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## Modeling of Solidification

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A Thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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## Contents

	Ré	SUMÉ <b>v</b>	ii
	AB	STRACT vi	ii
	Ac	KNOWLEDGMENTS	$\mathbf{x}$
1	IN' 1.1 1.2	RODUCTION Dynamical Models	<b>1</b> 4 6
2	Mo 2.1 2.2 2.3 2.4	DELS OF SOLIDIFICATION         The Basic Model of Solidification         2.1.1 The Planar Stationary Solution         2.1.2 Linear Stability Analysis         Directional Solidification         Directional Solidification         Local Models of Solidification         2.3.1 The Geometrical Model         2.3.2 The Boundary-Layer Model         Phase-Field Models	8 8 10 12 14 18 19 20 22
3	DE 3.1 3.2 3.3 3.4 3.5	NDRITIC GROWTH       2         Introduction       2         Phase-Field Models of Dendritic Growth       2         The Model of Kobayashi       3         Thermodynamically-Consistent Models       3         Dendritic Growth in a Polymorphous Material       3	27 30 34 36 37
4	DI: 4.1 4.2 4.3	ECTIONAL SOLIDIFICATION       4         Some Local Descriptions of Directional Solidification       4         Phase-Field Model of Directional Solidification       4         4.2.1 The Phase Diagram       4         Numerical Simulations       5	. <b>4</b> 15 17 19
5	EL 5.1 5.2	ASTIC EFFECTS 5 Dendritic Growth due to Elastic Fields	<b>3</b> 54 59 55 57 59 71 72
6	Cc	NCLUSION 7	<b>9</b>

.

Ар	PENDICES	81
A.1	Linear Stability of the Planar Front in Directional Solidification	81
A.2	Sharp-interface limit	84
Re	FERENCES	89

-

.

## LIST OF FIGURES

1.1	Scanning electron micrograph showing the development of dendrites in a nickel-based superalloy single-crystal weld	2
2.1	Sketch of the solid-liquid interface	9
2.2	Temperature profile of the planar stationary solution	11
2.3	Growth rate spectrum	13
2.4	Schematic plot of the directional solidification setup	14
2.5	Phase diagram for dilute alloys	15
2.6	Growth rate spectrum for directional solidification	17
2.7	Coordinate system for the local models	19
2.8	Thermal field $u$ in front of the interface $\ldots$ $\ldots$ $\ldots$ $\ldots$	21
2.9	Double well structure of the free energy density	23
2.10	The equilibrium interfacial profile	24
3.1	The needle crystal	28
3.2	Growth of a dendrite in an undercooled melt	35
3.3	Free energy curve of the liquid and the amorphous phase with respect	
	to b.c.c. solid solution for a concentration of Ti-55 at.%Cr	38
3.4	Contour plot of the free energy	39
3.5	Free energy curve for different orientations of the phase-field	40
3.6	Dendritic amorphization of a bilayer of crystal	41
3.7	Many dendrites growing in an undercooled melt	43
4.1	Breathing-mode pattern	45
4.2	Experimental dispersion relation for the breathing-mode	46
4.3	Neutral curve of the stabilized Kuramoto-Sivashinsky equation	47
4.4	Interface dynamics exhibiting a vacillating-breathing mode	48
4.5	Part of the phase diagram for the model of directional solidification .	50
4.6	Non-steady state interfaces showing tip splitting and collision of two	
	solitary modes.	50
4.7	Numerical simulation of a breathing-mode	51
4.8	Numerical dispersion relation for the breathing-mode	52
5.1	Scanning tunneling micrograph overview of 0.1 ML Co deposited at	
	400K on Pt(111)	54
5.2	Magnification of the dendrite region	55
5.3	Growth in the presence of isotropic elastic field	<u> </u>
5.4	Quasidendritic growth in the presence of anisotropic elastic field (	62
5.5	Quasidendritic growth in the presence of anisotropic elastic field and a	
	phase dependent shear modulus	63
5.6	Growth of a dendrite in the presence of anisotropic elastic field	54

5.7	Contour plot of the functional derivative of the elastic energy 6	5
5.8	Definition of the Burgers vector	6
5.9	Stable equilibrium of two edge dislocations	3
5.10	Dynamics of the dislocations	4
5.11	Dislocation pileup	5
5.12	Initial configuration for the study of the pileup	6
5.13	Numerical simulation of the dislocation pileup	7
5.14	Dendritic growth in presence of dislocations	8

## Résumé

Nous développons des modèles de solidification permettant de traiter la phase solide de façon plus réaliste. Tout d'abord, nous modifions un modèle assez récent de croissance dendritique dû à Kobayashi [93] afin d'étudier la croissance polymorphe de dendrites. Pour cela, nous introduisons un paramètre d'ordre vectoriel au lieu d'un paramètre d'ordre scalaire. Ceci nous permet d'avoir des joints de grain dans les solides. Ce modèle est utilisé pour l'étude de l'amorphisation d'un matériau polycristallin ainsi que pour l'étude de la croissance de plusieurs dendrites d'orientations différentes.

Un modèle de phase développé par Grossmann et al. [93] est utilisé afin d'étudier une technique importante en métallurgie, la solidification dirigée. Plus précisément, nous examinons une des instabilités secondaires, le mode optique ou oscillatoire. Nous trouvons que la fréquence de l'oscillation est reliée au nombre d'onde du motif selon la loi  $\omega \sim q$ . Ceci est en accord avec l'expérience de Cladis et al. [91].

Finalement, nous examinons l'effet de l'élasticité sur la croissance. Un modèle est proposé afin expliquer la croissance quasi-dendritique des îlots de Co déposé sur une surface Pt(111) telle qu'observée lors d'une expérience récente de Grütter et Dürig [95]. Une ressemblence qualitative est trouvée entre nos simulations et ces résultats expérimentaux. L'importance des dislocations est abordée à la fin de cette thèse. Un modèle de la dynamique des dislocations est présenté qui permet d'inclure des interfaces. Ce modèle qui a été construit afin d'étudier l'effet des dislocations sur la solidification nous permet aussi de reproduire certains résultats bien connus de la théorie des dislocations tels l'empilement.

## Abstract

Some models of solidification are developed by treating the solid in a more realistic manner than that has been done to date. In order to further investigate the polymorphous dendritic growth, a recent phase-field model of dendritic growth due to Kobayashi [93] is modified by introducing a vectorial order parameter. This new model allows for the existence of grain boundaries and is used to study the amorphization of polycrystalline material as well as the growth of many dendrites of different orientations.

One of the major techniques of solidification, namely the directional solidification is further analyzed by using the phase field model proposed by Grossmann et al. [93]. More precisely, a particular secondary instability, the vacillating breathing mode, is investigated. The relation between the frequency and the wavenumber,  $\omega \sim q$ , found in the experiment of Cladis et al. [91] is recovered through qualitative simulations.

The effect of elasticity on growth is investigated. A model is proposed to explain the quasidendritic growth of the Co islands deposited on a Pt(111) surface observed in a recent experiment of Grütter and Dürig [95]. Qualitative resemblance between their experimental results and our simulations is found. The importance of dislocations is addressed by presenting a model of dislocation dynamics that takes into account the possibility of interfaces. This model not only incorporates the effect of dislocations on solidification, but also qualitatively reproduces some well known phenomena of dislocation theory known as "pile up".

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> Karim Aguenaou Montréal, 1997

Modeling of Solidification

1

Solidification, the growth of a stable phase of material into the unstable liquid phase, has been studied for many years for practical reasons. During solidification, diverse microstructures can appear which influence greatly the mechanical properties of the material. The most spectacular example of such a microstructure is the dendrite. The term dendrite was apparently first introduced to the world of crystal growth by Tschernoff<sup>1</sup> at the end of the 19<sup>th</sup> century. He used it to describe the branched structure he found in the center of a metal ingot. A dendrite is characterized by its tree-like shape<sup>2</sup> as clearly seen in figure 1.1. Dendrites are found in every kind of crystal growth process. The most common dendrites are snow flakes, which are characterized by six dendritic branches<sup>3</sup>. Because of its increased surface free energy, a dendritic crystal is thermodynamically unstable as compared to a droplet, its equilibrium shape. Thus, the shapes of the crystal are of dynamical origin.

Metallurgists have also encountered other types of regular structures. These include lamellar eutectics and the cellular growth of dilute alloys. In the solidification of an impure melt, segregation of solute takes place since the solid and the liquid phases of a given mixture have different concentrations at equilibrium. This chemical inhomogeneity has a profound impact on the mechanical as well as electronic performance of the material.

The growth patterns mentioned above have a typical size of  $10 - 100 \,\mu\text{m}$ . A mesoscopic description of the solidification, *i.e.* where we consider the liquid and

<sup>&</sup>lt;sup>3</sup>A standard reference in the study of snowflakes is the book of the Japanese scientist Nakaya [54] who investigated during 20 years in the island of Hokkaido the shape of the snow crystals, in nature and in laboratory.



<sup>&</sup>lt;sup>1</sup>Doherty [75]. More historical details can be found in the book of Smith [60].

<sup>&</sup>lt;sup>2</sup>This explains the etymology of the word dendrite.  $\delta\epsilon\nu\tau\rho\rho\nu$  (dendron) means a tree.



Figure 1.1: Scanning electron micrograph showing the development of dendrites in a nickel-based superalloy single-crystal weld [picture reproduced from David, DebRoy and Vitek [94]].

solid phase as continuous media, is then legitimate. Solidification will be described throughout this dissertation as a *first-order phase transition* characterized by the release of latent heat at the interface or, in the case of a mixture, by the rejection of the component of the mixture that has a lower concentration in the solid, *i.e.*, the solute.

This minimal model neglects effects such as fluid flow due to temperature, concentration gradient as well as volume changes, and elastic effects. These elastic effects are particularly important in the solid/solid transition, or in the growth of solid on solid, and therefore will be discussed later in this thesis. It is well known that the structural (Martensitic) transformations also have a strong influence on the properties of the material. The best example is steel. As these transformations do not involve any diffusion of atoms they will not be studied in this thesis.

The interest in the mathematical problem of solidification goes back to the middle of the  $18^{\text{th}}$  century<sup>1</sup> with the work of Lamé and Clapeyron. The problem was posed in its standard form by Stefan in 1889. The fundamental mechanism limiting the growth of a solid is the diffusion away from the interface of the latent heat released by the solidification or, in the case of a mixture, the diffusion away of the solute. The problem <sup>1</sup>Rubinstein [71].

of solidification has thus as a basic ingredient a field obeying a diffusion equation in both phases. This equation has to be supplemented by two boundary conditions at the solidification front: Heat (or solute) conservation at a point on the moving interface and a statement of local thermodynamic equilibrium which determines the temperature at the interface. The latter condition will bring into the problem the surface tension which is the crucial stabilizing force necessary for pattern formation. This free-boundary problem, the Stefan problem, is representative of one of the most challenging areas of applied mathematics.

Solidification started to attract the attention of statistical physicists in the late 70's. Solidification, an out-of-equilibrium process, is a subclass of the general problem of pattern formation in dissipative systems. Other examples<sup>1</sup> can be found in hydrodynamics with the Rayleigh-Bénard convection of fluid heated from below, in chemistry with the well studied Belousov-Zhabotinsky reaction and also in biology. A better understanding of one of these problems can shed new light on the solidification problem and vice versa.

The study of pattern formation has benefited greatly from recent careful experiments. Also, new concepts as well as new analytical and numerical tools have been introduced. In this thesis some of them will be explained. However, the *phase-field model* will be the major method expounded. The basic idea behind this model is to replace the dynamics of the boundary by an equation of motion for a phase-field which changes from one value to the other quickly but smoothly, corresponding, for example, to liquid and solid phases. The explicit interface motion is thus described by two coupled partial differential equations, one for the temperature (or concentration) and the other for the phase-field. As will be seen later in this thesis, phase-field models have been successful in reproducing the intricate pattern of dendrites as well as some other growth structures.

The phase-field model is closely related to model C introduced by Halperin, Hohenberg and Ma [74] in their study of non-equilibrium phenomena. We will briefly review the three dynamical models, namely models A, B and C that are often encountered in the study of dynamic critical phenomena. They also describe the dynamical

<sup>&</sup>lt;sup>1</sup>See Cross and Hohenberg [93] and the references therein.

properties of a large class of first-order transitions phenomena such as nucleation and spinodal decomposition.

## 1.1 Dynamical Models

The field theoretical approach to the dynamics of metastable states is well known to statistical physicists for the last thirty years. One focuses on a small set of semimacroscopic variables whose dynamical evolution is *slow* compared to the remaining degrees of freedom. The dynamical equations of motion for the slow variables are obtained, either by phenomenological arguments or projection operator techniques. The remaining variables enter only in the form of random forces.

A simple dynamical model is *model* A, in which  $\psi$  is a nonconserved order parameter reflecting the degree of local ordering in the system. It obeys the following dynamics

$$\frac{\partial \psi(\mathbf{r},t)}{\partial t} = -\Gamma \frac{\delta \mathcal{F}}{\delta \psi(\mathbf{r})} + \zeta(\mathbf{r},t) . \qquad (1.1)$$

 $\mathcal{F}$  is a *coarse-grained* free energy functional usually assumed to be of the Ginzburg-Landau form,

$$\mathcal{F}\{\psi\} = \int d\boldsymbol{r} \left[\frac{1}{2}K_{\psi}|\boldsymbol{\nabla}\psi|^2 + f(\psi)\right] , \qquad (1.2)$$

where the function  $f(\psi)$  has the double well structure

$$f(\psi) = -\frac{r(T)}{2}\psi^2 + \frac{u}{4}\psi^4$$

 $K_{\psi}$  and u are positive constant while r(T) is dependent on the temperature T in the following way: For  $T > T_c$  (r < 0) only a single minimum exists at  $\psi = 0$ . For  $T < T_c$  (r > 0), there are two degenerate stable minima. They correspond to the two phases coexisting at equilibrium. The mobility  $\Gamma$  gives the rate at which the system dynamically evolves.

The term  $\zeta(\mathbf{r}, t)$  is a Gaussian white noise with zero mean

$$\langle \zeta(\boldsymbol{r},t) \rangle = 0 \tag{1.3}$$

and its correlation is

$$\langle \zeta(\mathbf{r},t)\zeta(\mathbf{r}',t')\rangle = D\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$$
, (1.4)

where D is a constant. For consistency with equilibrium, the strength of the fluctuations D must be related to the temperature and the strength of the dissipation  $\Gamma$ by

$$D = 2\Gamma k_B T$$

where  $k_B$  is the Boltzmann's constant. This is known as the fluctuation-dissipation relation.

Without the noise term, equation (1.1) simply states that the rate at which the system releases back to equilibrium  $(\partial \psi / \partial t)$  is proportional to the deviation from equilibrium  $(\delta \mathcal{F} / \delta \psi)$ . It is a purely relaxational dynamics. The noise term makes sure that it evolves towards a global and not a local minimum.

Model A is used to describe the dynamics of binary alloys undergoing orderdisorder transition, and magnetic phase transitions, for example.

The dynamics of phase separation in a binary system is governed by the diffusion of the chemical potential gradient. The conservation of material is expressed by

$$rac{\partial c({m r},t)}{\partial t} = - {m 
abla} \cdot {m j}({m r},t) \; ,$$

where c(r,t) denotes the local concentration of one of the species. The diffusion current j(r,t) is

$$m{j}(m{r},t) = -\Gamma' m{
abla} rac{\delta \mathcal{F}}{\delta c(m{r})} \; ,$$

where  $\Gamma'$  is a kinetic coefficient. The local chemical potential is defined as

$$\mu(\mathbf{r}) \equiv rac{\delta \mathcal{F}}{\delta c(\mathbf{r})}$$

with

$$\mathcal{F}\{c\} = \int d\mathbf{r} \left[ \frac{1}{2} K_c |\nabla c|^2 - \frac{r(T)}{2} c^2 + \frac{u}{4} c^4 \right] \,. \tag{1.5}$$

The free energy functional (1.5) was studied by Cahn and Hilliard [58], in the context of binary alloys. The dynamical equation for the concentration becomes

$$\frac{\partial c(\boldsymbol{r},t)}{\partial t} = \Gamma' \nabla^2 \left[ -K_c \nabla^2 c + \frac{\partial f}{\partial c} \right] . \tag{1.6}$$

Cook [70] observed that it was necessary to add a noise term to (1.6) to have a correct statistical description of the alloy dynamics.

The dynamical equation for the concentration is the Cahn-Hilliard-Cook equation

$$\frac{\partial c(\boldsymbol{r},t)}{\partial t} = \Gamma' \nabla^2 \left[ -K_c \nabla^2 c + \frac{\partial f}{\partial c} \right] + \zeta(\boldsymbol{r},t) ,$$

which is also known as *model* B following the classification of Hohenberg and Halperin [77].  $\zeta(\mathbf{r}, t)$  satisfies equation (1.3) but its correlation is now

$$<\zeta(\mathbf{r},t)\zeta(\mathbf{r}',t')>=-2\Gamma'k_BT\nabla^2\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$$

The factor of  $-\nabla^2$  arises because of the conservation law.

The dynamics of a system with two coupled dynamical variables, a nonconserved order parameter  $\psi$  and a conserved variable c, is described by model C,

$$\frac{\partial \psi(\boldsymbol{r},t)}{\partial t} = -\Gamma_{\psi} \left[ -K_{\psi} \nabla^2 \psi + \frac{\partial f}{\partial \psi} \right] + \zeta_{\psi}(\boldsymbol{r},t)$$

and

$$\frac{\partial c(\boldsymbol{r},t)}{\partial t} = \Gamma_c \nabla^2 \left[ -K_c \nabla^2 c + \frac{\partial f}{\partial c} \right] + \zeta_c(\boldsymbol{r},t)$$

The terms  $\zeta_{\psi}(\mathbf{r},t)$  and  $\zeta_{c}(\mathbf{r},t)$  are Gaussian white noise satisfying (1.3) and the correlations are

$$<\zeta_{\psi}(\boldsymbol{r},t)\zeta_{\psi}(\boldsymbol{r}',t')>=2\Gamma_{\psi}k_{B}T\delta(\boldsymbol{r}-\boldsymbol{r}')\delta(t-t')$$

and

$$<\zeta_c(\mathbf{r},t)\zeta_c(\mathbf{r}',t')>=-2\Gamma_c k_B T \nabla^2 \delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$$

The cross correlation functions are zero.

## 1.2 Thesis Overview

The aim of this thesis is to serve as an illustration of the usefulness of the phase-field models to further develop successful models of solidification. In particular, we treat the solid phase in a much more realistic manner than has been done to date. The thesis is divided into four main chapters. Original results are found in chapters 3, 4 and 5.

The most common models of solidification are presented in chapter 2. After presenting the usual thermodynamics description of the free growth of a pure solid, we

introduce another important system pertaining to solidification, directional solidification. The local models of solidification are briefly presented, even though they will not be of great use in this thesis. Their historical importance however justifies their presence in this dissertation. A general presentation of the phase-field model concludes the chapter.

Chapter 3 deals with phase-field models of dendritic growth. Recent models of dendritic growth are reviewed and we show how to incorporate grain boundaries and polymorphous crystallization into these models.

In chapter 4, we show how to address recent experiments on directional solidification with a more realistic model. This phase-field model developed recently by Grossmann et al. [93] is used to study one of the secondary instabilities encountered in directional solidification, namely the vacillating-breathing mode.

In chapter 5, we incorporate the fundamental feature of the liquid-solid transition – elasticity – into models of solidification. In the first part of this chapter, the elastic field is coupled to growth. This is motivated by recent experimental results of Grütter and Dürig [95] on the quasidendritic growth of Co islands deposited on a Pt(111) surface. In the other half of the chapter, a model of dislocation dynamics is introduced and some qualitative results are discussed.

## 2

## MODELS OF SOLIDIFICATION

## 2.1 The Basic Model of Solidification

In the conventional model of the solidification of a pure substance from its melt, the diffusion of latent heat produced at the interface between the solid and the liquid is the fundamental mechanism controlling solidification. The heat in the neighborhood of the interface has to diffuse away from the interface, before further solidification can take place. The liquid is assumed to be free of any impurities whose slow diffusion would limit the crystal growth. Here the growth is limited solely by the diffusion of latent heat. The purely chemical model, where the diffusion of impurities is the limiting process, is similar to this thermal model<sup>1</sup> and will be discussed later in the context of directional solidification.

The dimensionless thermal diffusion field is chosen to be

$$u = \frac{T - T_{\infty}}{L/C} , \qquad (2.1)$$

where  $T_{\infty}$  is the temperature of the liquid far from the solid, L is the latent heat and C is the specific heat. The temperature field u obeys the diffusion equation

$$\frac{\partial u}{\partial t} = D\nabla^2 u , \qquad (2.2)$$

where D is the thermal diffusion constant. We shall consider here the simplest limit, namely the symmetric model where D is the same in both liquid and solid phases<sup>2</sup>. It greatly simplifies the calculations without altering too much the physical results. This is because it is the difference in free energy, not transport coefficients, which drives the transformation from the metastable liquid to the stable solid.

<sup>&</sup>lt;sup>1</sup>Langer [80].

<sup>&</sup>lt;sup>2</sup>The other limit useful in the study of the solidification of an impure melt is the *one-sided model* where the chemical diffusion in the solid is neglected.



Figure 2.1: Sketch of the solid-liquid interface.

The crucial equations of this model are the boundary equations imposed at the solidification front. First, there is *heat balance*<sup>1</sup> across the solid (S) – liquid (L) interface, which expresses the conservation of the total energy when some matter is transformed from liquid into the solid:

$$v_n = D(\nabla u|_{\mathbf{S}} - \nabla u|_{\mathbf{L}}) \cdot \hat{\boldsymbol{n}} , \qquad (2.3)$$

where  $\hat{n}$  is the unit normal directed outward from the solid as shown in figure 2.1 and  $v_n$  is the normal interface velocity. The left-hand side of (2.3) is the rate at which latent heat is generated at the interface and the right-hand side is the rate at which it is diffused away.

