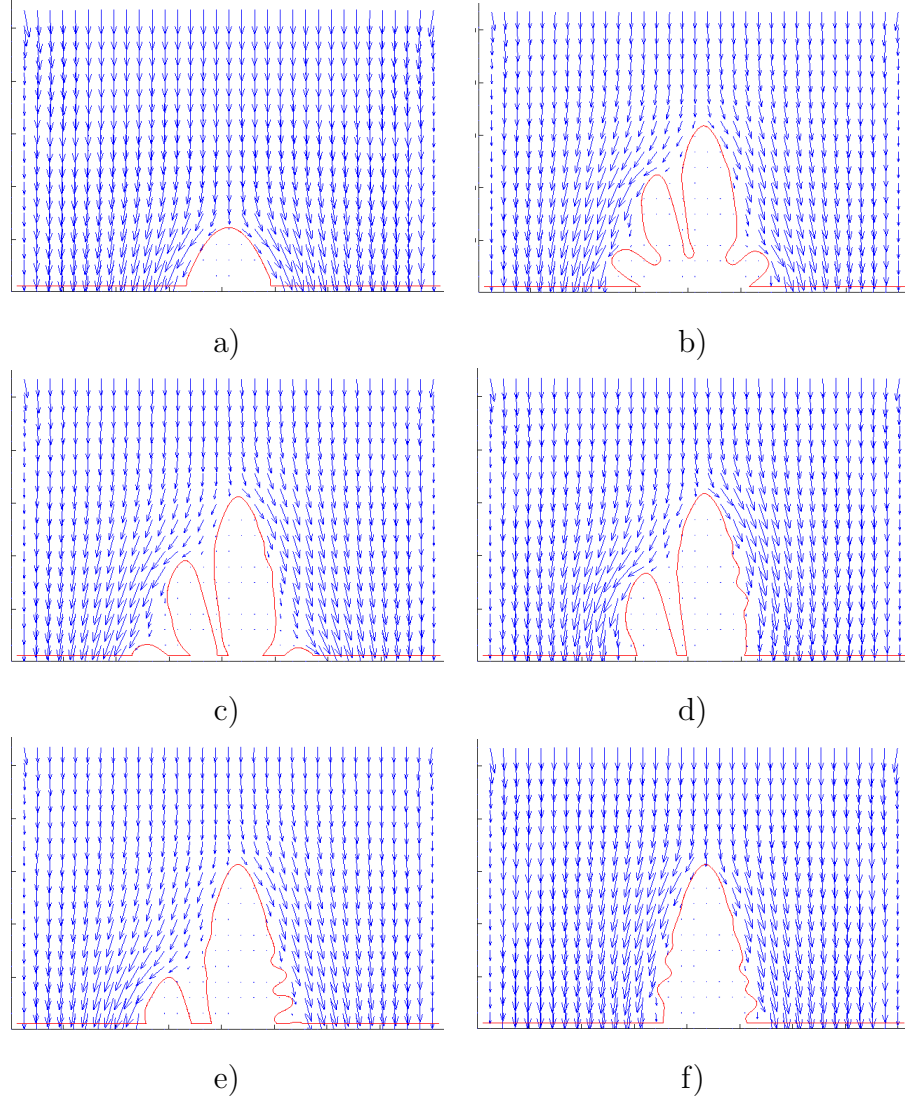


Figure 1.13: Metastable transitions from a double-peak to a dendritic morphology in the new dendritic parameter regime. The pictures describe the time evolution of the simulation which goes from left to right and from up to down. The parameters used are $d_0^* = 0.2$, $\Delta = 0.5$, $\epsilon_4 = 0.35$, $Pr = 1.4$, strength of inflow velocity $U_{inf} = 0.1$ and lattice size $600d_0 \times 600d_0$. For better visualization we have interpolated the velocities onto a grid that is almost 20 times coarser than the one used in the computations.

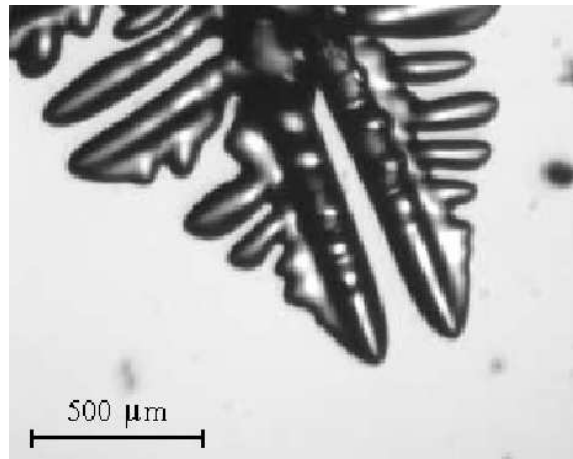


Figure 1.14: Doublon morphology formed after the tip splitting at the front of the growing interface. This picture was taken from the reference [70].

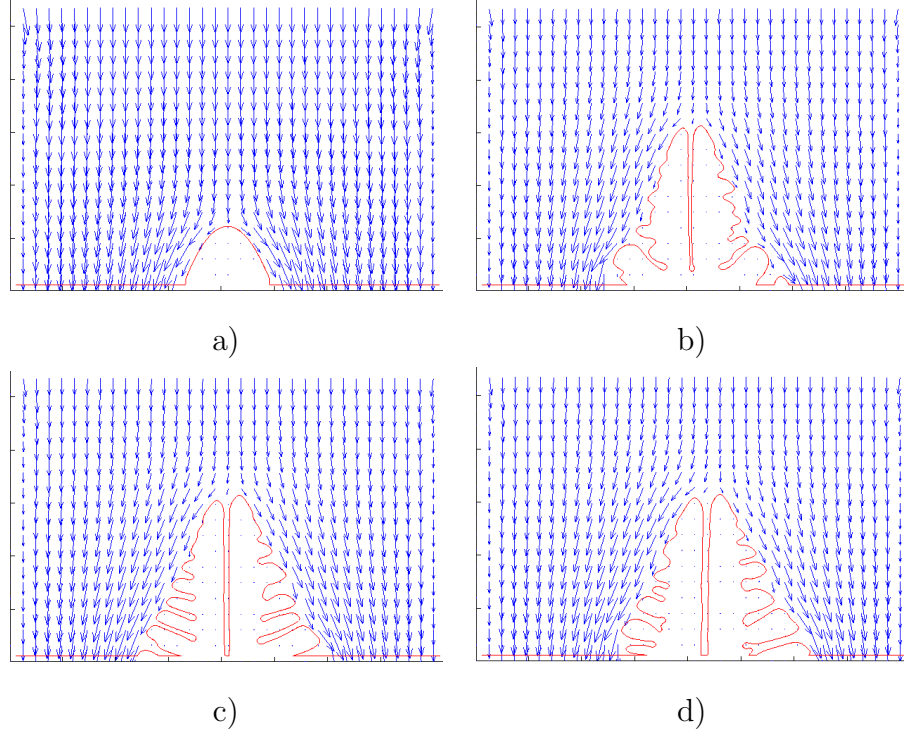


Figure 1.15: Stable transitions from a dendritic to doublon morphology. The pictures describe the time evolution of the simulation which goes from left to right and from up to down. The parameters used are $d_0^* = 0.2$, $\Delta = 0.8$, $\epsilon_4 = 0.35$, $Pr = 1.4$, strength of inflow velocity $U_{inf} = 0.1$ and lattice size $600d_0 \times 600d_0$. For better visualization we have interpolated the velocities onto a grid that is almost 20 times coarser than the one used in the computations.

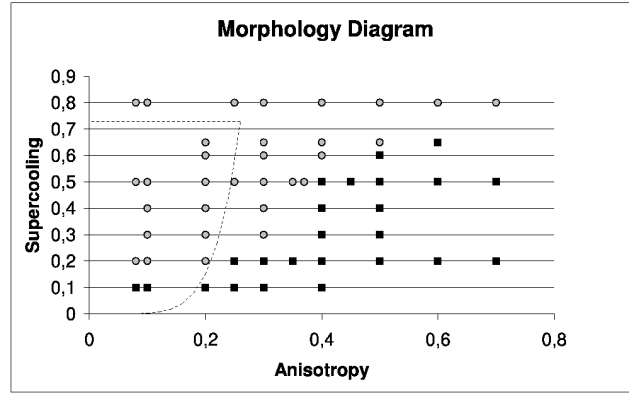


Figure 1.16: New morphology diagram for the dendrite-doublon morphology transition under opposed flow. The parameters used are $d_0 = 0.2$, $Pr = 1.4$, strength of inflow velocity $U_{inf} = 0.1$ and lattice size $700d_0 \times 700d_0$.

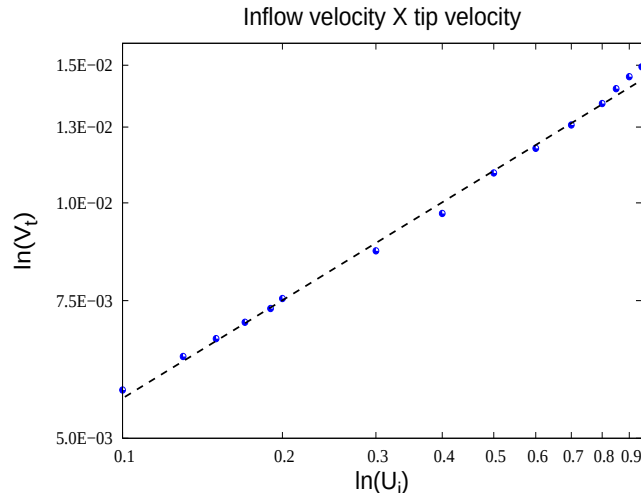


Figure 1.17: Comparison of the numerical tip velocity for different strengthes of flow (dots) with the improved scaling relation represented by the dashed line. The parameters used are $d_0 = 0.2$, $\Delta = 0.5$, $\epsilon_4 = 0.4$ and lattice size $600d_0 \times 600d_0$.

Chapter 2

Quantitative phase-field model for binary alloy system in presence of convection

In this chapter we introduce a new class of methods for the numerical simulation of alloy solidification. This new class of methods is called “phase-field models”. Until now we have obtained quantitative results for dendritic growth problems using the sharp interface technique. In sharp interface models the solidifying front is given explicitly. Hence, we have the problem of how to numerically track the solid-liquid interface and at the same time reproduce results free of unphysical effects caused by numerical artifacts. In chapter 1 we have presented a numerical technique which was able to deal with this issue. Moreover we have described one of many techniques to solve solidification problems using sharp-interface models [37, 42, 2, 3, 81, 12, 83]. Although several techniques have been developed to overcome many of the

drawbacks of the sharp interface approach, it is still difficult to extend this approach to treat a more realistic (physical) problem as e.g. multi-component alloy solidification or problems involving more than one solid phase (multi-phase systems).

Phase-field models on the other hand have the advantage of being prone to generalizations e.g. including the effects of convection in the liquid phase on microstructure development [72], including the contributions of elastic energy on the free energy of the system, and taking into account, in a proper way, the effects of attachment kinetics on the interface of the pattern formation during solidification. Over the past two decades, they have become a standard tool for solving many physical and material science problems. The phase-field approach belongs to a group of methods that rely on treating a microscopically sharp interface as a diffuse region immersed in the calculation domain.

The attractiveness of the phase-field method is that its evolutionary equations are derived in a thermodynamically consistent manner and there is no need to track the interface, since the interface is part of the solution. The phase-field equations are defined over the whole domain where we introduce the phase-field variable ϕ that varies smoothly from -1 to 1 between bulk phases over the diffuse interface region of width W (see Fig. 2.1). The phase field variable ϕ serves to distribute the interfacial forces and other source terms over the diffuse interface region.

These evolution equations are considered to be a relaxation in direction to the minimum of the free energy functional, similar to the time-dependent Ginzburg-Landau models for the out-of-equilibrium thermody-

namics of phase transitions [48]. The price to pay for this simple choice of the equations is the introduction of the new scale W into the problem. The typical size of the solid-liquid interface is of the order of nanometers whereas typical microstructural patterns are in the microscale. Hence, to numerically solve such a multiscale problem is clearly unfeasible. In order to reduce the gap between the scales of the interface thickness and the pattern, the solid-liquid interface needs to be chosen several orders of magnitude thicker than in the real physical problem. Doing so, it is clear that the simulations will become dependent of the choice of W . To overcome this problem Karma & Rappel [44, 45] developed the so called “thin-interface limit” approach in which W is considered small but finite. In this approach the sharp-interface limit of the phase-field model is checked by matching, order by order, terms of the asymptotic expansions for the field in power of W in region of slow (the bulk) and rapid (the interface) variation of the fields. At the lowest order in the interface thickness W , this procedure is quite straightforward and yields a Free Boundary Problem (FBP) that does not exhibit a dependence on W [43, 24, 28]. The solution of the FBP now becomes independent of the choice of W but it still produces unphysical effects associated with the thickness of the interface W . To eliminate it, Karma & Rappel [45] developed an anti-trapping term which counterbalances these effects. This approach was first developed for the pure substance in two and three dimensions [45]. Recently, it has been extended to simulate the solidification of a dilute binary alloy, where the diffusivity is unequal in solid and liquid [43, 24].

