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# Study of Stress-Induced Morphological Instabilities

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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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Für meine Eltern.

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## Résumé

Nous proposons un model pour étudier un méchanisme de relaxation des contraintes à une interface libre d'un solide sous contraintes non-hydrostatique, communement observé dans la croissance de films minces. Nous utilisons une approche Ginzburg-Landau. Cette instabilité évoluante dans le temps, connue sous le nom d'instabilité de Grinfeld, est d'une grande importance technologique. Elle peut être associée au mode de croissance par epitaxy d'ilôts sur couche sans dislocation, un procédé essentiel utilisé dans l'industrie de semi-conducteurs.

Dans notre model, le champ élastique est couplé à un paramètre d'ordre de telle façon que le solide puisse supporter les forces de cisaillement tandis que le liquide ne le puisse pas. Ainsi, le paramètre d'ordre est défini clairement dans le contexte de la transition entre les phases liquide et solide.

Nous montrons que, dans les limites appropriées, notre model est réduit à l'équation d'interface droite, ce qui est la formulation traditionelle du problème. Le traitement des non-linéarités est inhérent à notre description. Il évite les déficiences numériques des approches précédentes et permet des études numériques en deux et trois dimensions.

Pour tester notre model, nous faisons une analyse numérique de la stabilité linéaire et obtenons une relation de dispersion qui est en accord avec les résultats analytiques. Nous étudions le régime non-linéaire en mesurant la transformé de Fourier de la fonction de corrélation de crète à crète. Lorsque la contrainte est levée, nous observons que les structures interfaciale correspondant à différents nombres d'onde deviennent plus grossières. Nous nous attendons à ce que nos résultats sur les phénomènes transitoires de diminution des fréquences spatiales soient mesurables par microscopie ou par la diffraction de rayons X.

#### ABSTRACT

We propose a model based on a Ginzburg-Landau approach to study a strain relief mechanism at a free interface of a non-hydrostatically stressed solid, commonly observed in thin-film growth. The evolving instability, known as the Grinfeld instability, is of high technological importance. It can be associated with the dislocation-free island-on-layer growth mode in epitaxy which is an essential process used in the semiconductor industry.

In our model, the elastic field is coupled to a scalar order parameter in such a way that the solid supports shear whereas the liquid phase does not. Thus, the order parameter has a transparent meaning in the context of liquid-solid phase transitions.

We show that our model reduces in the appropriate limits to the sharp-interface equation, which is the traditional formulation of the problem. Inherent in our description is the proper treatment of non-linearities which avoids the numerical deficiencies of previous approaches and allows numerical studies in two and three dimensions.

To test our model, we perform a numerical linear stability analysis and obtain a dispersion relation which agrees with analytical results. We study the non-linear regime by measuring the Fourier transform of the height-height correlation function. We observe that, as strain is relieved, interfacial structures, corresponding to different wave numbers, coarsen. Furthermore, we find that the structure factor shows scale invariance. We expect that our result on transient coarsening phenomena can be measured through microscopy or x-ray diffraction.

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Study of Stress-Induced Morphological Instabilities

## INTRODUCTION

1

It has long been realized that mechanical and optical properties, as well as electronic performances of many materials, are strongly influenced by their micro-structure. This micro-structure includes features such as the atomic and crystallographic arrangements, the nature and density of defects, as well as the degree of chemical homogeneity. Understanding the basic mechanisms responsible for micro-structural changes is therefore of technological and scientific interest. It is, and has been, an active field of research, which comprises different disciplines, such as chemistry, metallurgy, crystal growth, material science and physics.

Traditional studies have been focused primarily on symmetries of atomic arrangements, surface anisotropies, and, more generally, on those near-equilibrium properties which are dominated by atomic and crystallographic effects. However, the formation of complex solidification patterns is intrinsically a non-equilibrium phenomena, and hence has a dynamical origin. The reason is that diffusion coefficients in solids are very small: at room temperature they are typically of order  $10^{-11} - 10^{-13} cm^2/s$ , implying that only crystals of small dimensions, i.e., in the micron range, can evolve on run-of-the-mill time scales of no more than the order of a few hours to their equilibrium shape, which minimizes the thermodynamic potential. A typical example is a dendrite, which is a tree-like or snowflake-like micro-structure. Its characteristics are quasi-periodic branches, which, as they grow, emit secondary branches. Another example is directional solidification, in which a dilute alloy is pulled at a given velocity in an externally imposed temperature gradient. If the pulling velocity v exceeds a threshold velocity  $v_c$ , cellular structures emerge. The threshold velocity depends on the thermal gradient and the impurity concentration, and is typically  $v_c \geq 1 \mu m/s$ . As a consequence, the solid alloy becomes inhomogeneous and periodic patterns perpendicular to the growth front appear whose typical scales are in the  $50 - 100 \mu m$  range.

For practical reasons, metallurgists would like to be able to predict how dynamical growth conditions influence the structure of the growing solids. Then one would know what kind of growth method and condition should be chosen to either avoid as much as possible deformations of the solidification front, which results in inhomogeneity, or to control conditions to grow structure with desired properties. Hence, one must understand the underlying mechanisms for the growth of these self-organized structures. Also, geologists and geophysicists are interested in these issues, although from a slightly different perspective. They are less interested in controlling the growth process, since this is impractical in geophysics. However, they may be able to obtain, at least qualitatively, information from some rock structures about the conditions which prevailed when they grew.

More recently, solidification has become a subject of interest for condensed matter physicists and statistical physicists due to its non-equilibrium character. Growth front morphologies are a subclass of the general problem of pattern formation in dissipative systems. Other well studied examples<sup>1</sup> are found, in hydrodynamics such as Rayleigh-Bénard convection, in chemistry with the Belousov-Zhabotinsky reactions as prototypes, in laser physics, and so on. These examples have the common characteristics that their final state is a non-equilibrium one, and the evolving pattern is a consequence of their non-equilibrium boundary conditions. However, the systems we shall study evolve towards thermodynamic equilibrium, implying that a well defined free energy functional exists, which provides the driving force for the dynamical evolution. A central question in pattern formation is to understand how patterns emerge from a structureless environment and what determines the selection, if any, of the observed structures. One would like to find a general selection principle for out-of-equilibrium systems which would play the same role as the free-energy minimization principle for systems in equilibrium. Although no general scheme for the behavior of out-of-equilibrium processes has been identified, some phenomena appear to be "generic", while some are controlled by microscopic properties of the system

<sup>&</sup>lt;sup>1</sup>Cross and Hohenberg [93].

under study. Generally growth patterns evolve on long length scales, typically, in the  $10 - 100\mu m$  range, and long time scales, implying a "mesoscopic" or continuum description. On this scale, which is large enough that the details of atomic organization and motion do not appear explicitly, it is sufficient to describe solidification simply as a first-order transition.

The basic model of solidification is a phenomenological, minimal model which is based on the release of latent heat at the transition. The moving solid-liquid interface can therefore be viewed as a source (or sink) of heat which, once produced, diffuses to the adjacent phase. If transport did not take place, heat would accumulate close to the front and the temperature would rise so that the liquid would become locally stable again and the solidification process would stop. Thus, there is a dynamical balance between production and transport of heat. This is responsible for the growth modes for given external conditions. This basic model of solidification usually gives rise to a morphological instability, the *Mullins-Sekerka instability*, which drives a pattern-forming process and characteristically produces dendrites.

Many features of the solidification process are generic to first-order transitions and hence are also observed in micro-structures, thermodynamically metastable states which evolve with time. The driving force for their temporal evolution usually consists of one or more of the following:

- A reduction in the bulk-chemical free energy.
- A decrease of the total interfacial energy between different phases or between different orientation domains or grains of the same phase.
- Relaxation of elastic-strain energy generated by the lattice mismatch between different phases or different orientation domains.
- External fields such as applied stress, electrical, temperature, and magnetic fields.

Asaro and Tiller [72] predicted a different morphological instability which is induced by stress. Like the Mullins-Sekerka instability, it is a long wavelength instability. Experimentally it was observed for the first time by Torii and Balibar [92]. It is also associated with the dislocation-free island-on-layer growth, a growth mode which is encountered in epitaxy. The instability is technologically relevant, since the stability of strained epitaxial films is of fundamental importance to the fabrication of modern electronic devices. Although much research<sup>1</sup> has been dedicated to the study of this stress-induced morphological instability in the last decade, it is much less well understood than the Mullins-Sekerka instability. Little is known about the non-linear regime. An analytical treatment is intricate since the elastic fields are tensorial quantities which are of long range. A systematic numerical study has been impossible due to numerical instabilities which are encountered at very early times<sup>2</sup>. Hence, basic questions, such as whether the instability eventually settles to a steady state or coarsens indefinitely have not been answered yet. We will propose another model to study this stress-induced instability, or Grinfeld instability as it is often referred to, which is based on a Ginzburg-Landau approach. Such an approach has previously been used very successfully to study dendritic growth and other manifestations of the Mullins-Sekerka instability.

Different methods have been employed to study the basic model of solidification and the dynamics of phase transformations. They are either based on a kinetic interface equation with appropriate boundary conditions, or on a Ginzburg-Landau approach, which is a field theoretical description. Both formulations have their merits and drawbacks. The interface formulation, being the conventional method for the treatment of phase changes, is often the most convenient form for analytical calculations. In this formalism, a multi-phase and/or multi-domain heterogeneous micro-structure is characterized solely by the geometry of sharp interfacial boundaries between structural domains of different orientations. These boundaries are mathematical interfaces of zero thickness. The phases and domains are assumed to have fixed composition and structure. The dynamical evolution of a micro-structure is then obtained by solving a set of differential equations in each phase and/or domain with boundary conditions specified at the interfaces that are moving with time. However, for complicated micro-structures, such as a *moving-boundary* or *free-boundary* 

<sup>&</sup>lt;sup>1</sup>Nozières [93]; Spencer, Voorhees and Davis [93]; Spencer, Davis and Voorhees [93]; Spencer and Meiron [94]; Kassner and Misbah [94].

<sup>&</sup>lt;sup>2</sup>Spencer, Davis and Voorhees [93]; Spencer and Meiron [94].

problem, it is impossible to solve analytically and very difficult to solve numerically. Moreover, different processes (e.g. phase transformations, grain growth, and Ostwald ripening) have usually been treated separately using different physical models. The field theoretical description, referred to as a phase-field or diffuse-interface model, overcomes the numerical difficulties and hence is a convenient method to model solidification processes and micro-structural evolution. The basic idea behind this approach is to replace the dynamics of the boundary by an equation of motion for a phase-field which is constant in the bulk phases but changes smoothly but quickly across a thin interfacial region. Thus, the explicit interfacial motion is described by, for example, two coupled partial differential equations, one for the temperature and the other for the phase-field. 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 *model* C together with two other dynamical models, namely model A and model B, that are often encountered in the study of critical phenomena. They also describe dynamical properties near a first-order transitions such as nucleation, spinodal decomposition, late stage growth and coarsening. A typical situation is a rapid quench from a one-phase, thermal equilibrium state to a two-phase, nonequilibrium state within a coexistence curve. Once initiated by spatial fluctuations, such a quenched system gradually evolves from this non-equilibrium state through a sequence of highly inhomogeneous states, which are far-from-equilibrium, to an equilibrium thermodynamic state which consists of two coexisting phases.

One might criticize the phenomenological level of description, and wonder if a microscopic description derived from first principles combined with a numerical simulation method is not a more rigorous approach. However, the pattern and instabilities we are interested in evolve on time and length scales which are not accessible by molecular dynamics methods. State-of-the-art molecular dynamics simulations allow systems sizes of up to  $10^9$  particles, which translates to 500 Ångström for three dimensions and up to  $0.5 \,\mu m$  for two dimensions. The time scale they may achieve is  $10^{-7}$  s. Furthermore, we expect details at the microscopic level to be irrelevant, and hence it does not seem promising that such a microscopic approach will help understand the underlying physical mechanism.



Figure 1.1: Sketch of double-well potential:  $f(\phi) = -\frac{r}{2}\phi^2 + \frac{u}{4}\phi^4$ . On the left, where, r < 0 and only one stable minimum exists at  $\phi \cong 0$ , the system is disordered. On the right, where r > 0 and two stable minima exist at  $\phi \cong \pm \sqrt{r/u}$ , the system is ordered.

## 1.1 Field Theoretical Models

The field theoretical description of non-equilibrium dynamics is a semi-phenomenological approach in which one focuses attention on a small set of semi-macroscopic variables, whose dynamical evolution is slow compared to the remaining microscopic degrees of freedom. Using either phenomenological arguments, or formal projection-operator techniques, dynamical equations of motion for the slow variables are obtained in which the remaining microscopic fast variables enter only in the form of random forces. Central to this approach is the coarse-grained Ginzburg-Landau free energy functional  $\mathcal{F}$  of the order parameter  $\phi$ :

$$\mathcal{F}\{\phi\} = \int d\vec{r} \left[\frac{l_{\phi}}{2}|\nabla\phi|^2 + f(\phi)\right],\tag{1.1}$$

where  $l_{\phi}$  is a positive constant and the function  $f(\phi)$  is

$$f(\phi) = -\frac{r}{2}\phi^2 + \frac{u}{4}\phi^4, \qquad (1.2)$$

where u is a positive constant. If r > 0,  $f(\phi)$  has a double well structure with two degenerate stable minima which correspond to the two phases coexisting at equilibrium. For r < 0 only one stable minimum exists. Hence, r is a control parameter determining whether the system is disordered ( $\phi \approx 0$ ) or in an ordered phase ( $\phi \approx \pm \sqrt{r/u}$ ). Figure 1.1 shows a sketch of the two cases.

Model A, in Hohenberg and Halperin [77] notation, describes the dynamics of a non-conserved order parameter  $\phi$ , which reflects the degree of local order in the system. Its equation of motion is given by:

$$\frac{\partial \phi(\vec{r},t)}{\partial t} = -\Gamma \frac{\delta \mathcal{F}}{\delta \phi(\vec{r})} + \xi(\vec{r},t), \qquad (1.3)$$

where  $\Gamma$  is a mobility, and  $\xi$  is thermal noise. By replacing  $\mathcal{F}$  by equation (1.1) we obtain

$$\frac{\partial \phi(\vec{r},t)}{\partial t} = -\Gamma \left[ \frac{\partial f}{\partial \phi} - l_{\phi}^2 \nabla^2 \phi \right] + \xi(\vec{r},t), \qquad (1.4)$$

which describes relaxational dynamics driven by a thermodynamic force  $\partial f/\partial \phi$  and a noise term  $\xi(\vec{r}, t)$ . The noise is assumed to be Gaussian and white, generated by the fast microscopic variables. Its mean  $\langle \xi(\vec{r}, t) \rangle = 0$ , and its correlation function

$$<\xi(\vec{r},t)\xi(\vec{r}',t')>=D\,\delta(\vec{r}-\vec{r}')\delta(t-t'),$$
(1.5)

where D is a constant, which is related to the temperature T and the strength of the dissipation  $\Gamma$  via the fluctuation-dissipation relation:

$$D = 2\,\Gamma\,k_B\,T,\tag{1.6}$$

where  $k_B$  is the Boltzmann constant. Typically, model A is used to describe the dynamics of binary alloys undergoing order-disorder transitions as well as magnetic phase transitions. Equation (1.4) without the noise term is known as the Allen-Cahn equation. Contrary to the dynamics of critical phenomena, where thermal fluctuations are essential to understand the basic physics of second order phase transitions, thermal noise often plays a minor role in pattern forming systems. since the length and energy scales of interest are normally very large.

If the order parameter is conserved, its dynamics is more constrained. A typical example is the phase separation of a binary alloy, after a quench from a high temperature homogeneous phase to a two phase system at lower temperature. The concentration of one alloy component is the order parameter  $\phi$ . The continuity equation

$$\frac{\partial \phi}{\partial t} = -\nabla \cdot \vec{j}(\vec{r}, t), \qquad (1.7)$$

describes the conservation of material. The diffusion current  $\vec{j}(\vec{r},t)$  is given by:

$$\vec{j}(\vec{r},t) = -\Gamma \nabla \frac{\delta \mathcal{F}}{\delta \phi(\vec{r})},\tag{1.8}$$

where  $\Gamma$  is a kinetic coefficient. The functional derivative on the right hand side of the equation describes a local chemical potential. The free energy functional is again given by equation (1.1). Upon substituting equation (1.1) in equation (1.8) we obtain a dynamical equation of motion for the conserved order parameter:

$$\frac{\partial \phi(\vec{r},t)}{\partial t} = \Gamma \nabla^2 \left[ -l_{\phi}^2 \nabla^2 \phi + \frac{\partial f}{\partial \phi} \right].$$
(1.9)

This equation was studied by Cahn and Hilliard [58] and is called the Cahn-Hilliard equation. Cook [70] realized that to achieve the correct statistical description of the alloy dynamics a noise term had to be added:

$$\frac{\partial \phi(\vec{r},t)}{\partial t} = \Gamma \nabla^2 \left[ -l_{\phi}^2 \nabla^2 \phi + \frac{\partial f}{\partial \phi} \right] + \xi(\vec{r},t).$$
(1.10)

This equation is known as Cahn-Hilliard-Cook equation, or, within the classification scheme of Hohenberg and Halperin [77], as model B.  $\xi(\vec{r}, t)$  is a Gaussian white noise with zero mean and the correlation function:

$$<\xi(\vec{r},t)\xi(\vec{r}',t')>=-2\Gamma k_B T \nabla^2 \delta(\vec{r}-\vec{r}') \,\delta(t-t').$$
 (1.11)

Model C describes the dynamics of a system with two coupled dynamical variables, a non-conserved order parameter  $\phi$  and a conserved variable c:

$$\frac{\partial \phi(\vec{r},t)}{\partial t} = -\Gamma \left[ \frac{\partial f}{\partial \phi} - l_{\phi}^2 \nabla^2 \phi \right] + \xi_{\phi}(\vec{r},t), \qquad (1.12)$$

and

$$\frac{\partial c(\vec{r},t)}{\partial t} = \Gamma \nabla^2 \left[ \frac{\partial f}{\partial c} - l_c^2 \nabla^2 c \right] + \xi_c(\vec{r},t), \qquad (1.13)$$

where  $\xi_{\phi}(\vec{r}, t)$  and  $\xi_{c}(\vec{r}, t)$  are Gaussian white noise with zero mean and the correlation functions:

$$\langle \xi_{\phi}(\vec{r},t)\xi_{\phi}(\vec{r}',t')\rangle = 2\Gamma_{\phi}k_BT\delta(\vec{r}-\vec{r}')\delta(t-t'), \qquad (1.14)$$

and

$$<\xi_{c}(\vec{r},t)\xi_{c}(\vec{r}',t')>=-2\Gamma_{c}k_{B}T\nabla^{2}\delta(\vec{r}-\vec{r}')\delta(t-t')$$
. (1.15)

The variable c and  $\phi$  are coupled through a term in the free energy which has to be motivated in much the same way as the other terms of the free energy. A typical example is:

$$f(\phi) = -\frac{1}{2}\phi^2 + \frac{1}{4}\phi^4 + c\phi^2 + \frac{c^2}{2}.$$
 (1.16)

## 1.2 Overview of thesis

In the following three chapters we introduce and review the main concepts and notions which are going to be used to study and analyze the stress-induced morphological instability in chapter 6, the main subject of original research in this thesis. This instability was first predicted by Asaro and Tiller [72]. However, since its rediscovery by Grinfeld [86], it is often called the Grinfeld instability. We will follow this nomenclature.

In chapter 2 the Mullins-Sekerka instability is summarized. An understanding of the physical mechanism underlying the Mullins-Sekerka instability will be helpful in understanding the Grinfeld instability. Further, concepts and methods being successfully employed in the study of the Mullins-Sekerka instability, such as linear stability analysis, can be used to investigate the Grinfeld instability. We will also give some typical examples of where the Mullins-Sekerka instability is encountered.