When the interface is assumed to be rough, the attachment of the atoms or molecules of the liquid onto the liquid-solid interface is quasi-instantaneous, *i.e.*, very fast ( $\sim 10^{-12}$  s) compared to the time of growth of an atomic layer of solid (in typical experiments where the velocity of the interface is of the order of 10  $\mu$ m/s, this time is  $\sim 10^{-4}$  s).

The interface is then considered to be in a local equilibrium. In practice, most metal interfaces as well as organic materials (*e.g.* succinonitrile and  $CBr_4$ ) on which many of the most precise experiments have been performed, are rough.

The second boundary condition determines the temperature  $u_i$  of the interface

$$u_i = \Delta - d_0 \kappa , \qquad (2.4)$$

where

$$\Delta = \frac{T_M - T_\infty}{L/C} \,. \tag{2.5}$$

Equation (2.4) is known as the Gibbs-Thomson equation for a pure material.  $\Delta$  denotes the dimensionless undercooling and  $T_M$  the melting temperature.  $\kappa$  is the  $\overline{}^{1}$ Also known as the Stefan-Lamé condition.

total curvature of the interface, defined as positive for a convex solid, and  $d_0 = \gamma CT_M/L^2$  is the *capillary length*. The capillary length is proportional to the solidliquid surface tension  $\gamma$  and is typically of the order of a few Ångströms. When a bulge of solid penetrates inside the melt, the temperature at the tip of the bulge is lower than the melting temperature of the planar interface.

More generally, one has to add to (2.4) a kinetic correction

$$u_i = \Delta - d_0 \kappa - \beta(v_n) \tag{2.6}$$

where  $\beta(v_n)$  is a function of the normal interface velocity. A linear function  $\beta = \beta_0 v_n$ would be accurate for a rough interface. For faceted interfaces,  $\beta$  is an orienteddependent function which can be highly non-linear. In that case, both  $d_0$  and  $\beta$  carry information about the orientation of the solidification front relative to the crystalline axes.

The set of equations (2.2, 2.3 and 2.4) supplemented by initial data, and boundary conditions for u far from the solidification front, constitutes a closed mathematical problem of the *free-boundary* type. It is known as the modified *Stefan problem* which has been extensively studied by mathematicians<sup>1</sup>. With zero surface tension ( $d_0 = 0$ ), it becomes the classical Stefan problem.

This basic model of solidification is also known as the minimal model. We assume that there is no flow in the liquid phase: convection and advection are neglected. However, even with these simplifications, the mathematical problem is highly nontrivial. Non-linearities come into play via the curvature (equation (2.4)) and the unit normal vector (equation (2.3)). For a one-dimensional interface, given by z = z(x) in the two dimensional x - z plane,  $\kappa = -z_{xx}(1 + z_x^2)^{-3/2}$  and  $n_z = (1 + z_x^2)^{-1/2}$ .

### 2.1.1 The Planar Stationary Solution

The planar solidification front constitutes the simplest problem. Consider a planar front moving forward in the z direction at a constant velocity  $v_0$ . The stationary diffusion equation in the reference frame of the interface takes the following form

$$D\frac{\partial^2 u}{\partial \bar{z}^2} + v_0 \frac{\partial u}{\partial \bar{z}} = 0 , \qquad (2.7)$$

<sup>1</sup>Rubinstein [71].

where  $\tilde{z} = z - v_0 t$ . With the boundary condition for the classical Stefan problem,  $\kappa = 0, u(0) = \Delta$ , the solution of (2.7) becomes

$$u(\tilde{z}) = \begin{cases} \Delta e^{-2\tilde{z}/\ell} & \text{for } \tilde{z} > 0; \\ \Delta & \text{for } \tilde{z} < 0, \end{cases}$$
(2.8)

where  $\ell = 2D/v_0$  is the thermal diffusion length. For growth velocities in the 10  $\mu$ m/s range,  $\ell$  is of the order of centimeters. This solution must satisfy the other boundary condition, heat balance (2.3). We find that a planar stationary growth is possible only when  $\Delta$  is equal unity ( $T_{\infty} = -80^{\circ}$ C for water). This could have been deduced directly from the heat balance equation: when  $\Delta = 1$ , the latent heat released is exactly equal to the heat necessary to bring the temperature of the liquid from  $T_{\infty}$  to  $T_M$ . Figure 2.2 shows the behavior of the field u(z).



Figure 2.2: Temperature profile of the planar stationary solution.

If  $\Delta < 1$  (and indeed, most experiments are conducted at very low undercooling, *i.e.*  $\Delta \ll 1$ ) not all the latent heat is absorbed by the solid and this heat builds up in front of the interface. As a result, the solidification rate decreases and the planar front moves following a diffusion law  $z_I \sim t^{1/2}$ . This law can be derived using a similarity transformation<sup>1</sup>.

<sup>&</sup>lt;sup>1</sup>See for instance Langer [87] and the literature related to the one dimensional Stefan problem in the book of Rubinstein [71].

## 2.1.2 Linear Stability Analysis

The most interesting feature of the planar solidification front described above is its morphological instability<sup>1</sup>. Let us consider the stability of the planar solidification moving at a constant velocity<sup>2</sup>  $v_0$ . The diffusion equation in the moving frame of the interface is

$$\frac{1}{D}\frac{\partial u}{\partial t} = \nabla^2 u + \frac{2}{\ell}\frac{\partial u}{\partial z}, \qquad (2.9)$$

where the tildes have been omitted on the z for simplicity. Say the unperturbed solidification front is  $\zeta_I(x) = 0$ , where x denotes positions in the plane perpendicular to z. The perturbed solidification front takes the form

$$\zeta_I(\boldsymbol{x}) + \delta\zeta(\boldsymbol{x},t)$$
.

Similarly, the perturbed temperature fields

$$u^L(\boldsymbol{x}, z, t) = e^{-2z/\ell} + \delta u^L(\boldsymbol{x}, z, t)$$

and,

$$u^{S}(\boldsymbol{x},z,t) = 1 + \delta u^{S}(\boldsymbol{x},z,t) \; .$$

We write the perturbations as the sum of their Fourier components

$$egin{aligned} \delta u^L(m{x},z,t) &= \hat{u}^L(m{k})\,e^{(im{k}\cdotm{x}-qz+\omega t)}\ , \ \delta u^S(m{x},z,t) &= \hat{u}^S(m{k})\,e^{(im{k}\cdotm{x}+ar{q}z+\omega t)} \end{aligned}$$

and

$$\delta \zeta(\boldsymbol{x},t) = \hat{\zeta}(\boldsymbol{k}) \, e^{(i \boldsymbol{k} \cdot \boldsymbol{x} + \omega t)}$$

From the diffusion equation (2.9), we obtain

$$\frac{\omega}{D} = q^2 - \frac{2}{\ell}q - k^2 = \bar{q}^2 + \frac{2}{\ell}\tilde{q} - k^2 . \qquad (2.10)$$

Using the Gibbs-Thomson condition and the heat balance equation, we obtain the two following equations after linearizing:

$$-rac{2}{\ell}\hat{\zeta}(m{k})+\hat{u}^L(m{k})=\hat{u}^S(m{k})=-d_0k^2\hat{\zeta}(m{k})$$

<sup>&</sup>lt;sup>1</sup>Langer [87]; Caroli, Caroli and Roulet [92].

<sup>&</sup>lt;sup>2</sup>This linear stability analysis is performed for the academic case  $\Delta = 1$  which allows one to identify the main mechanisms responsible for most of the front instabilities. Moreover, this algebra is also valid in the *quasistationary approximation* where the diffusive growth is approximated as constant growth on the time scale of the instability.

and

$$\frac{\omega}{D}\hat{\zeta}(\boldsymbol{k}) = -\left(\frac{2}{\ell}\right)^2 \hat{\zeta}(\boldsymbol{k}) + q\hat{u}^L(\boldsymbol{k}) + \tilde{q}\hat{u}^S(\boldsymbol{k}) \ .$$

Eliminating  $\hat{\zeta}$  and  $\hat{u}$  from the last two equations, we get

$$\omega = \frac{2D}{\ell} \left( q - \frac{2}{\ell} \right) - Dd_0 k^2 (q + \tilde{q}) . \qquad (2.11)$$

The physical interpretation of the last equation becomes easier after two common approximations. First, the thermal diffusion length is considered to be much greater than the wavelength of the perturbation  $(k\ell \gg 1)$ . Secondly, the diffusion of heat along the perturbation is fast compared to the growth of the solid. This is known as the quasistationary condition ( $\omega \ll Dk^2$ ). The front moves slowly enough to let the temperature field adapts to its instantaneous shape as if it were stationary. It amounts to neglecting  $\partial u/\partial t$  in equation (2.9). We deduce then from (2.10) that  $q \simeq \tilde{q} \simeq |\mathbf{k}|$ , and thus (2.11) simplifies to

$$\omega \simeq v_0 |k| (1 - d_0 \ell k^2) . \tag{2.12}$$

As shown in figure 2.3, the planar solidification front is linearly unstable against



Figure 2.3: Growth rate spectrum.

 $(\omega > 0)$  long wavelength deformations. This is known as the Mullins-Sekerka instability<sup>1</sup>. Also, the front is stable ( $\omega < 0$ ) against short wavelength fluctuations. <sup>1</sup>Mullins and Sekerka [63].



Figure 2.4: Schematic plot of the directional solidification setup.

The  $k^3$ -term responsible for this in (2.12) is proportional to the capillary length  $d_0$ . The capillarity acts as a stabilizing agent whereas the diffusion destabilizes the planar front. The typical scale of the patterns resulting from this instability is  $\lambda_s = 2\pi/k_s = 2\pi\sqrt{\ell d_0}$  which is the geometrical mean of the capillary length  $d_0$  and the diffusion length  $\ell$ . The scale of the front structure is typically of the order of microns.

## 2.2 Directional Solidification

Directional solidification is a well known technique in metallurgy which is used for purifying solids and preparing materials with specific properties<sup>1</sup>. The principle of directional solidification is illustrated by figure 2.4 and a typical phase diagram, which defines the parameters used, is shown in figure 2.5. An impure solid is grown at the expense of a liquid by pulling the sample at a constant velocity v in a temperature gradient established by hot and cold contacts. The contacts A and B are at a temperature respectively higher and lower than the liquidus and solidus temperature. In the study of non-linear dynamics, the experiments are usually carried out using liquids

<sup>&</sup>lt;sup>1</sup>Kurz and Fisher [92].



Figure 2.5: Phase diagram for dilute alloys.

instead of solids. The group of Libchaber pioneered the use of the isotropic/nematic transition occurring in some liquid crystals to study directional solidification<sup>1</sup>. The other liquid crystal phases that can be used are cholesteric/isotropic<sup>2</sup> There are experimental and theoretical advantages to work with liquids. For instance, the crystal anisotropy is absent and the two phases are more symmetric, thus the system is closer to the simple theoretical models.

Solidification of an impure melt is similar to the pure liquid solidification described in the last section but the diffusion of solute is now the rate limiting process. In directional solidification, the imposed external temperature gradient serves to limit the instability and allows one to study patterns closer to the planar interface. We assume that the thermal diffusion is instantaneous<sup>3</sup> which allows us to neglect the effect of the latent heat released on the imposed linear temperature gradient. Let c denote the concentration of the impurities. The diffusion of the concentration expressed in the laboratory frame is:

$$\frac{\partial c}{\partial t} = D\nabla^2 c + v \frac{\partial c}{\partial z} ,$$

<sup>&</sup>lt;sup>1</sup>Oswald, Bechhoefer and Libchaber [87]; Simon, Bechhoefer and Libchaber [88]; Flesselles, Simon and Libchaber [91].

<sup>&</sup>lt;sup>2</sup>See for example Cladis et al. [91].

<sup>&</sup>lt;sup>3</sup>The diffusion constants of the solute are  $D \sim 10^{-5} \text{cm}^2/\text{s}$  whereas the thermal diffusion constants range from  $10^{-1} \text{cm}^2/\text{s}$  for the metals to  $10^{-3} \text{cm}^2/\text{s}$  for organic materials.

where D is the diffusion constant assumed to be the same in the two phases. This equation has to be supplemented by the continuity conditions expressing the conservation of solute at the interface,

$$(\boldsymbol{v}\cdot\hat{\boldsymbol{n}})c_L(\zeta)(1-K)=D(\boldsymbol{\nabla}c_S-\boldsymbol{\nabla}c_L)\cdot\hat{\boldsymbol{n}}$$

and two local equilibrium equations, the Gibbs-Thomson condition

$$T=T_M-mc_L-T_Md_0\kappa\,,$$

and

$$c_S(\zeta) = K c_L(\zeta) ,$$

where  $\hat{n}$  is a unit vector normal to the interface, pointing from the solid phase into the liquid phase,  $\zeta$  is the position of the interface, m is the absolute value of the liquidus slope, K is the equilibrium segregation or partition coefficient (the ratio of the slopes of liquidus and solidus lines) which is close to unity in typical experiments,  $d_0$  is the capillary length, and  $\kappa$  is the curvature of the interface. Finally, another boundary condition for c is

$$\lim_{z\to\infty}c=c_0\;.$$

There are three typical lengths in the system. The diffusion length  $\ell \equiv 2D/v$ , the thermal length  $\ell_T \equiv \Delta T/G$  and the chemical capillary length  $\ell_c \equiv d_0 T_M/\Delta T$ . G is the applied thermal gradient,  $\Delta T \equiv m\Delta c$  is the temperature difference between the liquidus and the solidus line at the concentration  $c_0$  and  $\Delta c = c_0(1-K)/K$  is the equilibrium concentration gap.

As for the free growth problem, the planar stationary solution is easy to find. It is given in the liquid by

$$c(z > \zeta) = c_0 \left( 1 + \frac{1 - K}{K} e^{-2z/\ell} \right) = c_0 + \Delta c \, e^{-2z/\ell}$$

and in the solid

$$c(z<\zeta)=c_0.$$

The solidification gives rise to the build up of impurities in front of the interface. This layer of impurities is of thickness  $\ell$ .

#### 2: MODELS OF SOLIDIFICATION

As in section 2.1.2, a linear stability analysis of the planar stationary solution can be performed<sup>1</sup> to get:

$$\omega(k) = \frac{v}{\ell} \left[ \sqrt{1 + (k\ell)^2} (1 - \ell/\ell_T - \ell_c \ell k^2) - 1 \right] .$$

Here, the partition coefficient K is set to 1 as it is often done in the analytical studies of directional solidification<sup>2</sup>. The dispersion relation is shown in figure 2.6. At large  $k, \omega(k) \sim -2\ell_c Dk^3$ . Then the planar front is stabilized against short wavelength deformation by capillarity. On the other hand, the translation along the z axis is stable since  $\omega(k = 0) = -v/\ell_T < 0$ . This is due to the presence of the external thermal gradient. If the front moves ahead, the temperature becomes too high and it melts.



Figure 2.6: Growth rate spectrum for directional solidification.

The directional solidification has two controlling parameters, v and G. Let us assume that G is fixed and v varies. As the velocity is increased, the interface remains flat until a critical velocity  $v_c$  where a wavy pattern appears. This is the well known *cellular structure*. Such a morphological transition is called a *bifurcation*. Near this instability threshold, the interface can be described by simple models known as amplitude equations<sup>3</sup>. These models are used to characterize the bifurcation (supercritical

<sup>&</sup>lt;sup>1</sup>See appendix A.1 for the derivation.

<sup>&</sup>lt;sup>2</sup>In the experiments discussed in Flesselles, Simon and Libchaber [91],  $K \simeq 0.9$ .

<sup>&</sup>lt;sup>3</sup>For the amplitude equations as well as a discussion of the Eckhaus instability, see e.g. Caroli, Caroli and Roulet [92] and Cross and Hohenberg [93].

or subcritical), and to obtain the boundary of phase instability (Eckhaus instability).

For the symmetric model, the bifurcation is said to be *supercritical* or normal. The amplitude of the pattern close to the onset of the instability can be calculated by a linear analysis. Oswald, Bechhoefer and Libchaber [87] showed that the bifurcation is supercritical for the case of the nematic/isotropic transition. Just above the onset, they observed a sinusoidal interface deformation of arbitrarily small amplitude. In the one-sided model, the bifurcation is found experimentally<sup>1</sup> to be *subcritical* or inverted. Right above the onset of instability, the interface develop a highly non-linear state characterized by grooved cellular pattern. In this case, even the weakly non-linear theory is not appropriate. Subcritical bifurcation has been observed in organic materials as succinonitrile. This is another advantage of working with liquid crystals.

The instability of the structureless state is named as the *primary instability* while an instability of the cellular structure is known as a *secondary instability*. A well known secondary instability is the *solitary mode* discovered by Simon, Bechhoefer and Libchaber [88] in the context of the growth of a nematic. This mode is characterized by the inclusion of a few asymmetric cells connecting regions of "normal"-sized background cells which propagate along the interface at a constant velocity. Other secondary instabilities include tip splitting and optical modes. At higher speed, the interface motion enters a chaotic regime. We will focus later in this thesis on the optical modes where the cell width oscillates in phase opposition with its neighbors. These modes are also called *vacillating-breathing modes*.

## 2.3 Local Models of Solidification

Because of their spatial and temporal nonlocality, realistic models of solidification are difficult to solve, except for the geometrically most trivial situations. The local models of solidification were invented in the early eighties in order to simplify the mathematical problems.

The solidification front is modeled by a string moving in the two-dimensional space but having dynamical degrees of freedom associated only with the one-dimensional <sup>1</sup>See Caroli, Caroli and Roulet [92] and references therein.



Figure 2.7: Coordinate system for local models of solidification.

variable s. The local curvature  $\kappa(s, t)$  is defined by

$$\kappa(s,t) = \frac{\partial\theta}{\partial s} , \qquad (2.13)$$

where  $\theta$  is the angle between the normal to front and a fixed direction as shown in figure 2.7. If we have a form for  $\kappa(s,t)$ , then we can obtain  $\theta(s,t)$  from equation (2.13).

The equation of motion for  $\kappa$  is

$$\left(\frac{d\kappa}{dt}\right)_n = -\left(\frac{\partial^2}{\partial s^2} + \kappa^2\right) v_n , \qquad (2.14)$$

which must be supplemented by the metric condition

$$\left(\frac{ds}{dt}\right)_n = \int_0^s \kappa \, v_n \, ds' \,. \tag{2.15}$$

The subscript n indicates a differentiation along the outward normal to the front. Equations (2.14) and (2.15) are purely geometrical statements. A clear derivation of these equations can be found in Langer [87].

The oversimplification of these models comes from the assumption of *locality*. The motion of any piece of the string is determined only by its immediate neighborhood, e.g., its curvature and the derivatives of the latter.

### 2.3.1 The Geometrical Model

In the geometrical model<sup>1</sup>, one assumes that  $v_n = v_n(\kappa, \nabla \kappa, \cdots)$ . An attractive choice is

$$v_n = \kappa + \gamma \frac{\partial^2 \kappa}{\partial s^2} , \qquad (2.16)$$

<sup>&</sup>lt;sup>1</sup>Brower et al. [83]; Brower et al. [84].

#### 2: MODELS OF SOLIDIFICATION

where the second term of the right hand side stabilizes the system at short wavelengths for  $\gamma > 0$ . This is equivalent to the role played by the capillarity. However equation (2.16) lacks control parameters for the undercooling and the minimum nucleation size. Therefore, the most studied form is the following:

$$v_n = \kappa + \alpha \kappa^2 - \beta \kappa^3 + \gamma \frac{\partial^2 \kappa}{\partial s^2} \,. \tag{2.17}$$

As one can deduce from equation (2.17), a flat interface ( $\kappa = 0$ ) can never move. In fact, this is wrong since, as we saw in section 2.1, the velocity of such an interface follows  $v \sim 1/t^{1/2}$ . However, the geometrical model exhibits interesting pattern forming properties<sup>1</sup>, even though they are not quite dendrites. Despite these problems, the geometrical model has been extensively studied for its mathematical simplicity.

## 2.3.2 The Boundary-Layer Model

In the boundary-layer model<sup>2</sup>, some non-locality is introduced.

We want to solve the diffusion equation for u everywhere in the liquid subject to the usual boundary conditions at the solidification front. We suppose that the thermal field u (shown in figure 2.8) in front of the interface is<sup>3</sup>

$$u(z)\simeq u_i e^{-z/\ell}$$

where  $u_i = \Delta - d_0 \kappa$  as in (2.4).

If the range of the diffusion field  $\ell$  is much smaller than the radius of curvature, *i.e.*,  $\kappa \ell \ll 1$ , then the diffusion is confined to a small region, known as the *boundarylayer*. Now, instead of solving for the exact diffusion field u, we consider the dynamics of the heat content per unit length of this boundary layer. The heat content per unit length of this boundary layer is

$$\mathcal{H} = \int_0^\infty u \, dz \simeq \alpha u_i \ell \,\,, \tag{2.18}$$

where  $\alpha$  is an adjustable parameter of the order unity. The heat balance then becomes

$$v_n = \frac{Du_i}{\ell} = \frac{D\alpha u_i^2}{\mathcal{H}} . \tag{2.19}$$

<sup>&</sup>lt;sup>1</sup>Brower et al. [83]; Langer [87].

<sup>&</sup>lt;sup>2</sup>Ben-Jacob et al. [83]; Ben-Jacob et al. [84].

<sup>&</sup>lt;sup>3</sup>For simplicity, we omit the conventional factor 2 for  $\ell$ .



Figure 2.8: Thermal field u in front of the interface.