While the basic mechanisms of dendritic growth could be understood in many aspects using quantitative phase-field models [45, 43, 24, 56], the

relevance of this understanding for practical applications has been questioned by the fact that we can have direct quantitative comparisons between the experiments and the theory only in rare conditions.

Generally, this description refers to a situation at a small undercooling and without convection. Because in most real-life situations convection is inevitable, a better understanding of dendritic growth in presence of flow in the melt is an important theoretical and practical problem.

Under normal growth condition, i.e. if we do not have a microgravity setup, the inhomogeneous temperature distribution in the solidification sample will produce thermal convection [81, 83]. Even under microgravity the density difference between the two phases induces convection [51, 19, 83]. It is also clear that under gravity, natural convection can substantially influence the growth process and the features of the resulting pattern [81, 83, 73, 55, 54].

Numerical simulations of dendritic growth under convection influence for pure substance have been performed in diverse geometries [72, 9, 81, 54] and with both imposed flows and natural convection [7, 73, 81, 83, 54, 69]. For binary alloys much less has been done [83, 81] and many aspects of such processes still have to be investigated. Therefore, we present a phase-field model to investigate the influence of convection on dendritic growth of binary alloys.

Including fluid flow in phase-field models for binary alloys is a very demanding task. As we have seen in the chapter 1, fluid flow brings an additional length scale to the model which must be controlled during the simulations.

2.1 Description of the model

The approach presented in this chapter is based on the quantitative phase-field model for binary alloys defined in [43, 24]. In our extension, the phase field equations remain unchanged and we assume that the phase-field is not advected by the flow field. A no-slip condition at the solid-liquid interface is enforced by adding a source term [72] in the Navier-Stokes equations. Doing so, the no-slip condition is accurately reproduced regardless of the diffuse interface thickness [9].

We denote ϕ as the phase-field variable, where ϕ varies smoothly from 1 in the solid to -1 in the liquid. The interface is represented by the contour $\phi = 0$, see Fig. 2.1.

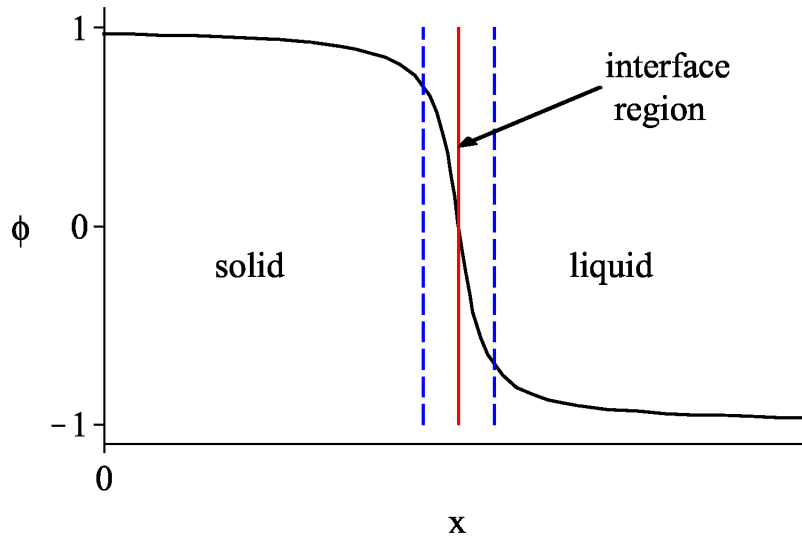


Figure 2.1: Phase-field profile.

The starting point for developing the model is the free energy functional of the system [24]

$$\mathcal{F} = \int_V f(\nabla\phi, \phi, c, T) dV, \quad (2.1)$$

with the free-energy density defined as

$$f(\nabla\phi, \phi, c, T) = K f_{grad}(\nabla\phi) + H f_\phi(\phi) + X f_c(\phi, c, T), \quad (2.2)$$

where f_ϕ depends only on the phase-field and provides the double well potential, f_c couples the phase fields to the concentration and temperature; f_{grad} sets a free energy cost for gradients in ϕ , forcing the interface to have a finite width; H and X are constants with dimensions of energy per unit volume and K has dimension of energy per unit length.

In the variational form the phase field equations read

$$\tau(\phi) \frac{\partial\phi}{\partial t} = -\frac{1}{H} \frac{\delta\mathcal{F}}{\delta\phi} \quad (2.3)$$

where H is introduced to remove the dimension of $\mathcal{F}$.

The conserved concentration field obey the continuity equation

$$\frac{\partial c}{\partial t} + (1 - \psi)(\mathbf{v} \cdot \vec{\nabla})c + \vec{\nabla} \cdot \vec{J} = 0 \quad (2.4)$$

where $\mathbf{v}$ is the fluid velocity, ψ is the solid fraction coupled with the phase-field ϕ by $\psi = (1+\phi)/2$, $\psi \in [0, 1]$ and $\vec{J}$ is the flux of the scaled concentration c

$$\vec{J} = -M(\phi, c) \vec{\nabla} \frac{\delta\mathcal{F}}{\delta c} \quad (2.5)$$

with $M(\phi, c)$ being a mobility.

The fluid motion is described by the modified Navier-Stokes equations

$$\begin{aligned} \frac{\partial(1 - \psi)\mathbf{v}}{\partial t} = & -(1 - \psi)(\mathbf{v} \cdot \vec{\nabla})\mathbf{v} - (1 - \psi)\vec{\nabla} \frac{p}{\rho_0} + \vec{\nabla}[\nu \vec{\nabla}(1 - \psi)\mathbf{v}] \\ & + M_1^2, \end{aligned} \quad (2.6)$$

where p is the pressure, ρ_0 is the liquid density, ν is the kinematic viscosity and M_1^2 is a dissipative interfacial force per unit volume given by

$$M_1^2 = -2h\nu \frac{\psi^2(1-\psi)}{W^2} \mathbf{v}, \quad (2.7)$$

with h being a constant [9] and $W = \sqrt{K/H}$.

The conservation equation for mass takes the following form:

$$\vec{\nabla} \cdot [(1-\psi)\mathbf{v}] = 0. \quad (2.8)$$

Taking the appropriate form for f_{grad} , f_ϕ , f_c and switching to a non-variational formulation, for reasons described in reference [24], we can write the phase-field equation as

$$\tau(T) \frac{\partial \phi}{\partial t} = W^2 \nabla^2 \phi - f'(\phi) - \frac{\tilde{\lambda}}{1-k} g'(\phi) \left(e^u - 1 - \frac{T-T_0}{mc_l^0} \right) \quad (2.9)$$

where $\tau(T) = \tau_0(1 + (T-T_0)/mc_l^0)$, $f(\phi) = -\phi^2/2 + \phi^4/4$, $g(\phi) = (15/8)(\phi - 2\phi^3/3 + \phi^5/5)$, k is the partition coefficient and u is the dimensionless measure of the deviation of the chemical potential from its equilibrium at a reference temperature, and it is defined as

$$u = \ln \left[\frac{2c/c_l^0}{1+k-(1-k)h(\phi)} \right] \quad (2.10)$$

with $h(\phi) = \phi$ and c_l^0 represents the liquidus concentration. $\tilde{\lambda}$ can be defined as

$$\tilde{\lambda} = \frac{L|m|(1-k)c_l^0}{2HT_m}, \quad (2.11)$$

where L is the latent heat of fusion, T_m is the melting temperature and H can be expressed in terms of the surface tension [24]. The term proportional to $\tilde{\lambda}$ represents the driving force for the solidification.

The flux $\vec{J}$ of equation (2.5) is then defined as

$$\vec{J} = -Dc\tilde{q}(\phi)\vec{\nabla}u - \vec{J}_{anti}, \quad (2.12)$$

where $\tilde{q}(\phi)$ is given by

$$\tilde{q}(\phi) = \frac{1 - \phi}{1 + k - (1 - k)h(\phi)} + \frac{(1 + \phi)}{2D}D_s \quad (2.13)$$

which is only valid for small solid diffusivity and

$$\vec{J}_{anti} = aWc_l^0(1 - k)e^u \frac{\partial \phi}{\partial t} \frac{\vec{\nabla} \phi}{|\vec{\nabla} \phi|}, \quad (2.14)$$

is the anti-trapping current [24], with $a = 1/2\sqrt{2}$. The anti-trapping current is needed here in order to counterbalance spurious effects when the interface thickness is enlarged. This effect is well known as artificial solute trapping effect, the solute atoms cannot “escape” fast enough into the liquid in order to maintain local equilibrium. Rather, they are trapped by advancing solidification front and the partition relation becomes invalid [60]

It is convenient to rewrite the equations above in terms of a new variable $U = \frac{e^u - 1}{1 - k}$ [43, 24].

Thus, making the change of variable the equations become:

$$\tau(T) \frac{\partial \phi}{\partial t} = W^2 \nabla^2 \phi + \phi - \phi^3 - \lambda g'(\phi) \left(U + \frac{T - T_0}{(1 - k)mc_l^0} \right) \quad (2.15)$$

and

$$\begin{aligned} \left(\frac{1+k}{2} - \frac{1-k}{2} h(\phi) \right) \frac{\partial U}{\partial t} &= -(1-\psi)(\mathbf{v} \cdot \vec{\nabla})c \\ &+ \vec{\nabla} \left(Dq(\phi) \vec{\nabla} U + aW[1 + (1-k)U] \times \frac{\partial \phi}{\partial t} \frac{\vec{\nabla} \phi}{|\vec{\nabla} \phi|} \right) \\ &+ [1 + (1-k)U] \frac{1}{2} \frac{\partial h(\phi)}{\partial t} \end{aligned} \quad (2.16)$$

where

$$\lambda = \frac{15}{8} \tilde{\lambda}.$$

This model reduces in its thin-interface limit to the standard FBP of alloy solidification. The relation between the phase-field parameters and the physical quantities are given by the capillary length

$$d_0 = \frac{a_1 W}{\lambda}$$

and the kinetic coefficient

$$\beta = a_1 \frac{\tau(T)}{\lambda W} \left[1 - a_2 \lambda \frac{W^2}{\tau_0 D} \right],$$

where the constants a_1 and a_2 are given by $a_1 = 5\sqrt{2}/8$ and $a_2 = 0.6267$ as in Ref. [43, 24]. In this chapter β is assumed to vanish by making $\tau_0 = a_2 \lambda W^2 / D$.

2.2 Anisotropic and dimensionless model

Before we present the complete model in dimensionless form, we include anisotropy in the model by making W and τ orientation dependent [45]. Thus,

$$W(\theta) = Wa_s(\theta) = W(1 + \epsilon_4 \cos(4\theta)), \quad (2.17)$$

$$\tau(\theta) = \tau_0 a_s(\theta)^2, \quad (2.18)$$

where $\theta = \arctan(\partial_y \phi / \partial_x \phi)$, is the angle between the direction normal to the phase-field interface and the x axis, and ϵ_4 is the anisotropy strength.

The equations (2.7), (2.15) and (2.17) are transformed in a dimensionless form by scaling length in units of W and time in units of τ_0 . Moreover, using length and time scale we can scale almost all other parameters. An overview of the scaled variables can be seen in Table 2.1.

Forthmore, the complete anisotropic phase-field model for binary alloys taking into account fluid flow in the melt phase can be written in dimensionless form:

Phase field equation:

$$\begin{aligned} a_s(\theta)^2 \frac{\partial \phi}{\partial \tilde{t}} = & \tilde{\nabla} \cdot [a_s(\theta)^2 \tilde{\nabla} \phi] + \partial_x \left(|\vec{\nabla} \phi|^2 a_s(\theta) \frac{\partial a_s(\theta)}{\partial (\partial_x \phi)} \right) \\ & + \partial_y \left(|\vec{\nabla} \phi|^2 a_s(\theta) \frac{\partial a_s(\theta)}{\partial (\partial_y \phi)} \right) + \phi - \phi^3 \\ & - \lambda g'(\phi) \left(U + \frac{T - T_0}{(1 - k)mc_l^0} \right), \end{aligned}$$

Variable	Unscaled	Scaled
Space	x	$\tilde{x} = x/W$
Time	t	$\tilde{t} = t/\tau_0$
Diffusion coefficient	D	$\tilde{D} = \frac{\tau_0}{W^2} D$
Velocity	$\bar{v}$	$\tilde{v} = \frac{\tau_0}{W} \bar{v}$
Viscosity	ν	$\tilde{\nu} = \frac{\tau_0}{W^2} \nu$
Pressure	p	$\frac{\tilde{p}}{\rho_0} = \frac{\tau_0^2}{W^2} \frac{p}{\rho_0}$

Table 2.1: Resume of the scale variables for the phase-field model equations.