Chapter 3 outlines and discusses the phase-field model in the context of dendritic growth, where it has been studied intensively. We show how the phase-field model is related to the sharp-interface equations.

Chapter 4 introduces the structure factor as a convenient measure to study coarsening, a late stage phenomena characteristic of first-order transitions. During this stage the dynamics of a phase-ordering or phase separating system is highly nonlinear and mainly driven by interfacial energy. The concept of dynamical scaling and its application is also presented.

In chapter 5 we explain the basic mechanism of the Grinfeld instability and provide experimental evidence. Traditional approaches and formulations of the Grinfeld instability and their results are summarized.

In chapter 6 we propose a new model for the Grinfeld instability which is based on a Ginzburg-Landau approach<sup>1</sup>. The model is first motivated and discussed. An asymptotic expansion is performed which shows that in the sharp-interface limit, the sharp-interface equation of the traditional approach are recovered. The model is then analyzed numerically in two and three dimensions. The thesis ends with a conclusion in chapter 7.

<sup>&</sup>lt;sup>1</sup>Müller and Grant [98].



## Mullins-Sekerka Instability

The Mullins-Sekerka instability is a thermally induced morphological instability which can be observed during the solidification of a pure substance from its undercooled melt. Since it is the simplest model which comprises an interfacial (morphological) instability which drives a pattern-forming process, it is a prototype of pattern forming systems. It has has been intensively studied in the last three decades. Good introductions and review articles have been written by Langer<sup>1</sup>. Mullins and Sekerka [63] were the first to perform linear stability analyses which characterized the instability and pointed out the underlying kinetic nature of the process.

## 2.1 Basic Model of Solidification

The basic model of solidification describes the propagation of a solid into an undercooled liquid. During this process, latent heat is generated at the solidification front. This heat must diffuse away before further solidification can take place. Hence, the rate limiting process is the propagation of heat, which is described by the following diffusion equation:

$$\frac{\partial u}{\partial t} = D \,\nabla^2 u \,, \tag{2.1}$$

where  $u = c_P \frac{T-T_M}{L}$  denotes the dimensionless temperature field.  $T_M$  is the melting temperature, L is the latent heat of melting,  $c_P$  is the specific heat at constant pressure, and D is the thermal diffusion coefficient, which in the simplest limit, the symmetric model, is the same in the liquid and solid phases. To complete the specification of the model, the following boundary conditions at the solidification front

<sup>&</sup>lt;sup>1</sup>Langer [80]; Langer [87]; Langer [89]; Langer [92].



Figure 2.1: Sketch of the solid-liquid interface.

have to be introduced:

$$v_n = D\left[ (\nabla u)^s - (\nabla u)^l \right] \cdot \vec{n} \,, \tag{2.2}$$

which implies that the normal velocity component  $v_n$  is determined by the condition of conservation of heat. Here,  $\vec{n}$  is the unit normal pointing from the solid (s) towards the liquid (l) as shown in figure 2.1. The temperature at the interface is determined by:

$$u_i = -d_0 \kappa_c - \beta(v_n) , \qquad (2.3)$$

which is the dynamical *Gibbs-Thomson condition*. The first term on the right hand side describes the Gibbs-Thomson condition which assumes local mechanical equilibrium at the interface. It accounts for the change in temperature due to a surface characterized by the curvature  $\kappa_c$ , being defined positive for a convex solid.  $d_0 = \frac{\gamma T_M c_P}{L^2}$ is the capillary length, which is proportional to the surface tension  $\gamma$  and typically of the order of a few Angström. The second term corrects for the departure from local equilibrium associated with the motion of the interface. Often a linear law is assumed,  $\beta(v_n) = \beta_0 v_n$ .  $\beta_0 = 0$  would describe the limit of pure diffusion control. which is the case of rough interfaces, in which the attachment of molecules of the liquid onto the solid-liquid interface can be assumed as quasi-instantaneous, *i.e.*, much faster (~  $10^{-12}s$ ) than the time the interface requires to grow by one atomic layer (typically the velocity of the interface is of the order of  $10\mu m/s$ , which implies a time of the order of  $10^4 s$ ). The above equations, supplemented by initial conditions and boundary conditions far from the solidification front, constitute a closed mathematical model of moving-boundary or free-boundary type. It is known as the modified Stefan model which has been studied extensively by mathematicians.

Figure 2.2 illustrates schematically why the solidification model develops a morphological instability. Comparing a planar solidification front with a deformed in-



Figure 2.2: Schematic illustration of Mullins-Sekerka instability. The solid line marks the solid-liquid interface, whereas the dashed lines mark isotherms.

terface shows that a forward bulge steepens the thermal gradient ahead in the fluid, implying that heat can diffuse away more rapidly in front of the bulge. Hence, the bulge grows faster and faster. This instability is compensated by the stabilizing effect of surface tension, which tries to minimize the surface area. A way to quantitatively characterize the instability is via a dispersion relation which is obtained from a systematic linear stability analysis.

## 2.2 Linear Stability Analysis

Linear stability analysis determines whether a small perturbation of wavelength  $\lambda$  of the steady-state planar interface will grow in time, in which case the interface is unstable, or whether it will decay, in which case it will be stable. First, the planar steady-state solution has to be determined. In the reference frame moving in the z direction with the interfacial velocity v, the steady-state diffusion equation has the following form:

$$\nabla^2 u + \frac{2}{l} \frac{\partial u}{\partial z} = 0, \qquad (2.4)$$

where  $l = \frac{2D}{v}$  is the diffusion length. Its solution for the boundary conditions (2.2) and (2.3) is given by:

$$u(z) = \begin{cases} \exp(-\frac{2z}{l}) - 1 & \text{for } z > 0 \text{ (liquid)} \\ 0 & \text{for } z < 0 \text{ (solid)}, \end{cases}$$

where the flat interface has been placed at z = 0. Note that the steady-state solution exists for any positive v, but requires a unit undercooling at infinity; that is,  $u \to -1$ as  $z \to -\infty$ . This implies that the latent heat released at the solidification front is equal to the heat necessary to bring the temperature of the liquid from  $T_{\infty}$  to  $T_M$ . However, if the undercooling at infinity is smaller than unity, only a fraction of the latent heat is absorbed by the solid, and hence heat builds up in front of the interface and no planar steady-state solution exists.

The linear stability analysis can be performed in complete generality<sup>1</sup>. However, here the "quasi-stationary approximation", a valid approximation in most situations of interest, is used. In that case it is assumed that the relaxation of the diffusion field is much faster than the motion of the interface. Hence, the problem can be solved approximately by first solving the time-independent diffusion equation (2.4), subject to the thermodynamic boundary condition (2.3) on the quasi-stationary interface  $\xi(x, t)$ , and then inserting this result into the continuity condition (2.2) to find an explicit expression for  $\partial \xi / \partial t$ . The solidification front is given by:

$$\xi(\vec{r},t) = \xi_0(\vec{r}) + \delta\xi(\vec{r},t), \qquad (2.5)$$

where  $\xi_0(\vec{r}) = 0$  describes the planar steady-state solidification front and  $\vec{r}$  the position in the plane perpendicular to  $\vec{v}$ .  $\delta\xi(\vec{r},t)$  describes a small amplitude sinusoidal perturbation:

$$\xi(\vec{r},t) = \hat{\xi}(\vec{k}) \exp(i\vec{k}\cdot\vec{x} + \omega_k t), \qquad (2.6)$$

where  $\vec{k}$  is a two-dimensional wave vector perpendicular to  $\vec{v}$ , and  $\omega_k$  is the amplification rate whose sign determines stability. The corresponding solution of the diffusion equation (2.4)  $u^l$  and  $u^s$  for the liquid and solid, respectively, yields:

$$u^{l}(\vec{x}, z, t) = \exp(-\frac{2z}{l}) - 1 + \delta u^{l}(\vec{x}, z, t), \qquad (2.7)$$

and

$$u^{s}(\vec{x}, z, t) = \delta u^{s}(\vec{x}, z, t), \qquad (2.8)$$

where the perturbations are expressed in Fourier components:

$$\delta u^{l}(\vec{x}, z, t) = \hat{u}^{l}(\vec{k}) \exp(i\vec{k} \cdot \vec{x} - qz + \omega t), \qquad (2.9)$$

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

and

$$\delta u^{s}(\vec{x}, z, t) = \hat{u}^{s}(\vec{k}) \exp(i\vec{k}\cdot\vec{x} + \tilde{q}z + \omega t), \qquad (2.10)$$

where q and  $\tilde{q}$  are the positive solutions of the stationary diffusion equation (2.4):

$$-\frac{2}{l}q + q^2 - k^2 = 0, \qquad (2.11)$$

and

$$\frac{2}{l}\tilde{q} + \tilde{q}^2 - k^2 = 0.$$
 (2.12)

The amplitudes  $\hat{u}^{l}$  and  $\hat{u}^{s}$  are small, of order  $\hat{\xi}$ , and can therefore be obtained from linearizing the Gibbs-Thomson condition (2.3) with  $\beta = 0$ :

$$-\frac{2}{l}\hat{\xi}(\vec{k}) + \hat{u}^{l}(\vec{k}) = \hat{u}^{s}(\vec{k}) = -d_{0}k^{2}\hat{\xi}(\vec{k}). \qquad (2.13)$$

Linearizing the heat conservation condition (2.2) yields:

$$\omega_k \hat{\xi}(\vec{k}) = -\frac{2v}{l} \hat{\xi}(\vec{k}) + D \left[ q \, \hat{u}^l(\vec{k}) + \tilde{q} \, \hat{u}^s(\vec{k}) \right].$$
(2.14)

By expressing  $\hat{u}^l$  and  $\hat{u}^s$  by  $\hat{\xi}$  using equation (2.13),  $\hat{\xi}$ ,  $\hat{u}^l$  and  $\hat{u}^s$  can be eliminated in equation (2.14), which reduces to:

$$\omega_{k} = v \left( q - \frac{2}{l} \right) - D \left( q + \tilde{q} \right) d_{0} k^{2} .$$
(2.15)

Assuming that  $kl \gg 1$ , which implies that the diffusion length l is much larger than the wavelength of perturbation  $\lambda = 2\pi/q$ , equation (2.15) reduces to the dispersion relation:

$$\omega_k \cong k \, v \, [1 - d_0 \, l \, k^2] \,, \tag{2.16}$$

which is shown in figure 2.3. The interface is unstable for  $\omega > 0$ , which is true for sufficiently long wavelength perturbations. Perturbations with wavelengths for which  $\omega < 0$  are stabilized. The term  $k^3$ , which is stabilizing, has the capillary length  $d_0$  as a prefactor. Hence, diffusion destabilizes the planar solidification front whereas capillarity acts as stabilizing agent. The wavelength  $\lambda_c = 2\pi\sqrt{l d_0}$  at which  $\omega$  vanishes is called the *neutral* or *critical stability point*. It sets the length scale for the problem. The diffusion length l is usually macroscopic, while  $\lambda_c$  is of the order of microns, so that  $l/\lambda_c \gg 1$ . This is just the condition that was needed in



Figure 2.3: Dispersion relation for Mullins-Sekerka instability. $k_c$ is the critical wave number. Perturbations with  $k < k_c$  are unstable, whereas perturbations with  $k > k_c$  are stabilized by surface tension.

order to justify the "quasi-stationary approximation". Another way of motivating the approximation is by realizing that the dominant instabilities have growth rates of order  $\omega_{max} \sim k_c v$ . The relaxation rates for corresponding perturbations of the diffusion field are  $\omega_{diff} \sim D k_c^2$ . Thus, the ratio  $\omega_{diff}/\omega_{max}$  is of order  $k_c l \gg 1$ , as required.

## 2.3 Examples

There are different manifestations of the Mullins-Sekerka instability. The most studied one is the dendrite. It evolves from an initially featureless seed, which is immersed in an undercooled melt. Bulges then start to develop in crystallographically preferred directions. The bulges grow into needle-shaped arms whose tips move outward at constant speed. These primary arms are unstable against side-branching. The sidebranches, in turn, are unstable against further side-branching, so that each outward growing tip leaves behind itself a complicated dendritic structure. See figure 2.4 as an example. Neglecting the surface tension  $\gamma$  altogether in the problem, Ivantsov [47] found a continuous family of needle-like steady states for a fixed undercooling  $\Delta$ . However, these solutions fixed only the product of the tip radius and the growth speed, and not their values individually, as required by experiments. Including the effect of surface tension excluded Ivantsov's needle-like solutions. Instead, the existence of a steady state solution required a non-vanishing anisotropy in the surface tension, which then provided a discrete set of solutions for the problem. A selection mechanism proposed that the selected dendrite is the one for which a stable solution exists. This hypothesis has been supported by numerical simulations and is known



Figure 2.4: STM of dendrites in a single-crystal weld David, DebRoy and Vitek [94].

as "solvability theory". A good explanatory monograph is given by Pomeau and Ben Amar [92].

The Mullins-Sekerka instability is not limited to the diffusion of heat but has an analog in alloys, where the diffusion of chemical species controls the motion of the solidification front. Since thermal diffusion is always much faster than chemical diffusion<sup>1</sup>, we assume it to be instantaneous. This implies that the solidification of alloys is effectively isothermal. To see the analogy between the thermal and the chemical cases, consider a typical phase diagram of a binary alloy, a portion of which is illustrated schematically in figure 2.5. Here, c denotes the concentration of the solute, and  $T_0$  is the local temperature which is assumed to be constant over a large region of the sample. In a two-phase equilibrium, the solute concentration in the liquid is appreciably greater than in the solid. Thus an advancing solidification front rejects solute molecules in much the same way as, in the pure thermal case, it releases latent heat. Hence, the diffusion of the excess solute away from the interface determines how fast the interface can move. The analogy to the thermal case becomes even clearer if we write down the equation of motion in terms of chemical potentials of the solute relative to that of the solvent:

$$\tilde{\mu}^{s} = \mu^{s} - \mu_{0}(T_{0}) = \frac{\partial \mu^{s}}{\partial c_{c}} \delta c^{s}, \qquad (2.17)$$

and

$$\tilde{\mu}^{l} = \mu^{l} - \mu_{0}(T_{0}) = \frac{\partial \mu^{l}}{\partial c} \delta c^{l}, \qquad (2.18)$$

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



where  $\tilde{\mu}$  measures the difference of the chemical potential from its equilibrium value and c is the concentration. The diffusion equation then yields:

$$\frac{\partial \tilde{\mu}}{\partial t} = D_c \nabla^2 \tilde{\mu} \,, \tag{2.19}$$

with  $D_c$  being the chemical diffusion constant. The latent heat is replaced by the miscibility gap  $\Delta c$  shown in figure 2.5. The boundary conditions are then given by equation (2.2) and equation (2.3).

The last example of a Mullins-Sekerka-like instability presented here, is in *directional solidification*, a well known technique in metallurgy to purify solids or prepare materials with specific properties. As above, chemical diffusion is the dominant kinetic effect. However, in addition, a temperature gradient G is imposed which controls the orientation and velocity of the solidification front. The basic features of the system are shown in figure 2.6. A sample is pulled at a constant velocity v through a fixed temperature gradient established by hot and cold contacts, which are at temperatures above and below the liquidus and solidus line, respectively. Hence, the problem is



described by the diffusion equation for the solute or impurity concentration, and the modified boundary conditions incorporating the imposed thermal gradient. A linear stability analysis for the modified problem yields the following dispersion relation<sup>1</sup>:

$$\omega(k) \cong \frac{v}{l} \left[ \sqrt{1 + (kl)^2} (1 - \frac{l}{l_T} - d_0 l k^2) - 1 \right], \qquad (2.20)$$

which is shown in figure 2.7. Three different length scales are involved: the diffusion length l = 2D/v, the thermal length  $l_T = \Delta T/G$ , and the chemical capillary length  $d_0$ . The velocity v and G are two control parameters which control the complex behavior of the instability. Keeping G fixed and varying v, one observes that, for small pulling velocities, the flat interface is stable for all wavelength. This implies that the thermal gradient is stabilizing. As the pulling velocity is increased beyond  $v_c$ , the velocity at which the planar front becomes unstable, a finite band of unstable wavelength appears which eventually evolves to a characteristic cellular pattern<sup>2</sup>. Increasing the velocity further causes a dendritic pattern to appear.

<sup>&</sup>lt;sup>1</sup>The partition coefficient K, which is the ratio between the liquidus and solidus slope, was set to 1. <sup>2</sup>Weeks, van Saarloos and Grant [91].

## PHASE-FIELD MODEL

3

The basic model of solidification belongs to the class of moving or free boundary type problems. These problems are inherently non-linear since they include curvature contributions and thus are difficult to solve analytically. Even numerically, they turn out to be challenging problems since they involve explicit tracking of the phase boundaries. The phase-field approach, which is rooted in continuum models of phase transitions, avoids these problems by replacing the equation of motion of the macroscopically sharp phase boundaries by an equation of motion for a phase-field, which is definite in the whole domain. The phase variable, or order parameter, is constant in the bulk phases and changes smoothly but rapidly across the phase boundary, implying a diffuse phase boundary. Hence, the problem of simulating the advance of a sharp boundary is converted to solving a system of partial differential equations that governs the evolution of the phase and diffusion field. Langer introduced the phasefield model to describe the solidification of a pure melt, by reinterpreting "model C" of Halperin, Hohenberg and Ma [74] which was introduced in chapter 1.1. Fix<sup>1</sup> was the first who called the model the phase-field "approach", and implemented it numerically. Also, Collins and Levine [85] have proposed independently phase-field equations and analyzed one-dimensional steady-states. Since then, the original model has been modified and reformulated to address issues of thermodynamic consistency<sup>2</sup>. It has also been extended to model the solidification of binary<sup>3</sup> and eutectic alloys<sup>4</sup> as well as to polymorphous crystallization<sup>5</sup>. It has been also employed to study elastic

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

<sup>&</sup>lt;sup>2</sup>Wang et al. [93].

<sup>&</sup>lt;sup>3</sup>Wheeler, Boettinger and McFadden [92].

<sup>&</sup>lt;sup>4</sup>Elder et al. [94].

<sup>&</sup>lt;sup>5</sup>Morin et al. [95].
effects in phase separating solids<sup>1</sup>. However, most of the numerical work has been focused on the simulation of dendritic growth<sup>2</sup> which provides a non-trivial test case for the phase-field method. One drawback of the phase-field approach is that, in order to obtain quantitative results, the simulations have to be independent of computational parameters. This implies that the interfacial region has to be resolved sufficiently and fixes the grid size, which then constrains the length scale being simulated. Due to this constraint, it is only recently that three-dimensional simulations have been performed. One way of circumventing this constraint is by applying adaptive grid methods<sup>3</sup> and using the fact that only the interfacial region changes during time. The other approach is based on a reinterpretation of the "sharp-interface limit" by Karma and Rappel<sup>4</sup> and will be discussed in chapter 3.2 and appendix A.1.

### 3.1 Model

The basic equation of the phase-field model is given by:

$$\frac{\partial \phi}{\partial t} = -\Gamma \frac{\delta \mathcal{F}}{\delta \phi} \,, \tag{3.1}$$

where  $\Gamma$  is the kinetic coefficient and  $\mathcal{F}$  is a Ginzburg-Landau free energy functional:

$$\mathcal{F}(\phi) = \int d\vec{x} [f(\phi) + \frac{l^2}{2} |\nabla \phi|^2 + \lambda g(\phi)u].$$
(3.2)

Here,  $f(\phi)$  is a free energy density with a double well structure in  $\phi$ 

$$f(\phi) = \frac{\phi^2(\phi - 1)^2}{a},$$
(3.3)

whose minima  $\phi = 0, 1$  determine the bulk phases, such as liquid and solid. The parameter *a* measures the potential depth, and will be related to the surface tension and interfacial width. Figure 3.1 shows the double well structure of the free energy density for  $g(\phi) = \phi - \frac{1}{2}$ . The dimensionless diffusion field is  $u = c_P \frac{T-T_M}{L}$ , as in chapter 2.1. It is coupled to the phase-field  $\phi$  by  $g(\phi)$ . The gradient term  $|\nabla \phi|^2$  is the contribution due to the interface. The interpretation of the different contributions

<sup>&</sup>lt;sup>1</sup>Onuki [89a]; Onuki [89b]; Nishimori and Onuki [90]; Onuki and Nishimori [91]; Sagui, Somoza and Desai [94].