In this model,  $v_n$  is determined by the thickness of the interface. Consider the heat content  $\mathcal{H}\delta s$  in a length  $\delta s$  of the boundary layer. It obeys the following dynamical equation

$$\left(\frac{d}{dt}(\mathcal{H}\delta s)\right)_n \simeq \delta s \, v_n \left(1-u_i\right) + \alpha \, \delta s \, D \, \nabla_s \cdot \ell \, \nabla_s u_i$$

The first term of the right-hand side of this equation is the total rate of heat generation. The total rate of heat generation is  $v_n$ . An amount  $v_n u_i$  is used to heat the solidified liquid from u = 0 to  $u = u_i$  and  $v_n(1 - u_i)$  enters the boundary layer. The second term describes lateral heat diffusion. The geometrical formula<sup>1</sup>

$$\left(\frac{d}{dt}(\delta s)\right)_n = (\delta s)v_n\,\kappa$$

yields

$$\left(\frac{d\mathcal{H}}{dt}\right)_{n} \simeq v_{n}(1 - u_{i} - \mathcal{H}\kappa) + D\nabla_{s} \cdot \mathcal{H}\nabla_{s}(\ln u_{i}) .$$
(2.20)

The lateral diffusion term mimics the retarded non-local interaction between different points on the solidification front.

The basic model of solidification (section 2.1) and the boundary-layer model are in good agreement when  $\kappa \ell \ll 1$ . The flat interface can be shown to move with <sup>1</sup>Using equation (2.15). the appropriate law of  $t^{1/2}$ . The needle crystals in the Ivantsov limit  $d_0 = 0$  are parabolas (section 3.1). Furthermore the stability spectra of the two problems are similar for long wavelengths. However, discrepancies at small wavelengths  $(k\ell \gg 1)$  are important.

## 2.4 Phase-Field Models

The term *phase-field model* has been introduced by Fix<sup>1</sup>. His idea was to replace the dynamics of the boundary by an equation of motion of a phase-field which applies in the whole domain. In this sense, phase-field models are similar to the enthalpy or weak-formulation methods<sup>2</sup>. The phase-field (or the order parameter)  $\phi$  labels the liquid and solid phases. It takes a constant value in each bulk phase, *e.g.*  $\phi = 0$  in the liquid and  $\phi = 1$  in the solid. At the interface,  $\phi$  varies quickly but smoothly.

The equation of motion for  $\phi$  can be written as

$$\tau \frac{\partial \phi}{\partial t} = -\frac{\delta \mathcal{F}}{\delta \phi} , \qquad (2.21)$$

where  $\tau$  is a time scale for the kinetics of  $\phi$  and  $\mathcal{F}$ , a Landau-Ginzburg free energy functional

$$\mathcal{F} = \int d\mathbf{r} \left[ f(\phi, u) + \frac{\epsilon^2}{2} |\nabla \phi|^2 \right] \,. \tag{2.22}$$

The free energy density  $f(\phi, u)$  is a double well function with respect to  $\phi$  and  $u = (T - T_M)/(L/c)$  is the dimensionless diffusion field. The term  $|\nabla \phi|^2$  is the contribution of the interface. The surface tension is defined as the additional free energy per unit area introduced by requiring the presence of a planar phase boundary between two phases in equilibrium. For a one-dimensional system with  $\phi = \phi(x)$  and f(1,0) = f(0,0) = 0, the surface tension per unit area is given by<sup>3</sup>

$$\gamma = \int_{-\infty}^{+\infty} dx \left[ f(\phi, 0) + \frac{\epsilon^2}{2} \phi_x^2 \right] , \qquad (2.23)$$

At equilibrium and in one-dimension, the dynamical equation (2.21) reduces to

$$-\epsilon^2 \phi_{xx} + \frac{\partial f(\phi, 0)}{\partial \phi} = 0$$
 (2.24)

<sup>&</sup>lt;sup>1</sup>Fix [82]; Fix [83].

<sup>&</sup>lt;sup>2</sup>See for example Smith [81] and Fix [83].

<sup>&</sup>lt;sup>3</sup>Cahn and Hilliard [58]; Allen and Cahn [79].


Figure 2.9: Double well structure of the free energy density.

or

$$\frac{\epsilon^2}{2}\phi_x^2 = f(\phi, 0) \ . \tag{2.25}$$

The surface free energy  $\gamma$  is then

$$\gamma = \epsilon^2 \int_{-\infty}^{+\infty} \phi_x^2 \, dx \; . \tag{2.26}$$

Various precise forms of  $f(\phi, u)$  have been suggested. Let us consider the following<sup>1</sup>,

$$f(\phi, u) = \frac{\phi^2 (\phi - 1)^2}{4} + \alpha u \left(\phi - \frac{1}{2}\right) .$$
 (2.27)

The term  $\alpha u(\phi - 1/2)$  is a nonequilibrium driving force and the bulk free energy difference between the phases is  $\alpha u$ . From this consideration, one may determine  $\alpha = L^2/cT_M$ . When u is negative, the solid phase is favored and vice versa (figure 2.9). At equilibrium, the interfacial profile has the well-known hyperbolic tangent (figure 2.10). The parameter  $\epsilon$  introduced in (2.22) which measures the energy cost of the interface gives also the thickness of the interface.

The equation of heat diffusion is modified to take into account the latent heat released at the interface

$$\frac{\partial u}{\partial t} = D\nabla^2 u + \frac{1}{\Delta\phi} \frac{\partial\phi}{\partial t} , \qquad (2.28)$$

where  $\Delta \phi = \phi_+ - \phi_- = 1$  and the last term of (2.28) represents the interfacial source.

It can be worthwhile to keep  $\phi$  fixed in the bulk so that the latent heat is released at the interface only. We write the free energy density as

$$f(\phi, u) = \frac{1}{4}\phi^2(\phi - 1)^2 + \alpha g(\phi)u , \qquad (2.29)$$

<sup>&</sup>lt;sup>1</sup>See for instance Langer [86], Collins and Levine [85] and Collins, Chakrabarti and Gunton [89]



Figure 2.10: Equilibrium interfacial profile  $\phi(x)$ . The thickness of the interface is proportional to the parameter  $\epsilon$ .

where  $\delta g/\delta \phi|_{0,1} = 0$ . The obvious form of g would be a solution of  $\delta g/\delta \phi = [\phi(\phi-1)]^n$ where n is a positive integer. The simplest choice n = 1 leads to the model proposed by Kobayashi [93] with  $g(\phi) = \phi^3/3 - \phi^2/2$  (see section 3.3). Another solution, n = 2, gives the models proposed by Wang et al. [93] and Umantsev and Roitburd [88] (section 3.4).

### Effect of the noise

Up to now, we have not considered the influence of internal or external noise on the growth. Intrinsic thermal fluctuations are always present in the system but, as we will see below, the size of these fluctuations is small for the macroscopic phenomena we are dealing with in this thesis. The influence might become more important when the scale of the pattern decreases. The external noise that arises from defects in the apparatus, vibrations in a laboratory, or impurities in the sample, is not under the control or the observation of the experimentalist.

The effect of thermal noise is taken into care as in model A by adding to equation (2.21) a stochastic term  $\zeta(\mathbf{r}, t)$  such that

$$\frac{\partial \phi}{\partial t} = -\Gamma \frac{\delta \mathcal{F}}{\delta \phi} + \zeta ,$$

where  $\zeta$  is a Gaussian white noise with zero mean  $\langle \zeta(\boldsymbol{r},t) \rangle = 0$  and correlation

$$\langle \zeta(\mathbf{r},t)\zeta(\mathbf{r}',t')\rangle = 2\Gamma k_B T \delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$$
,

with T the temperature and  $k_B$  is the Boltzmann's constant. Thermal noise is important when  $k_BT \sim f_0\xi^d$  where  $f_0$  and  $\xi$  are respectively a typical energy density and a typical length scale in the system. For the succinonitrile system<sup>1</sup>, the bulk melting temperature is  $T_M = 58.2^{\circ}$ C, and the typical undercooling is  $T - T_M \sim 0.1 - 1.0^{\circ}$ C. The latent heat  $L = 4.5 \times 10^8 \text{ erg/cm}^3$  and  $L/C = 23.1^{\circ}$ C. The diffusion length  $\ell \sim 0.01 - 1.0 \text{ cm}$  and the capillary length  $d_0 = 192$  Å. The dendrites studied have tip radii  $\rho \sim 1 - 100 \,\mu\text{m}$ . The heat contained in a small volume  $\rho^3$  in front of the interface is  $C(T - T_M)\rho^3 \sim 10^{-2}$  erg which is much higher than  $k_BT \sim 10^{-13}$  erg.

There is no general way to introduce the effect of external noise. Usually, one makes the sensible hypothesis that the external noise is also uncorrelated and additive. The noise obeys the same relations as above. Its mean value is zero and the correlation is now

$$\langle \zeta(\mathbf{r},t)\zeta(\mathbf{r},t)\rangle = \Gamma F_A \delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$$
,

where  $F_A$  is a phenomenological parameter.

A discussion of the influence of noise in the Swift-Hohenberg equation (modeling the onset of the Rayleigh-Bénard convection) can be found in Cross and Hohenberg [93].

### Sharp-interface limit

The equations for the phase field and the temperature reduce to the basic equations of solidification in the so-called *sharp-interface limit*. The formal procedure is similar to the one employed by Caginalp [89] and is described at length in appendix A.2. It allows one to relate the coefficients  $\alpha$  and  $\tau$  to the capillary length and the kinetic coefficient. Following the usual method, one can write  $\tau \sim b\epsilon^2$  and  $\alpha \sim \epsilon\gamma$  where  $\epsilon$ , the interface thickness, is a small parameter. With the matched asymptotic expansion, we obtain  $d_0 \sim \epsilon/\alpha$  and  $\beta \sim \tau/\epsilon\alpha$ . Hence, this method introduces a kinetic term in the Gibbs-Thomson condition. This is not very appropriate if one wants to get quantitative results for the usual experiments where the kinetic correction  $\beta v$  is negligible. Also, with this method, the temperature u does not vary across the interface. This implies that the variation of the temperature across  $\epsilon$ ,  $|\delta u| \sim \epsilon v_n/D$  must

<sup>&</sup>lt;sup>1</sup>These are the values given in the review of Kessler, Koplik and Levine [88].

### 2: MODELS OF SOLIDIFICATION

be much smaller than  $\beta v_n$ . This leads to the constraint  $d_0 \gg \epsilon^3/D\tau$ . Hence, we have to deal with large lattices to get computational results that are independent of the computational parameters, as argued by Wang and Sekerka [96a].

Karma and Rappel [96b] have performed a sharp-interface limit calculation on the phase-field which includes a variation of u in the interface region. This is formally equivalent to choosing  $\tau \sim b\epsilon^2$  and  $\alpha \sim \gamma$ . They obtained  $d_0 \sim \epsilon/\alpha$  and  $\beta \sim (1 - \alpha \epsilon^2 A/D\tau)\tau/\alpha\epsilon$  where A is a numerical factor depending on the choice of the function  $g(\phi)$ . The form for the capillary length is similar to the previous one, but it is now possible to tune the parameters such as  $\beta = 0$ . The constraint  $d_0 \gg \epsilon^3/D\tau$ does not exist anymore and a small  $d_0$  is possible. It greatly enhances computational efficiency and makes 3-D simulations possible<sup>1</sup>. A similar calculation was performed earlier by Caginalp and Fife [88] where they obtained basically the same expressions for  $\beta$  and  $d_0$ .

<sup>&</sup>lt;sup>1</sup>Karma and Rappel [96a].

# 3

## DENDRITIC GROWTH

## 3.1 Introduction

In section 2.1, it has been mentioned that a steady-state planar solution is impossible for an undercooling  $\Delta$  different from one. Ivantsov [47] found that in the absence of surface tension ( $d_0 = 0$ ), a whole family of steady-state *needle crystal* (branchless dendrites) solutions exists for any  $\Delta < 1$ . A constant velocity is allowed by the needle shape because the heat produced at the interface can diffuse to the sides and therefore, there is no slowing down of the solid due to a build up of heat at the interface. The corresponding needle crystals are paraboloids in three-dimensions and parabolas in two-dimensions with tip radius  $\rho$ , moving with the constant velocity vin the direction Oz, the axis of revolution or symmetry, as seen in figure 3.1. Going to parabolic coordinates, one obtains in three-dimensions

$$\Delta = P e^P \int_P^\infty \frac{e^{-y}}{y} dy , \qquad (3.1)$$

where P is the thermal Péclet number defined as the ratio of the tip radius to the thermal diffusion length  $P = \rho/\ell = \rho v/2D$ . The velocity is not determined. For a given  $\Delta$ , only the product  $\rho v$  is determined.

The paraboloid shape of the needle crystal can be understood qualitatively by the following argument. The heat released at the interface is advected along Oz according to the law z = vt and it diffuses along a transverse direction as  $y = (Dt)^{1/2}$ . An equation of an isotherm is then  $z = y^2 v/D$  which describes the paraboloid.

The relation  $\Delta = \Delta(P)$  can be anticipated by a dimensionless analysis<sup>1</sup>. From the

<sup>&</sup>lt;sup>1</sup>See for instance Pelcé [88] and also Pomeau and Ben Amar [92]. The latter derived proper scaling laws from boundary layers estimates when only latent heat (or solute) diffusion limits the growth but also in the presence of an axial flow.



Figure 3.1: The needle crystal

parameters involved in the problem of the growth of needle crystal without surface tension, one can build only the following two dimensionless expressions:  $\Delta = C(T_M - T_\infty)/L$  and  $CT_M/L$ . The velocity of the crystal v cannot be related to  $\Delta$ . However, by adding a length  $\rho$ , another dimensionless expression involving the velocity is possible, the Péclet number  $P = \rho v/2D$ . Hence, one must have  $\Delta = \Delta(P)$ . The surface tension  $\gamma$  introduces a new length into the problem,  $\gamma/L$ . Thus, it is not necessary anymore to introduce  $\rho$  and the new dimensionless expression can be written as  $DL/v\gamma$ . The velocity must be related to the other dimensionless quantities as  $v = DL/\gamma f(\Delta)$ .

The Ivantsov solution has been verified quantitatively by many precise experiments on the growth of dendrites, such as the one of Huang and Glicksman [81] using succinonitrile. But these experiments also tell us that for a given  $\Delta$ , only dendrites of a given  $\rho$  and v can grow. Hence, the existence of a family of Ivantsov's solution was a puzzle and the object of research for forty years. Langer and Müller-Krumbhaar [78] put forward a theory of marginal stability to explain this selection mechanism. They conjectured that the naturally selected states are those which sit just at the margin of stability. The same idea was applied to front propagation by Dee and Langer [83] who suggested than the natural velocity  $v^*$  of fronts propagating into an unstable state is related to the stability of these fronts through the marginal stability. The fronts that move slower that  $v^*$  are unstable to perturbations, while those that move faster are stable. This is indeed the case in some situations as show by van Saarloos [87].

Coming back to the dendrite problem, we saw in section 2.1.2 that a planar solidification front moving at a speed v is linearly unstable against sinusoidal perturbation of wavelength greater than  $\lambda_s = 2\pi\sqrt{\ell d_0}$ . Essentially, Langer and Müller-Krumbhaar [78] conjectured that a dendrite with a tip radius  $\rho$  greater than  $\lambda_s$  will be unstable against splitting. In addition, they argued that a dendrite with a tip radius too small would thicken due a piling up of side branches in the tail of the dendrite. The operating point is at a state of marginal stability characterized by the dimensionless number

$$\sigma = \frac{2Dd_0}{v\rho^2} = \left(\frac{\lambda_s}{2\pi\rho}\right)^2 \tag{3.2}$$

which is independent of the dimensionless undercooling  $\Delta$ . If we set  $\rho = \lambda_s$  then  $\sigma^* \simeq (1/2\pi)^2 \simeq 0.025$  which is consistent with experiments<sup>1</sup> giving  $\sigma^* \simeq 0.0195$ . Equations (3.1) and (3.2) would determine the unique dynamical operating state.

However, intensive studies of the simplified models of solidification introduced in section 2.3, the geometrical and the boundary-layer models, as well as later calculations on the full model of solidification led to a major breakthrough in the mid 1980's. It was argued that a subtle mathematical mechanism called *microscopic solvability* was responsible for determining the operating conditions, that is the radius and velocity, of the tip of a dendrite. The main insight of the solvability mechanism was that the tip's operating conditions were determined by the smallest — the microscopic — length scale in the description. Unlike the marginal stability mechanism, which was dynamic, the microscopic solvability mechanism was based on the existence of steady-state solutions.

The problem can be divided into two regions. Far from the tip (the outer region), the effect of surface tension is negligible and the shape of the interface obeys the Ivantsov solution (3.1) which for small undercooling becomes

$$\frac{\rho v}{D} \simeq -\frac{\Delta}{\ln(\Delta)}$$
 (3.3)

<sup>&</sup>lt;sup>1</sup>For example, refer to Huang and Glicksman [81].

Close to the tip (the inner region), the integral equation reduces to a non-linear eigenvalue problem and the velocity of the dendrite is

$$v \simeq \frac{4}{C} \frac{D}{d_0} \left( \frac{\Delta}{\ln(\Delta)} \right)^2 ,$$
 (3.4)

where C is the eigenvalue of a non-linear integral equation. C is equal to  $8/\sigma$  where  $\sigma$  is given by (3.2). However,  $\rho$  is not the tip radius of the needle crystal but the tip radius of the Ivantsov paraboloid that describes the needle crystal at large distances from the tip. Numerical calculation of C has shown that there is no stationary solution of the needle crystal problem in the presence of isotropic surface tension. Thus, Langer and Müller-Krumbhaar [78] studied the dynamical stability of a solution that did not exist.

However, the introduction of anisotropy in the surface tension leads to a discrete set of steady-state solutions. Among those solutions, only one is stable with respect to small perturbation of the tip. The hypothesis that it is the unique solution and that it describes the tip of the dynamically selected dendrite is known as the *solvability theory*. A stationary solution of needle crystal exists *only if anisotropy in the surface tension is introduced*. Some reviews of the solvability theory can be found in Langer [89], Pelcé [88] and Ben Amar [88].

The work led to a clear new understanding of crystal growth but was very technical. Directly or indirectly, work began on microscopic models of crystal growth, wherein all length scales are well described. The most successful such approach is called the phase-field model.

## 3.2 Phase-Field Models of Dendritic Growth

Following is the free energy functional

$$\mathcal{F} = \int d\boldsymbol{r} \left[ f(\phi, u) + \frac{\epsilon(\theta)^2}{2} |\boldsymbol{\nabla}\phi|^2 \right] , \qquad (3.5)$$

where

$$f(\phi, u) = \frac{1}{4}\phi^2 (1 - \phi)^2 - \lambda u \phi^2 (1 - \phi)^2$$
(3.6)

with minima at  $\phi = 0$  and  $\phi = 1$  corresponding to the liquid and solid phases, respectively. The angle  $\theta$  is the angle between the normal to the interface and the x axis which we can assume has a crystallographic signification. It is more convenient to use dimensionless units. We rescale the space coordinates using a typical length scale w that could be the radius of the curvature of the interface. Thus, the diffusive time scale is  $w^2/D$ . In these units, the dynamics of the order parameter is described by

$$\tau \frac{\partial \phi}{\partial t} = -\frac{\delta \mathcal{F}}{\delta \phi} \tag{3.7}$$

and it is coupled to the equation of the diffusion field

$$\frac{\partial u}{\partial t} = \nabla^2 u + \frac{\partial \phi}{\partial t} . \tag{3.8}$$

In the sharp-interface limit<sup>1</sup> where  $\epsilon \kappa \ll 1$ , one can get the anisotropic form of the Gibbs-Thomson condition<sup>2</sup>,

$$u_i = -\left(d_0 + \frac{\partial^2 d_0}{\partial \theta^2}\right)\kappa - \beta(\theta)v_n .$$
(3.9)

### Numerical Implementation

For two dimensional calculations, equation (3.7) becomes

$$\tau \frac{\partial \phi}{\partial t} = -\frac{\delta f}{\delta \phi} - \bar{\epsilon}^2 \frac{\partial}{\partial x} \left( \eta(\theta) \eta'(\theta) \frac{\partial \phi}{\partial y} \right) + \bar{\epsilon}^2 \frac{\partial}{\partial y} \left( \eta(\theta) \eta'(\theta) \frac{\partial \phi}{\partial x} \right) + \bar{\epsilon}^2 \nabla \cdot \left( \eta^2(\theta) \nabla \phi \right) , \quad (3.10)$$

where we used  $\epsilon = \bar{\epsilon}\eta(\theta)$ . The prime denotes a derivative with respect to  $\theta$ . The normal to the interface is

$$\hat{n} = \frac{\nabla \phi}{|\nabla \phi|} = \cos \theta \ \hat{x} + \sin \theta \ \hat{y}$$

and

$$\tan\theta = \frac{\phi_y}{\phi_x}$$

Neumann boundary conditions are used for both fields:  $\nabla \phi \cdot \hat{n} = 0$  and  $\nabla u \cdot \hat{n} = 0$ where n is the normal to the boundary. In other terms, the change of phase is forbidden along n and the heat cannot leak outside the system.

We solve the equations (3.8) and (3.10) by discretization in a way that will be simple to implement. More elaborate computational techniques are described in Wang

<sup>&</sup>lt;sup>1</sup>McFadden et al. [93]; Karma and Rappel [96b].

<sup>&</sup>lt;sup>2</sup>Herring [53].