Diffusion equation:

$$\begin{aligned}
& \left(\frac{1+k}{2} - \frac{1-k}{2} h(\phi) \right) \frac{\partial U}{\partial \tilde{t}} = -(1-\psi)(\tilde{\mathbf{v}} \cdot \tilde{\nabla})c \quad (2.19) \\
& + \tilde{\nabla} \left(\tilde{D} q(\phi) \tilde{\nabla} U + \frac{1}{2\sqrt{2}} [1 + (1-k)U] \times \frac{\partial \phi}{\partial \tilde{t}} \frac{\tilde{\nabla} \phi}{|\tilde{\nabla} \phi|} \right) \\
& + [1 + (1-k)] U \frac{1}{2} \frac{\partial h(\phi)}{\partial \tilde{t}}
\end{aligned}$$

Momentum equation:

$$\frac{\partial(1-\psi)\tilde{\mathbf{v}}}{\partial t} = -(1-\psi)(\tilde{\mathbf{v}} \cdot \tilde{\nabla})\tilde{\mathbf{v}} - (1-\psi)\tilde{\nabla} \frac{\tilde{p}}{\tilde{\rho}_0} \quad (2.20)$$

$$+ \tilde{\nabla} [\tilde{\nu} \tilde{\nabla} (1-\psi)\tilde{\mathbf{v}}] - 2h\tilde{\nu}\psi^2(1-\psi)\tilde{\mathbf{v}} \quad (2.21)$$

Continuity equation:

$$\tilde{\nabla} \cdot (1-\psi)\tilde{\mathbf{v}} = 0 \quad (2.22)$$

2.3 Numerical approach

We use the model equation described in the previous section to numerically simulate dendritic growth of dilute binary alloys under the influence of an imposed flow field. The equations (2.19)-(2.22) are numerically discretized using a finite difference approach on an uniform spatial lattice with grid space Δx . We adopt second order discretization for the high order terms and an advanced first order approximation for the terms of low orders. To avoid numerical instability due convection transport, the convective term is discretized by using the up-wind scheme [35]. The phase-field equations are solved using an explicit Euler method with constant time step Δt . To solve the modified Navier-Stokes equations (2.21) a special scheme is required.

The equations (2.19)-(2.22) are discretized employing a finite difference approach, as discussed above. Nevertheless, there is a need to rearrange the components in a staggered grid (see section 1.2.4). To solve the Navier-Stokes equations we use a scheme which is based on the SMAC [5] method.

We treat the term (2.7) implicitly and the convective part of the Navier-Stokes equations explicitly. The resulting system of equations is solved by an iterative Gauss-Seidel method [6]. The system is solved until $\nabla \cdot \tilde{\mathbf{v}} \approx 0$ and the convergence of the method is controlled (in its explicit part) by

$$\Delta t < \Delta x^2 / 2D, \quad (2.23)$$

due to the diffusion field and the convective part through the Courant-Friedrichs-Levy (CFL) condition [35]

$$\Delta t < \Delta x / \tilde{\mathbf{v}}. \quad (2.24)$$

In its implicit part the convergence is controlled by limiting the maximum relative error like

$$MAX \left\{ \left| \frac{\tilde{\mathbf{v}}_i^{t+\Delta t} - \tilde{\mathbf{v}}_{i+1}^{t+\Delta t}}{\tilde{\mathbf{v}}_i^{t+\Delta t}} \right| \right\} < \epsilon_{error}, \quad (2.25)$$

where ϵ_{error} is a small constant.

The simulation domain is schematically illustrated in Fig. 2.2. A small crystal seed exists initially in the center of the domain. The seed is engulfed in a supersaturated melt at composition c_l^0 under forced flow conditions. As shown in figure 2.2, for symmetric reasons, only half of the domain is simulated. If flow is not considered, then the domain can still be reduced to only a quarter of the total domain of simulation.

The crystal axes are aligned with the coordinate axes. For these studies, we apply symmetric boundary conditions on the left side of the domain for all the fields ($\partial v_x / \partial x = 0$, $\partial \phi / \partial x = 0$, $\partial c / \partial x = 0$, $\partial p / \partial x = 0$ and $v_y = 0$). On the right side we use no-flux boundary conditions for the phase field

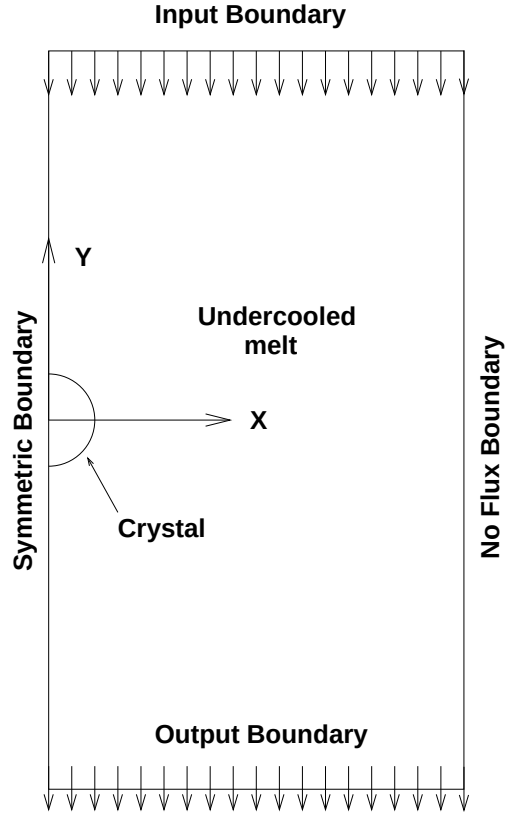


Figure 2.2: Computational configuration for the dendritic growth simulations.

and free-slip boundary condition for the flow field ($\partial v_x / \partial x = 0$, $\partial \phi / \partial x = 0$, $\partial c / \partial x = 0$, $\partial p / \partial x = 0$ and $v_y = 0$). On the top and bottom side we alternated constant inflow ($v_x = 0$, $v_y = V_\infty$, $\partial \phi / \partial y = 0$, $\partial c / \partial y = 0$ and $\partial p / \partial y = 0$) and outflow ($v_x = 0$, $\partial v_y / \partial y = 0$, $\partial \phi / \partial y = 0$, $\partial c / \partial y = 0$ and $\partial p / \partial y = 0$) boundary conditions.

2.4 Numerical simulations

In this section we investigate the influence of an imposed flow on solidification of Fe-Mn alloy. All the calculations are performed for the isothermal case $T = 1474^\circ\text{C}$ and initial alloy composition $c_l^0 = 9.8 \text{ mol\% Mn}$. In Fig. 2.3 we show the phase-diagram of Fe-Mn and a zoom in the region of interest for our simulations. The thermodynamic parameters can be seen in Table 2.2.

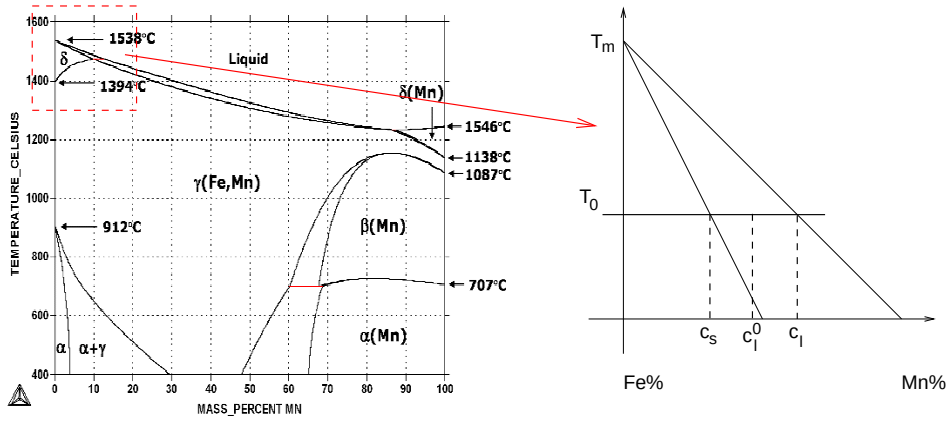


Figure 2.3: Fe-Mn phase-diagram and a zoom in the region of $c_l^0 = 9.8 \text{ mol\% Mn}$.

During the numerical calculation of the equations (2.19)-(2.22) we add a stochastic noise at the interface region in order to include fluctuations at the interface, which gives rise to the initial morphological instability.

In Fig. 2.4 we show the phase-field simulations of dendritic growth with and without flow. On the left side we present the time evolution of a dendritic growing under purely diffusive conditions. On the left side we present the case where the dendritic growth under forced flow conditions. The total domain

Table 2.2: Material parameters of Fe-Mn alloy (see Ref. [18]) used in the phase-field simulations and corresponding characteristic length scales for the isothermal solidification. The anisotropy of the interfacial free energy is taken as $\epsilon_4 = 0.05$. We use $W/d_0 = 19.45$ and $\Delta x = 0.8W$ in all the simulations

D (Diffusion coefficient in liquid)	$1.0 \times 10^{-9} \text{ m}^2/\text{s}$
m (Liquidus slope)	496.6 C/at
T_0 (Reference temperature)	1473°C
k (partition coefficient)	0.72
σ (solid/liquid interface energy)	0.4 J/m^2

size was assumed to be $2000W \times 1000W$ in our simplified domain. Note, however that in Fig. 2.4 as well as in the others snapshots in this section we show only the region near the solid phase (the dendritic).

A further comparison between the simulations show that convection decisively disturbs the symmetry of the equiaxed dendrite. At first, in the case without convection, all the primary dendrites grow with approximately equal velocities from the central nucleus. Secondly, sidebranches emanate from each main arm equally to the right and to the left side, showing approximate mirror symmetry in relation to the axis of the arm (see Fig. 2.4a)). In the case with convection, one easily notes that the growth velocity of the primary dendrite growing upstream is higher than that of the primary ones growing horizontally, which, in turn, is higher than that of the primary dendrite growing downstream. This can be explained as follows. In the pure diffusive situation, each dendrite has approximately the same growth condi-

tions because the solute boundary layer looks the same for each dendrite, i.e. the height of the solute pile-up is the same for each dendrite and also the thickness of the boundary layer is the same for each arm in equivalent regions. According to the phase-diagram Fig. 2.3, an increase in solute content brings about a decrease of the liquidus temperature, which tends to make the growth slower. In the case with convection, the solute boundary layer becomes unsymmetrical. In the region of the upstream growth, the flow steadily supplies fresh liquid (with the nominal alloy composition) to the phase front which keeps the supersaturation high and stimulates the growth. This is confirmed by the fact that, in this case, the pile-up is lower and the thickness of the boundary layer is smaller than in the situation without flow, see Fig. 2.5. On the other side, in the region of the downstream flow (wake region), there is an excess of solute, which tends to inhibit the growth by decreasing the local supersaturation. This is reflected in a higher solute pile-up and thicker boundary layer in comparison to the situation without flow see Fig. 2.5.

As a consequence of the stimulated growth in the upstream direction, the corresponding primary dendrites have the chance of emanating sidebranches earlier than the primary dendrites growing horizontally, see Fig. 2.6. The growth of these sidebranches tend to block the growth of the sidebranches from the dendrites growing horizontally. The opposite occurs in the case of the primary dendrite growing downstream. Because its growth is inhibited, its sidebranches lose the competition against the sidebranches of the neighbouring horizontal dendrites.

A comparison of the evolution of the dendritic microstructure for different

values of the imposed inflow velocity shows that the primary dendrites, which, in the situation without flow, grow along a perfectly horizontal line, deviate from this direction when the inflow velocity is progressively increased. The deviation of the tip from the original horizontal line increases with an increase of the inflow velocity, see Fig. 2.7. This asymmetry is brought about by the imposed flow and is related to the changes of local concentration (and consequently, local supersaturation) which are caused by the flow.

Observing Fig. 2.4 and Fig. 2.7, we note that the envelope of the equiaxed grain for the purely diffusive case corresponds to a square with concave sides (from the outside). This concavity tends to disappear in the upper half of the equiaxed dendrite when the flow is introduced in the system and its velocity is progressively increased. In addition to this, the sidebranches emanating from the upstream growing dendrite seem to "reorient" themselves with an increasing flow velocity, from an orientation which is initially orthogonal to the main arm (as it is usual for diffusive dendritic growth) to another one, which tends to be orthogonal to the flow lines (mainly for the highest inflow velocities). The number of sidebranches of the upstream growing primary dendrite also tends to reduce with increasing growth velocity, as if convection would stabilize the interface.

2.5 Discussion

In this chapter we have extended a quantitative phase-field approach [24] to simulate dendritic growth of Fe-0.98mol%Mn alloy under the influence of an imposed flow field. We have shown the influence of (macroscopic) convection on the pattern formation in the scale of the microstructure. On one side, convection alters the morphology of dendrites, by influencing, for instance, the solute boundary layer thickness and the solute pile-up. On the other in the neighbourhood of a dendrite, convection can bring about the enrichment/impoverishment of solute in the liquid phase. This alters the (local) supersaturation on the microscale, and this influences some characteristics of dendritic growth, e.g. tip velocity, sidebranching, but also the local evolution of the solid fraction.