<sup>&</sup>lt;sup>2</sup>Kobayashi [93]; McFadden et al. [93]; Wang and Sekerka [96]; Karma and Rappel [98].

<sup>&</sup>lt;sup>3</sup>Provatas, Goldenfeld and Dantzig [98].

<sup>&</sup>lt;sup>4</sup>Karma and Rappel [96b]; Karma and Rappel [96a]; Karma and Rappel [98].



Figure 3.1: Double well structure of the free energy density  $f(\phi)$  coupled to  $g(\phi)u = (\phi - 1/2)u$ .

will become more transparent by considering a one-dimensional system at equilibrium for u = 0. The equation of motion (3.1) reduces to:

$$-l^2\phi_{xx} + \frac{\partial f(\phi, 0)}{\partial \phi} = 0.$$
(3.4)

or

$$\frac{l^2}{2}\phi_x^2 = f(\phi, 0), \qquad (3.5)$$

where the subscript x denotes a derivative. The solution is given by the hyperbolic tangent, which describes the diffuse interfacial region between the two bulk phases:

$$\phi(x) = \frac{1}{2} \left[ 1 - \tanh(\frac{x}{\sqrt{2cl}}) \right].$$
(3.6)

Figure 3.2 shows the interfacial profile. The interfacial width, being the range in which  $\phi$  changes from 0.05 to 0.95, can be deduced from equation (3.6) to be

$$w \simeq 3\sqrt{2al} \,. \tag{3.7}$$

The surface tension, which is defined as the additional free energy per unit area generated by an interface between the two bulk phases in equilibrium, is given by:

$$\gamma = \int_{-\infty}^{\infty} dx \left[ f(\phi, 0) + \frac{l^2}{2} \phi_x^2 \right].$$
(3.8)

Using equation (3.5) and the fact that  $f(\phi, 0) = 0$  in the bulk phases, we obtain:

$$\gamma = l^2 \int_{-\infty}^{\infty} dx \, \phi_x^2 = \frac{l}{3\sqrt{2a}} \,. \tag{3.9}$$

Hence, parameter l, together with parameter a, determines the surface tension  $\gamma$  as





well as the interfacial thickness w.

The term  $\lambda g(\phi)u$  in equation (3.2) causes a bulk free energy difference between the two phases, and thus provides a thermodynamic driving force. Depending on the sign of u, one or the other phase is favored (see figure 3.1). To describe the full problem of solidification the heat diffusion equation has to be added:

$$\frac{\partial u}{\partial t} = D\nabla^2 u + \frac{1}{\Delta} \frac{\partial \phi}{\partial t} \,. \tag{3.10}$$

The first part is the diffusion equation as described in chapter 2.1. The second term on the right side represents the interfacial source term with  $\Delta = \dot{\gamma}^s - \phi^l$  being related to the release of latent heat. Substituting equation (3.2) in equation (3.1) results in:

$$\frac{\partial \phi}{\partial t} = -\Gamma \left[ f_{\phi}(\phi) - l^2 \nabla^2 \phi + \lambda g_{\phi}(\phi) u \right], \qquad (3.11)$$

for which different choices of  $g(\phi)$  have been proposed. In order to keep  $\phi$  fixed in the bulk phases, meaning that the latent heat is only released at the interface,  $g(\phi)$  has to fulfill the following condition:

$$\frac{\partial g}{\partial \phi}|_{0,1} = 0. \tag{3.12}$$

This can be fulfilled by choosing:

$$\frac{\partial g}{\partial \phi} = \left[\phi(\phi - 1)\right]^n,\tag{3.13}$$

where n is a positive integer. For n = 1, the model proposed by Kobayashi [93] is recovered. This will be discussed in chapter 3.3. Models for n = 2 have also been studied<sup>1</sup>.

<sup>&</sup>lt;sup>1</sup>Wang et al. [93]; Umantsev and Roitburd [88].

# 3.2 Sharp Interface Limit

The connection between the sharp interface formulation of the problem and the phasefield model is established via the sharp interface limit. In the sharp interface limit the phase-field model, consisting of a system of two non-linear coupled equations of motion for the temperature (3.10) and the order parameter (3.11), reduces to the basic model of solidification (equations (2.1) - (2.3)). The sharp interface limit is obtained by an asymptotic multiple-scale analysis, also often referred to as matching asymptotics. Caginalp and Fife [88] and Caginalp [89] showed that the different sharp interface models can all arise as particular scaling limits of the phase-field equations. The results are summarized in table 3.1. To obtain these limits, the phase-field equations have to be rescaled:

$$x' = \frac{x}{w}, \qquad t' = \frac{Dt}{w^2}, \qquad (3.14)$$

and,

$$\epsilon = \frac{l}{w}, \qquad \qquad \alpha = \frac{D}{\Gamma l^2}$$
(3.15)

where w is a mesoscopic length scale such as the diffusion length  $l_d$ . Omitting the primes we obtain:

$$\alpha \,\epsilon^2 \frac{\partial \phi}{\partial t} = \epsilon^2 \,\nabla^2 \phi - f_\phi(\phi) - \lambda \,g_\phi(\phi) \,u\,, \qquad (3.16)$$

and

$$\frac{\partial u}{\partial t} = D \,\nabla^2 u + \frac{1}{\Delta} \frac{\partial \phi}{\partial t} \,. \tag{3.17}$$

We are left with three parameters  $\epsilon$ ,  $\alpha$  and  $\lambda$ , whose scaling behavior determines the different results of the sharp interface limit.  $\epsilon$  is a small expansion parameter,  $\alpha$  is related to a microscopic relaxation time, and  $\lambda$  is a dimensionless parameter that controls the strength of the coupling between the phase and diffusion fields. Two physical parameters are involved:  $d_0$ , the capillary length, and  $\beta$ , the kinetic coefficient.

Caginalp [89] fixed one parameter by requiring that the surface tension  $\gamma$ , being a physical parameter, be independent of the scaling. Dividing equation (3.16) by  $\lambda$  we obtain:

$$\alpha \xi^2 \frac{\partial \phi}{\partial t} = \xi^2 \nabla^2 \phi - \frac{f_{\phi}(\phi)}{\lambda} - g_{\phi}(\phi) u , \qquad (3.18)$$

where  $\xi = \epsilon^2/\lambda$ . The surface tension in the phase-field model was determined by equation (3.9) to be proportional to the ratio  $\xi/\sqrt{\lambda}$ . Hence, the requirement of constant surface tension implies:

$$\frac{\xi}{\sqrt{\lambda}} = const. , \qquad (3.19)$$

which reduces the number of free parameters to two. With this assumption, the first three scaling limits in table 3.1 can be derived (Caginalp [89]). In order to use the phase-field approach for the study of dendritic growth, and other problems involving the Mullins-Sekerka instability, the convergence of the phase-field approach has to be studied. This was done by Wheeler, Murray and Schaefer [93], as well as by Wang and Sekerka [96], who observed that the lattice spacing  $\Delta x$  had to be chosen very small compared to the scale of the dendritic pattern. This permits convergence to a reliable quantitative solution of the sharp interface equations. It turns out that only the regime of a dimensionless undercooling of the order of one, in which the interfacial undercooling  $u_i$  is dominated by interfacial kinetics, is computational on a quantitative level. This constraint is a consequence of the scaling ansatz that  $\xi \to 0$ , which implies that the temperature is not allowed to change across the interfacial thickness. However, the magnitude of a variation of u across the interface scales as  $\delta u \sim \xi v/D$ , since u varies locally on a scale  $\sim D/v$  in the direction normal to the interface, where v is the local normal velocity of the interface. Therefore, neglecting this variation is equivalent to assuming that  $\delta u \ll \beta v$ , which yields, using equation (3.19), the constraint:

$$d_0 \gg \frac{\xi^3 \Gamma}{D} \,. \tag{3.20}$$

Since  $\Delta x \sim \xi$ , the constraint implies a very small grid spacing and restricts the system sizes which can be simulated.

However, considering the phase-field equation as a mathematical tool to solve the sharp interface limit, one has only to demand that, in the sharp interface limit, the sharp interface equations have to be recovered. Dropping the constraint (3.19), we are left with three model parameters and two physical parameters. Karma and Rappel<sup>1</sup> realized that using another scaling approach,  $\lambda$  can be used as a free parameter, which can be chosen for computational convenience. In their scaling limit, the interfacial

<sup>&</sup>lt;sup>1</sup>Karma and Rappel [96b]; Karma and Rappel [96a]; Karma and Rappel [98].

thickness is small compared to the mesoscale of the diffusion field, but it remains finite. They refer to it as the "thin-interface limit", since its limit includes corrections for variation of the temperature field across the interface:

$$\beta = \frac{\alpha I}{\lambda J} \left[ 1 + \lambda \frac{K + J F}{2 \alpha I} \right], \qquad (3.21)$$

where I, J, K and F are integration constants which depend on the precise form of  $g(\phi)$  and  $f(\phi)$ . They are determined in appendix A.1. The thin-interface limit is closely related to a limit derived by Caginalp and Fife [88], as will be shown in appendix A.1. This allows the constraint on  $d_0$  (3.20) to be lifted, which greatly enhances computational efficiency, and makes three-dimensional simulations possible without adaptive grid methods. However, at very low undercoolings adaptive grid methods have to be employed<sup>1</sup>.

	Stefan model	scaling limit	sharp interface limit
		$\lambda, \xi \to 0$	$\frac{\partial u}{\partial t} = D\nabla^2 u$
1	classical	lpha - fixed	$v = D(\nabla u^s - \nabla u^l) \cdot \vec{n}$
		$\frac{\xi}{\sqrt{\lambda}} \to 0$	$u_i = 0$
		$\lambda, \xi \to 0$	$\frac{\partial u}{\partial t} = D\nabla^2 u$
2	modified	$\alpha$ - fixed	$v = D(\nabla u^s - \nabla u^l) \cdot \vec{n}$
		$\frac{\xi}{\sqrt{\lambda}}$ - fixed	$u_i = -d_0\kappa - \alpha d_0v$
	alternative	$\lambda, \xi, \alpha \to 0$	$\frac{\partial u}{\partial t} = D\nabla^2 u$
3	modified A	$\frac{\xi}{\sqrt{\lambda}}$ - fixed	$v = D(\nabla u^s - \nabla u^l) \cdot \vec{n}$
l			$u_i = -d_0\kappa$
	alternative	$\xi \rightarrow 0$	$\frac{\partial u}{\partial t} = D\nabla^2 u$
4	modified B	$\lambda, \alpha$ - fixed	$v = D(\nabla u^s - \nabla u^l) \cdot \vec{n}$
			$u_i = -d_0\kappa + \beta v$

Table 3.1: Scaling relations between phase-field equation and sharp interface equations.

<sup>&</sup>lt;sup>1</sup>Provatas, Goldenfeld and Dantzig [98].

# 3.3 Dendritic Growth

Dendritic growth is the problem for which the phase-field approach was created. Here it was first introduced, here different questions of interpretation and thermodynamical consistency were discussed, as well as its numerical appeal and limitations. Since some analytical results are available, it is a good system to study all the questions mentioned above. We will present the phase-field model of Kobayashi [93], which was the first model which reproduced qualitatively distinct features characteristic of dendritic growth, such as tertiary side arms and the coarsening of side arms away from the tip. Since then, many contributions have been concerned with changing the model to obtain quantitative results. As the free energy functional, Kobayashi proposed:

$$\mathcal{F} = \int d\vec{r} \left[ f(\phi, u) + \frac{\epsilon(\theta)^2}{2} |\nabla \phi|^2 \right] , \qquad (3.22)$$

with an anisotropy in  $\epsilon = \hat{\epsilon}\eta(\theta)$  which will result in an anisotropy in the surface tension. The energy density is:

$$f(\phi, u) = \frac{1}{4}\phi^2(\phi - 1)^2 - g(\phi)m(u) , \qquad (3.23)$$

where  $u = (T - T_M)/(T_M - T_\infty)$  and |m(u)| < 1/2, so that together with the choice of  $g(\phi)$ :

$$g(\phi) = \frac{1}{2}\phi^2 - \frac{1}{3}\phi^3, \qquad (3.24)$$

the minima of the free energy stay at  $\phi = 0$  and  $\phi = 1$  as discussed in chapter 3.1.

One possible choice for m is  $m(u) = \alpha/\pi \arctan(-\gamma u)$  with  $\alpha < 1$ . To study the effect of the anisotropy in  $\epsilon$  we consider a planar interface. For the isothermal case the solution is:

$$\phi = \frac{1}{2} \left[ 1 - \tanh\left(\frac{\vec{r} \cdot \vec{n}}{2\sqrt{2}\,\epsilon(\theta)}\right) \right] \,, \tag{3.25}$$

implying that the width of the interface is proportional to  $\epsilon(\theta)$ . The surface energy as defined in equation (3.9) yields:

$$\gamma = \int_{-\infty}^{\infty} dx \,\epsilon^2(\theta) \,\phi_x^2 = \frac{\epsilon(\theta)}{6\sqrt{2}}, \qquad (3.26)$$

which motivates the choice of anisotropy. The dynamics of the order parameter is given by:

$$\tau \frac{\partial \phi}{\partial t} = -\hat{\epsilon}^2 \frac{\partial}{\partial x} \left[ \eta(\theta) \, \eta'(\theta) \, \frac{\partial \phi}{\partial y} \right] + \hat{\epsilon}^2 \frac{\partial}{\partial y} \left[ \eta(\theta) \, \eta'(\theta) \, \frac{\partial \phi}{\partial x} \right] + \hat{\epsilon}^2 \, \nabla \cdot (\eta^2(\theta) \, \nabla \phi)$$



Figure 3.3: Growth of a dendrite in an undercooled melt for 6-fold anisotropy in two dimensions. From left to right the number of times steps are:  $N_t = 500$ ,  $N_t = 1500$  and  $N_t = 4000$ .

+ 
$$\phi(1-\phi)\left[\phi-\frac{1}{2}+m(u)\right]+a\phi(1-\phi)\chi$$
, (3.27)

and the equation of diffusion of heat is

$$\frac{\partial u}{\partial t} = \nabla^2 u + \frac{1}{\Delta} \frac{\partial \phi}{\partial t} . \qquad (3.28)$$

with

$$\Delta = c_p \frac{T_M - T_\infty}{L} \,, \tag{3.29}$$

denoting the dimensionless undercooling, which is an important control parameter. The last term in equation (3.27) describes a noise with strength a which acts only at the interface to stimulate side branching.  $\chi$  is a random number uniformly distributed in the interval  $\left[-\frac{1}{2}, \frac{1}{2}\right]$ . An example of a dendritic growth simulation is shown in figure 3.3 for the parameters:  $\eta = 1 + \delta \cos(6\theta)$  where  $\delta = 0.04$ ,  $\bar{\epsilon} = 0.01$ ,  $\tau = 0.003$ ,  $\alpha = 0.9$ ,  $\gamma = 10$ , a = 0.01,  $\Delta = 0.6$ , a mesh size of 0.03 and system size  $N_x = N_y =$ 300. We start with a 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 transform to a 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 Criticism

The basic model of solidification is a minimal model. It only considers the thermal aspect of the phase transition, namely, the release of latent heat at the solidification front and its diffusion into the solid and liquid phase. Due to non-linearities, which come into play via the curvature  $\kappa_c$  and the normal vector  $\vec{n}$ , the mathematical problem is non-trivial and many interesting, complex patterns evolve, as can be seen in dendritic growth. Nevertheless, it is a crude simplification, which does not include flow in the liquid phase, nor does it include elastic effects in the solid phase. Indeed, the main distinction between a solid and a liquid is the shear modulus. Solids support shear, implying that their shear modulus is finite, whereas the shear modulus of a liquid is zero, implying that they do not support shear. One might expect that the basic model of solidification should capture this main distinction. However, it does not. The same criticism applies to the phase-field model. Here, although rooted in the continuum description of phase transition, indicating that the phase  $\phi$  is an order parameter,  $\phi$  does not have any physical content. It is merely a label to distinguish the solid from the liquid phase.

Below, we will propose a solidification model in which the order parameter is proportional to the shear modulus. Hence, it captures the main difference between the solid and liquid phase. That is, the shear modulus of the liquid phase will vanish, whereas the shear modulus of the solid will be finite. Thus, the phase-field obtains a physical meaning in the context of liquid-solid phase transition.

### COARSENING

4

Apart from the morphological instability discussed in the last two chapters, the firstorder phase transition shows other interesting dynamical properties which involve such phenomena as nucleation, spinodal decomposition, late stage growth, and coarsening. In the classical theory of first-order phase transitions, one distinguishes between two different types of instabilities which characterize the early stages of phase separation. The first is an instability against finite amplitude perturbations in which localized (droplet-like) fluctuations lead to the initial decay of a metastable state. The rate of birth of such droplets is described by homogeneous nucleation theory. The second is an instability against infinitesimal amplitude perturbations, non-localized (long wavelength) fluctuations which lead to the initial decay of an unstable state. This latter instability is termed spinodal decomposition. It should be noted that this sharp distinction between metastable and unstable states, put forward by the classical theory of first-order phase transitions, is not supported by modern field theoretical approaches. We now review the long wavelength instability observed in systems undergoing spinodal decomposition, and in the late-stage growth and coarsening regime as it is needed for the further discussion in chapter 6. We follow here the reviews by Gunton, San Miguel and Sahni [83] and Bray [94].

### 4.1 Linear Theory

The starting point for the analysis of the early stages of spinodal decomposition is the Cahn-Hillard equation (1.9), or model B without noise:

$$\frac{\partial \phi(\vec{r},t)}{\partial t} = \Gamma \nabla^2 \left[ \frac{\partial f}{\partial \phi} - l^2 \nabla^2 \phi \right] \,. \tag{4.1}$$

Cahn linearized this non-linear equation about the averaged concentration  $\phi_0$  to obtain:

$$\frac{\partial m(\vec{r},t)}{\partial t} = \Gamma \nabla^2 \left[ \frac{\partial^2 f}{\partial \phi_0^2} - l^2 \nabla^2 \right] m(\vec{r},t) , \qquad (4.2)$$

where

$$m(\vec{r}) = \phi(\vec{r}) - \phi_0.$$
 (4.3)

The Fourier transform of equation (4.2) yields:

$$\frac{\partial \hat{m}(\vec{k})}{\partial t} = -\omega(k) \,\hat{m}(\vec{k}), \qquad (4.4)$$

where  $\hat{m}(\vec{k})$  is the Fourier transform of  $m(\vec{r})$  and

$$\omega(k) = \Gamma l^2 k^2 \left[ k^2 + \frac{1}{l^2} \frac{\partial^2 f}{\partial \phi_0^2} \right] . \tag{4.5}$$

Thus, inside the spinodal regime, where  $\partial^2 f / \partial \phi_0^2 < 0$ ,  $\omega(k)$  is negative for  $k < k_c$ , where

$$k_c^2 = \frac{1}{l^2} \left| \frac{\partial^2 f}{\partial \phi_0^2} \right|. \tag{4.6}$$

Hence, long wavelengths grow exponentially

$$\hat{m}(\vec{k},t) = \hat{m}(\vec{k},0)e^{-\omega(k)t}.$$
(4.7)

The quantity of experimental interest is the structure function  $\hat{S}(\vec{k},t) = \langle |\hat{m}(\vec{k})|^2 \rangle$ , which is proportional to the small angle, diffuse scattering intensity. Linear theory therefore predicts

$$\hat{S}(\vec{k},t) = \hat{S}(\vec{k},0) e^{-2\omega(k)t}.$$
(4.8)

This implies an exponential growth in the scattering intensity for  $k < k_c$ , with a peak at a time-independent wave number  $k_m = k_c/\sqrt{2}$ . The behavior predicted by the linear theory, equation (4.8), is usually not observed in Monte-Carlo studies nor in experimental studies of alloys and fluids. However, Binder [84] studied the effect of a long-range force on the dynamics of first order phase transitions and found that the time regime in which the linear theory of spinodal decomposition holds increases logarithmically with the range of interaction. This prediction can be confirmed by numerically simulation of the Cahn-Hillard-Cook equation. See, for example, Laradji, Grant and Zuckermann [90] and references therein. They studied the effect of longrange interactions on the dynamics on first order transitions in two dimensional Ising models via Monte-Carlo simulations with Glauber<sup>1</sup> (spin-flip) and Kawasaki<sup>2</sup> (spinexchange) dynamics. They observed in both cases an agreement with the linear theory at early times.