#### 3: Dendritic Growth

and Sekerka [96a]. The grid spacings in the x and y directions are identical and equal to  $\Delta x$ . The time step is denoted by  $\Delta t$ . Hence,  $x_i = i\Delta x$ ,  $y_j = j\Delta x$  and  $t = n\Delta t$ . For the space derivatives, we use the usual central difference scheme

$$\begin{split} \frac{\partial \phi^n}{\partial x} \bigg|_{i,j} &= \frac{\phi^n_{i+1,j} - \phi^n_{i-1,j}}{2\Delta x} + \mathcal{O}(\Delta x^2) ,\\ \frac{\partial \phi^n}{\partial y} \bigg|_{i,j} &= \frac{\phi^n_{i,j+1} - \phi^n_{i,j-1}}{2\Delta x} + \mathcal{O}(\Delta x^2) ,\\ \frac{\partial^2 \phi^n}{\partial^2 x} \bigg|_{i,j} &= \frac{\phi^n_{i+1,j} - 2\phi^n_{i,j} + \phi^n_{i-1,j}}{\Delta x^2} + \mathcal{O}(\Delta x^2) ,\\ \frac{\partial^2 \phi^n}{\partial^2 y} \bigg|_{i,j} &= \frac{\phi^n_{i,j+1} - 2\phi^n_{i,j} + \phi^n_{i,j-1}}{\Delta x^2} + \mathcal{O}(\Delta x^2) . \end{split}$$

We have several choices for representing the time derivative term. If an explicit scheme is employed for both dynamical equations, then a von Neumann stability analysis leads to two stability conditions,  $\Delta t \leq \Delta x^2/(4\bar{\epsilon}^2/\tau)$  for (3.10) and  $\Delta t \leq \Delta x^2/4$  for (3.8). For the values that we will use, the condition on the dynamical equation for  $\phi$  is more restrictive. Hence to maximize computational efficiency, we use a forward time centered space scheme for (3.10) and an alternating direction implicit (ADI) scheme<sup>1</sup> for (3.8).

The discretized version of (3.10) is then

$$\phi_{i,j}^{n+1} = \phi_{i,j}^{n} + \frac{\Delta t}{\tau} \left[ -\frac{\delta f}{\delta \phi} - \bar{\epsilon}^{2} (\eta_{y} \eta' + \eta \eta'_{y} + 2\eta \eta_{x}) \phi_{x} + \bar{\epsilon}^{2} (-\eta_{x} \eta' - \eta \eta'_{x} + 2\eta \eta_{y}) \phi_{y} + \bar{\epsilon}^{2} \eta^{2} \nabla^{2} \phi \right] . \quad (3.11)$$

Equation (3.8) is discretized by the ADI method. We difference this equation in two half-steps

$$u_{i,j}^{n+1/2} = u_{i,j}^{n} + \frac{\Delta t/2}{\Delta x^2} (\mathcal{L}_x u_{i,j}^{n+1/2} + \mathcal{L}_y u_{i,j}^{n}) + N_{i,j}^{n+1} ,$$
  
$$u_{i,j}^{n+1} = u_{i,j}^{n+1/2} + \frac{\Delta t/2}{\Delta x^2} (\mathcal{L}_x u_{i,j}^{n+1/2} + \mathcal{L}_y u_{i,j}^{n+1}) + N_{i,j}^{n+1} ,$$

where we have used

$$N_{i,j}^{n+1} = \frac{\phi_{i,j}^{n+1} - \phi_{i,j}^{n}}{2}$$
(3.12)

<sup>1</sup>Press et al. [92].

and

$$\mathcal{L}_x u_{i,j} = u_{i+1,j} - 2 u_{i,j} + u_{i-1,j} ,$$
  
$$\mathcal{L}_y u_{i,j} = u_{i,j+1} - 2 u_{i,j} + u_{i,j-1} .$$

Putting the unknowns on one side in the matrix notation, we finally get

$$(1 - \alpha L_x) \cdot u^{n+1/2} = (1 + \alpha L_y) \cdot u^n + N^{n+1},$$
  
 $(1 - \alpha L_y) \cdot u^{n+1} = (1 + \alpha L_x) \cdot u^{n+1/2} + N^{n+1},$ 

where  $\alpha = \Delta t/2\Delta x^2$ . The matrices  $1 - \alpha L_x$  and  $1 - \alpha L_y$  are tridiagonal so the equations can be solved using a standard tridiagonal algorithm. Given  $u^n$ , we get first  $u^{n+1/2}$  and by substitution,  $u^{n+1}$ .

### Anisotropy

In the isothermal case with u = 0 and without anisotropy, using (3.6), equation (2.26) reduces to

$$\gamma = \epsilon^2 \int_{-\infty}^{+\infty} \phi_x^2 \, dx = \epsilon^2 \int_0^1 \phi_x \, d\phi = \frac{\epsilon}{6\sqrt{2}} \,, \tag{3.13}$$

where we have used in the last step that  $\phi_x = \sqrt{2f(\phi, 0)/\epsilon^2}$  (equation (2.25)).

Now, when anisotropy is introduced, a planar interface for the isothermal case will have the solution  $\phi = \phi(\mathbf{r} \cdot \hat{\mathbf{n}})$  where  $\hat{\mathbf{n}}$  is the normal to the interface. Then the phase-field obeys the equation

$$\phi = \frac{1}{2} \left[ 1 - \tanh\left(\frac{\boldsymbol{x} \cdot \hat{\boldsymbol{n}}}{2\sqrt{2}\epsilon(\theta)}\right) \right]$$
(3.14)

and the surface free energy then becomes

$$\gamma = \frac{\epsilon(\theta)}{6\sqrt{2}} \,. \tag{3.15}$$

Here, the interface width, defined as being the distance for  $\phi$  ranging from 0.05 to 0.95 is deduced from (3.14) to be

$$w \simeq 6\sqrt{2}\epsilon(\theta)$$
 . (3.16)

Hence, both  $\gamma$  and w are proportional to  $\epsilon(\theta)$ , *i.e.* they have the same anisotropy.

## 3.3 The Model of Kobayashi

Kobayashi [93] performed numerous simulations of a solid dendrite growing into an undercooled melt. He observed various dendritic patterns and realistic features such as tertiary side arms and the coarsening of side arms away from the tip. It was the first time that computation of a model of solidification had shown these features. His work was however purely qualitative.

As a free energy density, he chose

$$f(\phi, u) = \frac{1}{4}\phi^4 + \frac{m(u) - 3/2}{3}\phi^3 - \frac{m(u) - 1/2}{2}\phi^2 , \qquad (3.17)$$

where  $u = (T - T_M)/(T_M - T_\infty)$  and |m(u)| < 1/2 so that the minima of the free energy stay at  $\phi = 0$  and  $\phi = 1$ . A possible choice is  $m(u) = \alpha/\pi \arctan(-\gamma u)$  with  $\alpha < 1$ . The anisotropy is introduced via the parameter  $\epsilon(\theta) = \bar{\epsilon}\eta(\theta)$ . The dynamics of the order parameter is given by

$$\tau \frac{\partial \phi}{\partial t} = -\bar{\epsilon}^2 \frac{\partial}{\partial x} \left( \eta(\theta) \eta'(\theta) \frac{\partial \phi}{\partial y} \right) + \bar{\epsilon}^2 \frac{\partial}{\partial y} \left( \eta(\theta) \eta'(\theta) \frac{\partial \phi}{\partial x} \right) + \bar{\epsilon}^2 \nabla \cdot (\eta^2(\theta) \nabla \phi) + \phi (1 - \phi) \left( \phi - \frac{1}{2} + m(u) \right)$$
(3.18)

and the equation of diffusion of heat is

$$\frac{\partial u}{\partial t} = \nabla^2 u + \frac{1}{\Delta} \frac{\partial \phi}{\partial t} , \qquad (3.19)$$

where  $\Delta = (T_M - T_\infty)/(L/c)$  denotes the dimensionless undercooling.  $\Delta$  is an important tuning parameter in these simulations.

Following what has been done before, we will not include the external noise as in equation (1.1) but rather add a term  $a\phi(1-\phi)\chi$  to the dynamical equation (3.10), where  $\chi$  is a random number uniformly distributed in the interval  $\left[-\frac{1}{2},\frac{1}{2}\right]$  and a is the strength of the noise. In fact, this term adds noise only at the interface to stimulate side branching. This way of introducing noise is acceptable since we are not interested in, for example, nucleation process.

An example of a dendritic growth simulation is shown in figure 3.2. The parameters are the following:  $\eta = 1 + \delta \cos(6\theta)$  where  $\delta = 0.04$ ,  $\bar{\epsilon} = 0.01$ ,  $\tau = 0.0003$ ,  $\alpha = 0.9$ ,  $\gamma = 10$ , a = 0.01,  $\Delta = 0.6$  and the mesh size is taken to be 0.03. We start with a 3: Dendritic Growth



Figure 3.2: Growth of a dendrite in an undercooled melt for a 6-fold (left) and a 4-fold (right) anisotropy. The large dots show the phase field contour ( $\phi = 0.5$ ) while the small dots represent the isotherm (u = -0.5). From top to bottom, the times are: 0.06, 0.15 and 0.3.

small solid disk at the center of the system. At the beginning of the simulations, the system is at the undercooling temperature u = -1.

Because of the boundary conditions used, the whole liquid will change to crystal for  $\Delta$  greater than 1. If  $\Delta$  is less that 1, a fraction  $\Delta$  of the whole region will solidify and the system will lose all its supercooling.

# 3.4 Thermodynamically-Consistent Models

Arguing that the approach above is not appropriate for the non-isothermal case, Wang et al. [93] used an entropy functional for the system,

$$S = \int d\boldsymbol{r} \left[ s(\phi, u) - \frac{\tilde{\epsilon}^2}{2} |\boldsymbol{\nabla}\phi|^2 \right]$$
(3.20)

instead of the Helmholtz free energy.

The evolution equations for the temperature and the phase-field are derived by requiring that u and  $\phi$  evolve so as to ensure positive locally entropy production. This phase field model is discussed at length in Wang et al. [93]. It leads to a pair of coupled partial differential equations:

$$\frac{\tilde{\epsilon}^2}{m}\frac{\partial\phi}{\partial t} = \phi(1-\phi)\left[\phi - \frac{1}{2} + 30\tilde{\epsilon}\alpha\Delta u\phi(1-\phi) + \tilde{\epsilon}^2\nabla^2\phi\right]$$

 $\operatorname{and}$ 

$$\frac{\partial u}{\partial t} = \nabla^2 u - \frac{1}{\Delta} p'(\phi) \frac{\partial \phi}{\partial t} ,$$

where  $p(\phi) = \phi^3(10 - 15\phi + 6\phi^2)$  and the prime denotes differentiation with respect to  $\phi$ . In this model, the order parameter  $\phi$  is 0 in the solid and 1 in the liquid. These equations result from the following choice of the entropy density functional:

$$s(\phi, u) = \int_0^{\phi} \left[ \zeta(1-\zeta) \left(\zeta - \frac{1}{2}\right) + \tilde{\epsilon} \alpha \Delta u p'(\zeta) \right] d\zeta$$

As in the Kobayashi model, the two states are given by *fixed* values of  $\phi$ . Using this model, Wheeler, Murray and Schaefer [93] have conducted a detailed study of dendritic growth. They compared the results of their computations of dendritic growth with the current theories of dendritic tip selection (see section 3.1). With the same model, Wang and Sekerka [96b] have also carried out simulations of dendrites grown from pure melts where they have carefully considered the diverse length scales: the

capillary length, the interface thickness, the tip radius and the computational domain size. They showed that results independent of computational parameters can only be obtained at very large supercoolings. In contrast to Kobayashi, these works are quantitative. The reader is referred to these articles for a detailed account of their results.

Umantsev and Roitburd [88] have developed a similar thermodynamically consistent approach. Their model is based on a Ginzburg-Landau functional which is an integral of the Gibbs free energy density of the homogeneous phase and a gradient energy contribution.

## 3.5 Dendritic Growth in a Polymorphous Material

In the last sections, the problem of the free growth of a dendrite into a melt was discussed. The technique used can be generalized to address two other problems: the growth of a dendrite in a polymorphous crystal and the growth of many dendrites of different orientations in a melt.

According to Johnson [86], the melting phenomenon is equivalent to solid state amorphization, because thermodynamically, the amorphous phase is the low temperature state of the undercooled liquid. Numerous investigations on amorphization have been carried out on Ti-Cr systems<sup>1</sup>. Analyses of the thermodynamics of the system and of the transformation behavior have shown that *inverse melting* of the b.c.c. solid in the concentration range between 40 and 65 at.% Cr is possible. Furthermore, complete amorphization is possible for alloys containing 55 at.% Cr. For this system, the free energies of the liquid and amorphous phases are shown with respect to the b.c.c. solid in figure 3.3. Below the inverse melting temperature  $T_{IM}$ , the crystalline phase is a metastable state of the solid.

Following the work of Morin et al. [95], we introduce a *d*-component non-conserved vector field,  $\phi$ . The direction of  $\phi$  mimics the local orientation of the crystal while its magnitude,  $|\phi|$ , indicates if we are in the solid or the amorphous phase. Grain boundaries exist between the crystallites composing the system. Hence, one has to add a term that will explicitly break the continuous symmetry of the free energy and <sup>1</sup>Bormann [94].



Figure 3.3: Free energy curve of the liquid and the amorphous phase with respect to b.c.c. solid solution for a concentration of Ti-55 at.%Cr. H.c.p. Ti and b.c.c. Cr are taken as energy reference states at each temperature.  $T_M$  and  $T_{IM}$  denote the melting and the inverse melting temperature respectively [from Bormann [94]].

the spin waves associated with it. Since there is no reason why the crystal orientation should depend on the temperature, the temperature u is coupled symmetrically to  $\phi$ .

The distortion free energy, which has to be invariant under a rigid rotation of the system, is built following the Frank free energy for the nematic phase<sup>1</sup>:

$$\mathcal{F}_n = \frac{1}{2} \int d\boldsymbol{r} \left[ K_1 (\boldsymbol{\nabla} \cdot \hat{\boldsymbol{n}})^2 + K_2 (\hat{\boldsymbol{n}} \cdot \boldsymbol{\nabla}_{\wedge} \hat{\boldsymbol{n}})^2 + K_3 (\hat{\boldsymbol{n}}_{\wedge} (\boldsymbol{\nabla}_{\wedge} \hat{\boldsymbol{n}}))^2 \right] ,$$

where  $\hat{n}(r)$  is the local director and  $K_1, K_2$  and  $K_3$  are respectively the elastic coefficients for the *splay*, *twist* and *bend* deformations. In two dimensions, there is obviously no twist. Also, the bend term reduces to  $(\nabla_{\wedge} \hat{n})^2$ . This free energy can be simplified more by assuming  $K_1 = K_3 = \epsilon^2$ .

Then, the free energy functional reads

$$\mathcal{F} = \int d\mathbf{r} \left[ \frac{\epsilon^2}{2} ((\nabla \cdot \phi)^2 + (\nabla_{\wedge} \phi)^2) + \frac{1 + b \cos(n\theta)}{1 + b} \frac{(|\phi|^2)^2}{4} + \frac{m(u) - \frac{3}{2}}{3} (|\phi|^2)^{3/2} - \frac{m(u) - \frac{1}{2}}{2} |\phi|^2 \right] . \quad (3.21)$$

The term  $cos(n\theta)$  is an important term of this model that breaks the rotational symmetry of the free energy by introducing *n* wells in  $\theta$  (figure 3.4). Here,  $cos(\theta) = \hat{x} \cdot \phi/|\phi|$ . Physically, a crystallite can take any orientation and we should have an <sup>1</sup>See for instance de Gennes and Prost [93].



Figure 3.4: Contour plot of the free energy (3.21) with u = 0 and b = -0.03

infinite number of wells. However, we choose n = 12 or n = 15 in the next simulations. If n is too large, the domain wall between neighboring orientations becomes very small and we have to reduce the mesh size  $\Delta x$ , and hence the time step, to avoid numerical instabilities. This would increase the simulation time.

The reduced temperature u is defined with respect to  $T_{IM}$  instead of  $T_M$ . At the temperature u = 0, it can be shown that in order to have saddle points at  $\theta = (2n+1) \cdot 15^{\circ}$  (in the case of n = 12), b has to obey the condition  $-1/16 \leq b < 0$ . The value of the free energy at a saddle point (see figure 3.5) is then

$$f(oldsymbol{\phi}_s, u=0)\simeq -b/2$$
 .

So, b dictates the type of domain walls which will form. For small values of |b|, it is energetically favorable for  $\phi$  to jump between neighboring orientations. It mimics a grain boundary. For large values of |b|, a zero  $|\phi|$  is favored and amorphous material is trapped at the grain boundary. When m(u) becomes negative, the saddle point can disappear. This introduces another constraint. Choosing  $m = \frac{\alpha}{\pi} \arctan(-\delta u)$ , we have to select  $\alpha$  depending on the value of b.



Figure 3.5: Free energy curve for different orientations of the phase-field.

The system evolves to its equilibrium state according to the following equations

$$\tau \frac{\partial \phi_x}{\partial t} = \left[ \epsilon^2 \nabla^2 - \frac{1 + b \cos(n\theta)}{1 + b} |\phi|^2 - \left(m - \frac{3}{2}\right) |\phi| + m - \frac{1}{2} \right] \phi_x$$
$$-\frac{nb}{4(1+b)} \sin(n\theta) |\phi|^2 \phi_y , \qquad (3.22)$$

$$\tau \frac{\partial \phi_y}{\partial t} = \left[ \epsilon^2 \nabla^2 - \frac{1 + b \cos(n\theta)}{1 + b} |\phi|^2 - \left(m - \frac{3}{2}\right) |\phi| + m - \frac{1}{2} \right] \phi_y + \frac{nb}{4(1 + b)} \sin(n\theta) |\phi|^2 \phi_x$$
(3.23)

 $\operatorname{and}$ 

$$\frac{\partial u}{\partial t} = \nabla^2 u + \frac{1}{\Delta} \frac{\partial |\phi|}{\partial t} . \qquad (3.24)$$

Noise is introduced in the same way as in the model of Kobayashi.

The growth on an amorphous seed was studied in diverse conditions. Figure 3.6 shows the dendritic amorphization of a bilayer of solid. It is observed experimentally that amorphization takes place at the grain boundaries as well as at other defects. Hence, the seed is placed originally at the grain boundary. The initial "undercooling" temperature of the system is u = -1. The parameters used for this simulation are the following:  $\bar{\epsilon} = 0.01$ ,  $\tau = 0.0003$ ,  $\alpha = 0.9$ ,  $\gamma = 10$ , a = 0.01,  $\Delta = 0.6$  and b = -0.001. The top layer is a crystal of orientation  $\theta = 30^{\circ}$  and at the bottom layer,  $\theta = 60^{\circ}$ .



Figure 3.6: Dendritic amorphization of a bilayer of crystal. From left to right, top to bottom the times are: 0.036, 0.12, 0.24 and 0.36.

It is important to stress that anisotropy is not introduced by hand through the parameter  $\epsilon$ . However, the branches growing along the grain boundary exhibit a dendritic behavior. In the other directions, the tips are subject to repeated splitting as expected for the case of a growth in absence of anisotropic surface tension. The existence of an interface between the two layers costs energy ( $\sim |\nabla \phi|^2$ ) but less than the cost of energy of an amorphous/crystal interface. The growth of a dendrite at the grain boundary is favored as it will remove an extra energy cost.

The same model can be used to model the free growth of many dendrites. Since each well in the free energy corresponds to a crystal of different orientation, it is now possible to grow dendrites of different orientations (different  $\theta$ ). We will now introduce an anisotropic surface tension by letting the parameter  $\epsilon$  depend on the surface orientation  $\vartheta$ . Then

$$\epsilon(\vartheta) = \overline{\epsilon}(1 + \eta \cos(\vartheta - \theta)),$$

where

$$\tan(\vartheta) = \frac{\partial |\phi| / \partial y}{\partial |\phi| / \partial x}.$$

The terms  $\epsilon^2 \nabla^2 \phi_{\alpha}$  with  $\alpha = x, y$  in equations (3.22) and (3.23) have to be replaced

by

$$\bar{\epsilon}^2 \frac{\partial}{\partial x} \left( \eta(\vartheta) \eta'(\vartheta) \frac{\partial \phi_{\alpha}}{\partial y} \right) + \bar{\epsilon}^2 \frac{\partial}{\partial y} \left( \eta(\vartheta) \eta'(\vartheta) \frac{\partial \phi_{\alpha}}{\partial x} \right) + \bar{\epsilon}^2 \nabla \cdot \left( \eta^2(\vartheta) \nabla \phi_{\alpha} \right) \,.$$

We simulate now the growth of three six-fold dendrites. We choose n = 15 so that the six-fold dendrites with orientation  $\theta = 0$ , 24° and 48° will all look differently oriented. We use boundary conditions with the system size 256 × 256. All the other parameters are the same as before. The results of the simulation are shown in figure 3.7. At the beginning, as long as the dendrites are far enough from each other, their growth does not differ from the case of the isolated dendrite. However, when they come close enough to each other, because of the latent heat released in front of the interface, they will melt each other and particularly the small structures as the secondary branches. At longer times, when the system has reached the melting temperature, the growth takes place only through the curvature. The system will reduce its energy by minimizing the interface. At this time, the secondary branches will completely disappear.



Figure 3.7: Many dendrites growing in an undercooled melt. From left to right, top to bottom, the times are: 0.1, 0.2, 0.3, 0.5, 1.0, and 2.0.

## DIRECTIONAL SOLIDIFICATION

Contrary to dendritic growth, the amplitude of the patterns developing at the solid/ liquid interface in directional solidification experiments can be made as small as we want by tuning the external imposed gradient. This problem then has a lot in common with other pattern forming systems such as Rayleigh-Bénard convection. In this chapter, we limit our discussion to the study of a particular secondary instability, the vacillating-breathing mode.

Cladis et al. [91] studied the directional growth from the isotropic phase of a cholesteric liquid crystal. They used a mixture of the nematic liquid crystal 8CB (cyano-octyl biphenyl) and the chiral impurity C15 (cyano (methyl) butoxybiphenyl) at a concentration 9% of weight. An important length scale in the cholesteric liquid crystals is the pitch defined as the distance for a  $2\pi$  rotation of the director n. In the experiments detailed in Cladis et al. [91], the temperature gradient is  $G = 7.5 \pm 0.01 K/cm$  and the critical velocity  $v_c = 19 \pm 0.5 \mu m/s$ . At a value of  $\epsilon \equiv (v - v_c)/v_c = 0.56$ , they found a bifurcation to an oscillatory or breathing mode as shown in figure 4.1.