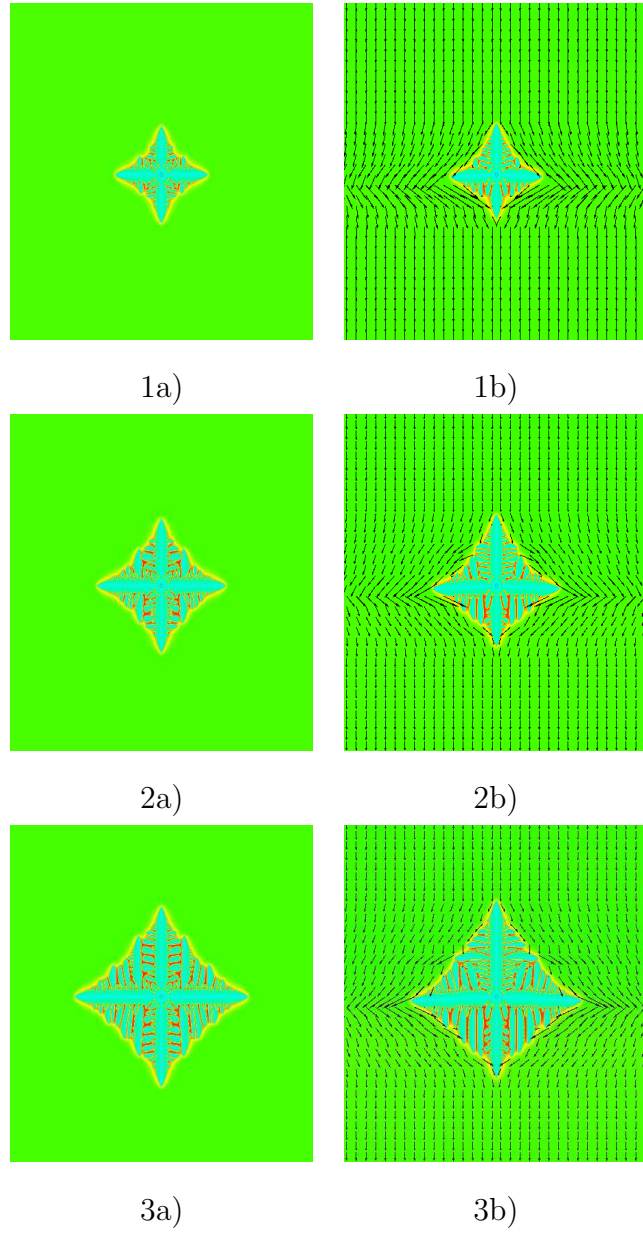


Figure 2.4: Phase-field simulation of dendritic growth of Fe-9.8 mol% Mn alloy. The time evolves from top to bottom. a) Purely diffusive growth conditions b) With an imposed inflow velocity $V_\infty = 2\mu\text{m/s}$.

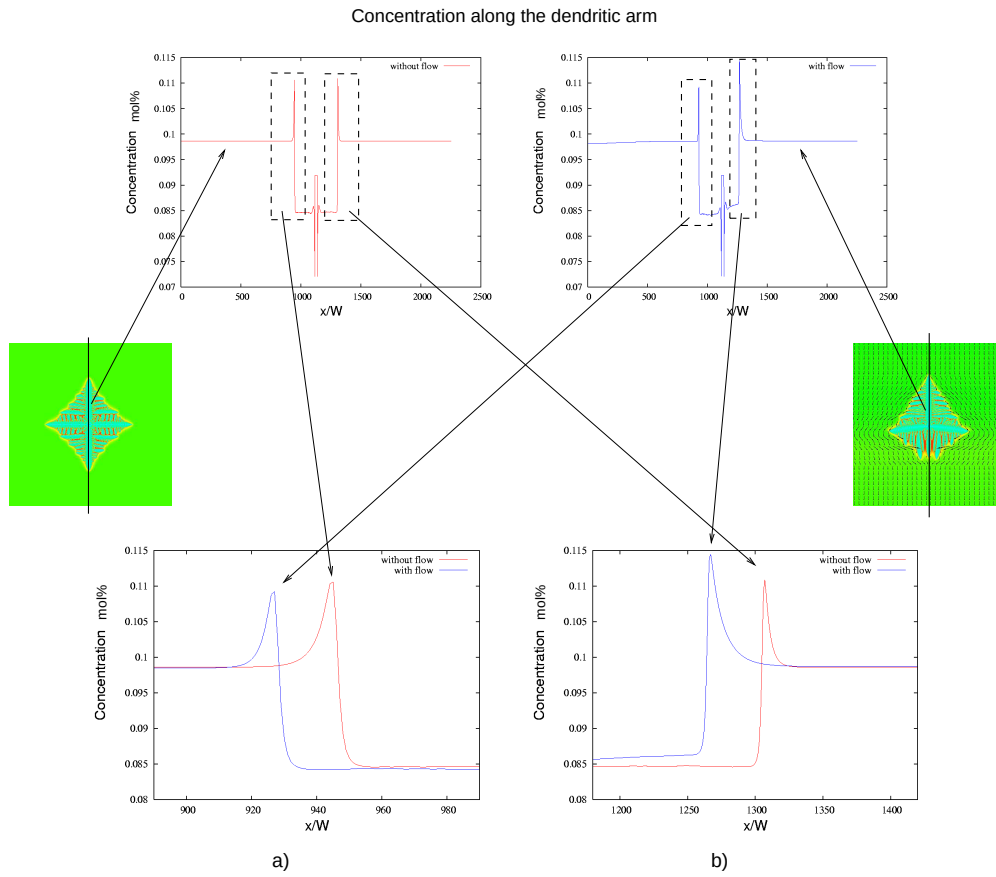


Figure 2.5: In this picture we compare the solute pile-up in front of the a) the upstream dendritic tip and b) the downstream tip, for the case with and without flow.

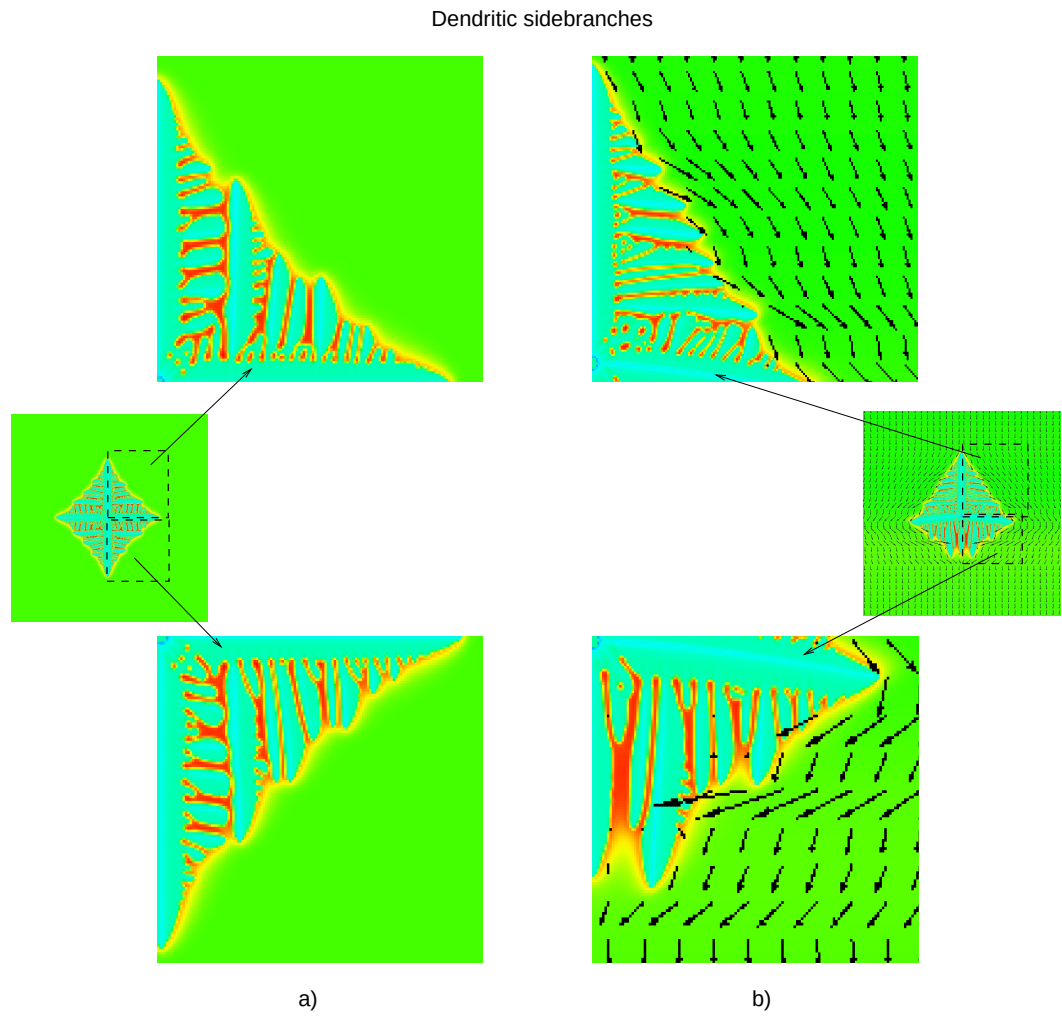


Figure 2.6: Dendritic sidebranches a) without flow and b) with flow.

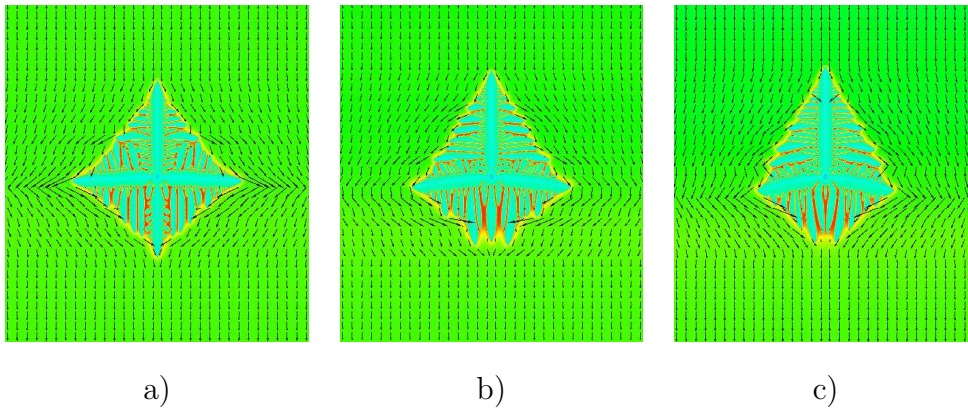


Figure 2.7: Dendritic growth under different imposed inflow velocity.

a) $V_\infty = 2\mu\text{m/s}$, b) $V_\infty = 4\mu\text{m/s}$, c) $V_\infty = 6\mu\text{m/s}$.

Chapter 3

Quantitative phase-field modelling of two-phase growth with fluid flow

In this chapter we present an extension of the quantitative phase-field model proposed by Folch & Plapp [28] to investigate the influence of fluid flow on the two-phase solidification of binary alloy systems. The model approach for purely diffusive growth is described in detail in reference [28]. Originally, the phase-field model of Folch & Plapp [28] was developed having its bases on the model approach described in chapter 2. This was one of the first models that allowed for quantitative simulations of low-speed eutectic and peritectic solidification under typical experimental conditions. The extension to incorporate fluid flow in the melt phase allows us to simulate two-phase growth of binary alloys in the presence of convection. In the following section we will give a brief description of the phase-field approach given by Folch and

Plapp and explain how we have extended it to incorporate convection in the melting phase. The results in this chapter will be presented in two parts. First we will present the influence of convection on the growth of eutectic systems and then we will study heterogeneous nucleation and microstructure formation of peritectic growth in the presence of convection.

3.1 Phase-field model

In the following we extend the phase-field model described in [28] to simulate eutectic/peritectic growth including hydrodynamic convection in the molten phase. We use three phase fields, with $p_i \in [0, 1]$ and $p_\alpha + p_\beta + p_L = 1$. p_i label the Alpha phase for $i = \alpha$, Beta phase for $i = \beta$ and liquid phase for $i = L$, respectively. We denote $\vec{p} \equiv (p_\alpha, p_\beta, p_L)$.

The model approach is based on the free energy functional of a representative volume of the investigated material system, which is given by

$$\mathcal{F} = \int_V \sum_i \frac{W(\theta_i)^2}{2} (\nabla p_i)^2 + f dV, \quad (3.1)$$

where $W(\theta_i) = W(1 + \epsilon_{p_i} \cos 4\theta_i)$ depends on the orientation of the solid-liquid interface [44], with $\theta_i = \arctan \partial_y p_i / \partial_x p_i$ and ϵ_{p_i} being the measure of the anisotropy¹. The free-energy density is defined as

$$f = \sum_i p_i^2 (1 - p_i)^2 + \tilde{\lambda} \left[\frac{1}{2} \left[c - \sum_i A_i(T) g_i(\vec{p}) \right]^2 + \sum_i B_i(T) g_i(\vec{p}) \right] \quad (3.2)$$

where $\tilde{\lambda}$ is a coupling constant given by

$$\tilde{\lambda} = \frac{W}{d} \frac{a_1}{2} \left(\frac{1}{|A_\alpha|} + \frac{1}{|A_\beta|} \right),$$

¹here we consider ϵ_{p_β} always equal to zero

with $\bar{d} = (d_\alpha + d_\beta)/2$ being the average capillary length² and $a_1 = \sqrt{2}/3$. The function g_i couples the phase-field to the concentration and the temperature. The coefficients $A_i(T)$ and $B_i(T)$ define the equilibrium phase diagram [26] and they can be defined for isothermal solidification or for directional solidification [28]. For the isotherm case they read:

$$\begin{aligned} A_i(T) &= c_i + (k_i - 1)U_i, & A_L &= 0, \\ B_i(T) &= A_i U_i & B_L &= 0, \end{aligned}$$

where $U_i = (T_R - T)/(|m_i|\Delta C)$ is the dimensionless undercooling, k_i are the partition coefficients, A_L, B_L are the corresponding liquid coefficients, m_i are the liquidus slope and $c_i = (C_i - C_R)/\Delta C$ is the scaled concentration, where C_R is the liquidus concentration at a certain reference temperature T_R . We use $\Delta C = c_\beta - c_\alpha$. For directional solidification they can be written as:

$$\begin{aligned} A_i(T) &= c_i + (k_i - 1)\frac{z - v_p t}{l_T^i}, & A_L &= 0, \\ B_i(T) &= \mp A_i \frac{z - v_p t}{l_T^i} & B_L &= 0, \end{aligned}$$

where v_p is the pulling speed, t is the time and $l_T^i = |m_i|\Delta C/G$ are the thermal lengths, and G is the thermal gradient.