# 4.2 Non-linear Theory: Early Stage

Although the linear theory predicts correctly the long wavelength instability, it is clear from its prediction of exponential growth of the fluctuations that it will be valid at most at very early times. However, it cannot account for non-linear effects such as coarsening, which stabilizes the system before it finally reaches its two-phase equilibrium. Many attempts have been made to incorporate non-linear effects into a theory of spinodal decomposition. The starting point is the dynamical equation of the correlation function of model B. Using equation (1.2) we obtain:

$$\frac{\partial}{\partial t} < \phi(\vec{r}, t) \phi(\vec{r'}, t) > = -2 \Gamma \nabla^2 \left[ r + l^2 \nabla^2 \right] < \phi(\vec{r}, t) \phi(\vec{r'}, t) > + (4.9) 
+ 2 \Gamma u \nabla^2 < \phi^3(\vec{r}, t) \phi(\vec{r'}, t) > -2 \Gamma k_B T \nabla^2 \delta(\vec{r} - \vec{r'}),$$

which is formally exact. However,  $\langle \phi(\vec{r},t) \phi(\vec{r'},t) \rangle$  is coupled to  $\langle \phi^3(\vec{r},t) \phi(\vec{r'},t) \rangle$ implying that equation (4.9) is the first of a hierarchy of coupled equations of motion. This is a common problem in many-body physics, however with the difference here that one is dealing with two-phase phenomena, far-from equilibrium. Hence, the standard techniques, such as factorizing the non-linear term by a single peaked Gaussian approximation, are difficult to justify. However, coarsening does result from the Gaussian approximation done by Langer. The Fourier transform of equation (4.9) is

$$\frac{\partial \hat{S}(\vec{k},t)}{\partial t} = -2\Gamma k^2 \left[ \left( l^2 k^2 + \frac{\partial^2 f}{\partial \phi_0^2} \right) \hat{S}(\vec{k},t) + \sum_{n=3}^{\infty} \frac{1}{(n-1)!} \frac{\partial^n f}{\partial \phi_0^n} \hat{S}_n(\vec{k},t) - k_B T \right].$$
(4.10)

The first higher order structure factor in the Gaussian approximation is given by:

$$\hat{S}_4(\vec{k},t) = 3 < s^2(t) > \hat{S}(\vec{k},t),$$
(4.11)

<sup>&</sup>lt;sup>1</sup>Ising model with Glauber dynamics is a microscopic formulation of model A.

<sup>&</sup>lt;sup>2</sup>Ising model with Kawasaki dynamics is a microscopic formulation of model B.

with

$$\langle s^{2}(t) \rangle = \frac{1}{(2\pi)^{3}} \int d\vec{k} \, S(\vec{k}, t).$$
 (4.12)

Hence, the equation of motion for the structure factor is given by:

$$\frac{\partial \hat{S}(\vec{k},t)}{\partial t} = -2\,\Gamma k^2 \left[ l^2 k^2 + A(t) \right] \hat{S}(\vec{k},t) + 2\,\Gamma k_B T k^2 \,, \tag{4.13}$$

with

$$A(t) = \frac{\partial^2 f}{\partial \phi_0^2} + \frac{1}{2} \frac{\partial^4 f}{\partial \phi_0^4} < s^2(t) > .$$
(4.14)

As a consequence, the characteristic wave number  $k_c$  now decreases with time, since  $\langle s^2(t) \rangle$  is a positive, increasing function of time. The most important result of this approximation, however, is a qualitative explanation of coarsening.

Langer, Bar-on and Miller [75] suggested a physical approximation which is based on the assumption that the spatial dependence of the higher-order correlation functions is the same as that of the two-point correlation function  $S(\vec{r}, t)$ . This leads to

$$S_n(\vec{r},t) \simeq \frac{\langle s^n(t) \rangle}{\langle s^2(t) \rangle} S(\vec{r},t) \,. \tag{4.15}$$

This approximation seems reasonable for large length scales, but is less accurate for short length scales. Its biggest drawback lies in the fact that it is an uncontrolled approximation. Using this approximation in the dynamical equation of the structure factor with

$$A(t) = \sum_{n=2}^{\infty} \frac{1}{(n-1)!} \frac{\partial^n f}{\partial \phi^n}_{\phi_0} \frac{\langle s^n(t) \rangle}{\langle s^2(t) \rangle}.$$
 (4.16)

 $\hat{S}(\vec{k},t)$  can be obtained numerically. For a critical quench, the theory is in qualitative agreement with Monte Carlo and experimental studies. It shows a "crossing of the tails" of the structure factor for different times which has been observed in numerical and experimental studies of phase separation.

Grant et al. [85] have developed a systematic perturbation theory for the early stages of spinodal decomposition for a system with long range interaction in which the small parameter of the theory is proportional to the inverse of the range of the force. The first order perturbative correction acts to substantially slow down the evolution predicted by the linear theory and shifts the effective critical wave number with time to small wave numbers which implies coarsening. The "crossing of tails"

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of the structure factor is also observed. However, perturbation calculations were performed to order  $\epsilon^2$ , in which the probability distribution function corresponded to a time-dependent Gaussian form, not to a bimodal one.

### 4.3 Non-linear Theory: Late Stage

Whereas the early stage is characterized by the formation of interfaces, separating regions of space where the system approaches one of the final coexisting states, the late stages are dominated by the motion of these interfaces as the system acts to minimize its surface free energy. During this time, the size of the domains grow, while the total amount of interface decreases.

Much of the theoretical framework for understanding the dynamics of phase separation has arisen from of the pioneering work of Lifshitz and Slyosov, and Wagner, hereafter called LSW-theory. It describes the asymptotic  $(t \to \infty)$  growth of droplets of a minority phase of small volume fraction in a slightly supersaturated phase of a solid solution. They calculated analytically the asymptotic behavior of the droplet distribution function, f(R, t), where R denotes the radius of a given droplet of the minority phase. In particular, they showed that the average droplet size obeys the growth law:

$$\bar{R} \sim t^{1/3}$$
. (4.17)

They also derived an expression for the droplet distribution function f(R, t) which showed dynamical scaling namely,

$$f(R,t) = t^{\alpha}g(\frac{R}{t^{\beta}}), \qquad (4.18)$$

where

$$\alpha = -(d+1)\beta, \qquad (4.19)$$

$$\beta = \frac{1}{3}.\tag{4.20}$$

and,

The physical mechanism behind the coarsening process is that larger droplets grow at the expense of smaller droplets by evaporation-condensation. Particles of the minority phase diffuse through the majority phase from smaller droplets that are dissolving, to larger droplets that are growing. This late stage growth is called Ostwald ripening and is characteristic for the dynamics of systems with conserved order parameters.

(4.24)

(4.26)

#### A. Scaling approach to late-stage coarsening

Much progress in understanding the late stage growth regime is based on a dynamical scaling hypothesis<sup>i</sup> which states that, at late times, there exists a single characteristic length scale L(t) such that the domain structure is (in a statistical sense) independent of time when lengths are scaled by L(t). Hence, the evolution of the system in the late stage regime is self-similar. The hypothesis is supported by many experimental studies of, for example, binary alloys, binary fluids, and polymer blends. It is also supported by the LSW-theory, as well as by numerical work.

An important quantity to characterize the domain structure is the equal time pair correlation function:

$$C(\vec{r},t) = \langle \phi(\vec{x}+\vec{r},t) \phi(\vec{x},t) \rangle, \qquad (4.21)$$

and its Fourier transform, the equal time structure factor:

$$S(\vec{q},t) = \langle \phi_{\vec{q}}(t) \phi_{-\vec{q}}(t) \rangle, \qquad (4.22)$$

where the angular brackets indicate an average over initial condition. Experimentally, the evolution of the structure factor can be monitored using small angle scattering of X-rays or neutrons, whereas the evolution of the correlation function can be obtained by microscopy. The existence of a single characteristic length scale, implies that the pair correlation function and the structure factor have, after some transient time  $t_0$ , the following scaling form:

$$C(\vec{r},t) = f(x),$$
 (4.23)

with

 $x=\frac{r}{L(t)}.$ Hence, the Fourier transform satisfies

$$S(\vec{q}, t) = L^{d}(t) g(y), \qquad (4.25)$$

with

where d is the spatial dimension, and 
$$g(y)$$
 is the Fourier transform of  $f(x)$ . It should  
be noted that, various choices for the definition of this length exists. For example, one

 $y = q L(t) \, ,$ 

<sup>&</sup>lt;sup>1</sup>It should be noted that scaling has not been proven, except in some simple models and the LSWtheory.

could define L(t) as  $q_1^{-1}$ , the first moment of S(q, t), as well as  $q_P^{-1}$ , the peak position of S(q, t). Many attempts have been made to predict the scaling forms f(x) and g(y)as well as the dynamical behavior of L(t). The determination of the growth law for L(t) has been done by examining interface dynamics of phase-ordering systems. The determination of the scaling forms f(x) and g(y) turns out to be very challenging. A number of approximate scaling functions for non-conserved fields have been proposed. None of them seem to be completely satisfactory. For conserved fields the theory is even less well understood.

#### **B.** Interface Dynamics

The interface dynamics approach has been used to analyze late stage phenomena and to obtain growth laws for L(t). Depending on whether the order parameter is conserved or not, the growth mechanisms are quite different. The interfacial motion for the different cases can be studied using the field theoretical description discussed in chapter 1.1. An order-disorder transition, in which the order parameter is not conserved, can be described by the Allen-Cahn equation (1.4) or model A without noise. As shown in appendix A.1<sup>1</sup> the interface dynamics yields:

$$v = -\kappa_c \,, \tag{4.27}$$

where v is the velocity of the interface (normal to itself) and  $\kappa_c$  is the curvature. Hence, the growth of a non-conserved field during coarsening proceeds through an independent motion of the interface driven by curvature forces. From this Allen-Cahn result we obtain an equation for a characteristic scale L(t):

$$\frac{\partial L}{\partial t} \sim \frac{1}{L} \,, \tag{4.28}$$

which yields the growth law:

$$L(t) \sim t^{1/2}$$
. (4.29)

In the presence of a conservation law the motion of the interface is slower, and a coupling between the bulk phases and the interface exists. Numerical studies and

<sup>&</sup>lt;sup>1</sup>There, the more complex case is discussed. However, if one sets the temperature u to zero, model A is obtained.

analytical investigations<sup>1</sup> have shown that in the symmetrical as well as highly asymmetric quenches the late stage grows is described by:

$$L(t) \sim t^{1/3}$$
, (4.30)

which generalizes the result by the LSW-theory.

<sup>1</sup>Bray [94].

# 5

# **GRINFELD INSTABILITY**

Elastic effects can strongly influence the morphology of materials and consequently influence material properties. Their effect on phase transformation has been studied intensively by metallurgists (Khachaturyan [83]). The micro-structure of even simple binary alloys involves an intricate system of domains of distinct compositions, separated by phase and grain boundaries. Included are defects such as impurities and vacancies, as well as dislocations. Each of these components influences the elastic state of the solid. Work by Cahn and Larché<sup>1</sup> has been dedicated to the study of the thermodynamics of multi-phase solids under stress. A good introduction to the thermodynamics of inhomogeneous solids, in the presence of stress, has been given by Nozières [92]. More recently, the influence of elasticity on phase-separating alloys has been studied<sup>2</sup>. Elasticity always provides a positive energy contribution. Thus, solids try to release their elastic energy in the process of energy minimization. There are different ways for solids to release that elastic energy. One is by plastic deformation, which involves dislocations, the other is by elastic deformation, which is commonly seen in thin-film growth. A non-hydrostatically, i.e. uni-axially, strained solid, which is in contact with its own melt or vapor, can release its elastic energy by a morphological instability at the interface. This strain release mechanism was first predicted by Asaro and Tiller [72]. They performed a linear stability analysis, and obtained a dispersion relation which showed a long-wavelength instability. The instability was driven by elastic stress, and stabilized by surface tension at short wavelengths. As background for our investigation, we now introduce the basic quantities and concepts of elasticity<sup>3</sup> which are needed for the study of the Grinfeld instability. Since the

<sup>&</sup>lt;sup>1</sup>Larché and Cahn [78]; Larché and Cahn [85]; Cahn [89].

<sup>&</sup>lt;sup>2</sup>Sagui, Somoza and Desai [94]; Onuki [89b]; Léonard and Desai [97].

<sup>&</sup>lt;sup>3</sup>Landau and Lifshitz [83].

Grinfeld instability is a long length scale effect, a continuum description is appropriate.

# 5.1 Basic quantities and concepts of elasticity

In contrast to liquids, solids sustain shear, which implies that solids respond to an external force with a deformation. The external force can either act on the whole volume, such as in the case of gravity, or on the surface of the solid. The deformation is characterized by a *strain*:

$$u_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) , \qquad (5.1)$$

with  $u_i$  being the displacements of the atoms from a reference state, which can be a stress-free or pre-stressed state.

The most fundamental condition of elasticity is the mechanical equilibrium condition, which states that, at equilibrium, all forces per unit volume in the solid,  $f_i$ , vanish:

$$f_i = \frac{\partial \sigma_{ij}}{\partial x_j} + f_i^b = 0, \qquad (5.2)$$

where  $\sigma_{ij}$  is the stress tensor and  $f_i^b$  are external body forces. A summation convention over repeated indices is implicit. Solving this system of partial differential equations for appropriate boundary conditions, which are either given in terms of externally applied surface forces  $F_i$ , or in terms of displacements, determines the stress state of the solid.

The deformation of the solid is then determined using *Hooke's law*, which describes the linear relationship between the stress  $\sigma_{ij}$  and the strain  $u_{ij}$ :

$$\sigma_{ij} = K_{ijkl} u_{kl} \,, \tag{5.3}$$

where  $K_{ijkl}$  is a tensor of rank four, whose components are elastic constants. In the case of an isotropic solid,  $K_{ijkl}$  reduces to a tensor with only two components, so that Hooke's law can be written as:

$$\sigma_{ij} = \kappa u_{ll} \delta_{ij} + 2\mu \left( u_{ij} - \frac{1}{d} \delta_{ij} u_{ll} \right) , \qquad (5.4)$$

where  $\kappa$  is the *bulk modulus*, which accounts for volume changes,  $\mu$  is the *shear* modulus, which accounts for shape changes without volume changes, and d is the dimension of space. Hooke's law can also be expressed in the following form:

$$\sigma_{ij} = \frac{E}{1+\nu} \left( u_{ij} + \frac{\nu}{1-(d-1)\nu} u_{ll} \delta_{ij} \right) , \qquad (5.5)$$

where E is the Young's modulus, and  $\nu$  is the Poisson ratio. The motivation for the choice of these coefficients is based on considering homogeneous deformation. The relation between both sets of coefficients is given by:

$$E = \frac{2d^2\mu\kappa}{2\mu + d(d-1)\kappa},$$
(5.6)

and

$$\nu = \frac{d\kappa - 2\mu}{2\mu + d(d-1)\kappa}.$$
(5.7)

Depending on the particular problem, one or the other formulation is more appropriate.

Often it is more convenient to express the mechanical equilibrium condition (5.2) in terms of displacements. This can be achieved using Hooke's law:

$$\nabla (\nabla \cdot \vec{u}) + (1 - 2\nu)(\nabla^2 \vec{u}) = 0, \qquad (5.8)$$

which is known as the Lamé equation. As will be seen in appendix A.2, equation (5.8) can be solved in a straightforward way for two-dimensional systems. In many cases an elastic problem can be posed by assuming that the displacement field in the y-dimension vanishes, and that the displacement fields in the remaining two directions do not dependent on y. This implies that  $u_{xy} = u_{yy} = u_{zy} = 0$ , and reduces the three-dimensional problem to a two-dimensional one. It is called the *plane strain* case.

### 5.2 Stress relief mechanism

To understand the physical mechanism for the stress-driven morphological instability, we consider an uni-axially and uniformly stressed semi-infinite solid as shown in figure 5.1. If the surface is flat, the solid will be strained uniformly. Then the elastic energy density, being proportional to the product of strain and stress, will also be uniform and always positive, since the applied stress and the resultant strain always have the same sign. If, however, the surface is perturbed, the applied stress results in a non-uniform stress distribution throughout the solid. Independent of the sign of the applied stress, stress relaxation occurs at the peaks which are less constrained, whereas a high stress concentration is observed in the valleys which are more constrained. The resulting stress gradient along the surface drives a mass flow from the valleys to the peaks. Thus, valleys will grow deeper and increase the stress gradient even more. This positive feedback will sustain the mass flow and drive the instability. However, the instability is balanced by the surface tension which tries to minimize the surface area. The competition between the destabilizing effect due to the stress relief mechanism, and the stabilizing effect due to surface tension, is characterized by a dispersion relation which can be obtained by a linear stability analysis. Like the Mullins-Sekerka instability, where during solidification the temperature can overcome the surface free energy and destabilize a planar solidification front at long wavelengths, a stress in a solid is capable of destabilizing an otherwise flat surface at long wavelengths. Before continuing with a quantitative approach, we would like to emphasize that the buckling of the surface is due to the fact that surface corrugation reduces the stored elastic energy. It should not be confused with the bending of a solid when one applies a longitutional stress to a thin rod.

Nozières [92] explains the above-described stress relief mechanism in more quantitative terms. Consider a two dimensional, uni-axially stressed solid where

$$\sigma_{xx}^{(0)} = \sigma_0 - p_l \neq \sigma_{zz}^{(0)} , \qquad (5.9)$$

$$\sigma_{xz}^{(0)} = 0, \qquad (5.10)$$

$$\sigma_{zz}^{(0)} = -p_l \,. \tag{5.11}$$

The solid is in contact with its liquid phase at a planar interface along z = 0 and pressure  $p_l$ . Figure 5.1 shows a sketch of the set-up. The two phases have equal enthalpies per unit mass, so

$$\frac{g}{\rho} = \frac{f + p_l}{\rho},\tag{5.12}$$

where f is the free energy per unit volume and  $\rho$  the mass density. We assume now that the solid grows locally, so that the interface gets displaced by an amount h(x) =



Figure 5.1: Sketch of Grinfeld instability. A stress  $\sigma_0$  is applied to the edges of a semi-infinite, isotropic solid which is in free contact with its own melt or vapor at pressure p.