Following the groove positions in time, Cladis et al. [91] obtained the dispersion relation shown in figure 4.2. These data show that  $\omega \sim q$ . Their best fit is  $\omega/\omega_{el} = -0.23 + 1.13q/2q_0$  where  $2\pi/q_0$  is the helical pitch and  $\omega_{el}$  is the characteristic frequency for the director diffusion.

In this experiment, the helical pitch plays an important rôle. However, the breathingmode is generic. It has also been observed in eutectic systems<sup>1</sup> and in addition, an optical mode has been reported by Flesselles, Simon and Libchaber [91] for the case of the nematic/isotropic transition.

<sup>&</sup>lt;sup>1</sup>Zimmermann, Karma and Carrard [90].



Figure 4.1: Breathing-mode pattern decorated behind the interface by disclination lines when  $\epsilon = 0.56$ . The black region at the extreme left is the isotropic phase. The bright band next to it is the cholesteric-isotropic meniscus [from Cladis et al. [91]].

## 4.1 Some Local Descriptions of Directional Solidification

The *Kuramoto-Sivashinsky* (K-S) equation models pattern formation in different systems. Kuramoto and Tsuzuki [76] derived it in the context of reaction-diffusion equations modeling the Belousov-Zhabotinsky reaction. Sivashinsky [77] derived it to model instability of the plane front of a laminar flame. Most of the studies focused on the chaotic behavior of the K-S equation,

$$h_t = -h_{xx} - h_{xxxx} + h_x^2 , (4.1)$$

where the function h(x,t) describes the position of the front at time t, at height h above the point x.

Misbah and Valance [94] have studied the instabilities displayed by a modified version of the K-S equation, which they named the *stabilized* Kuramoto-Sivashinsky equation

$$h_t = -\alpha h - h_{xx} - h_{xxxx} + h_x^2 , \qquad (4.2)$$

where  $\alpha$  is a parameter that mimics a stabilizing effect, as the imposed thermal gradient in directional solidification. The surprising feature is that despite the simplicity of



Figure 4.2: Dispersion relation for the breathing-mode. The frequency  $\omega$  is scaled with an elastic frequency  $\omega_{el}$  and q/2 by  $q_0$ . The sample thickness are  $41\mu$ m (•) and  $37\mu$ m (•). See Cladis et al. [91] for more details.

this equation, Misbah and Valance [94] found five secondary instabilities: (i) the Eckhaus instability, (ii) the Parity-Broken instability, (iii) the period-halving instability, (iv) the vacillating-breathing instability, and (v) an oscillatory instability which they named as the irrational vacillating-breathing. From equation (4.2), the dispersion relation for an infinitesimal perturbation around the solution h = 0 is given by

$$\omega = -\alpha + q^2 - q^4 . \tag{4.3}$$

Figure 4.3 shows the neutral curve ( $\omega = 0$ ) below which the solution h = 0 is unstable.

Close to the instability threshold, a weakly nonlinear analysis is possible and has been performed by Misbah and Valance [94]. We perform numerical simulations on (4.2) to recover the breathing-modes. Figure 4.4 displays the dynamics of a vacillating-breathing mode.

The numerical simulations are performed as follows. The spatial derivatives are calculated by Fourier transforming h(x, t) and multiplying by the power of the wavevector corresponding to the derivative and then, by transforming everything back in real space. For the time integration we use the semi-implicit extrapolation method due to Bader and Deuflhard<sup>1</sup>, an implicit scheme that is appropriate for stiff differential

<sup>&</sup>lt;sup>1</sup>Press et al. [92].



Figure 4.3: Neutral curve of the stabilized Kuramoto-Sivashinsky equation.

equations. However, when the system is large, the efficiency of this method may suffer as the matrix (the Jacobian) to be inverted is not sparse. Even then, for the system shown in figure 4.4, the method of Bader and Deuflhard is very competitive.

By realizing that in the directional solidification experiments most of the dynamical phenomena appear in a regime where the wavelength is much larger than the diffusion length (typically  $\lambda/\ell \simeq 10$ ), Kassner, Misbah and Müller-Krumbhaar [91] have derived an equation of motion for the interface in a quasilocal regime. They discovered that this equation supports a vacillating-breathing instability. More details on the calculations can be found in Ghazali and Misbah [92].

## 4.2 Phase-Field Model of Directional Solidification

Grossmann et al. [93] introduced a phase-field model to study directional solidification in two and three dimensions. Here, the free energy used is given by

$$\mathcal{F} = \int d\mathbf{r} \left[ \frac{1}{2} D_{\phi} |\nabla\phi|^2 + \frac{1}{4} \beta (\phi^2 - 1)^2 + \frac{1}{2} \gamma \,\Delta\phi \, U^2 + \Delta T \phi \right] , \qquad (4.4)$$

where  $\phi$  is the non-conserved field describing the liquid/solid transition,  $U \equiv c + \phi/\Delta \phi$ with c, the dimensionless concentration field of impurities and  $\Delta T \equiv T - T_M$  with T the temperature and  $T_M$ , the melting temperature. Furthermore,  $\Delta \phi$  is the miscibility gap and  $D_{\phi}$ ,  $\beta$  and  $\gamma$  are phenomenological constants. The dynamical equation for c



Figure 4.4: Interface dynamics exhibiting a vacillating-breathing mode ( $\alpha = 0.1$  and q = 0.64).

and  $\phi$  are

$$\frac{\partial \phi}{\partial t} = -\Gamma_{\phi} \frac{\delta \mathcal{F}}{\delta \phi}$$

and

$$\frac{\partial c}{\partial t} = \frac{\Gamma_c}{\gamma \Delta \phi} \nabla^2 \frac{\delta \mathcal{F}}{\delta c}$$

where  $\Gamma_{\phi}$  and  $\Gamma_{c}$  are the mobilities for  $\phi$  and c respectively. In the frame moving in the  $\hat{z}$  direction at speed v, the dynamics becomes

$$\frac{d\phi}{d\tau} = D_{\phi} \nabla^2 \phi + \beta (\phi - \phi^3) - \gamma U - \Delta T(z')$$
(4.5)

and

$$\frac{dU}{d\tau} = D_U \nabla^2 U + \frac{1}{\Delta \phi} \frac{d\phi}{d\tau} , \qquad (4.6)$$

where  $z' \equiv z - v\tau$ ,  $d/d\tau \equiv \partial/\partial \tau - v\partial/\partial z'$ ,  $D_U \equiv \Gamma_c/\Gamma_{\phi}$  and  $\tau \equiv \Gamma_{\phi}t$ . The moving temperature gradient  $\Delta T(z')$  is  $-\Delta T_0$  for z' < -W, z'G for |z'| < W and  $\Delta_0$  for z' > W with  $G \equiv \Delta T_0/W$  the external imposed temperature gradient. The average concentration is taken to be  $c_0 = 0$ . The partition coefficient is assumed to be equal to unity. This model can be shown to lead to the basic equations of solidification in the appropriate limit and the phenomenological constants are then related to the physical lengths:  $\ell_T \equiv \gamma/G$ ,  $d_0 \equiv \sigma/2\gamma$  and  $\sigma \equiv D_{\phi} \int du (\partial \phi^{1D}/\partial u)$  where  $\phi^{1D}$  is the one dimensional solution of equation (4.5).

### 4.2.1 The Phase Diagram

A phase diagram can be built by minimizing the free energy with respect to  $\phi$ . This minimization leads to

$$\phi^{3} + \phi \left(\frac{\gamma}{\beta \Delta \phi} - 1\right) + \frac{\gamma c + \Delta T}{\beta} = 0$$

For small of  $\gamma/\beta \Delta \phi$  and  $(\gamma c + \Delta T)/\beta$ , the values of  $\phi$  in the solid and the liquid are

$$\phi_{\rm sol} = 1 - \frac{\frac{\gamma}{\beta \Delta \phi} + \frac{\gamma c + \Delta T}{\beta}}{2}$$

and

$$\phi_{\rm liq} = -1 + \frac{\frac{\gamma}{\beta \Delta \phi} - \frac{\gamma c + \Delta T}{\beta}}{2}$$

respectively. With the same approximations, the free energy of each phase is

$$\mathcal{F}_{\rm sol} = \Delta T + \frac{\gamma}{2\Delta\phi} + \gamma c + \frac{\gamma\Delta\phi}{2}c^2$$

and

$$\mathcal{F}_{\text{liq}} = -\Delta T + \frac{\gamma}{2\Delta\phi} - \gamma c + \frac{\gamma\Delta\phi}{2}c^2$$

By using the double tangent construction, we finally find equations for the liquidus and solidus lines as follows:

$$(\Delta T)_{\text{solidus}} = \gamma \left( -\frac{1}{\Delta \phi} - c \right)$$

and

$$(\Delta T)_{\text{liquidus}} = \gamma \left( \frac{1}{\Delta \phi} - c \right)$$

Figure 4.5 indicates the part of the phase diagram corresponding to the above approximation. We deduce from this phase diagram that the hot contact has to be at a temperature  $\Delta T > \gamma/\Delta \phi$  and the cold contact at  $\Delta T < -\gamma/\Delta \phi$  for directional solidification experiments with the average impurities concentration  $c_0$  around 0.



Figure 4.5: Part of the phase diagram for the model of directional solidification.

## 4.3 Numerical Simulations

Numerical simulations of (4.5) and (4.6) were performed on a discrete lattice with free boundary in the  $\hat{z}$  direction and periodic in the  $\hat{x}$  direction. For the Laplacian, the usual central difference scheme with the nearest neighbors was used. The Euler's method was used for the time derivatives. In the following simulations, the parameters  $\beta = 1$  and  $\Delta T_0 = 0.38$ . Various non-steady state effects can be seen, such as the tipsplitting instability and the colliding solitary modes (figure 4.6).



Figure 4.6: Non-steady state interfaces showing tip splitting (left) and collision of two solitary modes (right) [from Grossmann et al. [93]].

A simulation of a breathing-mode is shown in figure 4.7(a). The oscillation of

### 4: DIRECTIONAL SOLIDIFICATION



Figure 4.7: Example of a numerical simulation of a breathing-mode pattern with  $2\pi/q = 43$  and v = 0.195: (a) a large system,  $L_x = 516$ , (b) the small system where most of the simulations have been performed,  $L_x = \lambda = 43$ .

neighboring grooves are in antiphase while the next-nearest neighbors are in phase. This breathing-mode is obtained by starting with an interface of the form  $\zeta(x, t = 0) = \cos(24\pi x/L_x) + \cos(12\pi x/L_x)$  with  $L_x = 495$ ,  $\gamma = 0.63$ ,  $D_{\phi} = 1.5$ ,  $D_U = 1$ , W = 100 and v = 0.2.

We perform numerical simulations on the breathing-modes. We assume that the breathing-mode exists and for numerical efficiency, we work on a smaller system containing only one groove (figure 4.7(b)). Neumann conditions at the boundaries in the  $\hat{x}$  direction (gradients of the fields are zero) are used. We fix the wavelength and look for the velocity giving rise to the breathing-mode. This is the inverse of what is done experimentally where the pulling velocity is the control parameter. The results of the simulations are summarized in figure 4.8. As observed experimentally, the wavelength decreases when the velocity increases (figure 4.8(a)). However, in addition, these results show the existence of breathing-modes of different velocities (and of different vacillating frequencies) for a given wavelength, contradicting what is



Figure 4.8: Results of the numerical simulations : (a) v versus q, (b) Dispersion relation for the breathing-mode.

known from the experiments. The dispersion relation is plotted in figure 4.8(b). As before, the numerical results agree qualitatively with the experiment of Cladis et al. [91],  $\omega \sim q$ , but the broadening prevents us to make any strong statements. Noise has been added to the Langevin equations but it did not change the results.

This raises the issue of whether or not true selection occurs during directional solidification. However, long transients may be present in our numerical work which we have not identified. Nevertheless, it is clear that further study of this phenomena would be of use.

# $\mathbf{5}$

## ELASTIC EFFECTS

It is known that the domain morphology in phase-separating alloys can be strongly influenced by elastic fields (Khachaturyan [83]). These long-range fields originate from lattice misfit or the difference in the lattice constants of the two phases.

Onuki and Nishimori<sup>1</sup> introduced a Ginzburg-Landau approach to analyze the elastic effects in phase-separating alloys in a model B system. They assumed the coherent condition, which states that the planes are continuous through the interfaces. In their scheme, the elastic strain is a subsidiary tensor variable coupled to a conserved order parameter, the concentration c, in the free energy. They obtained a closed description of c by eliminating the elastic field from the mechanical equilibrium. Sagui, Somoza and Desai [94] applied this formalism to the study of the effect of an elastic field in an order-disorder phase transition described by dynamics corresponding to a model C system. The elastic field was coupled to both the concentration and the order parameter.

A recent experiment by Grütter and Dürig [95] illustrates the importance of the elastic field. They reported on the observation of the dendritic growth of Co on Pt(111) surface. An example is shown in figure 5.1.

The dendrite arms are 3-5 nm wide, 0.20 nm high (a monolayer of Co) and can be up to 250 nm long. The lattice constant of Co is 9.7% smaller than that of Pt. Hence, the Co islands cause substantial surface strain which induces the reconstruction of the Pt(111) surface. These reconstructed areas act in turn as templates for the growth of the Co islands. Figure 5.2 shows the reconstruction of the Pt surface in front of the dendrites characterized by parallel double lines.

<sup>&</sup>lt;sup>1</sup>Onuki [89a]; Onuki [89b]; Nishimori and Onuki [90]; Onuki and Nishimori [91].



Figure 5.1: Scanning tunneling micrograph overview of 0.1 ML Co deposited at 400K on Pt(111) [From Grütter and Dürig [95]].

## 5.1 Dendritic Growth due to Elastic Fields

We will simulate the growth of the Co islands on the Pt(111) using a phase field model. The field  $\phi$  is 1 when the atoms of Co are present and 0 when the substrate is free of Co adatoms. The external driving force, h, models the deposition of Co onto the Pt(111) surface. This driving force is assumed to be constant. The total free energy  $\mathcal{F}$  is

$$\mathcal{F} = \int d\mathbf{r} \left[ \tilde{f}(\phi, h, u_{ij}) + \frac{l_{\phi}^2}{2} |\nabla \phi|^2 \right] \,. \tag{5.1}$$

The bulk free energy density  $f(\phi, h, u_{ij})$  is given by

$$\tilde{f}(\phi, h, u_{ij}) = \frac{1}{4}\phi^4 + \frac{h - 3/2}{3}\phi^3 - \frac{h - 1/2}{2}\phi^2 + \epsilon_{\phi}\phi\nabla\cdot\boldsymbol{u} + f_{\rm el} , \qquad (5.2)$$

where  $\epsilon_{\phi}$  is the coupling constant between  $\phi$  and  $\nabla \cdot u$ . With this linear coupling, the Pt(111) surface is strained only when some Co atoms ( $\phi = 1$ ) are present.  $f_{\rm el}$  is



Figure 5.2: Left: Magnification of the dendrite region (200 nm  $\times$  200 nm). A localized reconstruction of the Pt(111) surface is seen in front of the Co branch. Right: Zoom of the reconstruction (15 nm  $\times$  36 nm) [From Grütter and Dürig [95]].

the isotropic elastic free energy given  $by^1$ 

$$f_{\rm el} = \frac{1}{2} \kappa (\boldsymbol{\nabla} \cdot \boldsymbol{u})^2 + \mu \sum_{i,j} \left( u_{ij} - \frac{\delta_{ij}}{2} \boldsymbol{\nabla} \cdot \boldsymbol{u} \right)^2 \,. \tag{5.3}$$

Here,  $\kappa$  and  $\mu$  are the bulk and shear moduli respectively and  $u_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$  is the elastic strain.

### A. Constant Elastic Moduli

First, we consider constant elastic moduli. Later, we will consider the case where the elastic moduli depend on  $\phi$ .

The elastic field instantaneously relaxes to adjust to a given  $\phi$ . This is the condition of mechanical equilibrium,

$$\frac{\delta \mathcal{F}}{\delta u_i} = \sum_j \frac{\partial \sigma_{ij}}{\partial x_j} = 0.$$
(5.4)

With the definition of the elastic stress tensor

$$\sigma_{ij} = \frac{\partial \mathcal{F}}{\partial u_{ij}} = (\epsilon_{\phi}\phi + \kappa \nabla \cdot \boldsymbol{u})\delta_{ij} + 2\mu \left(u_{ij} - \frac{\delta_{ij}}{2} \nabla \cdot \boldsymbol{u}\right) , \qquad (5.5)$$

<sup>&</sup>lt;sup>1</sup>Landau and Lifshitz [90].

the condition of mechanical equilibrium (5.4) becomes

$$\kappa \nabla \nabla \cdot \boldsymbol{u} + \epsilon_{\phi} \nabla \phi + \mu \nabla^2 \boldsymbol{u} = 0 .$$
 (5.6)

Under the assumption of zero external stress, the solution of this equation is<sup>1</sup>

$$\boldsymbol{\nabla} \cdot \boldsymbol{u} = -\frac{\epsilon_{\phi}}{\alpha}\phi , \qquad (5.7)$$

where  $\alpha \equiv \kappa + \mu$ . In agreement with what Cahn [61] has shown in the case of spinodal decomposition, if the system is isotropic and the elastic moduli are independent of  $\phi$ , then the induced elastic field is simply proportional to  $\phi$  and thus there will be no long-range interaction present.

After substituting the expression for  $\nabla \cdot \boldsymbol{u}$  in (5.6), we find

$$\frac{\partial u_i}{\partial x_j} = -\frac{\epsilon_\phi}{\alpha} \frac{\partial^2 W_\phi}{\partial x_j \partial x_i} , \qquad (5.8)$$

with

$$abla^2 W_\phi = \phi$$
 or  $W_\phi = rac{1}{
abla^2} \phi$ .

If we substitute equation (5.8) in (5.2), we find<sup>2</sup>

$$\tilde{f}(\phi,h) = \frac{1}{4}\phi^4 + \frac{h - 3/2}{3}\phi^3 - \frac{h - 1/2}{2}\phi^2 - \frac{\epsilon_{\phi}^2}{2\alpha}\phi^2 .$$
(5.9)

Hence, the coupling with the elastic field favors the growth of the Co islands even if h is zero. We remove this undesirable effect by using the free energy density

$$f(\phi, h, u_{ij}) = \frac{1}{4}\phi^4 + \frac{h - 3/2}{3}\phi^3 - \frac{h - 1/2}{2}\phi^2 + \frac{\epsilon_{\phi}^2}{2\alpha}\phi^2 + \epsilon_{\phi}\phi\nabla\cdot\boldsymbol{u} + f_{\rm el} .$$
(5.10)

### B. The Effect of Anisotropy

The dendritic pattern in the experiment of Grütter and Dürig [95] is due mainly to the anisotropy of the lattice strain. For simplicity, only a four-fold anisotropy is considered.

<sup>1</sup>We apply  $\nabla \cdot$  to equation (5.6) and use the identity  $\nabla^2 u = \nabla \nabla \cdot u - \nabla_{\wedge} (\nabla_{\wedge} u)$ .

<sup>&</sup>lt;sup>2</sup>Notice that  $\int dr \sum_{ij} \left( \frac{\partial^2 W_{\phi}}{\partial x_i \partial x_j} \right)^2$  is equal to  $\int dr \left( \nabla^2 W_{\phi} \right)^2$  because of the periodic boundary conditions.

#### 5: Elastic Effects

The elastic energy for a two-dimensional crystal with the point group symmetry of a square is given by<sup>1</sup>

$$f_{\rm el} = \frac{1}{2}C_{11}(u_{xx}^2 + u_{yy}^2) + \frac{1}{2}C_{12}(u_{xx}u_{yy}) + C_{44}u_{xy}^2 .$$
(5.11)

This energy can be rewritten  $as^2$ 

$$f_{\rm el} = \frac{1}{2}\kappa(\boldsymbol{\nabla}\cdot\boldsymbol{u})^2 + \mu\sum_{i,j}\left(u_{ij} - \frac{\delta_{ij}}{2}\boldsymbol{\nabla}\cdot\boldsymbol{u}\right)^2 + \frac{1}{2}\beta\sum_i u_{ii}^2 , \qquad (5.12)$$

which is the isotropic elastic energy plus a part due to the square anisotropy. The elastic moduli are given by

$$\begin{split} \mu &= C_{44} \; , \\ \kappa &= C_{12} + C_{44} \; , \\ \beta &= C_{11} - C_{12} - 2C_{44} \end{split}$$

and the anisotropy is defined<sup>3</sup> as  $\xi \equiv \beta/C_{44}$ .

The elastic strain tensor becomes

$$\sigma_{ij} = (\epsilon_{\phi}\phi + \kappa \nabla \cdot \boldsymbol{u} + \beta u_{ii})\delta_{ij} + 2\mu \left(u_{ij} - \frac{\delta_{ij}}{2} \nabla \cdot \boldsymbol{u}\right)$$
(5.13)

and the condition of mechanical equilibrium reads in Fourier space as

$$i\boldsymbol{k}\cdot\hat{\boldsymbol{u}}(\boldsymbol{k}) = \frac{\epsilon_{\phi}\hat{\chi}(\boldsymbol{k})\hat{\phi}(\boldsymbol{k})}{1+\kappa\hat{\chi}(\boldsymbol{k})}, \qquad (5.14)$$

where we introduce

$$\hat{\chi}(\boldsymbol{k}) = \sum_{i} \frac{\hat{k_i}^2}{\mu(1 + \xi \hat{k_i}^2)} \,.$$
(5.15)

A linear approximation in the anisotropy  $\xi$  gives

$$i\boldsymbol{k}\cdot\hat{\boldsymbol{u}}(\boldsymbol{k}) = \frac{\epsilon_{\phi}}{\alpha}\hat{\phi}(\boldsymbol{k}) - \xi\mu\frac{\epsilon_{\phi}}{\alpha^2}\left(1 - 2\frac{k_x^2k_y^2}{k^4}\right)\hat{\phi}(\boldsymbol{k})$$
(5.16)

or in real space

$$\boldsymbol{\nabla} \cdot \boldsymbol{u} = -\frac{\epsilon_{\phi}}{\alpha}\phi + \xi \mu \frac{\epsilon_{\phi}}{\alpha^2} \left(1 - 2\frac{\nabla_x^2 \nabla_y^2}{\nabla^4}\right)\phi .$$
 (5.17)

Hence the anisotropy introduces a long-range interaction.