The dynamic of the phases is derived from the free energy functional $\mathcal{F}$ as

$$\tau(\vec{p}) \frac{\partial p_i}{\partial t} = -\frac{1}{H} \frac{\delta \mathcal{F}}{\delta p_i}, \quad (3.3)$$

where $\tau(\vec{p})$ is a relaxation time. In this work we neglect interface kinetics (low undercooling), by choosing $\tau_i = a_2 A_i^2 \tilde{\lambda} W^2 / D$, with $a_2 = 1.175$.

²The capillary length for each phase is defined as $d_i = \frac{\sigma_{iL} T_R}{L_i |m_i| \Delta C}$, where L_i are the latent heat of fusion per unit volume, T_R is a reference temperature and σ_{iL} are the solid-liquid surface tensions

The concentration field is given by:

$$\frac{\partial c}{\partial t} + p_L(\mathbf{v} \cdot \vec{\nabla})c - \vec{\nabla} \cdot (M(\vec{p})\vec{\nabla} \frac{\delta \mathcal{F}}{\delta c} - \vec{J}_{AT}) = 0, \quad (3.4)$$

where $M(\vec{p})$ is a mobility and $\vec{J}_{AT}$ is the anti-trapping term [28] given by

$$\vec{J}_{AT} = 2aW\hat{n}_L \sum_{i=\alpha,\beta} (A_L(T) - A_i(T))(-\hat{n}_L \cdot \hat{n}_i) \frac{\partial p_i}{\partial t}, \quad (3.5)$$

where $\hat{n}_i = \vec{\nabla} p_i / |\vec{\nabla} p_i|$.

The flow field is modeled by coupling the Navier-Stokes equations to the phase-field [26],

$$\frac{\partial p_L \mathbf{v}}{\partial t} = -p_L(\mathbf{v} \cdot \vec{\nabla})\mathbf{v} - p_L \vec{\nabla} \frac{p}{\rho_0} + \nabla[\nu \nabla p_L \mathbf{v}] + p_L \beta_c \mathbf{g} - 2h\nu \frac{\mathbf{v}}{W^2} p_L^2, \quad (3.6)$$

$$\vec{\nabla} \cdot p_L \mathbf{v} = 0. \quad (3.7)$$

where $\beta_c = \frac{\partial \rho}{\partial c} \frac{1}{\rho_0} (c - c_0)$ is the coefficient of solutal expansion, p is the pressure, ν is the kinematic viscosity, ρ_0 is the liquid density and $\mathbf{g}$ is the gravitational constant.

The set of equations (3.3)-(3.7) are made dimensionless by using the same scale parameters as discussed in section 2.2, more details about the dimensionless system of equations can be seen in the reference [28].

For the set of equations in this chapter we use a similar numerical procedure as described in section 2.3. The equations (3.3)-(3.7) are discretized using a finite difference approach and we use an Euler explicit scheme to solve the phase-field equations (3.3)-(3.4) and a semi-implicit scheme to solve the Navier-Stokes equations (3.6)-(3.7).

As part of the optimization/implementation procedure we compute the equation (3.3) for p_α and p_β only and use the fact that $p_L = 1 - p_\alpha - p_\beta$ to identify the liquid phase.

The model approach described in this chapter can be used to simulate solidification processes of binary alloys with an Eutectic/Peritectic phase diagram and it also take into account the effect of natural/forced convection in the molten phase. Next, we will use our numerical implementation to investigate typical problems of eutectic/peritectic microstructure evolution under the influence of convection.

Before starting the description of the simulations, it is useful to write down some reference non-dimensional numbers which will be used as parameters in the simulations. When fluid flow is added, we define the flow Peclet number as $P_{ef} = V_{\infty}H/D_L$, where V_{∞} is a reference flow velocity in the system and H is a reference length (to be defined in the individual cases). The solutal Rayleigh number is defined as $Ra = gH^3\beta_c\Delta C/\nu D_L$.

3.2 Eutectic growth under the influence of convection

An eutectic alloy is characterized by having a composition at which the melting temperature of the alloy is minimal. At this composition, which we call the eutectic composition, the liquid can coexist with two distinct solid phases of different compositions (see Fig. 3.1).

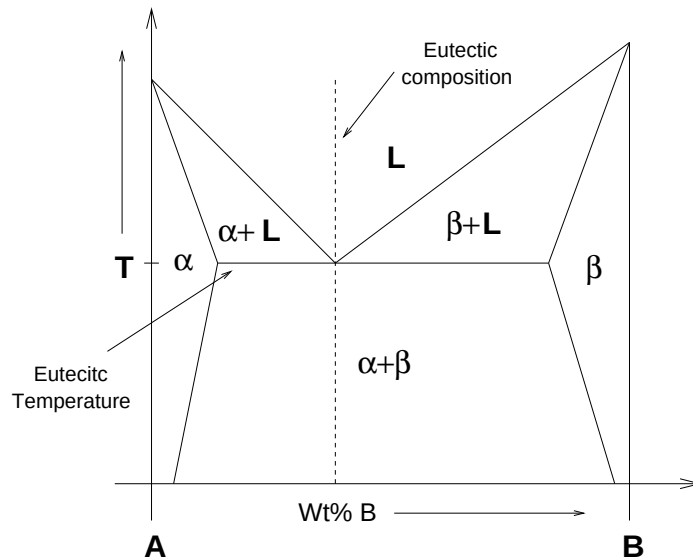


Figure 3.1: Schematic eutectic phase diagram of an A-B alloy.

The formation of lamellar microstructures during eutectic solidification (see Fig. 3.2) has been intensively investigated, both from the point of view of engineering applications and from the theoretical point of view [62, 51].

Many of these studies are based on the classical theory of Jackson and Hunt [40] for the lamellar and rod-like eutectic growth.

Over the years many authors have discussed the need to take convection

effects into account for the simulation of eutectic lamellae growth [62, 53].

It is known that convection can not be avoided in a solidification process and that it drastically alters the dynamic of the growth microstructure. The origin of convection can be natural phenomena - a case we call natural convection - or externally applied phenomena as magnetic stirring, rotation, etc. The influence of convection on eutectic growth has been a field of many controversial studies; the discussion started in 1976 when Larson reported his Apollo-Soyuz Test Project (ASTP) experiment that directional solidification in microgravity causes a significant reduction in the fiber spacing of the MnBi-Bi eutectic [50]. Since Larson's ASTP experiment on MnBi-Bi, a large number of experimental and theoretical studies has been performed to try to understand the influence of convection on eutectic microstructure - see [8, 51] and references therein. Among them, Baskaran and Wilcox [8] have performed numerical calculations on the uniform shear-flow system. Ma *et al.* [53] studied the effect of a weak convection by using analytical perturbation methods taking the flow shear rate as a small parameter. Coriel *et al.* [19] extended the Jackson-Hunt model to the case where fluid flow is induced by the different densities of the phases. In their studies they showed that the eutectic spacing (see Fig. 3.2) can increase, decrease, or remain constant in a low-gravity environment, depending on the alloy system. Lee *et al.* [51] have carried out experimental investigations in Al-Cu systems to study the effect of fluid flow on eutectic microstructures. They showed how different modes of convection can influence the eutectic spacing and the microstructure growth. Zhang *et al.* [82] carried out numerical studies where they describe changes on the lamellae spacing due to an imposed transverse flow ahead of

the solidified interface. They showed that transverse fluid flow increases the interlamellar spacing and that fluid flow strongly alters the microstructure growth.

Although there have been many investigations about eutectic growth under convection effects, none of these studies have considered the phase-field approach. In order to cover this research field in the state of the art on microstructure solidification, we developed a quantitative phase-field model which is able to simulate the growth of lamellae taking into account the effect of natural and forced convection in the melt phase. To our knowledge, this is the first phase-field approach which is able to deal with this open issue.

3.2.1 Numerical simulations

In this section we perform numerical simulation of directional solidification of eutectic lamellae. In figure 3.2 we show an example of the two-dimensional lamellae geometry we will simulate.

We apply periodic boundary conditions on the left/right side of the domain, symmetric boundary conditions on the top and no-flux boundary conditions on the bottom. The total simulation box is chosen to be $n_x \times n_z$, where n_x and n_z are the number of grid points perpendicular and parallel to the thermal gradient, respectively. Typically, the number of grid points required in the z direction is much larger than in the x direction, since diffusion and thermal lengths are much larger than the lamellar spacing.

Moreover, we start with completely flat interfaces, and the phase fields are initialized as step functions. These step functions then quickly relax to the smooth solutions for the phase fields, while the interfaces begin to curve and

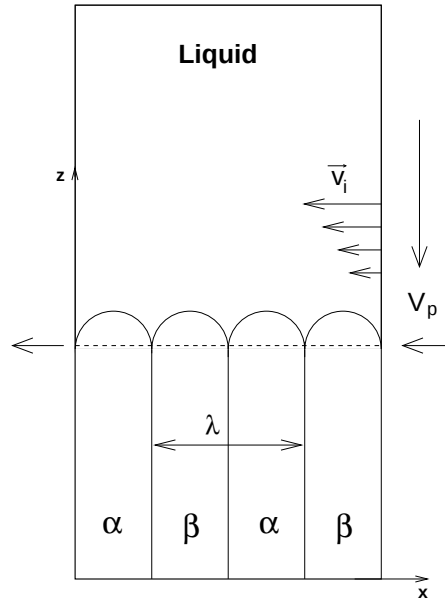


Figure 3.2: Schematic illustration of eutectic lamellae growth with fluid flow. λ is the lamellar spacing.

drift to adjust their average undercooling. We consider the one-sided model. To allow long time run observation, our numerical scheme is implemented in a frame which follows the solidifying front. This is done by shifting the simulation box from time to time along the growth direction.

Basically we will investigate two types of convection in directional solidification: one is convection caused by a concentration difference in the system, the so called natural convection or buoyancy convection, the second is convection induced by an imposed shear flow ahead of the solidifying front (forced convection).

Effect of natural convection on the growth of eutectic lamellae

Before we start to use the model described in section 3.1, we need first to test its convergence. In reference [28] Folch and Plapp show that the model presented in section 3.1 - for the case where fluid flow is neglected - is convergent to the thin-interface limit. This was done by performing a series of simulations where they fix the physical parameters and decrease the interface width W . They showed that the results become independent of the choice of W for $\lambda/W \geq 64$ (in their parameters range). Their results were compared with the numerical solution obtained from the boundary integral model.

In this section we test the convergence of our approach by investigating the steady state lamellar growth when natural convection is taken into account in the liquid phase. We perform the same series of simulation as described in Ref. [28]. Unfortunately, we can not compare our results with a sharp-interface approach since to our knowledge there is no sharp-interface approach for eutectic problem with fluid flow.

We adopt the same input parameters as given in [28]: we take $l_D/\bar{d} = 51200$ and $\bar{l}_T/l_D = 4$ where $l_D \approx D/v_p$ is the diffusion length. This corresponds to the typical experimental values $G \approx 100K/cm$ and $v_p \approx 1\mu m/s$ for $CBr_4-C_2Cl_6$ [29]. We use $m_\alpha = -m_\beta$, $c_\alpha = -c_\beta$ (symmetric phase diagram) and eutectic composition in the liquid. For the fluid flow we take $Ra = 1.34 \times 10^{-2}$ and $Ra = 3.85 \times 10^{-2}$. We compute the solutal Rayleigh number based on the thickness of the solutal boundary layer where the concentration gradient exists. We define this thickness as the distance from the interface to the position where the concentration drooped 99% in the bound-

ary layer. Following the simulations given in reference [28] the tests are done by decreasing W (increasing λ/W) while keeping all the ratios above and λ/λ_{min} fixed, where $\lambda_{min} \propto \sqrt{dl_D}$ is the minimum undercooling spacing. Thus, we take $\lambda/W = 32, 64, 96$ and 128 , and fix all others ratios. For each simulation, the interface profile and the interface undercooling are monitored to check when the steady state is reached. As you can take from figure 3.3 the convergence in the case with convection is somewhat slower than in the case without convection. Note that the results for $\lambda/W = 32$ are not plotted in figure 3.3, since they are far from the converged lamellae profile. Nevertheless, we achieve convergence for $\lambda/W \geq 96$.