 $h_0 \cos qx$ . If we ignore capillarity, the total enthalpy is unchanged as long as the growth occurs at constant stress  $\sigma_{ij}$ . However, the mechanical matching conditions at the interface are violated. To first order, a shear component appears:

$$\sigma_{nt}^{(0)} = n_i \sigma_{ij} t_j = \left[ \sigma_{zz}^{(0)} - \sigma_{xx}^{(0)} \right] \frac{dh}{dx} = -\sigma_0 \frac{dh}{dx}, \qquad (5.13)$$

where  $n_i$  and  $t_j$  are components of the normal and tangential vector on the interface. To maintain mechanical equilibrium, an extra tangential force has to be applied to the interface in order to compensate for the bulk stress:

$$dF_t = \sigma_{nt}^{(0)} ds \,, \tag{5.14}$$

where ds is an infinitesimal surface element. If not, the solid relaxes elastically, thereby lowering its enthalpy. The change in elastic enthalpy due to an infinitesimal deformation is

$$\delta G = \int d\vec{r} \left[ \sigma_{ij} \delta u_{ij} + p_l \delta u_{ll} \right] \,. \tag{5.15}$$

Using the fact that  $p_l = -\sigma_{zz}^{(0)}$ , we expand the stress as:

$$\sigma_{ij} = \sigma_{ij}^{(0)} + \Delta \sigma_{ij} , \qquad (5.16)$$

where  $\Delta \sigma_{ij}$  is the additional stress due to relaxation. Hence, the change in elastic enthalpy for a finite deformation is:

$$\Delta G = \int d\vec{r} \left[ (\sigma_0 u_{xx} + \frac{1}{2} \Delta \sigma_{ij} u_{ij}) \right], \qquad (5.17)$$

where  $\Delta \sigma_{ij}$  can be calculated, as pointed out above and see appendix A.2. Using Hooke's law, the strains  $u_{ij}$  are known as well and one obtains:

$$\Delta G = -\frac{1-\nu^2}{E}\sigma_0^2 h^2 q \,. \tag{5.18}$$

This is only the elastic contribution to the free enthalpy, which is destabilizing. However, the contribution due to capillarity will stabilize the interface at large q.

# 5.3 Experimental Evidence

There are different experimental systems in which the Grinfeld instability has been observed and studied.

#### $^{4}He$

The first quantitative experiment on the equilibrium shape of crystals under nonhydrostatic stress were performed by Torii and Balibar [92] in 1992 using solid <sup>4</sup>He in contact with its own melt. <sup>4</sup>He is often used to study theories of crystal growth, since one can obtain large single crystals, free of grain boundaries and defects. Since it also grows and melts rapidly, experiments can be performed in a reasonable amount of time. However, it has the drawback of being difficult to cool without leaks. Torii and Balibar [92] grew a very pure  ${}^{4}$ He crystal in a glass box, in which from one side the crystal could be strained via a piezoelectric ceramic. This allowed a straining up to  $u_{xx} = \pm 3.2 \cdot 10^{-4}$ . The strain was measured using a Fabry-Perot interferometer as was the height of the interface. Due to the slight difference in the refractive index between solid and liquid helium,  $\Delta n = 0.0034$ , melting or growth, i.e., displacement of the interface, produces a phase shift and, hence, a fringe pattern. They first observed macroscopic melting. At a critical strain of  $\delta u_c = \pm 7 \cdot 10^{-5}$ , grooves appeared with a critical wavelength of 8mm. Since the onset of the instability was sudden, and the disappearance for decreasing strain showed strong hysteresis, the instability was of first order. The shape of the grooves was independent of the sign of the applied strain, i.e., cusps were always pointing towards the solid. Further, it was observed that the corrugations vanished with time, implying that other relaxation mechanisms were present which showed a clear temperature dependence. The typical relaxation time varied from tenths of seconds at 1.2K to an hour at 0.9K. Additional experiments on <sup>4</sup>He liquid-solid interfaces were also performed by Bowley [92].

#### Polymer crystal

Another interesting quantitative study of the Grinfeld instability was performed by Berréhar et al. [92]. Their experimental system is a single-crystal film of polymerized polydiacetylene, grown in epitaxy with a monomer substrate. The polymerization is initiated by low-energy electrons and induces a uniaxial stress in the polymerized film, which is generated by the difference in the chain parameter between the monomer and the polymer. The polymer chains grow along the binary axis  $\vec{b}$ . The relative lattice mismatch in the chain direction varies continuously with the polymer content. Polymer content as well as the film thickness can be controlled by the electron dose and electron energy, respectively. The thicknesses of the film studied ranged from 50 to 500*nm*. The surface profile was analyzed with an AFM (atomic force microscope). For films up to 150nm the surface was covered with a wavy parallel wrinkle pattern perpendicular to the chain direction  $\vec{b}$ . The surface height variations were typically 5nm and the spacing  $\lambda$  in the range of 150 - 350nm. The pattern was independent of the film thickness and the polymer content X for X > 10%. For films thicker than 200nm, the whole sample surface showed rather regular patterns of long parallel cracks, again perpendicular to the chain direction  $\vec{b}$ , with fairly regular spacings in the range of a few  $\mu m$ . The cracks were straight and ran straight through steps, implying that they were not preferentially initiated by surface defects. For the crack depth, a lower limit of 100nm could be obtained, comparable to the film thickness. By comparing the spacing of the wrinkles with the predicted wavelength derived from the linear stability analysis of the Grinfeld instability, and the time scale of the appearance of the wrinkle pattern which was consistent with surface diffusion, it was argued that the wrinkle pattern is due to the Grinfeld instability, and that the cracking was a secondary instability initiated by the Grinfeld instability, which also determines the crack spacing.

#### Dislocation-free Stranski-Krastanov growth

The Grinfeld instability is also associated with the dislocation-free Stranski-Krastanov growth, which describes the island-on-layer growth mode in epitaxy. Typically, one distinguishes three growth modes in epitaxy:

- Frank-van der Merwe growth (layer-by-layer growth),
- Stranski-Krastanov growth (island-on-layer growth),
- Volmer-Weber growth (island-growth).

Figure 5.2: Different growth modes in epitaxy. From left to right: Frank-van der Merwe growth (layer-by-layer growth), Stransky-Krastanov growth (island-on-layer growth), Volmer-Weber growth (island growth).

Which growth mode will be adopted in a given system will depend on the interfacial free energy terms and on the lattice mismatch. In lattice matched systems, only the first two growth modes can occur. Whether the film wets the substrate (layer-by-layer growth) or does not (island-on-layer growth) depends then only on three energies: the interfacial energies  $\gamma_{fs}$ , the film surface energy  $\gamma_f$  and the substrate surface energy  $\gamma_s$ . If  $\gamma_{fs} + \gamma_f < \gamma_s$  island growth occurs. Otherwise layer-by-layer growth happens. By adding a surfactant,  $\gamma_{fs} + \gamma_f$  can be changed, and island growth can be suppressed. If film and substrate have different lattice constants, a coherently growing film will be strained. As the film thickness increases, so does the elastic energy stored within the film. At some thickness, it becomes energetically favorable to relieve this misfit strain. This happens either elastically by the dislocation-free Stranski-Krastanov mode or plastically by the formation of dislocations, or both.

For a long time it was assumed that dislocations provided the only stress relief mechanism. However, in 1990, Eaglesham and Cerullo [90] showed that the islands formed in Stranski-Krastanov growth of Ge on Si(100) are initially dislocation-free. Since then, many more systems have been found which show dislocation-free Stranski-Krastanov growth<sup>1</sup>. Two examples are shown in figure 5.3 and figure 5.4. In both cases Ge is grown coherently on Si and shows an undulating surface structure. In figure 5.3, the surfactant Sb was present. It should be noted that there is some evidence that the dislocation-free Stranski-Krastanov mode is only a transient stage towards the plastic relaxation. It has been realized that surface morphology plays an important role in the dislocation nucleation process. As we will see in chapter 6, inhomogeneities in the surface morphology imply regions of high stress concentrations which may provide enough energy to nucleate dislocations. Traditional theories of stress relaxation via dislocations are based on the above mentioned energy balance

<sup>&</sup>lt;sup>1</sup>LeGoues, Copel and Tromp [90]; Guha, Madhukar and Rajkumar [90]; Tersoff and LeGoues [94]; Okada, Weatherly and McComb [97].



Figure 5.3: STM image of 8 mono-layers Ge on Si(100) deposited at  $700^{\circ}C$  with Sb as a surfactant (Horn von Hoegen [97]).

between elastic energy and surface free energy. They do not include the nucleation process. The earliest treatment was the continuum theory of Frank and van der Merwe for an array of non-interacting dislocation at the film-substrate interface. Matthews and Blakeslee [74] assumed pre-existing dislocations in the substrate, which were assumed to move into the film once the mean stress caused by the misfit exceeded the dislocation line tension. However, these approaches do not consider the mechanism by which the dislocations nucleate. Dong et al. [98] performed a two-dimensional molecular dynamics simulation in which they studied the temporal evolution of the surface morphology and the mechanisms for misfit dislocation nucleation and stress relaxation. Their results show that the critical thickness depends sensitively on the film morphology. Tersoff and LeGoues [94] indicated, by calculating the nucleation rate of dislocations, that strain-induced surface "roughening" is the dominant mechanism for the introduction of dislocations in strained layers at high misfit. It is therefore important to study the pre-dislocation morphological changes, though ultimately dislocations must be included for complete understanding.



Figure 5.4: TEM micrograph of a section of Ge grown on Si(100). The 8 mono-layers of Ge on Si are pseudomorphic, i.e. have the same lattice-spacing (LeGoues, Copel and Tromp [90]).

### 5.4 Traditional Approach

The Grinfeld instability has been studied theoretically quite intensively in the last decade. There have been basically two approaches. The first uses a variational principle, in which the the analysis of the second variation determines whether the system under consideration is stable or unstable. Grinfeld<sup>1</sup> used this approach to study various configurations. However, these thermodynamic energy minimization calculations are static and do not permit a description of the evolution of the instability, nor can they describe the morphology and stability of a growing film. The other approach being used by Asaro and Tiller [72], Srolovitz [89], Spencer, Voorhees and Davis [91], Spencer, Voorhees and Davis [93], Spencer. Davis and Voorhees [93], Spencer and Meiron [94], Grilhé [93], Yang and Srolovitz [93] and Kassner and Misbah [94] is based on a dynamical continuum model, in which mass transport mechanisms, such as condensation-evaporation or surface diffusion, are driven by the chemical potential or the gradient of the chemical potential which comprises surface free energy as well as elastic energy. We will present here the second approach, which is at the same time the sharp-interface formulation of the problem. It can be related to our phase-field formulation, as will be seen later.

It has been seen in the experimental set-ups described above that the solid can be strained uni-axially in different ways. In the experiment by Torii and Balibar [92] a He<sup>4</sup> crystal was strained by applying an external force at the edges of the sample. In the case of epitaxial strained films, the film is attached coherently to the

<sup>1</sup>Grinfeld [82]; Grinfeld [86]; Grinfeld [89].

substrate. The difference between the lattice constant of the film  $a_f$  and the substrate  $a_s$  generated a lattice mismatch  $\epsilon = \frac{a_f - a_s}{a_s}$  and strained the film. If the lattice constant of the film is greater than that of the substrate,  $\epsilon > 0$ , the film is compressed in the horizontal directions in order to match with the substrate.

#### A. Model

To be more precise, let us consider the set-up shown in figure 5.5. A stress  $\sigma_{xx} = \sigma_0$  is applied to the vertical sides of a semi-infinite, isotropic solid which is in free contact with its own melt or vapor in z-direction, constrained in x-direction and infinite in ydirection. Initially the surface lies along z = 0. In addition, the system is assumed to be isothermal and the pressure of the vapor or melt is assumed to be small compared to stress in the solid. The solid responds to the applied stress through a deformation, which can easily be determined if the surface of the solid is flat. Since the solid is constrained in the x-direction, it is convenient to use a reference frame for which  $u_x = 0$  in the stressed state. Hooke's law is then given by:

$$\sigma_{ij} = \frac{E}{1+\nu} \left( u_{ij} + \frac{\nu}{1-2\nu} u_{ll} \,\delta_{ij} - \frac{1+\nu}{1-2\nu} \,\epsilon \,\delta_{ij} \right) \,, \tag{5.19}$$

where  $\epsilon$  is the strain of the reference frame. Due to that choice:

$$u_{xx} = 0.$$
 (5.20)

Since the surface is flat, the boundary condition (5.24) reads:

$$\sigma_{zz} = 0. \tag{5.21}$$

 $u_z$  however will be uniformly strained due to Poisson relaxation:

$$u_{zz} = \frac{1+\nu}{1-\nu} \epsilon \,. \tag{5.22}$$

This can be seen by replacing equation (5.20) and equation (5.21) in Hooke's law (5.19). Hence, the stressed state is uniform. However, if the surface is not flat, the stress field will *not* be uniform. To determine the stress state then, one has to solve the mechanical equilibrium condition (5.2):

$$\frac{\partial \sigma_{ij}}{\partial x_j} = 0, \qquad (5.23)$$



Figure 5.5: Sketch of Grinfeld instability. A stress  $\sigma_0$  is applied to the edges of a semi-infinite, isotropic solid which is in free contact with its own melt or vapor.

with the appropriate boundary condition at the surface:

$$\sigma_{ij}n_j = 0, \qquad (5.24)$$

on the surface z = h(x), where  $n_j$  is the normal vector to the surface pointing towards the liquid or vapor. The other boundary conditions at  $z \to -\infty$  are:

$$\sigma_{zz} = 0 \tag{5.25}$$

$$\sigma_{xx} = \sigma_0 \,. \tag{5.26}$$

With equation (5.23) and boundary conditions (5.24), (5.25) and (5.26), the stress state of the solid for a given configuration of the free surface z = h(x) is defined. The equation is solved in appendix A.2. Knowing the stress state at the surface of the film, the chemical potential along the surface can be calculated:

$$\mu^{s}(x) = \mu_{0} + \gamma \kappa_{c}(x) \Omega + \frac{1+\nu}{2E} \left[\sigma_{ij}^{2} - \nu(\sigma_{ll})^{2}\right] \Omega, \qquad (5.27)$$

where  $\mu_0$  is the chemical potential for the flat interface,  $\gamma$  is the surface tension,  $\Omega$  is an atomic volume, and  $\kappa_c$  the curvature:

$$\kappa_{c} = \frac{\frac{\partial^{2}h}{\partial x^{2}}}{\sqrt[3]{1 + (\frac{\partial h}{\partial x})^{2}}}.$$
(5.28)

Since  $\sigma_{nn} = \sigma_{nt} = 0$  are zero along the surface due to the mechanical equilibrium condition (5.24), the only non-zero stress contribution at the interface is  $\sigma_{tt}$ :

$$\mu^{s}(x) = \mu_{0} + \gamma \kappa_{c} \Omega + \frac{1 - \nu^{2}}{2E} \sigma_{tt}^{2} \Omega. \qquad (5.29)$$

Essential for the development of the instability is mass transport, through which the solid can reach its equilibrium state. There are mainly two mass transport mechanisms: evaporation-condensation, or melting-freezing, and surface diffusion. In the

and,

case of evaporation-condensation the mass transport occurs through an attachmentdetachment process at the front. We assume that the system is above the roughening transition, without facets, so that the attachment kinetics are fast. This implies that the growth velocity of the surface  $v_n$  (normal to itself) is proportional to the difference in the chemical potential between the solid and liquid:

$$v_n = -\Gamma\left(\mu^s - \mu^l\right),\tag{5.30}$$

where  $\Gamma$  is a kinetic coefficient. Since we assumed that the planar solid is in equilibrium with the liquid phase, and further assumed that the liquid pressure  $p_l$  is very small, we obtain

$$\Delta \mu = \mu^{s} - \mu^{l} = \gamma \kappa_{c} \Omega + \frac{1 - \nu^{2}}{2E} \sigma_{tt}^{2} \Omega.$$
(5.31)

Hence, equation (5.30) yields:

$$v_n = -\Gamma \left[ \gamma \kappa_c + \frac{1 - \nu^2}{2E} \sigma_{tt}^2 \right] , \qquad (5.32)$$

or in terms of the surface profile h(x):

$$\frac{\partial h}{\partial t} = \Gamma \frac{1}{\sqrt{1 + h_x^2}} \left[ \gamma \kappa_c + \frac{1 - \nu^2}{2E} \sigma_{tt}^2 \right] \,. \tag{5.33}$$

If the transport mechanism is surface diffusion, the total amount of material is conserved:

$$v_n = -\nabla_s \vec{j}_s \,, \tag{5.34}$$

where  $\nabla_s$  is the Laplace-Beltrani operator, which ensures that diffusion occurs only along the surface, and  $\vec{j}_s$  is the material current at the surface which is proportional to the gradient in the chemical potential of the solid:

$$\vec{j}_s = -D\nabla_s \mu^s \,, \tag{5.35}$$

where  $D = D_s \Omega \delta / k_B T$ ,  $D_s$  is the surface diffusivity,  $\delta$  is the number of atoms per unit area, and  $k_B T$  is the thermal energy. The equation of motion for the interface becomes:

$$v_n = D \, \nabla_s^2 \mu^s \,, \tag{5.36}$$

and in terms of the surface profile h(x):

$$\frac{\partial h}{\partial t} = D \frac{1}{\sqrt{1 + h_x^2}} \frac{\partial^2}{\partial s^2} \mu^s \,. \tag{5.37}$$

### **B.** Linear Stability Analyses

Linear stability analysis characterizes the instability. To do so, we study the dynamics of a small amplitude sinusoidal surface profile,

$$h(x) = h_0 \sin qx \,, \tag{5.38}$$

which implies that the stress field in the film is no longer uniform. To calculate the equation of motion of the interface, the stress state at the interface has to be known. This can be achieved by solving the mechanical equilibrium condition with the boundary conditions (5.24) and (5.25). The algebra is done in appendix A.2. The stress in the infinitely thick solid is given by

$$\sigma_{xx} = \sigma_0 \left[ 1 - h_0 q(qz+2) e^{qz} \sin(qx) \right], \qquad (5.39)$$

$$\sigma_{xz} = \sigma_0 h_0 q^2 z e^{qz} \sin(qx) , \qquad (5.40)$$

$$\sigma_{zz} = \sigma_0 h_0 q^2 (1 - qz) e^{qz} \cos(qx) \,. \tag{5.41}$$

This shows that the perturbation of the uniform stress field due to the sinusoidal surface profile decays exponentially into the film (z < 0) with a decay length proportional to the wavelength of the surface profile. At the surface only the tangential stress component  $\sigma_{tt}$  is non-zero. To lowest order in  $qh_0$  it is given by:

$$\sigma_{tt} = \sigma_0 \left[ 1 - 2qh \right] \,. \tag{5.42}$$

The first term is a zeroth-order contribution which accounts for the fact that stress increases the chemical potential, and melts even a planar front. This term should be subtracted from the chemical potential in equation (5.29). The second term is the first order term which shows that the stress in the peaks is the lowest, whereas in the valleys it is the highest.

Replacing equation (5.42) in the linearized equation of motion for the surface, in the case of evaporation-condensation, results in

$$\frac{\partial h}{\partial t} = -\Gamma \left[ \gamma q^2 - 2 \frac{1 - \nu^2}{E} \sigma_0^2 q \right] h , \qquad (5.43)$$

and in the case of surface diffusion,

$$\frac{\partial h}{\partial t} = -D \left[ \gamma q^4 - 2 \frac{1 - \nu^2}{E} \sigma_0^2 q^3 \right] h.$$
(5.44)

and



Figure 5.6: Dispersion relations for Grinfeld instability for evaporation-condenstion on the left and for surface diffusion on the right.  $q_c$  is the critical wave number. Perturbations with  $q < q_c$  are unstable, whereas perturbations with  $q > q_c$  are stabilized by surface tension.

These linearized equations can be solved by:

$$h(t) = h_0 \exp\left(\omega t\right), \tag{5.45}$$

where  $\omega$  describes the normal-mode growth rate, which is determined by a dispersion relation. In the case of evaporation-condensation. or melting-freezing, we obtain

$$\omega = \Gamma \left[ 2 \, \frac{1 - \nu^2}{E} \sigma_0^2 q - \gamma \, q^2 \right] \,, \tag{5.46}$$

and in the case of surface diffusion,

$$\omega = D \left[ 2 \frac{1 - \nu^2}{E} \sigma_0^2 q^3 - \gamma q^4 \right] .$$
 (5.47)

Figure 5.6 shows the dispersion relation for both cases. In both cases, modes  $q > q_c$  are stable, whereas modes  $q < q_c$  are linearly unstable to small perturbations of the surface. The neutral or critical wave number is in both cases given by:

$$q_c = 2 \frac{1 - \nu^2}{E} \frac{\sigma_0^2}{\gamma} \,. \tag{5.48}$$

As can be seen from the sign in both equations, the elastic field destabilizes the surface at long wavelength, whereas surface tension stabilizes short wavelength perturbations. Therefore, the stress-induced morphological instability is also a long-wavelength instability. Note that the dispersion relation passes through the origin, meaning that the flat interface is marginally stable to linear order.