<sup>&</sup>lt;sup>1</sup>Landau and Lifshitz [90].

<sup>&</sup>lt;sup>2</sup>Sagui, Somoza and Desai [94].

<sup>&</sup>lt;sup>3</sup>A cubic lattice is considered to be isotropic when  $C_{44} = (C_{11} - C_{12})/2$ . At this value of the elastic moduli, the sound speed for the transversal and longitudinal waves are equal (see *e.g.* Weißmantel and Hamann [89] and Nishimori and Onuki [90]). This definition of anisotropy differs from the one of Chaikin and Lubensky [95] for whom the ratio  $(C_{11} - C_{44})/C_{12}$  is the measure of the anisotropy of cubic solid.

## C. Order Parameter Dependent Elastic Moduli

Now we will consider the case when the elastic moduli depend on the order parameter  $\phi$  as follows:

$$\kappa = \kappa_0 + \kappa_\phi \phi \; ,$$
  
 $\mu = \mu_0 + \mu_\phi \phi$ 

and

$$\beta = \beta_0 + \beta_\phi \phi \; .$$

This dependence of the elastic moduli on the order parameter will also introduce long-range interactions.

As before, we want to express the elastic field in terms of order parameter. The part of the free energy depending on the elastic field will be computed to first order in the elastic coefficients,  $\kappa_{\phi}$ ,  $\mu_{\phi}$  and  $\beta$ .

The condition of mechanical equilibrium now reads

$$\epsilon_{\phi} \frac{\partial \phi}{\partial x_{i}} + \kappa_{0} \frac{\partial}{\partial x_{i}} \nabla \cdot \boldsymbol{u} + \kappa_{\phi} \frac{\partial}{\partial x_{i}} (\phi \nabla \cdot \boldsymbol{u}) + 2\mu_{0} \sum_{j} \frac{\partial}{\partial x_{j}} \left( u_{ij} - \frac{\delta_{ij}}{2} \nabla \cdot \boldsymbol{u} \right) + 2\mu_{\phi} \sum_{j} \frac{\partial}{\partial x_{j}} \phi \left( u_{ij} - \frac{\delta_{ij}}{2} \nabla \cdot \boldsymbol{u} \right) + \beta_{0} \frac{\partial}{\partial x_{i}} u_{ii} + \beta_{\phi} \frac{\partial}{\partial x_{i}} (\phi u_{ii}) = 0.$$
(5.18)

To zeroth order, the strain tensor is given as before by

$$rac{\partial u_i}{\partial x_j} = -rac{\epsilon_\phi}{lpha} rac{\partial^2 W_\phi}{\partial x_j \partial x_i}$$

Applying  $\sum_i \partial / \partial x_i$  to (5.18), we find

$$\begin{split} \epsilon_{\phi} \nabla^{2} \phi + \kappa_{0} \nabla^{2} \nabla \cdot \boldsymbol{u} + 2\mu_{0} \sum_{i,j} \frac{\partial^{2}}{\partial x_{i} \partial x_{j}} \left( u_{ij} - \frac{\delta_{ij}}{2} \nabla \cdot \boldsymbol{u} \right) + \beta_{0} \sum_{i} \frac{\partial^{2}}{\partial x_{i}^{2}} u_{ii} \\ + \kappa_{\phi} \nabla^{2} (\phi \nabla \cdot \boldsymbol{u}) + 2\mu_{\phi} \sum_{i,j} \frac{\partial^{2}}{\partial x_{i} \partial x_{j}} \phi \left( u_{ij} - \frac{\delta_{ij}}{2} \nabla \cdot \boldsymbol{u} \right) + \beta_{\phi} \sum_{i} \frac{\partial^{2}}{\partial x_{i}^{2}} (\phi u_{ii}) = 0 \; . \end{split}$$

In the terms containing  $\kappa_{\phi}$  and  $\mu_{\phi}$  as well as  $\beta_0$  and  $\beta_{\phi}$ , we replace  $\nabla \cdot u$  by its zeroth order. The condition of mechanical equilibrium now reads

$$\nabla \cdot \boldsymbol{u} = -\frac{\epsilon_{\phi}}{\alpha}\phi + \kappa_{\phi}\frac{\epsilon_{\phi}}{\alpha^{2}}\phi^{2} + 2\frac{1}{\alpha}\frac{1}{\nabla^{2}}\sum_{i,j}\frac{\partial^{2}}{\partial x_{i}\partial x_{j}}\mu_{\phi}\phi\left(\frac{\epsilon_{\phi}}{\alpha}\right)\left(\frac{\partial^{2}W_{\phi}}{\partial x_{j}\partial x_{i}} - \frac{\delta_{ij}}{2}\phi\right) + \beta_{0}\frac{\epsilon_{\phi}}{\alpha^{2}}\left(1 - 2\frac{\nabla_{x}^{2}\nabla_{y}^{2}}{\nabla^{4}}\right)\phi + \beta_{\phi}\frac{\epsilon_{\phi}}{\alpha^{2}}\frac{1}{\nabla^{2}}\sum_{i}\frac{\partial^{2}}{\partial x_{i}^{2}}\left(\phi\frac{\partial^{2}W_{\phi}}{\partial x_{i}^{2}}\right).$$
The part of the functional derivative of the free energy due to the elastic terms is

$$\Delta_{\rm el} = \epsilon_{\phi} \nabla \cdot \boldsymbol{u} + \frac{1}{2} \kappa_{\phi} (\nabla \cdot \boldsymbol{u})^2 + \mu_{\phi} \sum_{i,j} \left( u_{ij} - \frac{\delta_{ij}}{2} \nabla \cdot \boldsymbol{u} \right)^2 + \frac{\beta_{\phi}}{2} \sum_i u_{ii}^2 \,.$$

After we substitute the expression for  $\nabla \cdot \boldsymbol{u}$  and  $u_{ij}$ ,  $\Delta_{el}$  translates to

$$\Delta_{\rm el} = -\frac{\epsilon_{\phi}^2}{\alpha}\phi + \frac{3}{2}\kappa_{\phi}\left(\frac{\epsilon_{\phi}}{\alpha}\right)^2\phi^2 + 2\mu_{\phi}\frac{\epsilon_{\phi}}{\alpha}\frac{1}{\nabla^2}\sum_{i,j}\frac{\partial^2}{\partial x_i\partial x_j}\left[\phi\left(\frac{\epsilon_{\phi}}{\alpha}\right)\left(\frac{\partial^2 W_{\phi}}{\partial x_j\partial x_i} - \frac{\delta_{ij}}{2}\phi\right)\right] + \mu_{\phi}\sum_{i,j}\left(\frac{\epsilon_{\phi}}{\alpha}\right)^2\left(\frac{\partial^2 W_{\phi}}{\partial x_j\partial x_i} - \frac{\delta_{ij}}{2}\phi\right)^2 + \beta_0\left(\frac{\epsilon_{\phi}}{\alpha}\right)^2\left(1 - 2\frac{\nabla_x^2 \nabla_y^2}{\nabla^4}\right)\phi + \frac{\beta_{\phi}}{2}\left(\frac{\epsilon_{\phi}}{\alpha}\right)^2\sum_i\left(\frac{\partial^2 W_{\phi}}{\partial x_i^2}\right)^2 + \beta_{\phi}\left(\frac{\epsilon_{\phi}}{\alpha}\right)^2\frac{1}{\nabla^2}\sum_i\frac{\partial^2}{\partial x_i^2}\left(\phi\frac{\partial^2 W_{\phi}}{\partial x_i^2}\right) .$$
 (5.19)

Finally, the Langevin equation for the order parameter is

$$\frac{\partial \phi}{\partial t} = -\Gamma_{\phi} \left[ \phi^{3} + \left(h - \frac{3}{2}\right) \phi^{2} - \left(h - \frac{1}{2}\right) \phi + \frac{3}{2} \kappa_{\phi} \epsilon_{\phi}^{2} \phi^{2} + \mu_{\phi} Q 
+ 2\epsilon_{\phi} \frac{1}{\nabla^{2}} \sum_{i,j} \frac{\partial^{2}}{\partial x_{i} \partial x_{j}} \left(\mu_{\phi} \phi b_{ij}\right) + \beta_{0} \epsilon_{\phi}^{2} \left(1 - 2 \frac{\nabla_{x}^{2} \nabla_{y}^{2}}{\nabla^{4}}\right) \phi 
+ \beta_{\phi} \epsilon_{\phi}^{2} \sum_{i} \left(\frac{\partial^{2} W_{\phi}}{\partial x_{i}^{2}}\right)^{2} + \beta_{\phi} \epsilon_{\phi}^{2} \frac{1}{\nabla^{2}} \sum_{i} \frac{\partial^{2}}{\partial x_{i}^{2}} \left(\phi \frac{\partial^{2} W_{\phi}}{\partial x_{i}^{2}}\right) - l_{\phi}^{2} \nabla^{2} \phi \right] , \quad (5.20)$$

where  $b_{ij} = \epsilon_{\phi} \left( \frac{\partial^2 W_{\phi}}{\partial x_j \partial x_i} - \frac{\delta_{ij}}{2} \phi \right)$  and  $Q = \sum_{ij} b_{ij}^2$ . Also, the coefficient  $\epsilon_{\phi}$  is redefined so that  $\epsilon_{\phi} \equiv \epsilon_{\phi} / \alpha$ .

# 5.1.1 Numerical Simulations

Because of the terms  $\frac{1}{\nabla^2}$  in equation (5.20), it is necessary to go to Fourier space. We use an isotropic form for the Laplacian  $\Delta_k = (\cos(k_x \Delta x) \cos(k_x \Delta y) + \cos(k_x \Delta x) + \cos(k_y \Delta y) - 3)/\Delta x^2$  as well as for  $\nabla_x$ ,  $\nabla_y$ ,  $\nabla_x^2$  and  $\nabla_y^2$ . The system size is 256 × 256 and periodic boundary conditions are used throughout the simulations. The time integration is performed using the standard Euler's method. We have neglected noise in these simulations.

# A. Quasidendritic growth

In the following simulations,  $l_{\phi} = 0.33$ ,  $\Gamma_{\phi} = 3$  and  $\epsilon_{\phi} = 0.5$ . Also,  $\kappa_0 = 0.9$ ,  $\mu_0 = 0.3$ and  $\beta_{\phi} = 0$ . Moreover, we set  $\kappa_{\phi} = 0$  since the dependence of the bulk modulus on  $\phi$  is small compared to the dependence of  $\mu$  over  $\phi$ . The other parameters,  $\beta_0$ ,  $\kappa_{\phi}$ and  $\mu_{\phi}$  take different values during the simulations. The spatial mesh is taken to be  $\Delta x = \Delta y = 1.0$  whereas  $\Delta t = 0.1$ . The time integration is performed using the standard Euler's method. Finally, the external field is chosen to be h = 0.45.

Figure 5.3 shows the time evolution for a system with isotropic elastic constants. The time sequence (a) corresponds to the case where the difference of the elastic



Figure 5.3: Growth in the presence of isotropic elastic field. The anisotropy is chosen to be  $\beta_0 = 0$ . The pictures shown correspond to t = 40 and t = 70 from top to bottom. (a)  $\mu_{\phi} = 0$ , (b)  $\mu_{\phi} = 0.05$ and (c)  $\mu_{\phi} = -0.05$ . In (b), the background gray color corresponds to  $\phi = 0$ . Around the black phase, the white ring is a region of small negative value of  $\phi$  due to the long range force. In (c), the white regions correspond to  $\phi = 0$  whereas in the gray ones,  $\phi$  has a small positive value.

moduli in the two phases is zero, *i.e.*,  $\kappa_{\phi} = \mu_{\phi} = 0$  and thus elasticity has no effect on the growth. In (b) and (c), we include the dependence of the elastic modulus  $\mu_{\phi}$ on  $\phi$ . We choose  $\mu_{\phi} = 0.05$  in (b) and  $\mu_{\phi} = -0.05$  in (c).

When  $\mu_{\phi} > 0$ ,  $\Delta \mu \equiv \mu(\phi = 1) - \mu(\phi = 0) = \mu_{\phi} > 0$  and  $\phi = 1$  is the hard phase, while when  $\mu_{\phi} < 0$ ,  $\phi = 1$  is the soft phase. The integration of the two terms containing  $\mu_{\phi}$  in (5.19) give  $\mu_{\phi}\phi Q$ . Hence, this contribution is positive when  $\phi = 1$ is the hard phase ( $\mu_{\phi}\phi > 0$ ) and it is minimized for spherical morphologies of this phase. In this case, the elastic forces slow down the growth. The elastic contribution is negative when  $\phi = 1$  is the soft phase ( $\mu_{\phi}\phi < 0$ ) and this phase will deform anisotropically. Here, the elastic forces favor the growth. The four-fold symmetry exhibited in (c) is due to the anisotropy induced by the underlying grid used in the numerical calculations.

The introduction of an anisotropy in the elastic moduli changes drastically the morphology of the  $\phi = 1$  domains (hereafter named as the black phase) as well as the speed of growth. This is illustrated by the left side of figure 5.4 where  $\beta_0 = -0.1$  and  $\beta_{\phi} = \mu_{\phi} = 0$ . After the black domain has reached a critical radius, we observe the growth of branches exhibiting a four-fold anisotropy. The growth of the black phase in front of the tip is greatly favored. This can be visualized by the contour plot of  $\Delta_{el}$  (equation (5.19)). The contour plots are shown on the right side of figure 5.4. Lighter colors correspond to positive values of the functional derivatives. These positive regions repel the particles from the dark regions and the growth takes place preferentially in the darker regions of the contour plot. This quasidendritic growth is characterized by an absence of secondary branching.

Figure 5.5 illustrates the effect of the introduction of a dependence of  $\mu$  on the order parameter. For a positive  $\mu_{\phi}$ , it slows down the growth as expected but do not alter the quasidendritic structure.

The morphology of the growth is similar to the one observed in the experiment of Grütter and Dürig [95], except that we used a square anisotropy to simplify the algebra.

### B. Dendritic growth

One can use the same model to check if the main features of a solid, *i.e.*, its rigidity and often its anisotropy, are enough to obtain the dendritic growth. This approach is more natural than introducing by hand an anisotropy in the surface tension as we did before in section 3.3. To reach this goal, we will use equation (5.20), but now the field h is given by  $h(u) = \alpha/\pi \arctan(-\delta u)$  where u is the reduced temperature of section 3.3. It obeys the following equation

$$\frac{\partial u}{\partial t} = \nabla^2 u + \frac{1}{\Delta} \frac{\partial \phi}{\partial t} \; , \label{eq:eq:electropy}$$



Figure 5.4: Quasidendritic growth in the presence of anisotropic elastic field. On the left, the phase field is plotted. On the right, the corresponding contour plot of the functional derivative of the elastic free energy is shown. The anisotropy  $\beta_0 = -0.1$ ,  $\mu_{\phi} = 0$  and  $\kappa_{\phi} = 0$ . The pictures shown correspond to t = 10, t = 25, and t = 40 from top to bottom.

62



Figure 5.5: Quasidendritic growth in the presence of anisotropic elastic field and a phase dependent shear modulus.  $\beta_0 = -0.1$  and  $\mu_{\phi} = 0.05$ . The pictures shown correspond to t = 10, t = 25, t = 40 and t = 50 from top to bottom and left to right.



Figure 5.6: Growth of a dendrite in the presence of anisotropic elastic field.  $\beta_{\phi} = -0.2$  and  $\mu_{\phi} = 0.05$ . The pictures shown correspond to t = 0.1, t = 0.2, t = 0.3 and t = 0.4 from top to bottom and left to right.

where  $\Delta = (T_M - T_\infty)/(L/c)$  denotes the dimensionless undercooling.

In the following simulations,  $l_{\phi} = 0.01$ ,  $\Gamma = 3333$ ,  $\epsilon_{\phi} = 0.2$  and  $\Delta = 0.6$ . Noise has been added at the interface as in section 3.3 with an amplitude a = 0.03. Also,  $\kappa_0 = 0.9$ ,  $\mu_0 = 0$  and  $\beta_0 = 0$  so that the liquid has no anisotropy and does not support shear. As before, we neglect the dependence of the bulk modulus on the phase,  $\kappa_{\phi} = 0$ . The spatial mesh is taken to be  $\Delta x = \Delta y = 0.03$  whereas  $\Delta t = 0.0001$ . Figure 5.6 shows the result of a simulation for  $\mu_{\phi} = 0.05$  and  $\beta_{\phi} = -0.2$  and a contour plot  $\Delta_{el}$ is shown in Figure 5.7.

We recover indeed dendritic features. Simulations have also been performed for different values of the shear modulus and the anisotropy. As before, in front of the main branches of the dendrites, one observes a long-range influence of the elasticity.



Figure 5.7: Contour plot of the functional derivative of the elastic energy of the dendrite at t = 0.3.

Growth in the x and y axis is favored or, equivalently, the growth of the dendrite in the diagonal direction is impeded. This feature is observed also for the secondary branches where we note higher values of  $\Delta_{el}$  in the diagonal direction.

# 5.2 Modeling of the Dislocations Dynamics

The presence of dislocations is known to have a major impact on the strength of materials. It is the major reason for the plastic mechanical properties of crystalline solids. The density of the dislocations defined as the number of dislocation lines intersecting a unit area in the crystal ranges from well below  $10^2$  dislocations/cm<sup>2</sup> in the best germanium and silicon crystals to  $10^{11}$  or  $10^{12}$  dislocations/cm<sup>2</sup> in some heavily deformed metal crystals. Dislocations may also be a controlling factor in crystal growth. For example, the presence of a screw dislocation will favor the growth of the crystal in a spiral fashion. Due to the misfit between the substrate and the film, dislocations are often present in the first few layers of the epitaxial growth. Given the impact of the dislocations on the materials, much research has been devoted to the problem of dislocation dynamics. The reader is referred to Kosevich [79] and Kröner [81] for comprehensive reviews of the field.

The model presented below is inspired partly by the work of Nelson and cowork-

ers<sup>1</sup> on melting in two dimensions. In their theory of dislocation-mediated melting, the transition from liquid to solid takes place in two steps with increasing temperature. Dissociation of dislocation pairs first is responsible for the transition from a solid phase with long-range translational and orientational order to an hexatic phase characterized by a short-range translational order but a quasilong-range orientational order. Dissociation of disclination pairs at a higher temperature then produces an isotropic fluid. In the various stages of the derivation of the model of dislocation dynamics, some ideas of the two dimensional melting will be used.

Let us imagine that in a crystalline solid represented in figure 5.8, an extra half



Figure 5.8: Definition of the Burgers vector by means of a Frank's circuit [from Kröner [81]].

crystalline plane (parallel to the plane z-y in the figure) is inserted. The edge of this half-plane (parallel to the z axis) is called an *edge dislocation*. We form in the real crystal (a) a Frank's circuit which lies entirely in the good material (as opposed to the *bad* region near the dislocation where the displacements are large) and encloses the dislocation. Then we draw the same circuit in the reference crystal (b). This circuit does not close in the reference crystal. The closure failure, here denoted by  $\vec{EA}$  is called the Burgers vector, **b**. The Burgers vector is equal in magnitude and direction to a lattice vector. Macroscopically, this is written as

$$\oint_{\Gamma} d\boldsymbol{u} = \boldsymbol{b} \;. \tag{5.21}$$

When b is parallel to the dislocation line, it is a *screw dislocation*. For an edge dislocation, b is perpendicular to the dislocation line. In two dimensions, we obviously

<sup>&</sup>lt;sup>1</sup>Nelson [78]; Nelson and Halperin [79]; Nelson [83]; Toner and Nelson [81]; Nelson, Rubinstein and Spaepen [82].

have only the edge dislocations.

It is convenient to introduce the notation

$$w_{ji} = \frac{\partial u_i}{\partial x_j} \tag{5.22}$$

allows us to rewrite equation (5.21) as

$$\oint_{\Gamma} du_i = \oint_{\Gamma} \frac{\partial u_i}{\partial x_j} dx_j = \oint_{\Gamma} w_{ji} dx_j = b_i .$$
(5.23)

This equation can also be written in a differential form. The integral over the contour  $\Gamma$  transforms to an integral over the surface  $\Sigma$  spanned by  $\Gamma$  to give

$$\oint_{\Gamma} w_{ji} dx_j = \int_{\Sigma} d\mathbf{r} \,\epsilon_{kj} \nabla_k w_{ji} = \sum_{\alpha} b_{\alpha i} \,, \qquad (5.24)$$

where the sum is over the Burgers vectors  $b_{\alpha}$  of all the dislocations enclosed in  $\Gamma$ .  $\epsilon_{ij}$ is the antisymmetric tensor,  $\epsilon_{ij} = -\epsilon_{ji}$ . In terms of the dislocation density<sup>1</sup>, b(r),

$$\epsilon_{kj} \nabla_k w_{ji} = b_i(\boldsymbol{r}) \ . \tag{5.25}$$

Because of the large number of dislocations in solid, we shall not consider the microscopic details of the configuration, but rather the "large scale" properties. We will hence work with a continuous description of the problem or, in other words, with the dislocation density.