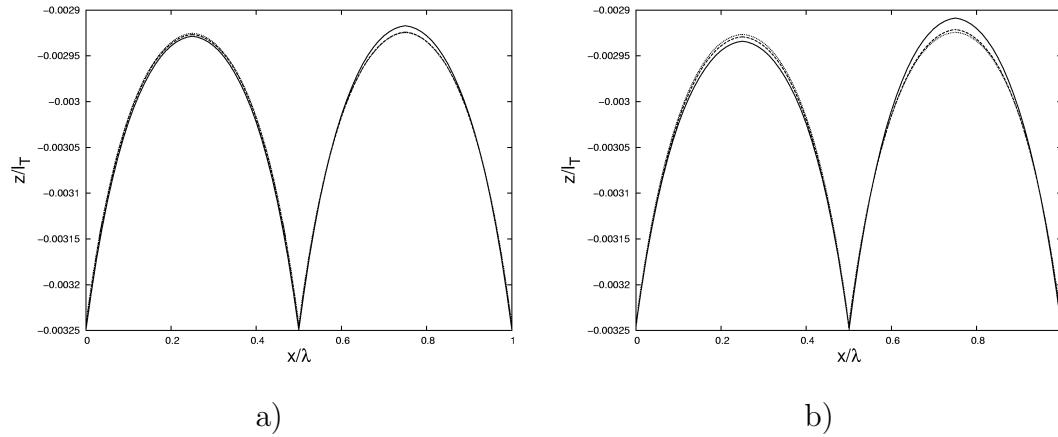


Figure 3.3: Steady-state lamellae growth with fluid flow. The parameters for all the runs are given in the text above. Solid line, $\lambda/W = 64$; dashed lines, $\lambda/W = 96$; dotted lines, $\lambda/W = 128$. a) $Ra = 1.34 \times 10^{-2}$ and b) $Ra = 3.85 \times 10^{-2}$.

If we examine the microstructure growth in Fig. 3.3 we see that they are not drastically altered by natural convection. Moreover the lamellae pair are

slightly asymmetric and this asymmetry is less pronounced for small Rayleigh number (case where convections effect are smaller, see Fig. 3.3a)).

The asymmetry can be explained by the fact that in the presence of a gravitational field, the difference in the concentration field of α , β and liquid phase produces natural convection which induces a fluid motion in the central part of the liquid close to the interface triple point (see Fig. 3.4). This means that the concentration field ahead of the solid-liquid interface is not symmetric any longer. In our case, the fluid motion increases the solute transport in front of the β phase (lamellae in red, see Fig. 3.4) and it enriches the solute field in front of the α phase (lamellae in blue, see Fig. 3.4). Since these effects are quite small we can see only a slight asymmetry on the growth of the lamellae.

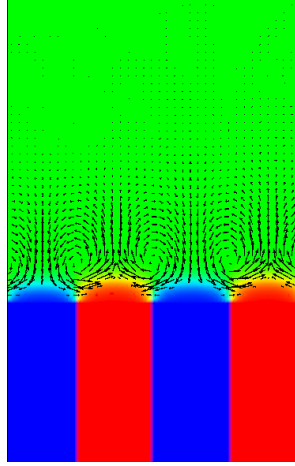


Figure 3.4: This picture shows a snapshot of the phase-field simulation of eutectic growth in the presence of natural convection. The arrows represent the fluid motion and the colors the concentration field. The phase α is represented by the blue color and β by red.

Now, we consider the same material and computational parameters as above and we investigate the influence of natural convection on the interfacial undercooling for varying lamellar spacing. This is done by plotting the average interfacial undercooling ΔT versus the lamellar spacing λ , which, for the purely diffusive case is known as the Jackson and Hunt curve [40]. For the resolution, we take $\lambda/W = 96$, since, on the basis of Fig. 3.3 we expect results to be converged for $\lambda/W \geq 96$. The lamellar spacing λ can be changed by changing the size of the simulation box. We investigate three different growth rates and we use $Ra = 1.34 \times 10^{-2}$ and $Ra = 3.85 \times 10^{-2}$. In Fig. 3.5, 3.6 and 3.7 we plot the average undercooling versus the lamellar spacing considering the cases with and without convection effects.

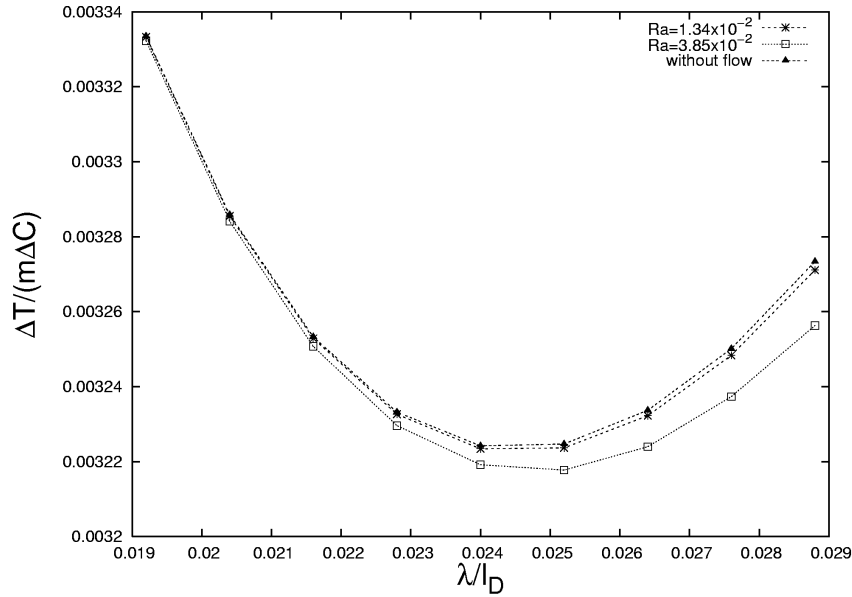


Figure 3.5: Average undercooling versus lamellar spacing for $l_D/\bar{d} = 45000$.

Following the Jackson and Hunt theory the interfacial undercooling has

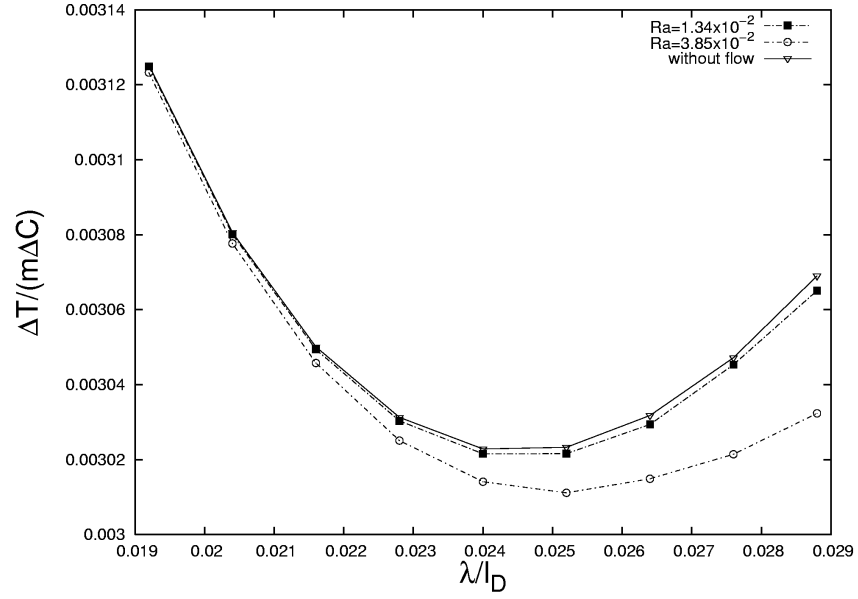


Figure 3.6: Average undercooling versus lamellar spacing for $l_D/\bar{d} = 51200$.

a minimum, $\Delta T = \Delta T_{JH}$, for the spacing λ_{JH} , which constitutes a reference length for lamellar eutectics. In reference [28] Folch and Plapp show a very good agreement between the Jackson and Hunt parameters (λ_{JH}/l_D and $\Delta T_{JH}/(m\Delta C)$) and the values (λ/l_D and $\Delta T/(m\Delta C)$) computed with their phase-field model. Here we compute these values again and compare them with the minimum undercooling when convection effects are taken into account.

The results are summarized in Table 3.1. A graphical description of them can also be seen in Fig. 3.5, 3.6 and 3.7.

As you can take from the pictures (see Fig. 3.5, 3.6 and 3.7) the higher the growth rate the less the effect of buoyancy forces on the minimum interfacial undercooling. In figure 3.5 we see almost no convection influence

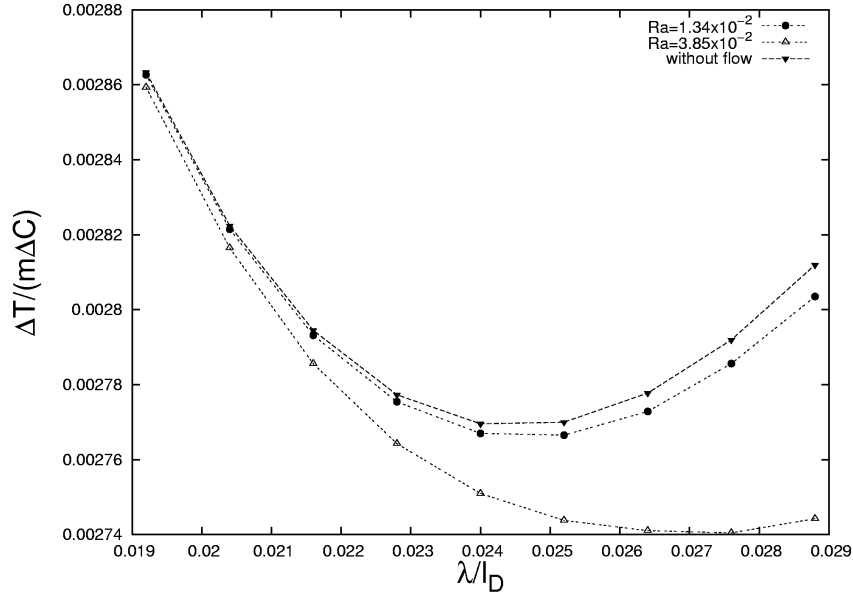


Figure 3.7: Average undercooling versus lamellar spacing for $l_D/\bar{d} = 61000$.

	$l_D/\bar{d} = 45000$		$l_D/\bar{d} = 51200$		$l_D/\bar{d} = 61000$	
	λ_{min}	ΔT_{min}	λ_{min}	ΔT_{min}	λ_{min}	ΔT_{min}
Without flow	0.02403	0.003224	0.02403	0.003023	0.02401	0.00277
Ra_1	0.02403	0.003223	0.024402	0.003020	0.025188	0.00276
Ra_2	0.02520	0.003217	0.025201	0.003011	0.027603	0.00274

Table 3.1: Minimum interfacial undercooling and minimum lamellar spacing computed with the phase-field model. As a matter of simplification we represent $\lambda_{min} = (\lambda/l_D)_{min}$, $\Delta T_{min} = \Delta T/(m\Delta C)$, $Ra_1 = 1.34 \times 10^{-2}$ and $Ra_2 = 3.85 \times 10^{-2}$.

on the minimum interface undercooling or minimum lamellar spacing for $Ra = 1.34 \times 10^{-2}$. For $Ra = 3.85 \times 10^{-2}$ the minimum interfacial undercool-

ing decreases and the corresponding minimum lamellar spacing increases in relation to the purely diffusive case (see also Table 3.1). When we decrease the growth rate (see Fig. 3.6 and 3.7) we still can see a stronger convection effect on the minimum interfacial undercooling and minimum lamellar spacing. As we decrease the growth rate, the minimum lamellar spacing in the presence of convection increases with respect to the purely diffusive case. We also observe that the effect of natural convection is more pronounced when the interfacial energy is lower.

Moreover, the results above clearly show that natural convection can modify the minimum lamellar spacing to such an extent that the Jackson and Hunt predictions are no longer valid. Similar results were also found by Zhang et al. [82] but they consider a fixed shear flow ahead of the solid-liquid interface.

Effect of forced flow on directional solidification of eutectic lamellae

In this section we investigate the effect of a shear flow ahead of the solid-liquid interface. Again, we use the same material parameters as in section 3.2.1 and resolution $\lambda/W = 96$.

In figure 3.8, we present numerical simulations of eutectic lamellae growth under forced convection effects. We impose a fixed shear flow $V_\infty = 7.06 \times 10^{-7} m/s$ ahead of the solid-liquid interface. The corresponding simulations for the purely diffusive case ($V_\infty = 0$) can be seen in the figure 3.9.