#### C. Summary of other Results

Spencer, Voorhees and Davis [93] extended the linear stability analyses to a threedimensional epitaxially strained film with surface diffusion. They included the substrate as well as an external flux. For the static film they observed that the neutral wave number  $q_c$  was a function of the film thickness,  $d_0$ , and the stiffness ratio  $\varrho = \frac{\mu^J}{\mu^s}$ ,  $\mu^{f}$  and  $\mu^{s}$  being the shear modulus of the film and substrate, respectively.  $\rho = 1$  represents the case where film and substrate have the same shear moduli, and hence are not distinguishable elastically. In this case, the system is equivalent to the semiinfinite solid discussed above. For  $\rho > 1$  the substrate is softer than the film. The neutral wave number  $q_c$  starts off larger than for a semi-infinite solid, decreases with increasing film thickness, and finally approaches the semi-infinite neutral wave number curve. For  $0 < \rho < 1$ , the substrate is stiffer than the film, and reduces the range of unstable modes compared to the semi-infinite solid. With increasing film thickness, the critical wave number increases and finally also approaches the semi-infinite solid curve. For a rigid substrate with g = 0, the stabilizing effect of the substrate is so pronounced that the instability is completely suppressed for film thicknesses less than a critical value. The effect of a constant deposition of particles on the film results in a growth rate change with time, since the growth rate depends on the film thickness as discussed above. Thus, there is no simple way of measuring the stability. However, since both the perturbation and the film are growing, the growth of the perturbation is only observable if the perturbation growth is faster than the rate at which the film thickens. The competition is quantified by a relative growth rate  $\Omega = \omega(\hat{d}) - \frac{V}{\hat{d}(t)}$ . Since the growth rate  $\omega$  is extremely sensitive to temperature, due to the temperature dependence of the surface diffusivity, low temperatures can suppress the instability.

By exploiting the long-wave nature of the instability Spencer, Davis and Voorhees [93] derived a non-linear evolution equation for the film surface of an epitaxially strained film on a rigid substrate ( $\rho = 0$ ), in the absence of particle deposition. As discussed above, linear stability analysis shows that for a rigid substrate there is a critical thickness  $d_c$  below which the film is stable, and that with increasing film thickness the range of unstable wave numbers extends from zero. Hence, in the vicinity of this critical thickness the unstable wave numbers are near zero. Introducing

the film thickness d as the characteristic length scale, they assume that the length scale in the lateral directions  $\lambda$  is much larger, so that  $\alpha = d/\lambda \ll 1$  is a small parameter. Hence, the displacement fields as well as the Lamé equation (5.8) can be expanded in  $\alpha$ , and solved to lowest order. They obtain a non-linear evolution equation for the surface and examine its two-dimensional steady states. They find sub-critical spatially periodic finite-amplitude rounded-cusp steady solutions, as well as near-critical spatially periodic small-amplitude steady state solutions. However, the stability analysis they performed showed that all these solutions are unstable. The absence of stable two-dimensional steady states leaves the eventual fate of the evolution of the instability unresolved. To gain insight into whether additional steady solution branches exist, or a type of coarsening occurs, they studied the time dependent behavior of their long-wave evolution equation. However, the equation breaks down before any of these issues are resolved.

By calculating the chemical potential of an uni-axially stressed, semi-infinite solid, and incorporating higher-order terms in the interfacial height h, Nozières [93] determined the instability to be first order (sub-critical). He also showed that the interface flattens on the liquid side and develops grooves on the solid side. He also found that gravity acts as a stabilizing influence.

Spencer and Meiron [94] studied numerically the non-linear evolution of the stressdriven morphological instability on the surface of a two-dimensional semi-infinite solid as a function of amplitude and wave number. They found that the solution branch of the steady states terminates with a cusp singularity which is numerically not accessible. At small amplitudes, the steady state solution had a sinusoidal shape, whereas at larger amplitudes the peaks were broader and the valleys sharper. They also studied the time dependent evolution of different small sinusoidal perturbation which also evolved to cusp singularities.

Another numerical study was performed by Yang and Srolovitz [93]. They used boundary integral equation methods to solve the elastic equations, and integrated the sharp interface equation for the case of surface diffusion. They observed deep cracklike grooves appearing, in which the growth rate for the grooves rapidly accelerated, and the time dependence of the groove depth became faster than exponential. They argued their observations were related to fracture.

#### D. Discussion

Experiments as well as simulations indicate that the Grinfeld instability might be transient and will ultimately lead either to fracture and/or to dislocation nucleation. By that stage the sharp-interface approach must have broken down since the problem can no longer be described by considering surface tension and linear elastic strain only. However, numerical simulations<sup>1</sup> encounter numerical instabilities already at much earlier times. Also three-dimensional simulations have proven impractically large using the sharp-interface equations.

The phase-field approach on the other hand is very robust against numerical instabilities. Also, since non-linearities are inherent in the description numerical simulations in two and three dimensions can easily be performed. Furthermore, the phasefield approach can easily be extended by coupling additional fields to the phase-field. Hence the nucleation of dislocations can be included by coupling a dislocation density field to the phase-field. Thus the formulation of the Grinfeld instability based on a Ginzburg-Landau approach is the first step towards a complete description of stress relaxation mechanisms in evolving structures.

<sup>&</sup>lt;u>56</u>

<sup>&</sup>lt;sup>1</sup>Spencer, Davis and Voorhees [93]; Spencer and Meiron [94].

### MODEL OF SURFACE INSTABILITIES INDUCED BY STRESS

We propose a new model to describe the Grinfeld instability which is based on a Ginzburg-Landau approach<sup>1</sup>. As discussed in chapter 3, the phase-field approach is a convenient way to simulate free-boundary or moving-boundary type problems. Since it has been employed successfully to study the Mullins-Sekerka instability, it seems also an appropriate formulation to study the Grinfeld instability. In the context of elasticity, it was first introduced by Nishimori<sup>2</sup> to analyze elastic effects in phase-separating alloys by coupling the elastic field to model B. In that scheme, the elastic strain is a subsidiary tensor which can be eliminated by assuming mechanical equilibrium. Thus it yielded a closed description for the equation of motion of the concentration. Sagui, Somoza and Desai [94] applied this formalism to model C, coupling the elastic field to both the concentration and the order parameter, in order to study the effect of an elastic field on an order-disorder transition. The approach has also been used by Aguenaou. Müller and Grant [98] to study quasidendritic growth due to elastic fields.

We modify that approach by coupling the elastic field to a non-conserved scalar order parameter field  $\phi(\vec{r})$  which determines whether one is in a hard solid phase which supports shear, or in a soft disordered phase, hereafter called the liquid phase, which does not. The position of the interface coincides with the rapid variation of this field. Coupled to the order parameter is the elastic strain  $u_{ij}$  which is a subsidiary tensor. The coarse-grained Ginzburg-Landau free energy is:

$$\mathcal{F}(\phi, u_{ij}) = \int d\vec{r} \left[ f(\phi, u_{ij}) + \frac{l^2}{2} |\nabla \phi|^2 \right], \qquad (6.1)$$

where  $u_{ij}$  is the strain and  $u_i$  is the displacement field.

<sup>&</sup>lt;sup>1</sup>Müller and Grant [98].

<sup>&</sup>lt;sup>2</sup>Onuki [89a]; Onuki [89b]; Onuki and Nishimori [91]; Nishimori and Onuki [90].


Figure 6.1: Sketch of three-well potential,  $\phi = 0$  is the liquid and  $\phi = \pm 1$  is the solid phase. There is no difference between the two solid phases. On the left solid and liquid are at coexistence, on the right the solid is meta-stable and will eventually melt.

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

$$f(\phi, u_{ij}) = \frac{1}{a}\phi^2(\phi^2 - 1)^2 + \frac{\eta_0^2}{2\kappa}g(\phi)^2 + \eta_0 \ g(\phi)\nabla \cdot \vec{u} + f_{el}(\phi, u_{ij}), \tag{6.2}$$

where the first part describes a three-well potential with  $\phi = 0$  being the liquid and  $\phi = \pm 1$  the solid phase, ensuring that the liquid-solid phase transition is first order. The potential depths *a* together with the parameter *l* fixes the interfacial thickness. The second term shifts the energy, so that, for constant elastic coefficients, solid and liquid are at coexistence. The coupling constant  $\eta_0$  is related to the externally applied stress. The trace of the strain tensor is  $\nabla \cdot \vec{u}$ , and  $f_{el}(\phi, u_{ij})$  is the isotropic elastic free energy for a *d*-dimensional system<sup>1</sup>:

$$f_{el}(\phi, u_{ij}) = \frac{1}{2}\kappa(\nabla \cdot \vec{u})^2 + \mu \sum_{ij} \left( u_{ij} - \frac{\delta_{ij}}{d} \nabla \cdot \vec{u} \right)^2, \qquad (6.3)$$

where  $\kappa$  is the bulk modulus and  $\mu$  the shear modulus which is  $\phi$  dependent:

$$\mu = \mu_1 g(\phi). \tag{6.4}$$

The convenient choice

$$g(\phi) = \frac{1}{2}\phi^2 - \frac{1}{4}\phi^4, \tag{6.5}$$

guarantees that both bulk phases keep their equilibrium values at  $\phi = 0$  (liquid) and  $\phi = \pm 1$  (solid). By construction, the shear modulus in the soft liquid phase is zero, whereas it stays non-zero and constant in the hard solid phase. Since the solid phase  $\sqrt{1}$  Landau and Lifshitz [83].

supports shear, whereas the liquid phase does not, our phase-field order parameter has a transparent meaning in the context of liquid-solid transition.

Since elastic forces propagate with the speed of sound, it is reasonable to suppose that the elastic field relaxes much faster than  $\phi$ . Thus, the elastic field can be solved in terms of the order parameter using the condition of mechanical equilibrium:

$$f_i = \frac{\delta \mathcal{F}}{\delta u_i} = \frac{\partial \sigma_{ij}}{\partial x_j} = 0.$$
(6.6)

The stress tensor  $\sigma_{ij}$  is then given by:

$$\sigma_{ij} = \frac{\partial \mathcal{F}}{\partial u_{ij}} = (\eta_0 g(\phi) + \kappa \nabla \cdot \vec{u}) \delta_{ij} + 2\mu_1 g(\phi) \left( u_{ij} - \frac{\delta_{ij}}{d} \nabla \cdot \vec{u} \right) .$$
(6.7)

Note, that the first term on the right hand side corresponds to a pre-strained reference frame and is proportional to the externally applied stress. The solution of the mechanical equilibrium condition, to first order in the shear modulus, is:

$$\nabla \cdot \vec{u} = Tr\mathbf{A} - \frac{\eta_0}{\kappa} g(\phi) + 2\mu_1 \frac{\eta_0}{\kappa^2} \int d\vec{r}' \int d\vec{r}'' G(\vec{r}, \vec{r'}) \frac{\partial^2}{\partial x'_i \partial x'_j} \left[ g(\vec{r'}) \ M_{ij}(\vec{r'}, \vec{r''}) \ g(\vec{r''}) \right], \quad (6.8)$$

and

$$\frac{\partial u_j}{\partial x_i} = \frac{\partial u_i}{\partial x_j} = A_{ij} - \frac{\eta_0}{\kappa} \frac{\partial^2}{\partial x_j \partial x_i} \int d\vec{r'} G(\vec{r}, \vec{r'}) g(\vec{r'}), \tag{6.9}$$

where

$$\nabla^2 G(\vec{r}, \vec{r'}) = \delta(\vec{r}, \vec{r'}) \tag{6.10}$$

and

$$M_{ij}(\vec{r},\vec{r'}) = \frac{\partial^2}{\partial x_i \partial x_j} G(\vec{r},\vec{r'}) - \frac{\delta_{ij}}{d} \delta(\vec{r}-\vec{r'}).$$
(6.11)

Equation (6.8) justifies the coupling term in equation (6.2), since in the absence of external strain, that is  $A_{ij} = 0$ , the solid will be stressed whereas the liquid is stress-free. For a flat surface, i.e.,  $\phi = \phi(z)$  being a function of z only, the solution of equation (6.8) in two dimension is:

$$u_{xx}(\vec{r}) = u_{xz}(\vec{r}) = 0, \qquad (6.12)$$

$$u_{zz}(\vec{r}) = -\frac{\eta_0}{\kappa} g(\vec{r}) \left( 1 - \mu_1 \frac{g(\vec{r})}{\kappa} \right) . \tag{6.13}$$

and,

Hence, the solid will be uni-axially strained, as discussed in chapter 5.4, with  $\eta_0$ determining the strength. The stress can be determined using Hooke's law (6.7):

$$\sigma_{xx} = 2\,\mu_1 \,\frac{\eta_0}{\kappa} g^2(\vec{r}) - \mu_1^2 \frac{\eta_0}{\kappa^2} g^3(\vec{r})\,, \tag{6.14}$$

and,

$$\sigma_{zz} = \sigma_{xz} = 0. \tag{6.15}$$

Hence  $\sigma_{xx}$  determines the stress which is externally applied.

The elastic field can now be expressed in terms of the order parameter. Substituting the strain from equation (6.8) and equation (6.9) in equation (6.3) leaves the total free energy to first order in  $\mu$  as function of  $\phi$  only:

$$\mathcal{F}(\phi) = \int d\vec{r} \left[ \frac{f(\phi)}{a} + \frac{l^2}{2} |\nabla \phi|^2 + \mu_1 \frac{\eta_0^2}{\kappa^2} g(\vec{r}) \int d\vec{r'} \int d\vec{r''} M_{ij}(\vec{r}, \vec{r'}) g(\vec{r'}) M_{ij}(\vec{r'}, \vec{r''}) g(\vec{r''}) \right].$$
(6.16)

The long-range character of the elastic field appears now in the non-local Green's function in  $\phi$ . One should also note that  $\eta_0$  enters quadratically in the free energy, implying that compressive as well as tensile stresses contribute equally to the energy. Assuming that the dynamics of  $\phi$  is relaxational, the equation of motion is given by:

$$\frac{\partial\phi}{\partial t} = -\Gamma \frac{\delta\mathcal{F}}{\delta\phi} = -\Gamma \left[ \frac{f_{\phi}(\phi)}{a} - l^2 \nabla^2 \phi + \mu_1 \frac{\eta_0^2}{\kappa^2} g_{\phi}(\phi) \ h(\phi) \right], \tag{6.17}$$

where the index  $\phi$  means differentiation by  $\phi$ .  $\Gamma$  is the mobility and

$$h(\phi) = 2 \int d\vec{r'} \int d\vec{r''} \left[ G(\vec{r}, \vec{r'}) \frac{\partial^2}{\partial'_i \partial'_j} M_{ij}(\vec{r'}, \vec{r''}) + M_{ij}(\vec{r}, \vec{r'}) M_{ij}(\vec{r'}, \vec{r''}) \right] g(\vec{r'}) g(\vec{r''}).$$
(6.18)

Rescaling length and time scales:

$$\vec{r'} = \frac{\vec{r}}{w}, \qquad (6.19)$$
$$t' = \frac{\Gamma t}{w^2}, \qquad (6.20)$$

(6.20)

where w is a characteristic length scale such as the wavelength of the perturbation, rescales the parameters to:

$$\epsilon = \frac{l\sqrt{a}}{w}, \qquad (6.21)$$

$$\beta = \frac{w^2}{a} \,, \tag{6.22}$$

$$c = \mu_1 a \frac{\eta_0^2}{\kappa^2} \,. \tag{6.23}$$

and,

Omitting the primes we obtain as equation of motion:

$$\frac{\partial \phi}{\partial t} = -\beta [f'(\phi) - \epsilon^2 \nabla^2 \phi + c \ g'(\phi) \ h(\phi)], \qquad (6.24)$$

with three parameters  $(\beta, \epsilon, c)$ , giving the mobility, capillarity, and shear strength, respectively.

# 6.1 Sharp Interface Limit

It has been argued in chapter 3 that the sharp interface equations and the phasefield formulation are equivalent if, in the sharp- or thin-interface limit, the phase-field equations converge to the sharp-interface equations. To obtain the sharp-interface limit, we will not integrate out the strain field, but instead we will keep the mechanical equilibrium condition explicitly. We obtain a system of coupled partial differential equations:

$$\frac{\partial\phi}{\partial t} = -\Gamma \left[ \frac{f_{\phi}}{a} - l^2 \nabla^2 \phi + \frac{\eta_0^2}{\kappa} g(\phi) g_{\phi}(\phi) + \eta_0 g_{\phi}(\phi) \nabla \cdot \vec{u} + \mu_1 g_{\phi}(\phi) \left( u_{ij} - \frac{\delta_{ij}}{d} \nabla \cdot \vec{u} \right)^2 \right]. \quad (6.25)$$

and

$$\frac{\partial \sigma_{ij}}{\partial x_j} = \frac{\partial}{\partial x_i} [\eta_0 g(\phi) + \kappa \nabla \cdot \vec{u}] + 2\mu_1 \frac{\partial}{\partial x_j} \left[ g(\phi) \left( u_{ij} - \frac{\delta_{ij}}{d} \nabla \cdot \vec{u} \right) \right] = 0.$$
(6.26)

To obtain a dimensionless equation, we rescale space as in equation (6.19) and time as:

$$t' = \frac{\Gamma l^2}{w^2} t \,, \tag{6.27}$$

and obtain as parameter:

 $\xi = \frac{l}{w} \,. \tag{6.28}$ 

This yields a dimensionless equation for  $\phi$ :

$$-\xi^{2} \frac{\partial \phi}{\partial t} = \frac{f_{\phi}}{a} - \xi^{2} \nabla^{2} \phi + \frac{\eta_{0}^{2}}{\kappa} g(\phi) g_{\phi}(\phi) + \eta_{0} g_{\phi}(\phi) \nabla \cdot \vec{u} + \mu_{1} g_{\phi}(\phi) \left( u_{ij} - \frac{\delta_{ij}}{d} \nabla \cdot \vec{u} \right)^{2} .$$
(6.29)

To perform the formal multiple-expansion we rescale the phase-field equation as:

ε

$$=\xi^2, \tag{6.30}$$

$$c = \frac{\xi}{\sqrt{a}},\tag{6.31}$$

and,

$$\bar{f}_{\phi} = c^2 f_{\phi} \,, \tag{6.32}$$

with c being fixed in the limit  $\epsilon \to 0$  as discussed by Caginalp [89]. The phase-field equation (6.29) yields:

$$-\epsilon^{2}\frac{\partial\phi}{\partial t} = \tilde{f}_{\phi} - \epsilon^{2}\nabla^{2}\phi + \epsilon \frac{\eta_{0}^{2}}{\kappa}g(\phi)g_{\phi}(\phi) + \epsilon \eta_{0} g_{\phi}(\phi)\nabla \cdot \vec{u} + \epsilon \mu_{1}g_{\phi}(\phi)\left(u_{ij} - \frac{\delta_{ij}}{d}\nabla \cdot \vec{u}\right)^{2}.$$
(6.33)