## 5.2.1 Energy of the Distribution of Dislocations

The displacement field u is a solution of the equilibrium equations

$$\nabla_j \sigma_{ij} = 2\mu \nabla_j u_{ij} + \lambda \nabla_i u_{kk} = 0 \tag{5.26}$$

everywhere except at the core of the dislocations. Due to the presence of the dislocations, u has a singular part. We write formally<sup>2</sup>

$$u_{ij}(r) = \phi_{ij}(r) + u_{ij}^{S}(r) , \qquad (5.27)$$

<sup>&</sup>lt;sup>1</sup>In general, the dislocation density is a second rank tensor named conventionally  $\alpha$ . It is defined as  $\int d\mathbf{S} \cdot \boldsymbol{\alpha} = b$  where b is the resulting Burgers vector of all the dislocations crossing the surface S spanned by any contour  $\Gamma$ . The first subscript in  $\alpha_{ij}$  indicates the average line direction of the dislocations piercing through the area element dS, whereas the second subscript gives the direction of the Burgers vector. In two dimensions with straight dislocation lines in the z axis, the only two components of  $\boldsymbol{\alpha}$  are  $b_x(r) \equiv \alpha_{zx}(r)$  and  $b_y(r) \equiv \alpha_{zy}(r)$ .

<sup>&</sup>lt;sup>2</sup>We follow in this section the notation and the derivation of Chaikin and Lubensky [95]. See also Nelson [78]; Nabarro [67].

where  $\phi_{ij}(r)$  is the strain associated with the smoothly varying displacements  $\phi(r)$ and  $u_{ij}^{S}(r)$  is the contribution from the dislocations.

By definition,  $\oint_{\Gamma} d\phi = 0$ . The singular part of the displacement has to obey the constraint  $\oint_{\Gamma} du^S = b$ . The solution is  $u^S = b\vartheta/2\pi$  where  $\vartheta$  is an angle in the plane perpendicular to l.

In two dimensions, the equilibrium condition equations (5.26) are fulfilled automatically if the stress tensor is written as

$$\sigma_{ij}^S = \epsilon_{ik} \epsilon_{jl} \nabla_k \nabla_l \chi , \qquad (5.28)$$

where  $\chi$  is the Airy stress function. The strain  $u_{ij}$  is related to the stress by the relation

$$u_{ij}^{S} = \frac{1}{2\mu} \sigma_{ij}^{S} - \frac{\lambda}{4\mu(\lambda+\mu)} \delta_{ij} \sigma_{kk}^{S}$$
$$= \frac{1+\sigma_{2}}{Y_{2}} \epsilon_{ik} \epsilon_{jl} \nabla_{k} \nabla_{l} \chi - \frac{\sigma_{2}}{Y_{2}} \nabla^{2} \chi \delta_{ij} , \qquad (5.29)$$

where in two dimensions, the Young's modulus is  $Y_2 = 4B\mu/(B + \mu)$ ,  $\sigma_2 = (B - \mu)/(B + \mu)$  is the Poisson ratio and  $B = \mu + \lambda$  denotes the bulk modulus.

Applying  $\epsilon_{ik}\epsilon_{jl}\nabla_k\nabla_l$  to both sides of the equation, we obtain

$$\frac{1}{Y_2} \nabla^4 \chi = \epsilon_{ik} \epsilon_{jl} \nabla_k \nabla_l u_{ij}^S = \frac{1}{2} \epsilon_{ik} \epsilon_{jl} \nabla_k \nabla_l (w_{ij}^S + w_{ji}^S) 
= \epsilon_{ik} \nabla_i b_k ,$$
(5.30)

where it is assumed that no disclination is present in the system.

Following Nelson [78], the elastic free energy breaks into two parts,

$$\mathcal{F}=\mathcal{F}_0+\mathcal{F}_D\;,$$

where  $\mathcal{F}_0$  is the purely harmonic contribution

$$\mathcal{F}_{0} = \frac{1}{2}\kappa(\boldsymbol{\nabla}\cdot\boldsymbol{\phi})^{2} + \mu\sum_{i,j}\left(\phi_{ij} - \frac{\delta_{ij}}{2}\boldsymbol{\nabla}\cdot\boldsymbol{\phi}\right)^{2}$$

and the dislocation contribution is given by

$$\mathcal{F}_{D} = \frac{1}{2} \int d\boldsymbol{r} \sigma_{ij}^{S} u_{ij}^{S}$$
  
$$= \frac{1}{2Y_{2}} \int d\boldsymbol{r} (\nabla^{2}\chi)^{2} + \frac{1+\sigma_{2}}{Y_{2}} \int d\boldsymbol{r} \epsilon_{ik} \epsilon_{jl} \nabla_{k} \nabla_{l} (\nabla_{i}\chi \nabla_{j}\chi) , \qquad (5.31)$$

where we have used (5.29). We consider the simple case where the total Burgers vector is zero, *i.e.*,  $\int d\mathbf{r} \ \mathbf{b} = 0$ . This means that there is no macroscopic bending of the crystal. Also we neglect disclinations, which are higher energy excitations. In this case, the last integral, which can be transformed into an integral over the boundary, vanishes. Then, the free energy of the dislocation reduces to

$$\mathcal{F}_D = \frac{1}{2Y_2} \int d\boldsymbol{r} (\nabla^2 \chi)^2 \tag{5.32}$$

which translates using (5.30) in Fourier space to

$$\mathcal{F}_{D} = \int \frac{dq}{(2\pi)^{2}} \left\{ \frac{Y_{2}}{2} \left[ \frac{1}{q^{2}} \left( \delta_{ij} - \frac{q_{i}q_{j}}{q^{2}} \right) \hat{b}_{i}(q) \hat{b}_{j}(-q) \right] + E_{c} \, \hat{b}_{i}(q) \hat{b}_{i}(-q) \right\} \,.$$
(5.33)

We have added to this equation the contribution of the core energy of a dislocation,  $E_c$ .

In real space, the free energy of the dislocations is<sup>1</sup>

$$\begin{split} \mathcal{F}_D &= \frac{Y_2}{8\pi} \int dr \int_{|\boldsymbol{r} - \boldsymbol{r}'| > a} dr' \bigg[ -b(r) \cdot b(r') \ln(|\boldsymbol{r} - \boldsymbol{r}'|) + \frac{b(r) \cdot (r - r') b(r') \cdot (r - r')}{|\boldsymbol{r} - \boldsymbol{r}'|^2} \bigg] \\ &+ E_c \int dr \ b^2(r) \ , \end{split}$$

where a is a short distance cut off. It can also be seen as the core diameter of the dislocations.

# 5.2.2 Local Formulation of the Dislocation Problem

It is possible to reformulate the interaction energy of the dislocations in a more convenient way. We introduce a local field  $\xi$  and write the dislocation free energy as

$$\mathcal{F}'_{D}[b,\xi] = \int d\mathbf{r} \left[ \frac{1}{2Y_{2}} \xi(\mathbf{r}) \nabla^{4} \xi(\mathbf{r}) + i\xi(\mathbf{r})\eta(\mathbf{r}) + E_{c} b^{2}(\mathbf{r}) \right] , \qquad (5.34)$$

where  $\eta(\mathbf{r}) \equiv \epsilon_{ij} \nabla_i b_j$ . The field  $\xi$  can be integrated out of the equilibrium distribution of the dislocation field  $b(\mathbf{r})$ 

$$\mathcal{P}[b] = \frac{\int \mathcal{D}[\xi] e^{-\mathcal{F}'_D[b,\xi]/k_B T}}{\int \mathcal{D}[\xi] \mathcal{D}[b] e^{-\mathcal{F}'_D[b,\xi]/k_B T}} = \frac{e^{-\mathcal{F}_D[b]/k_B T}}{\int \mathcal{D}[b] e^{-\mathcal{F}_D[b]/k_B T}} ,$$

where  $\mathcal{F}_D[b]$  in this equation is given by (5.33) as we will show below. Thus, the non-local interaction between the dislocations is introduced by integrating out the field  $\xi$ .

<sup>&</sup>lt;sup>1</sup>See Nelson and Halperin [79] for the mathematical details.

In Fourier space, the free energy (5.34) of the interacting dislocations is

$$\mathcal{F}'_{D} = \int \frac{dq}{(2\pi)^{2}} \left[ \frac{q^{4}}{2Y_{2}} \hat{\xi}(q) \hat{\xi}(-q) + i \hat{\xi}(q) \hat{\eta}(-q) + E_{c} \hat{b}(q) \cdot \hat{b}(-q) \right] \; .$$

With the change of variable

$$\hat{\xi}(q) = \hat{\psi}(q) - i \frac{Y_2}{q^4} \hat{\eta}(q)$$
 (5.35)

translates to

$$\mathcal{F}_{D}' = \int \frac{dq}{(2\pi)^{2}} \left[ \frac{q^{4}}{2Y_{2}} \hat{\psi}(q) \hat{\psi}(-q) + \frac{Y_{2}}{2q^{4}} \hat{\eta}(q) \hat{\eta}(-q) + E_{c} \hat{b}(q) \cdot \hat{b}(-q) \right]$$

The fields  $\psi$  and  $\eta$  are now separated and once  $\hat{\psi}(q)$  is integrated out, we end up with the desired form (5.33).

We assume now that the dynamics of  $\psi$  and b is entirely dissipative<sup>1</sup> and their motion is driven by the minimization of  $\mathcal{F}'_D$ . The dynamical equations read

$$\frac{\partial \hat{b}_x(q)}{\partial t} = -\Gamma_b q^2 \frac{\delta \mathcal{F}'_D}{\delta \hat{b}_x(-q)} = -\Gamma_b q^2 \left( \frac{Y_2}{q^4} \hat{\eta}(q)(-iq_y) + 2E_c \hat{b}_x(q) \right)$$
$$\frac{\partial \hat{b}_y(q)}{\partial t} = -\Gamma_b q^2 \frac{\delta \mathcal{F}'_D}{\delta \hat{b}_y(-q)} = -\Gamma_b q^2 \left( \frac{Y_2}{q^4} \hat{\eta}(q)(iq_x) + 2E_c \hat{b}_y(q) \right)$$

and

$$\frac{\partial \hat{\psi}(\boldsymbol{q})}{\partial t} = -\Gamma_{\psi} \frac{\delta \mathcal{F}_D'}{\delta \hat{\psi}(-\boldsymbol{q})} = -\Gamma_{\psi} \frac{q^4}{Y_2} \hat{\psi}(\boldsymbol{q}) \; ,$$

or in terms of the fields  $\xi$  using (5.35)

$$\begin{aligned} \frac{\partial \hat{b}_x(\boldsymbol{q})}{\partial t} &= -\Gamma_b \; q^2 \left( \frac{Y_2}{q^4} \hat{\eta}(\boldsymbol{q})(-iq_y) + 2E_c \, \hat{b}_x(\boldsymbol{q}) \right) \;, \\ \frac{\partial \hat{b}_y(\boldsymbol{q})}{\partial t} &= -\Gamma_b \; q^2 \left( \frac{Y_2}{q^4} \hat{\eta}(\boldsymbol{q})(iq_x) + 2E_c \, \hat{b}_y(\boldsymbol{q}) \right) \end{aligned}$$

and

$$rac{\partial \hat{\xi}(\boldsymbol{q})}{\partial t} = -\Gamma_{\psi}\left(rac{q^4}{Y_2}\hat{\xi}(\boldsymbol{q}) + i\hat{\eta}(\boldsymbol{q})
ight) - irac{Y_2}{q^4}rac{\partial \hat{\eta}(\boldsymbol{q})}{\partial t} \; .$$

,

<sup>&</sup>lt;sup>1</sup>In a recent paper, Rickman and Viñals [97] introduced a model of dislocation dynamics for the three-dimensional situation. They justify at length the choice of a dissipative dynamics as well as tackling the interesting situation where an external stress is present.

This dynamics does not discriminate between the glide and climb<sup>1</sup> motion of the dislocations. Also, we neglect the purely harmonic contribution to the free energy dissipation.

When the system has reached a steady state, the equation for  $\xi$  reduces to

$$\nabla^4 \xi(\boldsymbol{r}) = -iY_2 \eta(\boldsymbol{r}) = -iY_2 \epsilon_{lm} \nabla_l b_m(\boldsymbol{r})$$

Thus,  $\xi(\mathbf{r})$  is simply related to the Airy stress function

$$\xi(m{r})=i\chi(m{r})$$
 .

# 5.2.3 The Presence of a Liquid-Solid Interface

If one wished to study only a crystal with dislocations, working with (5.34), in other words introducing the field  $\xi$ , would be devoid of interest. The dynamical equations of the dislocation density can be derived directly from the free energy (5.33). The relevance of this method lies in the possibility of introducing an interface.

In the presence of a liquid/solid interface, one can use the same dislocation free energy

$$\mathcal{F}'_{D}[b,\xi,\phi] = \int d\mathbf{r} \left[ \frac{1}{2Y_{2}} \xi(\mathbf{r}) \nabla^{4} \xi(\mathbf{r}) + i\xi(\mathbf{r})\eta(\mathbf{r}) + E_{c} b^{2}(\mathbf{r}) \right] , \qquad (5.36)$$

where  $\eta$  is now given by  $\eta(\mathbf{r}) = \Phi(\mathbf{r})\epsilon_{lm}\nabla_l b_m$  with  $\Phi(\mathbf{r}) = \phi^2(\mathbf{r})$ .  $\phi$  is the phase-field chosen to be 0 in liquid and 1 in solid. Because of this coupling, the fields b and  $\xi$  decouple in the liquid phase. In this model, the liquid is described as a random distribution of dislocations that do not interact. Another approximation is made by having the same term  $1/Y_2$  for the solid and the liquid.

The algebra is very similar to the above. Following are the final equations for the dynamics of  $\xi$  and **b**:

$$\frac{\partial \hat{b}_x(\boldsymbol{q})}{\partial t} = -\Gamma_b q^2 \left( Y_2 \int \frac{d\boldsymbol{k}}{(2\pi)^2} \frac{\hat{\eta}(\boldsymbol{k})}{k^4} \hat{\Phi}(\boldsymbol{q}-\boldsymbol{k})(-iq_y) + 2E_c \, \hat{b}_x(\boldsymbol{q}) \right) ,$$
  
$$\frac{\partial \hat{b}_y(\boldsymbol{q})}{\partial t} = -\Gamma_b q^2 \left( Y_2 \int \frac{d\boldsymbol{k}}{(2\pi)^2} \frac{\hat{\eta}(\boldsymbol{k})}{k^4} \hat{\Phi}(\boldsymbol{q}-\boldsymbol{k})(iq_x) + 2E_c \, \hat{b}_y(\boldsymbol{q}) \right)$$

<sup>&</sup>lt;sup>1</sup>For a dislocation with a Burgers vector b and dislocation line l, the glide plane is defined as  $b \wedge l$ . It is particularly easy for the dislocation to move in this plane in a purely mechanical manner. This motion is called glide or conservative motion. It is different for climb or non-conservative motion. The climb takes place in the direction perpendicular to the Burgers vector. It requires the displacement of an entire plane of atoms and this is the reason why it is often neglected.

and

$$\frac{\partial \hat{\xi}(\boldsymbol{q})}{\partial t} = -\Gamma_{\psi} \left( \frac{q^4}{Y_2} \hat{\xi}(\boldsymbol{q}) + i\hat{\eta}(\boldsymbol{q}) \right) - i \frac{Y_2}{q^4} \frac{\partial \hat{\eta}(\boldsymbol{q})}{\partial t}$$

Following the model of Kobayashi [93] (section 3.3), the dynamics of the order parameter in real space is given by

$$\frac{\partial\phi}{\partial t} = \Gamma_{\phi} \left[ -\bar{\epsilon}^2 \frac{\partial}{\partial x} \left( \eta(\theta) \eta'(\theta) \frac{\partial\phi}{\partial y} \right) + \bar{\epsilon}^2 \frac{\partial}{\partial y} \left( \eta(\theta) \eta'(\theta) \frac{\partial\phi}{\partial x} \right) + \bar{\epsilon}^2 \nabla \cdot (\eta^2(\theta) \nabla \phi) 
+ \phi(1-\phi) \left( \phi - \frac{1}{2} + m(u) \right) + 2i\xi \phi \epsilon_{lm} \nabla_l b_m \right].$$
(5.37)

The equation of diffusion of heat is

$$\frac{\partial u}{\partial t} = \nabla^2 u + \frac{1}{\Delta} \frac{\partial \phi}{\partial t}$$

### 5.2.4 Numerical Simulations

As before, it is easier to integrate numerically the partial differential equations going into Fourier space. We use periodic boundary conditions throughout the simulations. For the dynamics of  $\phi$  and u, we choose  $\Gamma_{\phi} = 3.0$ ,  $\alpha = 0.9$ ,  $\delta = 10.0$ ,  $\gamma = 0.04$ ,  $\epsilon = 0.33$  and  $\Delta = 0.6$ . For the dynamics of b and  $\xi$ , the coefficients  $\Gamma_b$ ,  $\Gamma_{\chi}$ ,  $Y_2$  are set to unity throughout the simulations. Also,  $E_c = 0.05$ . The mesh size is taken to be  $\Delta x = \Delta y = 1.0$  whereas  $\Delta t$  varies for the different simulations depending on the system studied.

# Polygonization

Peach and Koehler [50] derived an expression for the force exerted on a dislocation line by a stress as well as an expression for the stress fields produced by the dislocations. This allows to describe the interaction between two dislocations. Let us consider two edge dislocations in the x - y plane and having their glide planes parallel to the x - zplane. If one dislocation  $b_1$  is along the z-axis, it exerts on the other dislocation  $b_2$  at the point  $(r, \theta)$ , a force whose component in the glide plane is

$$F_x = \frac{\mu}{2\pi(1-\nu)} b_1 b_2 \frac{\cos(\theta)\cos(2\theta)}{r} ,$$

where  $\nu = \lambda/2(\mu + \lambda)$  is the Poisson's ratio. It follows from this that if the dislocations have same signs,  $\theta = \pi/2$  is the stable configuration and if the dislocations have



Figure 5.9: Stable equilibrium of two edge dislocations. Left: the dislocations have same signs. Right: the dislocations have opposite signs.

opposite signs,  $\theta = \pi/4$  is the stable configuration as illustrated by figure 5.9. Hence, straight dislocations lying in parallel glide planes, and having same signs, will have the tendency to gather in one plane perpendicular to their glide planes and form a dislocation wall. This phenomena is known as polygonization.

In the model described above, the dynamics of b do not discriminate between the glide and climb motion. We expect however that some aspects of polygonization to be recovered. On the left side of figure 5.10, the time evolution of a simple system is shown. We start with two peaks of dislocation of value +1 and -1 places respectively at (16,16) and (48,32). It is important to stress that we work with a dislocation density, and hence the dislocations do not stay localized. As can be seen in this figure, the dislocations will organize in a stripe pattern. However, these vector graphs can be misleading because even if the length of the arrows do not vary much in time, the dislocation density reduces due to the annihilation of dislocations of opposite sign. To visualize the meaning of this pattern, it is more appropriate to consider the local orientation of the lattice.

The dislocation field produced by edge dislocations gives rise to an antisymmetric part in  $\partial_i u_i$  or, equivalently, to local rotations<sup>1</sup>

$$\theta(\boldsymbol{r}) = \frac{1}{2} (\partial_x u_y - \partial_y u_x) = \frac{1}{2\pi} \int d\boldsymbol{r}' \, \frac{\boldsymbol{b}(\boldsymbol{r}') \cdot (\boldsymbol{r} - \boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|^2} \; .$$

Upon Fourier transformation, it becomes

$$\hat{\theta}(q) = \frac{-iq \cdot \dot{b}(q)}{q^2} . \tag{5.38}$$

<sup>&</sup>lt;sup>1</sup>Nelson and Halperin [79]; Chaikin and Lubensky [95].



Figure 5.10: Dynamics of the dislocations. From top to bottom, the times are : 0, 300 and 1000. Left: configuration of the Burgers vector. Right: contour of the local orientation of the lattice as calculated from equation (5.38).

The local orientation of the lattice is shown on the right side of figure 5.10. As expected, the dislocations annihilate and the local orientation of the lattice reduces as time goes on.

Pileup



Figure 5.11: Dislocation pileup.

Let us consider a large number N of similar edge dislocations lying in the same glide plane and constrained by some obstacles (a lattice defect, a grain boundary or, as we will see, an interface) to a segment  $[-\ell/2, \ell/2]$  of the x axis. In the absence of an external applied field, the dislocations will repel each other and accumulate at the two ends as illustrated by figure 5.11. If N is large, we consider the dislocations to be continuously distributed, and look for their equilibrium distribution  $\mathcal{D}$ . It is known to be<sup>1</sup>

$$\mathcal{D}(x) = \frac{N}{\pi \left[ \left(\frac{\ell}{2}\right)^2 - x^2 \right]^{1/2}} \,. \tag{5.39}$$

As for the polygonization problem, the analytical results are derived for dislocations with a given glide plane. Our dynamics do not differentiate between the glide and climb and hence we expect to recover only qualitative behavior.

We start with the initial configuration illustrated by figure 5.12. Two squares of solids of width  $\ell = 20$  are placed in a liquid. Dislocations with Burgers vector pointing in the x and -x direction are placed in the middle of the squares. We choose to have two lines of Burgers vectors pointing in the opposite direction to obey the condition of zero total Burgers vector. On the lines,  $b_x(r) = \pm 1/\ell$  and  $b_y(r) = 0$ . The liquid is at a reduced temperature u = 0 so growth will not take place due to the undercooling. The results of the simulations are shown in figure 5.13. We observe along the line A the dislocation density. The distribution of dislocations given by equation (5.39) is also fitted on top of  $b_x$ . The only adjustable parameter in this <sup>1</sup>Kosevich [79]; Hirth and Lothe [82].



Figure 5.12: Initial configuration for the study of the pileup.

fitting is  $N/\pi$ . The dislocation density along A decreases in time due to the diffusion in the y direction. The dislocations distribution agrees well with the theoretical distribution at times  $t \simeq 5$ . Later, we believe that the differences between the actual dislocations distribution and the one assumed for deriving (5.39) (*i.e.*, dislocations constrained to their glide planes) are so large that any agreement is out of reach.