As you can take from Fig. 3.8, forced flow rapidly alters the growth of lamellae. Whereas in the purely diffusive case (Fig. 3.9) the lamellae grow parallel to the z direction, in Fig. 3.8 we see that forced convection tilts the

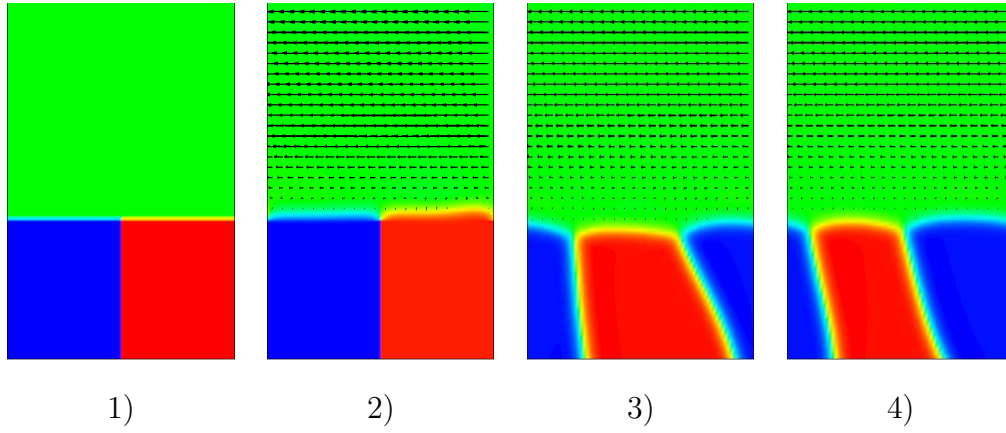


Figure 3.8: Time evolution of the phase-field simulations for eutectic lamellae growth with a shear flow ahead of the solid-liquid interface. Time evolves, from left to right. Note that we are showing only part of the simulation domain (the z direction is much larger than the x direction)

whole microstructure away from the flow direction. The solute field in front of the solid-liquid interface is taken away by the fluid flow, increasing the solute transport in this direction. When transverse flow is included in the system it increases the ability of the lateral migration of the atoms. The simulations presented in Fig. 3.8 correspond to the Peclet number (P_{ef}) in the range from $P_{ef} = 0.113$, based on the flow velocity near the solidifying front to $P_{ef} = 1.13$ based on the velocity ahead of the solidifying front (we choose $H = \lambda$).

More details about these investigations as well as a large range of parameter variations will be presented elsewhere in [66].

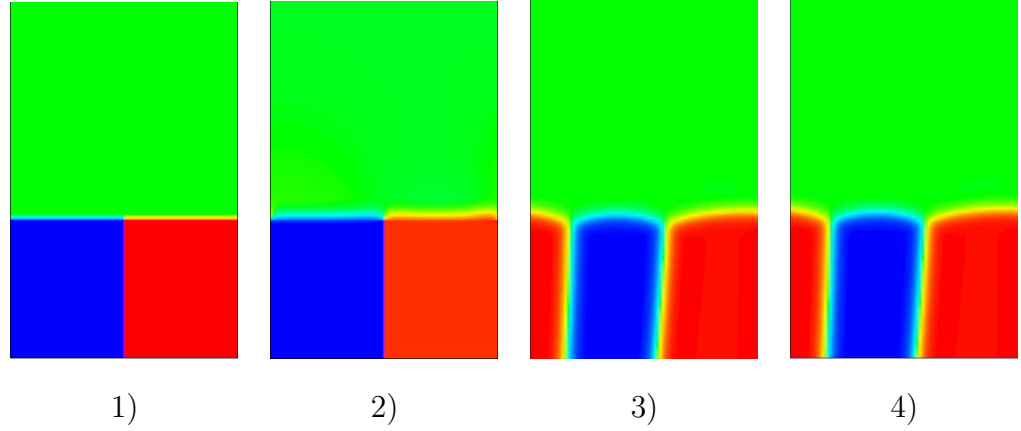


Figure 3.9: Time evolution of the phase-field simulations for eutectic lamellae growth under pure diffusive conditions. Time evolves, from left to right. Note that we are showing only part of the simulation domain (the z direction is much larger than the x direction)

3.2.2 Discussion

In this section we have presented phase-field simulations of eutectic lamellae growth under the effect of natural convection and the effect of a transverse shear flow fixed ahead of the solid-liquid interface. Moreover, we have done convergence studies by analyzing the lamellar steady state growth including convection in the molten phase. We show that even when taking the non-linear effects due to fluid flow in the melt into account, the phase-field model still exhibits thin-interface corrections. We have also demonstrated that natural convection can change the minimum lamellar spacing and that this will depend on the process parameters. In the case of transverse flow we have shown that fluid flow tilts the eutectic lamellae away from the flow direction, changing the whole microstructure in comparison to the case without fluid

flow effects.

The likewise important message of this section is that we have build a quantitative phase-field model which is able to simulate numerically eutectic growth under the effect of convection.

3.3 Peritectic growth under the influence of convection

In modeling nucleation it is essential to realize that the solid-liquid interface is known to extend to several molecular layers. This has successively been indicated by experiments [36], computer simulations [21], and statistical mechanical treatments based on the density functional theory [58]. The need to pay particular attention to this diffuse interface results from the fact that for nucleation the typical size of critical fluctuations is comparable to the physical thickness of the interface. The success of such careful treatment can be seen in modern nucleation theories for homogeneous nucleation, which do consider the molecular scale diffuseness of the interface. These theories could remove the difference of many orders of magnitude between nucleation rates from the classical sharp interface approach and experiment [31].

In heterogeneous nucleation we face an even more complex situation, since the main degrees of freedom of the process are larger than in homogeneous nucleation: First of all each phase can nucleate separately. Moreover, several phases can nucleate jointly, i.e. approximately at the same space and time. Finally one phase can nucleate on top of the other.

Here we are particularly interested in peritectic material systems. Even though many industrially important metallic alloy systems as well as ceramics are peritectics, much less is known about microstructural pattern formation in peritectic growth [12] than for example in eutectic growth. Similar to an eutectic system the phase diagram of a peritectic system contains a point – the peritectic point with peritectic temperature T_p – at which two different

solid phases, the parent (primary) and peritectic (secondary) phases, coexist with a liquid of higher composition than either solid phase. Above T_p , the parent phase is stable and the peritectic phase is meta-stable, whereas below T_p , the opposite is true. In the following we will consider C to be the concentration of the impurity and T_m the melting point of the pure phase. A schematic phase diagram of a peritectic material system can be seen in the figure 3.10.

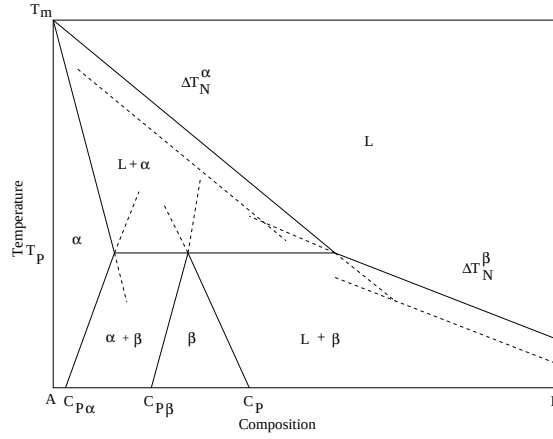


Figure 3.10: Schematic phase diagram of a peritectic alloy. C , concentration of impurity B; T_m , melting point of pure A; T_p , peritectic temperature. C_p , $C_{p\beta}$, and $C_{p\alpha}$ are the compositions of the liquid, β solid, and α solid that are in equilibrium at T_p . ΔT_N^α and ΔT_N^β are the nucleation undercoolings for α and β phases, respectively. Dashed lines are metastable extensions of the liquidus and solidus lines. This figure was taken from the reference [52].

In such peritectic material systems it is particularly relevant to understand the nucleation of the peritectic phase on top of the properitectic phase in detail, since this is the nucleation process yielding the stationary growth

morphology. For this specific nucleation process the precise configuration of the properitectic phase, i.e. its free energy on the one hand and its morphology on the other [39], should contribute to the precise nucleation rate.

Nevertheless the well established spherical cap model for the nucleation of a new phase β on a planar front of initial phase α predicts the following nucleation rate:

$$I = I_0 e^{-\Delta F^*/k_B T}, \quad (3.8)$$

where I_0 is a constant prefactor (with dimension equal to the number of nucleations per unit volume and unit time) and ΔF^* is the activation energy for heterogeneous nucleation. Assuming the critical nucleus of phase β to be spherical (see Fig. 3.11) the interfacial tensions $\gamma_{\alpha L}$, $\gamma_{\alpha\beta}$ and $\gamma_{\beta L}$ balance each other enclosing a contact angle θ if the following condition is fulfilled:

$$\gamma_{\alpha L} = \gamma_{\alpha\beta} + \gamma_{\beta L} \cos \theta. \quad (3.9)$$

ΔF^* is then given, respectively, in two and three dimensions by

$$\Delta F^* = \begin{cases} \frac{\gamma_{\beta L}^2}{\Delta F_\beta} \times \frac{\theta^2}{\theta - (1/2) \sin 2\theta}, & 2D \\ \frac{\gamma_{\beta L}^3}{\Delta F_\beta^2} \times \frac{16\pi(2 + \cos \theta)(1 - \cos \theta)^2}{12}, & 3D. \end{cases} \quad (3.10)$$

Here ΔF_β is the difference between the bulk free energy of the peritectic phase and of the liquid phase.

Equation (3.10) determines the classical local nucleation rate and hence the probability per unit time of a nucleus forming as a function of the local temperature at the solid-liquid interface. Thus morphological and energetical contributions to (3.10) resulting from the properitectic microstructure as discussed in [39] are neglected classically.

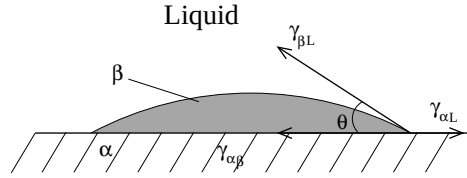


Figure 3.11: Heterogeneous nucleation of a “spherical cap”-shaped second phase β on a planar initial phase α according to the “spherical cap”-model. Figure following [61].

In the following we apply the phase-field model approach described in section 3.1 to treat this open issue. The way we proceed here is different from the further scientific advance of the authors of [32, 17, 33] in the sense, that we analyze the nucleation rate belonging to a heterogeneous nucleation event for a peritectic system. In contrast, the authors of [32] extended their own work to investigate several stochastically initialized homogeneous nucleation events of different phases and their subsequent growth in multi-phase systems [34]. More recently, Gránásy *et al.* [33] and Castro [17] investigate heterogeneous nucleation using a phase-field approach for a pure liquid crystal.

Here we will describe our new approach to investigate the rate of a nucleation event of a second phase on top of a first one in detail in section 3.3.1. Also in sections 3.3.1 and 3.3.1 we investigate microstructure growth in a peritectic system under the influence of hydrodynamic convection in the melt. We will then report on numerical investigations of the nucleation kinetics in such peritectic material systems, in particular on a morphological contribution from the properitectic phase to the activation energy, in section 3.3.1. Moreover, we will discuss the relation of our results to classical nu-

cleation theory in section 3.3.1. Finally we will conclude with a discussion of the general impact of our new approach for peritectic materials under the influence of convection.

3.3.1 Numerical simulations

The model described in section 3.1 allows us to investigate the peritectic transformation under the influence of fluid flow quantitatively. A representative evolution is shown in Fig. 3.12, where time runs from the left picture to the right. The row of pictures on the top represents the case where flow in the melt phase is taken into account, on the bottom the case without flow. The pictures (with and without flow) are depicted at the same time step for the same process parameters. The dark circle indicates the properitectic phase, the light structure the peritectic phase, which is nucleating on top of the properitectic one. Comparing peritectic growth with and without convection we find that hydrodynamic transport in the melt enhances the growth process considerably. To stress this effect we investigated a scale relation which describes the influence of the inflow velocity on the solid volume fraction of the microstructure evolution for a fixed time instant. In Fig. 3.13 we resume this finding by plotting the logarithm of the solid volume fraction versus the logarithm of the inflow velocity. We can see that for larger inflow velocity a linear regime was found. More details about these findings can be seen in [67]. Moreover, these results are in qualitative agreement with experimental investigation of the peritectic material system Fe-Ni in [75].

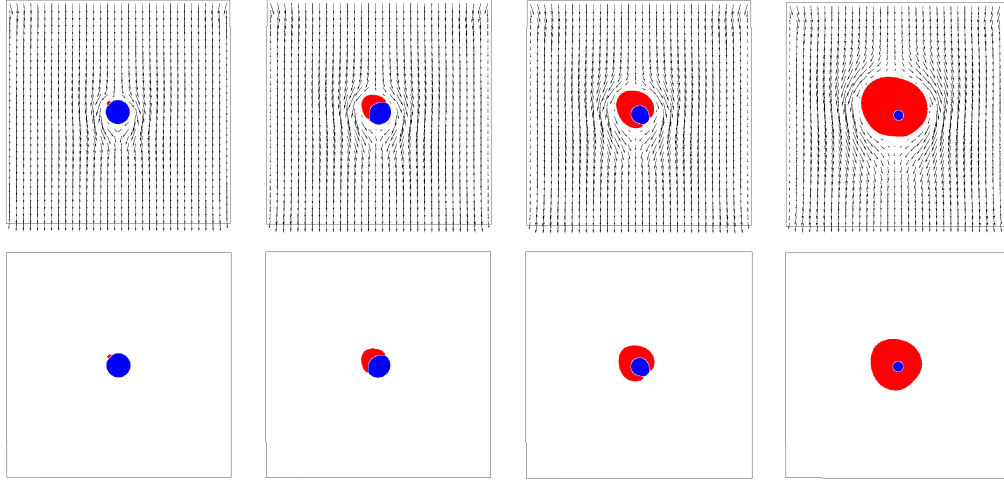


Figure 3.12: Numerical simulations of the peritectic transformation under the influence of convection (on the top) and without convection (on the bottom). The dark circle indicates the properitectic phase, the light structure the peritectic phase. Arrows are vectors indicating the velocity of the hydrodynamic field in the molten phase. The parameters used were: $m_\alpha = -3.73K/at\%$, $m_\beta = -0.6K/at\%$, $T_p = 1790.4K$, $D = 5.0 \times 10^{-9}m^2/s$ and the scaled concentrations $c_\alpha = -2.16$ and $c_\beta = -1.16$ [75].