Here we follow a formal expansion, as worked out in the appendix A.1 for the Mullins-Sekerka instability. The idea of the multiple-scale expansion, or matched asymptotics as it is often called, is to divide the total space into an outer region given by the bulk phases, and an inner region which contains the diffuse interface. In the inner region we define a local orthogonal set of curvilinear coordinates (r, s) that moves with the instantaneous velocity of the interface. Here, r measures the length along the normal direction, and s measures the arc length along the interface, defined by  $\phi = 1/2$ . Furthermore, we rescale the inner variable r to  $z = \frac{r}{\epsilon}$  and expand the outer solution in powers of  $\epsilon$ :

$$\phi = \phi(x, y, t, \epsilon) = \phi^{(0)}(x, y, t) + \epsilon \phi^{(1)}(x, y, t) + \epsilon^2 \phi^{(2)}(x, y, t) + \cdots, \quad (6.34)$$

and,

$$\sigma_{ij} = \sigma_{ij}(x, y, t, \epsilon) = \sigma_{ij}^{(0)}(x, y, t) + \epsilon \sigma_{ij}^{(1)}(x, y, t) + \epsilon^2 \sigma_{ij}^{(2)}(x, y, t) + \cdots$$
 (6.35)

For the inner solution, we obtain:

$$\phi(x,y,t,\epsilon) \equiv \Phi(z,s,t,\epsilon) = \Phi^{(0)}(z,s,t) + \epsilon \Phi^{(1)}(z,s,t) + \cdots, \qquad (6.36)$$

and,

$$\sigma_{ij}(x, y, t, \epsilon) \equiv \Sigma_{ij}(z, s, t, \epsilon) = \Sigma_{ij}^{(0)}(z, s, t) + \epsilon \Sigma_{ij}^{(1)}(z, s, t) + \cdots$$
(6.37)

### **Outer Solution**

Replacing the outer expansion in the equation of motion of  $\phi$ , we obtain to zeroth order in  $\epsilon$ :

$$\tilde{f}_{\phi}(\phi^{(0)}) = 0,$$
 (6.38)

which determines the bulk phases to be  $\phi^{(0)} = \pm 1, 0$ . The mechanical equilibrium condition, to zeroth order, results in:

$$\frac{\partial \sigma_{ij}^{(0)}}{\partial x_j} = \frac{\partial}{\partial x_i} \left[ \eta_0 \, g(\phi^{(0)}) + \kappa \nabla \cdot \vec{u} \right] + 2\mu_1 \frac{\partial}{\partial x_j} \left[ g(\phi^{(0)}) \left( u_{ij} - \frac{\delta_{ij}}{2} \nabla \cdot \vec{u} \right) \right] = 0 \quad (6.39)$$

which is the known mechanical equilibrium condition for the liquid:

$$\frac{\partial}{\partial x_i} \left[ \kappa \nabla \cdot \vec{u} \right] = \frac{\partial p}{\partial x_i} = 0 , \qquad (6.40)$$

where  $p = p_l$  is the liquid pressure, which is constant in the liquid phase. For the solid phase we have:

$$\frac{\partial}{\partial x_i} \left[ \eta_0 \, g(\phi^{(0)}) + \kappa \nabla \cdot \vec{u} \right] + 2 \, \mu_1 \, g(\pm 1) \frac{\partial}{\partial x_j} \left[ u_{ij} - \frac{\delta_{ij}}{2} \nabla \cdot \vec{u} \right] = 0 \,. \tag{6.41}$$

Since

$$\sigma_{ij} = (\eta_0 \, g(\phi) + \kappa \nabla \cdot \vec{u}) \delta_{ij} + 2 \, \mu \, \left( u_{ij} - \frac{\delta_{ij}}{2} \nabla \cdot \vec{u} \right) \tag{6.42}$$

is the stress tensor, equation (6.41) is the mechanical equilibrium condition (5.2).

### Inner Solution

Rewriting the equation of motion for  $\Phi$  in terms of z, and the expanded quantities, yields:

$$-\epsilon \ v \ \Phi_z = \tilde{f}_{\phi}(\Phi) - \epsilon^2 \left[ \Phi_{ss} + \frac{1}{\epsilon^2} \Phi_{zz} + \frac{\kappa_c}{\epsilon} \Phi_z \right] + \epsilon \left[ \frac{\eta_0^2}{\kappa} g(\Phi) \ g_{\phi}(\Phi) + \eta_0 \ g_{\phi}(\Phi) \nabla \cdot \vec{U} + \mu_1 \ g_{\phi}(\Phi) \left( U_{ij} - \frac{\delta_{ij}}{2} \nabla \cdot \vec{U} \right)^2 \right], \quad (6.43)$$

where  $v = \dot{r}$ . Note, that  $\kappa$  is the compressibility and  $\kappa_c$  is the curvature. Hence, O(1) is given by:

$$\tilde{f}_{\phi}(\Phi^{(0)}) - \Phi^{(0)}_{zz} = 0, \qquad (6.44)$$

which determines  $\Phi^{(0)}$ .

To first order in  $\epsilon$  we have:

$$-v \Phi_{z}^{(0)} = \tilde{f}_{\phi\phi}(\Phi^{(0)}) \Phi^{(1)} - \Phi_{zz}^{(1)} - \kappa_{c} \Phi_{z}^{(0)} + \frac{\eta_{0}^{2}}{\kappa} g_{\phi}(\Phi^{(0)}) g(\Phi^{(0)}) + \eta_{0} g_{\phi}(\Phi^{(0)}) \nabla \cdot \vec{U}^{(0)} + \mu_{1} g_{\phi}(\Phi^{(0)}) \left( U_{ij}^{(0)} - \frac{\delta_{ij}}{2} \nabla \cdot \vec{U}^{(0)} \right)^{2}, \quad (6.45)$$

which can be rewritten:

$$\mathcal{L}\Phi^{(1)} = - [\kappa_c - v] \Phi_z^{(0)} + \frac{\eta_0^2}{\kappa} g_\phi(\Phi^{(0)}) g(\Phi^{(0)}) + \eta_0 g_\phi(\Phi^{(0)}) \nabla \cdot \vec{U}^{(0)} + \mu_1 g_\phi(\Phi^{(0)}) \left( U_{ij}^{(0)} - \frac{\delta_{ij}}{2} \nabla \cdot \vec{U}^{(0)} \right)^2.$$
(6.46)

As explained in appendix A.1, this implies a solvability condition:

$$[\kappa_{c} - v] \int_{-\infty}^{\infty} dz \, (\Phi_{z}^{(0)})^{2} = \int_{-\infty}^{\infty} dz \, \Phi_{z}^{(0)} \left[ \frac{\eta_{0}^{2}}{\kappa} g_{\phi}(\Phi^{(0)}) \, g(\Phi^{(0)}) + \eta_{0} \, g_{\phi}(\Phi^{(0)}) \nabla \cdot \vec{U}^{(0)} \right. \\ \left. + \, \mu_{1} g_{\phi}(\Phi^{(0)}) \left( U_{ij}^{(0)} - \frac{\delta_{ij}}{2} \nabla \cdot \vec{U}^{(0)} \right)^{2} \right] .$$

$$(6.47)$$

The strain however will be determined, giving the inner mechanical equilibrium condition to leading order. To do so, we use

$$\frac{\partial}{\partial x_j} = t_j \frac{\partial}{\partial s} + n_j \frac{1}{\epsilon} \frac{\partial}{\partial z} , \qquad (6.48)$$

where  $n_i$  is the normal vector and  $t_i$  is the tangential vector to the interface. Replacing  $\partial/\partial x_j$  in the mechanical equilibrium condition (6.26) and keeping only the zeroth order terms yields:

$$\frac{\partial}{\partial z} \left\{ n_i \left[ \eta_0 \, g(\Phi^{(0)}) + \kappa \nabla \cdot \vec{U}^{(0)} \right] + 2\mu_1 n_j \left[ g(\Phi^{(0)}) \left( U_{ij}^{(0)} - \frac{\delta_{ij}}{2} \nabla \cdot \vec{U}^{(0)} \right) \right] \right\} = 0. \quad (6.49)$$

Integrating equation (6.49) over the interfacial region yields:

$$n_i \kappa \nabla \cdot \vec{u}^{(0)} - n_i \left( g_s + \kappa \nabla \cdot \vec{u}^{(0)} \right) - 2 \,\mu_1 \, n_j \, g_s \left( u_{ij}^{(0)} - \frac{\delta_{ij}}{2} \nabla \cdot \vec{u}^{(0)} \right) = 0 \,, \tag{6.50}$$

where the matching conditions determine  $\Phi$  to be the bulk values  $\phi = \pm 1,0$  and g(0) = 0 and  $g(\pm 1) = g_s$ . The above equation is simply the boundary condition at the interface:

$$n_i p_l^{(0)} - n_j \sigma_{ij}^{(0)} = 0, \qquad (6.51)$$

where  $p_l = \kappa \nabla \cdot \vec{u}$  is the pressure in the liquid, which was assumed to be negligible, and  $\sigma_{ij}$  is the stress:

$$\sigma_{ij}^{(0)} = (\eta_0 \, g_s + \kappa \nabla \cdot \vec{u}^{(0)}) \delta_{ij} + 2 \, \mu_1 \, g_s \left( u_{ij}^{(0)} - \frac{\delta_{ij}}{2} \nabla \cdot \vec{u}^{(0)} \right) \,, \tag{6.52}$$

as defined by equation (6.7). To determine the stress state at the interface we multiply equation (6.51) by the normal  $n_i$  and tangential vector  $t_i$ :

$$\sigma_{nn}^{(0)} = \eta_0 g_s + \kappa \nabla \cdot \vec{u}^{(0)} + 2 \mu_1 g_s n_j \left( u_{ij}^{(0)} - \frac{\delta_{ij}}{2} \nabla \cdot \vec{u}^{(0)} \right) n_i = 0, \quad (6.53)$$

and,

$$\sigma_{nt}^{(0)} = 2\mu_1 g_s n_j \left( u_{ij}^{(0)} - \frac{\delta_{ij}}{2} \nabla \cdot \vec{u}^{(0)} \right) t_i = 0.$$
(6.54)

Hence,  $\sigma_{tt}$  is not determined by the mechanical equilibrium condition (6.26). The mechanical equilibrium condition in the inner region is given by equation (6.49) and implies:

$$n_j \Sigma_{ij}^{(0)} = a_i \,, \tag{6.55}$$

with

$$\Sigma_{ij}^{(0)} = \left[\eta_0 \, g(\Phi^{(0)}) + \kappa \nabla \cdot \vec{U}^{(0)}\right] \delta_{ij} + 2\mu_1 \left[g(\Phi^{(0)}) \left(U_{ij}^{(0)} - \frac{\delta_{ij}}{2} \nabla \cdot \vec{U}^{(0)}\right)\right] \,. \tag{6.56}$$

Using the matching condition for  $\Sigma_{nn}^{(0)}$  and  $\Sigma_{nt}^{(0)}$  determines the constant  $a_i = 0$  and, hence

$$\Sigma_{nn}^{(0)} = 0, (6.57)$$

and,

$$\Sigma_{nt}^{(0)} = 0. (6.58)$$

The strain terms in equation (6.47) can be expressed in terms of the stress:

$$\nabla \cdot \vec{U}^{(0)} = \frac{1}{\kappa} \left( \frac{\Sigma_{ll}^{(0)}}{2} - \eta_0 g(\Phi^{(0)}) \right) , \qquad (6.59)$$

and,

$$U_{ij}^{(0)} - \frac{\delta_{ij}}{2} \nabla \cdot \vec{U}^{(0)} = \frac{1}{2\,\mu_1 g(\Phi^{(0)})} \left( \Sigma_{ij}^{(0)} - \frac{1}{2} \Sigma_{ll}^{(0)} \delta_{ij} \right) \,, \tag{6.60}$$

which, replaced in the solvability condition (6.47), yields:

$$(\kappa_{c} - v) I = \int_{-\infty}^{\infty} dz \, \Phi_{z}^{(0)} \left[ g_{\phi}(\Phi^{(0)}) \frac{\eta_{0}}{2 \kappa} \Sigma_{ll}^{(0)} + \frac{g_{\phi}(\Phi^{(0)})}{4 \,\mu_{1} g^{2}(\Phi^{(0)})} \left( \Sigma_{ij}^{(0)} - \frac{1}{2} \Sigma_{ll}^{(0)} \delta_{ij} \right)^{2} \right],$$
(6.61)

where we have introduced:

$$I = \int_{-\infty}^{\infty} dz \, (\Phi_z^{(0)})^2 = \frac{1}{2\sqrt{2}} \,. \tag{6.62}$$

Replacing equation (6.57) and equation (6.58) in the solvability condition (6.61), we obtain:

$$(\kappa_c - v) I = \int_{-\infty}^{\infty} dz \, \Phi_z^{(0)} g_{\phi}(\Phi^{(0)}) \left[ \frac{\eta_0}{2 \kappa} \Sigma_{tt}^{(0)} + \frac{1}{8 \,\mu_1 g^2(\Phi^{(0)})} \Sigma_{tt}^{(0) \, 2} \right] \,. \tag{6.63}$$

To obtain the linearized equation, we use the linearized expression for  $\Sigma_{tt}$  in terms of the externally applied stress  $\sigma_{xx}$  as is given by equation (5.42):

$$(\kappa_c - v) I = -\int_0^1 d\phi \left[ \frac{\eta_0}{\kappa} g_{\phi}(\phi) \sigma_{xx} + \frac{g_{\phi}(\phi)}{8\mu_1 g(\phi)^2} \sigma_{xx}^2 \right] qh$$
(6.64)

Substituting the externally applied stress  $\sigma_{xx}$  by equation (6.15) we obtain:

$$(\kappa_c - v) I = -\int_0^1 d\phi \, 4\mu_1 \frac{\eta_0^2}{\kappa^2} g_\phi(\phi) g^2(\phi) qh \,, \tag{6.65}$$

which after integration yields:

$$(\kappa_{\rm c} - v) I = -\frac{1}{48} \mu_1 \frac{\eta_0^2}{\kappa^2} qh \,. \tag{6.66}$$

Rewriting this results, we obtain the dimensionless sharp-interface equation (5.30):

$$v = \left[\frac{\sqrt{2}}{24}\mu_1 \frac{\eta_0^2}{\kappa^2} q - q^2\right] h.$$
 (6.67)

where we have replaced I by its value equation (6.62) and the curvature  $\kappa_c$  by its Fourier representation. Hence, we recover the sharp-interface equation (5.43) for the case of evaporation-condensation with:

$$A = \frac{\sqrt{2}}{24} \mu_1 \frac{\eta_0^2}{\kappa^2}, \qquad (6.68)$$

determined by the elastic parameters and

$$B = 1$$
. (6.69)

#### Numerical Implementation 6.2

To study our model, numerical simulations on a discrete square and simple cubic lattice with lattice constants  $\Delta x = \Delta y = \Delta z$  were performed in two and three dimensions. We will discuss the implementation for the two-dimensional case. However, it is straightforward to generalize it to three dimensions. Euler's method was used to integrate equation (6.24) in time. The Green's function was solved in Fourier space, where we used the isotropic form of the Laplacian:

$$\nabla^2(\vec{q}) = \frac{\cos(q_x \Delta x) \cos(q_z \Delta z) + \cos(q_x \Delta x) + \cos(q_z \Delta z) - 3}{\Delta x \Delta z}, \qquad (6.70)$$

$$\nabla_{xz}^2(\vec{q}) = -\frac{\sin(q_x \Delta x) \sin(q_z \Delta z)}{\Delta x \Delta z}, \qquad (6.71)$$

and,

$$\nabla_x^2(\vec{q}) = \frac{4\cos(q_x\Delta x)\cos(q_z\Delta z) - 4\cos(q_z\Delta z) + 2\cos(q_x\Delta x) - 2}{3\Delta x\Delta z}.$$
 (6.72)

The discretized forms of  $q_x$  and  $q_z$  are

$$q_x = \frac{2\pi j}{L_x},\tag{6.73}$$

$$q_z = \frac{2\pi i}{L_z},\tag{6.74}$$

where i and j are the index for row and column, respectively, and  $L_x = N_x \Delta x$  and  $L_z = N_z \Delta z$  give the system size.

The point  $\vec{q} = 0$  has to be treated carefully. Since only the quotients  $q_x^2/q^2$  and  $q_z^2/q^2$  appear in the equation of motion (6.24), and we also know that for the flat interface  $u_{zz} = \frac{n_0}{\kappa} g(\phi)$  and  $u_{xx} = u_{xz} = 0$ , the quotients are determined to be:

$$\frac{q_x^2}{q^2} = \frac{q_x q_z}{q^2} = 0, \qquad (6.75)$$

and,

 $\frac{q_z^2}{a^2} = 1 \, .$ Periodic boundary conditions were employed in all directions. Thus, the solid was in contact with its liquid phase at the bottom and at the top. It was ensured that the

solid was sufficiently thick that the interfaces at the top and bottom acted independently. Determining the appropriate mesh size and time step requires a compromise

(6.76)

between numerical efficiency, which is enhanced by big mesh sizes and time steps, and accuracy, which demands the smallest possible time step and mesh size. The von Neumann stability analysis, being a linear stability analysis of the discretized equation of motion, puts an upper bound on the time step  $\Delta t$  for a given mesh size  $\Delta x$ . For bigger time steps, the code is numerically unstable. The discretized, linearized form of equation (6.24) is

$$\phi(i,j;t+\Delta t) = \left\{ 1 - \frac{\Delta t}{\Delta x \Delta z} \left[ \Delta x \Delta z \right] + \epsilon^2 \left( 3 - \cos \frac{2\pi j}{N_x} \cos \frac{2\pi i}{N_z} - \cos \frac{2\pi j}{N_x} - \cos \frac{2\pi i}{N_z} \right) \right\} \phi(i,j;t) , \qquad (6.77)$$

where we have used that  $q_x = 2\pi/L_x$  and  $q_z = 2\pi/L_z$ . A numerical instability will occur if the term in curly brackets is greater than -1. Thus, to ensure numerical stability the following inequality has to be fulfilled:

$$1 - \frac{\Delta t}{\Delta x \Delta z} \left[ \Delta x \Delta z + \epsilon^2 \left( 3 - \cos \frac{2\pi i}{N_x} \cos \frac{2\pi j}{N_z} - \cos \frac{2\pi i}{N_x} - \cos \frac{2\pi j}{N_z} \right) \right] > -1, \quad (6.78)$$

or

$$\Delta t < \frac{2(\Delta x)^2}{(\Delta x)^2 + 6\epsilon^2},\tag{6.79}$$

where  $\Delta x = \Delta z$  was used as in all simulations being presented.  $\Delta x$  was chosen in such a way that the surface was resolved by at least 8 points. In any case, it was always tested that a decrease in mesh size and time step did not change our results. For all simulations presented here, the mesh size  $\Delta x = 0.01$  or 0.005, the time step  $\Delta t = 0.1$  or 0.05,  $\beta = 1.0$ , and  $\epsilon = 0.01$ . The parameter set,  $(N_x, N_y, N_z, h_0, c)$  will be specified below, where  $h_0$  gives the initial amplitude of the surface. Length scales will be measured in units of  $\Delta x$ .

# 6.3 Numerical Simulation

A typical time evolution of the Grinfeld instability is shown in figure 6.2. We prepare the system initially with a small undulation at the upper interface, and let it evolve in time. We observe that the valleys start to grow deeper and deeper. At the same time, we observe that the elastic field relaxes in the hills, whereas it increases in the valleys. Note that it seems that, in the liquid, the thermodynamic driving force  $h(\phi)$  close to the valleys has a finite value. However,  $h(\phi)$  represents only the strain field due to the geometry of the boundary. It still has to be multiplied by the shear modulus to contribute to the free energy as well as the driving force. The shear modulus is zero in the liquid phase. Thus,  $h(\phi)$  in the liquid phase does not contribute to the equation of motion of the phase field (6.24).