From this figure and also with the help of longer simulations, we can conclude that the interface acts like an obstacle. We have verified that the dislocations do not escape from the solid to annihilate with the dislocations of opposite sign in the other solid. In the language of electromagnetism, one can say that the liquid acts as an insulator. Also, one would expect that the solid domain would shrink to reduce the interfacial energy cost with a law  $v \sim 1/r$  where v is the velocity of the interface and r is the radius of curvature<sup>1</sup>. It is interesting to note that the dislocations trapped in the solid oppose this reduction of the domain size.

In the liquid, the dynamical equation for the **b** is  $\partial b(r)/\partial t = (2\Gamma_b E_c)\nabla^2 b(r)$ . Hence, the diffusivity  $2\Gamma_b E_c$  can be tuned by changing  $E_c$ . For a small value of  $E_c$ , the diffusion of the dislocations out into the liquid is suppressed and the interface acts as an obstacle. On the other hand, with a large value of  $E_c$ , this diffusion happens on shorter time scales. One would observe the dislocations leaving the solid.

<sup>1</sup>Allen and Cahn [79].



Figure 5.13: Numerical simulation of the dislocation pileup. The solid line corresponds to the x component of the dislocation density  $b_x$ . The dashed line is the fitted dislocations distribution as calculated from equation (5.39). The dotted line shows the position of the liquid/solid interface.

# Growth with a Dislocation Field

We demonstrate now the influence of the dislocations on the growth of the solid. We use the equation (5.37) to simulate the growth of a dendrite in the presence of dislocations.

In the liquid, we start with a random distribution of dislocations  $b_x = a\varrho_1$  and  $b_y = a\varrho_2$  where  $\varrho_1$  and  $\varrho_2$  are random numbers uniformly distributed in the interval  $\left[-\frac{1}{2},\frac{1}{2}\right]$  and a is the strength of the noise. We use a six-fold anisotropic surface tension.

Figure 5.14 illustrate the results. At small values of the dislocation density, these

defects do not influence greatly the growth. However, for higher values of this density, the defects act like a random noise at the interface and start to destroy the anisotropy.



Figure 5.14: Dendritic growth in presence of dislocations shown at t = 100. On the left: the phase field. On the right: a contour plot of |b|. Darker colors correspond to higher values of |b|. From top to bottom, the magnitude a of the noise increases: a = 0.05 and a = 0.1.

# CONCLUSION

6

In this thesis, we have developed some successful models of solidification by treating the solid phase in a more realistic manner than that has been done before. In chapter 3, we presented the recent phase-field models of dendritic solidification which have successfully reproduced some of the features of the dendritic growth. In the aim of accounting for elastic effect in solidification, we have extended these models by having a vectorial order parameter. This new model of polymorphous growth of dendrites allows for the existence of grain boundaries. First, this model was used to perform a study of the amorphization of a polycrystalline solid. Then, a slightly modified version was used to simulate the growth of dendrites of different orientations.

A study of a particular secondary instability in directional solidification, namely the vacillating-breathing mode, was performed in chapter 4 by using a phase-field model. The results of the simulations have shown qualitative agreements with the experiment of Cladis et al. [91]. In particular, the relation that the frequency of the vacillation is inversely proportional to the wavelengths ( $\omega \sim q$ ) was recovered. The reason for the apparent lack of selection in our results can be attributed to the fact that our simulations were performed on a small system with limited computer time. Thus it is necessary to carry out further studies of this phenomena on a larger system.

In chapter 5, we have addressed the influence of the elasticity on growth. At first, the strain field was coupled to the order parameter in a model A system. By assuming that the elastic field relaxes very fast, we have expressed it in terms of the order parameter. We have shown how this relatively simple coupling drastically modifies the growth and the morphology when anisotropy of the elastic field was taken into account. This simple model allows us to recover some of the experimental results of Grütter and Dürig [95], *i.e.*, the quasidendritic growth of Co deposited on a Pt(111)

### 6: CONCLUSION

surface. However, in order to facilitate our calculations, a four-fold anisotropy was used. In addition, the problem of the influence of the dislocation dynamics on the growth was tackled by introducing a model where the dislocation density field was coupled to the order parameter, and a passive field related to the Airy stress function. We have shown that this model can reproduce qualitatively well known phenomena of the dislocation theory such as the piling up. Furthermore, we have presented also qualitative results on the influence of this dislocation field on the growth.

The model of the dynamics of dislocations could be generalized in future works to take into account other effects such as the presence of an external stress and vacancies. It would be also interesting to investigate the influence of dislocations on the model of polymorphous growth that was introduced at the beginning of the thesis.

# APPENDICES

# A.1 Linear Stability of the Planar Front in Directional Solidification

Let c denote the concentration of the impurities. The diffusion of the concentration expressed in the laboratory frame is:

$$\frac{1}{D}\frac{\partial c}{\partial t} = \nabla^2 c + \frac{2}{\ell}\frac{\partial c}{\partial z} , \qquad (A.1)$$

where D is the diffusion constant assumed to be the same in the two phases,  $\ell \equiv 2D/v$  is the diffusion length and v is the pulling velocity. This equation is supplemented by the Gibbs-Thomson condition

$$T(\zeta) = T_M - mc_L - T_M d_0 \kappa , \qquad (A.2)$$

and the continuity condition

$$(\boldsymbol{v}\cdot\hat{\boldsymbol{n}})c_L(\zeta)(1-K) = D(\boldsymbol{\nabla}c_S - \boldsymbol{\nabla}c_L)\cdot\hat{\boldsymbol{n}}$$
(A.3)

Also, at the interface,

$$c_S(\zeta) = K c_L(\zeta) . \tag{A.4}$$

 $\hat{n}$  is a unit vector normal to the interface, pointing from the solid phase into the liquid phase,  $\zeta$  is the position of the interface, m is the absolute value of the liquidus slope, K is the partition coefficient,  $d_0$  is the capillary length, and  $\kappa$  is the curvature of the interface. Finally, the boundary conditions for c are

$$\lim_{z \to \infty} c_L = \lim_{z \to -\infty} c_S = c_0 . \tag{A.5}$$

There are three typical lengths in the system: the diffusion length  $\ell$ , the thermal length  $\ell_T \equiv \Delta T/G$  and the chemical capillary length  $\ell_c \equiv d_0 T_M / \Delta T$  where G is

the applied thermal gradient,  $\Delta T \equiv m \Delta c$  is the temperature difference between the liquidus and the solidus line at the concentration  $c_0$  and  $\Delta c = c_0(1 - K)/K$  is the equilibrium concentration gap (see figure 2.5 for the phase diagram).

The thermal profile is linear with a gradient G

$$T(z) = T_1 + Gz ,$$

where  $T_1$  is adjusted so that z = 0 corresponds to the position of the planar interface,  $\zeta_I$ . This planar interface solution is given by

$$c^L(z) = c_0 + \Delta c e^{-2z/\ell} ,$$
  
$$c^S(z) = c_0$$

and

$$\zeta_I(\boldsymbol{x},t)=0\;.$$

The perturbed solidification front takes the form

$$\zeta(\boldsymbol{x},t) = \zeta_I + \delta \zeta(\boldsymbol{x},t) \; .$$

Similarly, the perturbed concentration fields are

$$c^{L}(\boldsymbol{x}, z, t) = c_{0} + \Delta c \, e^{-2z/\ell} + \delta c^{L}(\boldsymbol{x}, z, t)$$

and,

$$c^{S}(\boldsymbol{x}, z, t) = c_{0} + \delta c^{S}(\boldsymbol{x}, z, t) .$$

We write the perturbations as the sum of their Fourier components

$$\delta c^{S}(\boldsymbol{x}, z, t) = \hat{c}^{S}(\boldsymbol{k}) e^{(i\boldsymbol{k}\cdot\boldsymbol{x}+\bar{q}z+\omega t)} ,$$
$$\delta c^{L}(\boldsymbol{x}, z, t) = \hat{c}^{L}(\boldsymbol{k}) e^{(i\boldsymbol{k}\cdot\boldsymbol{x}-qz+\omega t)} ,$$

and

$$\delta\zeta(\boldsymbol{x},t) = \hat{\zeta}(\boldsymbol{k}) e^{(i\boldsymbol{k}\cdot\boldsymbol{x}+\omega t)}$$

From the diffusion equation (A.1), we obtain

$$\omega \tau = \frac{(q\ell)^2}{2} - q\ell - \frac{(k\ell)^2}{2} = \frac{(\tilde{q}\ell)^2}{2} - \tilde{q}\ell - \frac{(k\ell)^2}{2}, \qquad (A.6)$$

where  $\tau = \ell/v$ .

In order to use the linearized version of the boundary conditions, we need the following approximations

$$T(\zeta) \simeq T(\zeta_I) + \frac{\partial T}{\partial z} \bigg|_{z=\zeta_I} \delta\zeta = T(0) + G \,\delta\zeta ,$$
  

$$\kappa = -\frac{\zeta_{xx}}{(1+\zeta_x^2)^{3/2}} \simeq k^2 \hat{\zeta}(k) ,$$
  

$$n_z = (1+\zeta_x^2)^{-1/2} \simeq 1 + \mathcal{O}(\delta\zeta^2) ,$$
  

$$n_x = -\zeta_x (1+\zeta_x^2)^{-1/2} \simeq \mathcal{O}(\delta\zeta)$$

and

$$\hat{\boldsymbol{n}}\cdot\boldsymbol{v}\simeq\boldsymbol{v}+\dot{\zeta}$$
.

Up to first order in the perturbation, the Gibbs-Thomson condition (A.2) gives

$$-m\hat{c}^{L}(\boldsymbol{k}) + \left[m\Delta c\left(\frac{2}{\ell}-\ell_{c}k^{2}\right)-G\right]\hat{\zeta}(\boldsymbol{k}) = 0$$

The continuity condition (A.3) leads to

$$\left(1-K-\frac{q\ell}{2}\right)\hat{c}^{L}(\boldsymbol{k})-\frac{\tilde{q}\ell}{2}\hat{c}^{S}(\boldsymbol{k})+2\frac{\Delta c}{\ell}\left(K+\frac{\omega\tau}{2}\right)\hat{\zeta}(\boldsymbol{k})=0$$

and finally (A.4)

$$K\hat{c}^{L}(\boldsymbol{k}) - \hat{c}^{S}(\boldsymbol{k}) - 2K\frac{\Delta c}{\ell}\hat{\zeta}(\boldsymbol{k}) = 0$$

We have to solve the set of equations

$$\begin{array}{rcl} -m \ \hat{c}^{L}(\mathbf{k}) & + (m\Delta c \left[2/\ell - \ell_{c}k^{2}\right] - G) \ \hat{\zeta}(\mathbf{k}) &= 0 \ , \\ (1 - K - q\ell/2) \ \hat{c}^{L}(\mathbf{k}) & -\tilde{q}\ell/2 \ \hat{c}^{S}(\mathbf{k}) & + 2\Delta c/(K + \omega\tau/2)/\ell \ \hat{\zeta}(\mathbf{k}) &= 0 \ , \\ K \ \hat{c}^{L}(\mathbf{k}) & - \hat{c}^{S}(\mathbf{k}) & - 2K\Delta c/\ell \ \hat{\zeta}(\mathbf{k}) &= 0 \ , \end{array}$$

with

$$\omega \tau = \frac{(q\ell)^2}{2} - q\ell - \frac{(k\ell)^2}{2} = \frac{(\tilde{q}\ell)^2}{2} - \tilde{q}\ell - \frac{(k\ell)^2}{2}$$

This set of equation has a non trivial solution if

$$-m\left[\tilde{q}K\Delta c + 2\frac{\Delta c}{\ell}\left(K + \frac{\omega\tau}{2}\right)\right] + \left[m\Delta c\left(\frac{2}{\ell} - \ell_c k^2\right) - G\right]\left[-\left(1 - K - \frac{q\ell}{2}\right) + K\frac{\tilde{q}\ell}{2}\right] = 0.$$

With the quasistationary approximation which amounts of neglecting  $\partial c/\partial t$  in (A.1), equation (A.6) reduces to

$$q\ell \simeq 1 + \sqrt{1 + (k\ell)^2} ,$$

and

$$\tilde{q}\ell \simeq 1 - \sqrt{1 + (k\ell)^2}$$
.

Also, we simplify further the problem by assuming that  $K \simeq 1$ . With these approximations, we finally get

$$\omega(k) = \frac{v}{\ell} \left[ \sqrt{1 + (k\ell)^2} (1 - \ell/\ell_T - \ell_c \ell k^2) - 1 \right] .$$

# A.2 Sharp-interface limit

The phase field equations are the following

$$\tau \frac{\partial \phi}{\partial t} = \epsilon^2 \nabla^2 \phi + \phi (1 - \phi) \left( \phi - \frac{1}{2} - m(u) \right)$$
(A.7)

and

$$\frac{\partial u}{\partial t} = \nabla^2 u + \frac{1}{\Delta} \frac{\partial \phi}{\partial t} . \tag{A.8}$$

Following Kobayashi [93], we write  $\tau = b\epsilon^2$  and  $m = \epsilon \gamma u/\sqrt{2}$ . We will obtain an interface equation in the limit of  $\epsilon$  tending to zero. For this, we use the method of matched asymptotic expansions<sup>1</sup>.

We divide our system in two subregions: 1. the *inner region* in the vicinity of the interface where the gradient of the order parameter is large and 2. the *outer region* in the bulk phases where the order parameter is approximatively constant.

# A. Outer solution

In this region where the variation of  $\phi$  is small and this variation is on an O(1) length scale, the solution is formally expanded in power of  $\epsilon$ ,

$$u = u^{(0)} + \epsilon u^{(1)} + \epsilon^2 u^{(2)} + \cdots$$

<sup>&</sup>lt;sup>1</sup>See for instance Caginalp and Fife [88] and Caginalp [89].

 $\operatorname{and}$ 

$$\phi = \phi^{(0)} + \epsilon \phi^{(1)} + \epsilon^2 \phi^{(2)} + \cdots$$

The leading order of the phase field equations (A.7) and (A.8) gives respectively,

$$\phi^{(0)}(1-\phi^{(0)})\left(\phi^{(0)}-\frac{1}{2}\right)=0$$
(A.9)

 $\operatorname{and}$ 

$$\frac{\partial u^{(0)}}{\partial t} = \nabla^2 u^{(0)} + \frac{1}{\Delta} \frac{\partial \phi^{(0)}}{\partial t} .$$
 (A.10)

The leading order solutions are given by  $\phi^{(0)} = 1$  and  $\phi^{(0)} = 0$  in the solid and the liquid respectively. For the temperature, we find the usual diffusion equation

$$\frac{\partial u^{(0)}}{\partial t} = \nabla^2 u^{(0)} . \tag{A.11}$$

# B. Inner solution

We introduce a local coordinate system based on a parameterization of the curve  $\phi(x, y, t) = 1/2$ . We use the arclength s as one of the local coordinates and r, the distance along the normal as the other coordinate. In the curvilinear coordinate system, the Laplacian and the time derivative take the following form:

$$\nabla^2 u = u_{rr} + \nabla^2 r \, u_r + |\nabla s|^2 u_{ss} + \nabla^2 s \, u_s \tag{A.12}$$

and

$$u_t = u_t + r_t \, u_r + s_t \, u_s \,. \tag{A.13}$$

We also introduce the scaled coordinate  $z = r/\epsilon$  and we write

$$u(x, y, t, \epsilon) \equiv U(z, s, t, \epsilon)$$
$$= U^{(0)}(z, s, t) + \epsilon U^{(1)}(z, s, t) + \cdots$$

and

$$\phi(x, y, t, \epsilon) \equiv \Phi(z, s, t, \epsilon)$$
$$= \Phi^{(0)}(z, s, t) + \epsilon \Phi^{(1)}(z, s, t) + \cdots$$

Now, the equations (A.7) and (A.8) can be written in the following form

$$\Phi_{zz} + \Phi(1-\Phi)\left(\Phi - \frac{1}{2}\right) + \epsilon \left\{\Phi(1-\Phi)\frac{\gamma}{\sqrt{2}}U - br_t\Phi_z + \nabla^2 r\Phi_z\right\} + \epsilon^2\{\cdots\} = 0 \quad (A.14)$$

and

$$U_{zz} + \epsilon \left\{ -r_t U_z + \frac{1}{\Delta} r_t \Phi_z + \nabla^2 r U_z \right\} + \epsilon^2 \{ \cdots \} = 0 .$$
 (A.15)

### 1. Matching conditions

Matching conditions provide the far field boundary condition for the inner solution<sup>1</sup>. The outer solution is written as a function of the inner variables and the resulting expressions are expanded in  $\epsilon$ . We drop the *s* variable since the matching conditions are with respect to only the coordinate orthogonal to the interface layer. Near the layer, we formally equate the two expansions

$$U(z, t, \epsilon) = u(\Gamma(t, \epsilon) + \epsilon z, t, \epsilon) , \qquad (A.16)$$

where  $z = (x - \Gamma(t, \epsilon))/\epsilon$  is the scaled coordinate and  $\Gamma(t, \epsilon)$  is the equation of the interface. The right hand side of (A.16) is expanded in a Taylor series in  $\epsilon$ 

$$U(z,t,\epsilon) = \sum_{n=0}^{N} \epsilon^n P_n(z,t) + \epsilon^{N+1} R_N , \qquad (A.17)$$

where

$$P_n(z,t) \equiv \frac{1}{n!} \frac{\partial^n}{\partial \epsilon^n} u(\Gamma(t,\epsilon) + \epsilon z, t, \epsilon)|_{\epsilon=0} .$$
 (A.18)

Matching is accomplished by letting  $\epsilon \to 0$  and  $z \to \pm \infty$  provided that  $\epsilon z^{N+1} \to 0$ . With this constraint, the remainder term in equation (A.18) is of lower order than any of the preceding terms.

The two first matching conditions are

$$U^{(0)}(\pm\infty,t) = P^{0}_{\pm}(\pm\infty,t) = u^{(0)}(\Gamma^{(0)}_{\pm},t)$$
(A.19)

and

$$U^{(1)}(z,t) = u^{(1)}(\Gamma_{\pm}^{(0)},t) + z u_r^{(0)}(\Gamma_{\pm}^{(0)},t) + \Gamma^{(1)}(t)u_r^{(0)}(\Gamma_{\pm}^{(0)},t)$$
(A.20)  
with  $z \to \pm \infty$ .

<sup>1</sup>Caginalp and Fife [88].

### 2. Leading order solution

The leading order solutions takes the form

$$U_{zz}^{(0)} = 0 (A.21)$$

and

$$\Phi_{zz}^{(0)} + \Phi^{(0)}(1 - \Phi^{(0)}) \left(\Phi^{(0)} - \frac{1}{2}\right) = 0.$$
 (A.22)

Using the matching condition (A.19) we have  $U^{(0)} = c(s, t)$  for the temperature.  $U^{(0)}$  is independent of the normal coordinate. The leading order solution of the phase field is

$$\Phi^{(0)}(z,s,t) = \frac{1}{2} \left\{ 1 - \tanh\left(\frac{z}{2\sqrt{2}}\right) \right\} .$$
 (A.23)

# 3. First-order solution

The first-order inner equation has the form

$$U_{zz}^{(1)} = r_t^0 \frac{1}{\Delta} \Phi_z^{(0)} , \qquad (A.24)$$

$$\mathcal{L}\Phi^{(1)} \equiv \Phi_{zz}^{(1)} + \Phi^{(1)} \left( 3\Phi^{(0)} - 3\left(\Phi^{(0)}\right)^2 - \frac{1}{2} \right)$$
  
=  $\Phi^{(0)} (\Phi^{(0)} - 1) \frac{\gamma}{\sqrt{2}} U^{(0)} - b v^{(0)} \Phi_z^{(0)} - \kappa^{(0)} \Phi_z^{(0)}$ . (A.25)

where we have used the normal velocity of  $\Gamma$ ,  $v = -r_t$  and its curvature,  $\kappa = \nabla^2 r$ .

Integration of equation (A.24) gives

$$U_z^{(1)} = -v^{(0)} \frac{1}{\Delta} \Phi^{(0)}(z) + d(s,t) .$$
 (A.26)

Using the matching condition (A.20)

$$\lim_{z \to \pm \infty} U_z^{(1)}(z,t) = u_r^{(0)}(\Gamma_{\pm}^0,t) , \qquad (A.27)$$

we get the appropriate heat balance condition

$$-v^{(0)}\frac{1}{\Delta} = [u_r^{(0)}]_{\Gamma_{\pm}^0}$$
(A.28)

Differentiation of (A.22) respect to z shows that  $\Phi_z^{(0)}$  is a homogeneous solution of (A.25), *i.e.*  $\mathcal{L}\Phi_z^{(0)} = 0$ . The right-hand-side of this equation must then be orthogonal to this function. This is known as the Fredholm alternative<sup>1</sup>. It provides the solvability condition

$$\int_{-\infty}^{+\infty} \Phi_z^{(0)} \left\{ \Phi^{(0)}(\Phi^{(0)} - 1) \frac{\gamma}{\sqrt{2}} U^{(0)} - b v^{(0)} \Phi_z^{(0)} - \kappa^{(0)} \Phi_z^{(0)} \right\} dz = 0 .$$
 (A.29)

Noticing that  $\Phi_z^{(0)} = \Phi^{(0)}(\Phi^{(0)} - 1)/\sqrt{2}$ , we get the Gibbs-Thomson equation

$$\gamma u^{(0)}(\Gamma_{\pm}, t) = -\kappa^{(0)} - b v^{(0)} . \tag{A.30}$$

<sup>&</sup>lt;sup>1</sup>See for example Haberman [87].

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IMAGE EVALUATION TEST TARGET (QA-3)







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