Investigating heterogeneous nucleation in peritectic materials via the phase-field method

In solidification experiments the final microstructure is determined by both the peritectic growth dynamics as well as the microstructure growth kinetics. Therefore, for a full quantitative comparison with experiments, it is essential to analyze the heterogeneous nucleation kinetics of the above peritectic material system, as well. For such a system a nucleation event arises as a critical fluctuation, which is a non-trivial time-independent so-

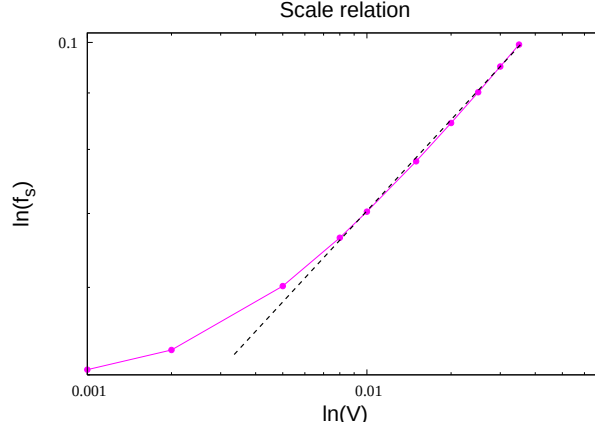


Figure 3.13: Plot of the logarithm of the solid volume fraction versus the logarithm of the inflow velocity.

lution of the governing equations we can derive from the underlying free energy functional. Our derivation follows the standard variational procedure of phase-field theory (for a review see e.g. [77, 13, 25]). Solving the equations (3.1)-(3.7) numerically under boundary conditions that prescribe bulk liquid properties far from the fluctuations ($p_L \rightarrow 1$, and $c \rightarrow c_\infty$ at the outer domain boundaries) and zero field-gradients at the center of the respective phases, one obtains the free energy of the nucleation event as

$$\Delta F^* = \mathcal{F} - \mathcal{F}_0 . \quad (3.11)$$

Here $\mathcal{F}$ is obtained by numerically evaluating the integration over $\mathcal{F}$ after having the time-independent solutions inserted, while $\mathcal{F}_0$ is the free energy of the initial liquid. The zero field-gradients arise naturally due to the stationarity of the problem if the “seed” phase is chosen large enough³. Based

³Thermodynamically this is always possible. The functioning of the underneath relax-

on the nucleation theory and (3.11) the nucleation rate is calculated as

$$I = I_0 \exp \{ -\Delta F^* / kT \} , \quad (3.12)$$

where the nucleation factor I_0 of the classical kinetic approach is used, which proved consistent with experiments [61, 46].

As introduced in the beginning of this section, in a peritectic material sample it is particularly relevant to understand the nucleation of the peritectic phase on top of the properitectic phase in detail, since this is the nucleation process yielding the stationary growth morphology. As demonstrated previously via analytical predictions and Monte Carlo studies (see e.g. [39, 65]), for this specific nucleation process the precise configuration of the properitectic phase, i.e. its free energy on the one hand and its morphology on the other, should contribute to the precise nucleation rate. This, as well as the experimental evidence for deviations from classical nucleation theory in the system Fe-Ni [75], motivated us to study the effect of two morphological features of the properitectic phase on the nucleation rate of the peritectic one, namely (I) the effect of facettes and (II) the effect of its radius. In this context the underlying faceted shape of the properitectic phase is initialized as “seed” for the peritectic phase to nucleate upon as depicted in Fig. 3.14. Fig. 3.14 reveals, too, that in our investigations the peritectic phase is nucleating at the corner of the properitectic phase. The anisotropic

 ation procedure does not depend on the volume of the properitectic phase as such, but on the relative volume of the properitectic phase to volume which we chose as initialization for the peritectic phase. This has to be tuned close to a ratio to be expected from the position in the phase diagram to ensure convergence within the limit of a reasonable number of variations.

form $W(\theta) = W_0(1 + \epsilon_{p_i} \cos 4\theta)$ for $W(\theta)$ allows us to obtain this state for the anisotropic case. However, we are aware that for a simulation of the full dynamic microstructure evolution into a faceted shape more elaborate anisotropic forms of $W(\theta)$ are required, as e.g. given in [22].

To calculate the nucleation rate of the peritectic phase on top of the properitectic phase (this faceted seed), it is then – as described above – essential to determine the corresponding time-independent configuration, at which neither of the two phases will grow ($\partial\mathcal{F}/\partial p_i = 0$), and at which also all diffuse fields are fully relaxed, i.e. stationary ($\partial c/\partial t = 0$). We find this state for various radius r (see Fig. 3.14) of the initial properitectic phase systematically, keeping the position of its center relative to the peritectic phase constant. For each variation we carry out the variational and the relaxation procedures and find the critical nucleation energy and nucleation rate for peritectic transformation. Note that a radius of the peritectic phase, where stationarity is achieved, is namely the radius of the critical nucleus (r_c). The precise morphology of the “two-phase” system with critical nucleus, in particular the size of properitectic phase and ratio of the volume of the two phases, depends on the kinetic of the previous transformation from liquid to properitectic phase.

In Fig. 3.15a) and Fig. 3.15b) we summarize our results. As you can take from Fig. 3.15a), the less faceted the properitectic phase, the larger the nucleation probability for a peritectic nucleation on top of it. For the contribution resulting from the radius of the properitectic phase a similar relation is true: the larger the radius of the properitectic phase, the larger the probability of a peritectic nucleation on top of it. Both findings are in

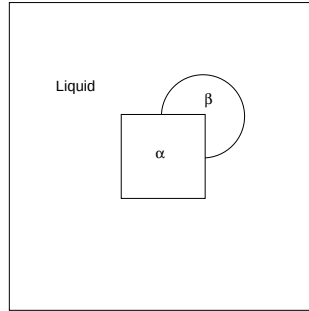


Figure 3.14: Schematic sketch to elucidate the initialization of the relaxation procedure and subsequent calculation to determine the heterogeneous nucleation rate via the phase field method for the case of an anisotropic “seed”.

qualitative agreement with the following atomistic picture: Unfacetted nuclei offer a great number of surface kinks for nucleation. This holds for nuclei of small radii, as well. However, small radius nuclei are also subject to large surface diffusion due to kink flow [59]. This overrides the first effect such that the overall nucleation rate turns out to be smaller for smaller radii. Moreover, these findings are in qualitative agreement with [39] and thus provide a first qualitative validation for our new approach towards heterogeneous nucleation. However, it should be noted that the atomistic picture is just given for a common sense estimation of what our model should do. In the continuum picture underlying our investigations, the differences of the different curves arise due to the fact that the total surface energy tied to the diffuse surface area of the proeutectic nucleus depends on its morphology. Thus the latter naturally has an impact on the nucleation rate just as indicated experimentally. This can be analyzed in more detail making use of the phase field profiles at the stationary point [66]. The benefit of using our contin-

uum model approach rather than atomistic models for the proposed studies is twofold: (1) The approach is computationally considerably more efficient, i.e. it will easily allow for subsequent 3D simulation and simulations of several nuclei competing in the course of initial growth. This also implies that the time scales which can be accessed are larger than for atomistic simulations. Only due to this does simulation of nucleation as well as initial growth become possible. (2) Moreover, it can easily be extended to additional physical mechanisms influencing the nucleation process as e.g. elastic ones [25] or anisotropies of the solid-liquid interfacial free energy [66].

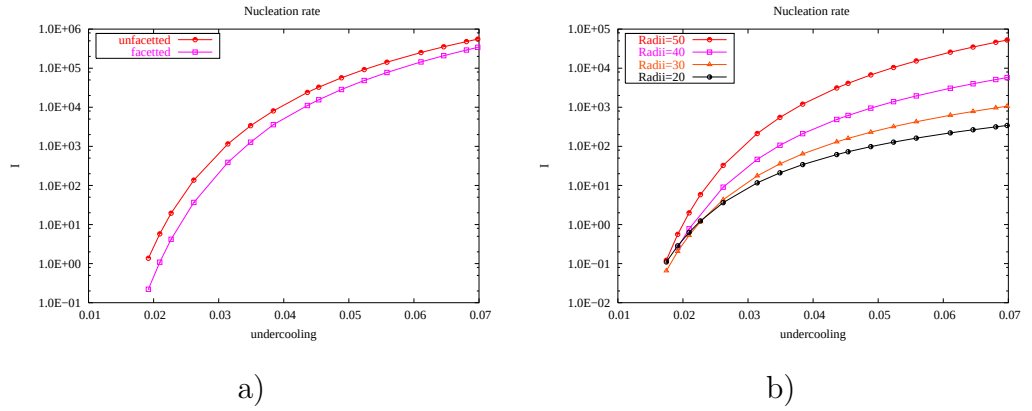


Figure 3.15: a) Comparison of the nucleation rate on top of a faceted nucleus to the one on top of an unfaceted nucleus. b) Comparison of the nucleation rate on unfaceted nuclei of different radii.

3.3.2 Discussion

To summarize in this section, we applied our phase-field approach successfully to investigate the influence of melt flow on the peritectic transfor-

mation. Moreover, we employ our model to identify the precise mechanisms of the heterogeneous nucleation kinetics in a peritectic system, i.e. essentially mechanisms beyond classical nucleation theory. In this context it is important to notice that the new features of our approach to heterogeneous nucleation inherently included are (I) the notion of a diffuse interface as well as (II) long-range interaction effects due to our continuum field approach towards the problem. Based on these features our model can explain differences between classical nucleation theory and experiments as morphological contributions to the nucleation rate. Moreover, it compares well to careful statistical studies of the effects of long-range interactions. In this sense it poses a valuable new approach towards heterogeneous nucleation in general taking into account kinetic, thermodynamic as well as long-range interaction effects, which still has to be developed further.

Summary and Outlook

In this work we have shown how important the influence of convection on the selected microstructure during solidification is. The influence of convection on microstructure solidification was investigated by using a classical sharp interface as well as phase-field models. First, a detailed description of our sharp interface approach with convection in the melt phase was presented. The quantitative aspects of our approach were elucidated through numerical validation and comparisons with existing literature results. The simulated results allow us to draw a new kinetic morphology diagram for dendritic growth under forced flow conditions. Next, we have included convection effects into the quantitative phase-field approach of Echebarria et al. [24] which are meant to simulate dendritic growth of a binary alloy. The description of our model extension as well as numerical investigations for the Fe-Mn system were also presented.

In order to simulate microstructure solidification of a two-phase system with convection, we have extended the quantitative phase-field approach of Folch and Plapp [28] to incorporate the effect of convection in the molten phase during solidification. The quantitative aspect of the model was proven to be preserved after the extension. The model was used to investigate direc-

tional solidification of eutectic lamellae under natural and forced convection influence. We have also applied the model to investigate the growth of the peritectic Fe-Ni alloy under the influence of convection. In the end, we propose the use of this phase-field approach as an alternative approach for the investigation of heterogeneous nucleation in peritectic systems.

The potential of the sharp interface approach and the phase-field models for the prediction of microstructure evolution during solidification under the influence of convection was demonstrated by the simulations presented in this work.

Furthermore, the models and results presented here call for future investigations and relevant model extensions:

- Extension of the sharp interface approach and the phase-field approach to investigate the influence of convection on microstructure evolution in 3 dimensions.
- Coupling the phase-field model with thermodynamic data bases.
- Generalization the phase-field approach to simulate multi-phase growth and multi-component alloy systems.
- Investigation the effect of convection on the free growth of eutectic lamellae.
- Investigation of the directional solidification of peritectic alloys under a transverse and ahead shear flow.

As a last point, a closer collaboration between numerical and experimental research efforts would be desirable to facilitate an exact matching of

numerical parameters and experimental conditions in the future.

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Curriculum Vitae

Personal Data

Name: Ricardo da Silva Siquieri

Date of Birth: 10th February 1978

Place: Born in Presidente Prudente - SP - Brazil

Citizen of Brazil

Education

1993 - 1995: High school, Pres. Prudente - SP - Brazil

1996 - 1999: Study of Mathematics, UNESP - Brazil

1998 - 1999: Research work, UNESP - Brazil

2000 - 2002: Master of Science, USP - São Carlos - Brazil

2004 - 2008: PhD Student, RWTH-Aachen - Germany

Professional Experience

2002 - 2004: Research scientist, Dortmund University - Department of Bio-chemical and Chemical Engineering, Chair of Thermodynamics

2004 - Research scientist, RWTH-Aachen - Faculty of Georesources and Materials Engineering, Chair of Computational Materials Engineering