# 6.4 Numerical Linear Stability Analysis

To analyze the Grinfeld instability and test our model, we perform a numerical linear stability analysis in two dimensions. To do so, we prepare the system initially with a small amplitude sinusoidal surface profile  $h(x, t = 0) = h_0 cos(qx)$ , where q is the wavenumber, and monitor its subsequent evolution. Figure 6.3 shows the time evolution of the amplitude of one Fourier mode as well as the evolution of the interfacial profile in real space. Initially the Fourier mode grows independently and exponentially obeying  $\exp(\omega(q)t)$ . Later it follows a slower growth regime, which can be seen in figure 6.3. By fitting an exponential through the initial regime,  $\omega$  was determined for different Fourier modes q. The obtained dispersion relation is shown in figure 6.4. It is consistent with

$$\omega = A q - B q^2, \qquad (6.80)$$

where

$$A \approx 28 \,, \tag{6.81}$$

and,

$$B \approx 1$$
. (6.82)

Perturbations with wavenumber larger than a critical wavenumber  $q_c$  are stabilized by surface tension, whereas wave numbers smaller than the critical wavenumber are unstable. Thus, we recover the long wavelength instability discussed in chapter 5.4. The flat interface however is stable. This result agrees with the linear stability analysis<sup>1</sup> which was performed in chapter 5.4 for the case where evaporation-condensation is the material transport mechanism, which is appropriate for our model.

In the sharp-interface limit the coefficients A and B are related to the model parameter via the linearized dimensionless sharp-interface equation (6.67). The prefactor in  $\overline{}^{1}$ Srolovitz [89].



Figure 6.2: Time evolution of the phase field (on the left) and the thermodynamic driving force (on the right). The pictures shown correspond to t = 1, t = 50, and t = 100 from top to bottom.



Figure 6.3: Growth of Fourier mode: On the left in Fourier space for  $N_x = N_z = 256$ ,  $h_0 = 4$ , c = 6.2, p = 6,  $\Delta x = 0.01$  and  $\Delta t = 0.1$ . On the right in real space for  $N_x = N_z = 512$ ,  $h_0 = 12$ , c = 6.2, p = 4,  $\Delta x = 0.005$ ,  $\Delta t = 0.05$  for equal distant time steps of 400.

front of the linear term A is given by equation (6.68) and comprises the elastic contribution. For the set of parameter of the simulation ( $\eta_0 = 1.0, \kappa = 0.9, \mu_1 = 600, a = 1$ ) it yields:

$$A = 34.5$$
. (6.83)

The prefactor in front of the quadratic term B is given by equation (6.69) and yields:

$$B = 1. \tag{6.84}$$

Hence, the simulations are in agreement with the sharp-interface equation.

It is interesting to note that the observability of the linear regime, which corresponds to the exponential growth mode, may be due to the long-range character of the elastic field. Binder [84] predicted that the linear regime increases with the range of interaction. It is interesting to note that the observability of the linear regime, which corresponds to the exponential growth mode, may be due to the long-range character of the elastic field. Binder [84] predicted that the linear regime increases with the range of interaction.

# 6.5 Non-linear Effects

Linear stability analysis predicts only the condition of onset of instability. To study the later-stage morphology and to compare with experiments, a complete non-linear description has to be employed. Further, the question of whether a steady state



Figure 6.4: Dispersion relation obtained from numerical linear stability analyses for different p and  $N_x = N_z = 256$ ,  $h_0 = 4$ , and c = 6.2. The inset shows a linear fit through the data which are plotted as  $\omega/q$  vs. q.

exists or asymptotic coarsening occurs has to be resolved. Neither Spencer, Davis and Voorhees [93] with their long-wave approach, nor Spencer and Meiron [94], could resolve that issue. Numerical instabilities and singularities limited their study, as grooves formed. We did not encounter numerical instabilities, and hence could study the groove formation. An advantage of the phase-field description is that nonlinearities are taken into account implicitly so that the non-linear regime does not provide any additional numerical problems.

### A. Interfacial Profile

A typical set of interfacial configurations is shown in figure 6.2 and figure 6.3. The nonlinear effect gives rise to a clear asymmetry between peaks and valleys, wherein deep grooves appear in the valleys. This behavior has been observed experimentally, as well as in previous theoretical studies<sup>1</sup>. It is interesting to note that in the early

<sup>&</sup>lt;sup>1</sup>Nozières [92]; Spencer, Davis and Voorhees [93]; Spencer and Meiron [94]; Yang and Srolovitz [93].



Figure 6.5: Section of interfacial profile smoothed by a low frequency pass to filter out high frequencies due to discretization of space.

stages of the instability we can fit the interfacial profile with a simple function

$$\kappa_c = \sum_i a_i(t)h^i. \tag{6.85}$$

where the curvature  $\kappa_c$  given by equation (5.28) is a low-order polynomial function of the height h(x) of the interface. The order of the polynomial is increasing with time. To estimate these dependences, the interfacial profile was smoothed by a low frequency pass to filter out high frequencies due to discretization of space. A typical profile with a fit is shown in figure 6.5. From this fit the curvature was calculated. Figure 6.6 shows the curvature versus the height at different times, together with higher order polynominal fits. The above described relationship between the curvature and the height variable can be understood by considering the sharp-interface equation (5.32):

$$\gamma \kappa_c = \frac{v_n}{\Gamma} - \frac{1 - \nu^2}{2E} \sigma_{tt}^2 , \qquad (6.86)$$

As we have discussed before, and worked out in appendix A.2,  $\sigma_{tt}$  is a function of the interfacial profile h(x). Hence,  $\sigma_{tt}$  can be expressed in terms of a polynomial in the amplitude of h:

$$\sigma_{tt} = \sum_{i} b_i h^i \,. \tag{6.87}$$

For very early times we showed that both the velocity (5.43), and the stress (5.42), are linear in h. As time progresses, the amplitude of h grows and non-linear terms become relevant, and must be considered in equation (6.86), which then yields equation (6.85).



Figure 6.6: Curvature versus high dependence of interfacial profile at different time steps. The data are represented by markers. Through the different data sets a polynominal was fitted. The order of the polynominal increased with time. At t = 100 the polynominal was of  $5^{th}$  order, at t = 200 of  $6^{th}$  order, at t = 300 of  $8^{th}$  order and at t = 400 of  $10^{th}$  order.

### B. Coarsening and Scaling

Experimentally, random fluctuations in the interface will give rise to the competitive growth of different structures corresponding to different wave numbers. To study this, we prepared the system with an interfacial profile consisting of a superposition of p linearly unstable modes,

$$h(x) = h_0 \sum_{i=1}^{p} \cos(q_i x + \phi_i)$$
(6.88)

with  $q_i < q_c$  and  $\phi$  being a uniformly distributed random variable in the interval  $[0, 2\pi]$ . A typical realization is shown in figure 6.7.

We averaged 100 runs over 500 time steps of a two-dimensional system with 100 unstable modes, where  $(N_x, N_y, N_z, c, h_0) = (1024, 512, 0, 12.3, 0.24)$ . Figure 6.8 shows the Fourier transform of the equal-time height-height correlation function, which we shall call the structure factor S(q, t), in different regimes. Note that the structure factor vanishes for  $q \rightarrow 0$  due to elasticity, not a conservation law. For very early times, in which the linear regime is valid, the structure factor can be derived from the dispersion relation by a Cahn-Hilliard-type theory. Figure 6.8 shows the data



Figure 6.7: Time evolution of the phase field in two dimension in the case of coarsening. The pictures shown correspond to t = 0.3, t = 5.0, t = 15.0 and t = 30.0 from left to right and top to bottom. The parameters were  $N_x = N_z = 256$ , c = 12.3 and  $h_0 = 0.4$ .



Figure 6.8: Structure factor of interfacial profile at equal time intervals. Solid lines show the structure factor derived from a linear Cahn-Hilliard-type theory, which only describes the data for early times.

together with the results of a linear theory. There is a strong similarity between this behavior and early-stage spinodal decomposition in long-range force systems<sup>1</sup>. For later times, when the non-linear effects come into play, the linear theory no longer describes the data. It is evident that the system coarsens. The location of the peak of the structure factor  $q_{\max}(t)$  moves to smaller wave numbers, as the peak height increases and sharpens. The peak height follows

$$S(q_{\max}, t) \sim t^{\alpha}, \tag{6.89}$$

where  $\alpha \approx 3$ , as can be seen in figure 6.9. This indicates that the interfacial length increases linearly with time for any unstable wavenumber, as expected from the linear analysis. As discussed in chapter 4.3, if a system displays dynamical scaling the structure factor scales as (4.25), which explains the exponent  $\alpha \approx 3$ , one for each height variable and one for the dimension. As shown in figure 6.10, the peak width sharpens with time as

$$\Delta_q \sim t^{-\gamma},\tag{6.90}$$

<sup>&</sup>lt;sup>1</sup>Laradji, Grant and Zuckermann [90].



Figure 6.9: Scaling of peak height of structure factor with time. As seen in the inset the peak height grows with time as  $S(q_{max}, t) \sim t^{\alpha}$  with  $\alpha \approx 3$ .



Figure 6.10: Scaling of width of structure factor with time. As seen in the inset the peak width sharpens with time as  $\Delta_q \sim t^{-\gamma}$  with  $\gamma \approx 0.5$ .

where  $\gamma \approx 0.5$ . This dependence is due to competitive ordering between different wave numbers, analogous to phase ordering systems with non-conserved order parameters, as discussed in chapter 4.3. Note however that the interfacial length increases linearly with time, while the peak width indicates a slower coarsening length  $\sim t^{1/2}$ . This is quite different from model A or B where only one characteristic length is observed. Even more interesting is figure 6.11, which shows that within the accuracy of our study, the structure factor shows scale invariance:

$$\frac{S(q,t)}{S(q_{\max},t)} = S^*(q^*), \tag{6.91}$$

where  $q^*$  is the scaled wave number  $q^* = (q - q_{\max})/\Delta_q$ . Fitting  $S^*$  to

$$S^* \sim (q^*)^\delta \tag{6.92}$$

for small  $q^*$  gives  $\delta \sim 1 - 2$  and,

$$S^* \sim (1/q^*)^{\psi},$$
 (6.93)

for large  $q^*$  gives  $\psi \sim 5 - 6$  as is seen in figure 6.12. We do not yet understand the origins of these exponents. We expect that our results on transient coarsening phenomena can be observed through microscopy or by x-ray diffraction (Sinha et al. [88]).

# 6.6 Three dimensional Growth

Since the elastic equations are much easier to solve in two dimensions, or in the plane strain case for which the elastic equations reduce to effectively two dimensions, almost all studies have been performed for these cases. Only Spencer, Voorhees and Davis [93] have performed a linear stability analysis for the full three-dimensional problem. All nonlinear approaches as well as all numerical studies had been limited to two dimensions. There has been speculation as to whether the third dimension will have an effect on the stress relief mechanism.

To study this, we simulated a system with  $N_x = N_y = N_z = 128$ , with z being the direction normal to the surface. Starting with a small amplitude sinusoidal perturbation in x, trenches with sharp deep grooves form, while a small amplitude



Figure 6.11: Scaling of structure factor. The structure factor shows scaling:  $S(q,t)/S(q_{max},t) = S^{\bullet}(q^{\bullet})$ , where the scaled wave number  $q^{\bullet} = (q - q_{max})/\Delta_q$ .



Figure 6.12: Fit of tails of structure factor. The rescaled structure factor is fitted to  $S^* \simeq (q^*)^{\delta}$  and small q, which gives  $\delta = 1.4$  and to  $S^* \simeq (1/q)^{\phi}$  which gives  $\phi = 5.9$ . The inset is a magnification of the tail region and its fit.

sinusoidal perturbation in the x and y directions resulted in islands. The instability is qualitatively the same as in two dimensions. If we start with a superposition of unstable modes, coarsening was again observed. Figure 6.13 shows a typical time evolution of the interfacial profile while coarsening is taking place. Figure 6.14 shows the corresponding side views of the interfacial profile, cut along the x = N/2 axis. The similarity to figure 6.7 which showed the interfacial profile of a two dimensional coarsening system is evident. We could not probe scaling for the three-dimensional system, since it required too much computer time. However, it is in principle possible.



Figure 6.13: Time evolution of the surface profile of the phase field in three dimension. The pictures shown correspond to t = 4.5, t = 7.5, t = 10.5 and t = 15.0 from left to right and top to bottom with the parameters  $N_x = N_y = N_z = 128$ ,  $h_0 = 1.0$ , and c = 18.5. Figure 6.14 shows the corresponding side view.



Figure 6.14: Side view of coarsening in three dimensions. The pictures shown correspond to t = 4.5, t = 7.5, t = 10.5 and t = 15.0 from left to right and top to bottom with the parameters  $N_x = N_y = N_z = 128$ ,  $h_0 = 1.0$ , and c = 18.5. Figure 6.13 shows the corresponding top view.

# CONCLUSION

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We have proposed a new model based on a Ginzburg-Landau approach to study a stress-induced morphological instability, commonly known as the Grinfeld instability. The instability has been observed experimentally and is often associated with the dislocation-free Stranski-Krastanov growth in epitaxy. Due to the technological relevance of epitaxial grown films in the semiconductor industry, understanding the instability is of fundamental importance.

In our approach, the elastic field is coupled to an order parameter in such a way that the solid supports shear, whereas the liquid phase does not. Hence, the order parameter obtains a transparent meaning in the context of liquid-solid phase transitions.

We have shown that our model reduces in the appropriate limit to the sharpinterface equation which have been used traditionally to study the instability. However, numerical studies using the sharp-interface equations had been limited to two dimensions and were constrained by numerical instabilities appearing at very early times. Hence, a systematic study of the non-linear regime was not possible. Important questions, such as whether the system moves towards a steady state or coarsens had not been answered yet.

In our description, the proper treatment of non-linearities is inherent. We also did not encounter any numerical instabilities, and could perform numerical simulations in two and three dimensions. To test our model, we first performed a numerical stability analysis and found that the growth of the amplitude of the Fourier modes was initially independent and exponential, obeying  $\exp(\omega(q)t)$ , followed by a slower growth. The fitted dispersion relation  $\omega(q)$  is consistent with  $\omega = Aq - Bq^2$  and agrees with the linear stability analysis carried out by Srolovitz [89]. We also observed that in the early stages of the instability, the interfacial profile could be fitted with a simple function  $\kappa_c = \sum_i a_i(t)h^i$ , where the curvature  $\kappa_c$  is a loworder polynomial function of the height h(x) of the interface. This observation could be explained by analyzing different contributions to the sharp-interface equation.

We studied the non-linear regime, which is characterized by competitive growth of different structures corresponding to different wave numbers by measuring the Fourier transform of the equal-time height-height correlation function. For early times we observed a strong similarity between its behavior and early-stage spinodal decomposition in long-range systems. For later times coarsening was evident: The location of the peak of the structure factor  $q_{max}(t)$  moves to smaller wave numbers, as the height increased and sharpened. The peak height followed  $S(q_{max}) \sim t^{\alpha}$ , where  $\alpha \approx 3$ , while the peak width sharpened with time as  $\Delta_q \sim t^{-\gamma}$ , where  $\gamma \approx 0.5$ . The former dependence was due to the interface length increasing linearly with time. The latter dependence was due to competitive ordering between different wave numbers, analogous to phase ordering. Within the accuracy of our study, we found that the structure factor showed scale invariance:  $S(q, t)/S(q_{max}, t) = S^*(q^*)$ , with the scaled wave number  $q^* = (q - q_{max})/\Delta_q$ . Fitting to  $S^* \sim (q^*)^{\delta}$  and  $S^* \sim (1/q^*)^{\Psi}$ , for small and large  $q^*$  respectively, gave  $\delta \sim 1-2$ , and  $\Psi \sim 5-6$ . We expect that these results can be observed through microscopy or by x-ray diffraction.

In our three-dimensional study we observed the same qualitative behavior as was observed in two dimensions. Starting with a small amplitude sinusoidal perturbation in one direction, trenches with sharp deep grooves form, while a small amplitude sinusoidal perturbation in two directions resulted in islands. Starting with a superposition of unstable modes, coarsening was again observed.

One advantage of our model is that it can be easily extended. Anisotropic effects can be studied by including anisotropy through the surface tension, the elastic coefficients, or the external stress. The effect of phase separation, or of impurities, can be analyzed by coupling an additional field to the phase-field. Also, instead of evaporation-condensation, surface diffusion can be chosen as the material transport mechanism. In addition, the influence of a constant flux can be studied. Furthermore, as has been discussed in the thesis, the stress field near the groove can become so high that dislocations might be nucleated. To study this, one can extend our model by coupling the phase-field to a dislocation density field. This latter extension is currently under investigation. 

# APPENDICES

# A.1 Sharp-interface limit

The starting point is the rescaled, generalized phase field equations from chapter 3.2:

$$\alpha \epsilon^2 \frac{\partial \phi}{\partial t} = \epsilon^2 \nabla^2 \phi - f_{\phi}(\phi) + \lambda g_{\phi}(\phi) u , \qquad (A.1)$$

and,

$$\frac{\partial u}{\partial t} = D\nabla^2 u + \frac{1}{2} \frac{\partial p(\phi)}{\partial t}.$$
 (A.2)

For

$$p(\phi) = \frac{2\phi}{\Delta} \tag{A.3}$$

we recover equation (3.16) and equation (3.17). Depending on the scaling of the parameters, four different sharp interface limits can be obtained, which describe different physical systems with distinct stability characteristics. We will show, for one particular scaling, how the sharp or thin interface interface limit is obtained using the method of *matched asymptotic expansions*. We will show that the scaling Karma and Rappel<sup>1</sup> have recently proposed, is equivalent to the scaling Caginalp and Fife [88] worked out previously. With this scaling ansatz, much larger systems can be simulated, including three-dimensional systems. An asymptotic analysis for  $\epsilon << 1$ will be carried out for a layered solution of the system (A.1) and (A.2), under the assumption that  $\alpha$  is of the order unity.

The interfacial curve is defined as the set of points at which  $\phi(x, y, t) = 1/2$ . A local orthogonal coordinate (r, s) system near the surface is introduced by:

$$r(x, y, t, \epsilon) = 0 \tag{A.4}$$

at the interface and

$$|\nabla r| = 1, \quad \text{and} \quad \nabla^2 r = \kappa,$$
 (A.5)

<sup>&</sup>lt;sup>1</sup>Karma and Rappel [96b]; Karma and Rappel [96a]; Karma and Rappel [98].

with  $\kappa$  being the curvature. Hence, r measures the distance along the normal, and s is the arclength.

The idea behind the matched asymptotic expansion is to divide the system into two subregions:

- 1. An *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 expansion

We formally expand the variables in their original coordinates in powers of  $\epsilon$ ,

$$\phi = \phi(x, y, t, \epsilon) = \phi^{(0)}(x, y, t) + \epsilon \phi^{(1)}(x, y, t) + \epsilon^2 \phi^{(2)}(x, y, t) + \cdots,$$
(A.6)

and,

$$u = u(x, y, t, \epsilon) = u^{(0)}(x, y, t) + \epsilon u^{(t)}(x, y, t) + \epsilon^2 u^{(2)}(x, y, t) + \cdots$$
 (A.7)

The leading order of the phase field equations (A.1) and (A.2) gives respectively,

$$f_{\phi}(\phi^{(0)}) + \lambda u^{(0)} g_{\phi}(\phi^{(0)}) = 0, \qquad (A.8)$$

and,

$$\frac{\partial u^{(0)}}{\partial t} = \nabla^2 u^{(0)} + \frac{1}{2} \frac{d \, p(\phi^{(0)})}{dt} \,. \tag{A.9}$$

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

$$\frac{\partial u^{(0)}}{\partial t} = \nabla^2 u^{(0)} . \tag{A.10}$$

To first order in  $\epsilon$ :

$$f_{\phi\phi}(\phi^{(0)})\phi^{(1)} + \lambda g_{\phi\phi}(\phi^{(0)})\phi^{(1)}u^{(0)} + \lambda g_{\phi}(\phi^{(0)})u^{(1)} = 0, \qquad (A.11)$$

and,

$$\frac{\partial u^{(1)}}{\partial t} = \nabla^2 u^{(1)} + \frac{1}{2} \frac{d}{dt} \left[ p'(\phi^{(0)}) \phi^{(1)} \right] \,. \tag{A.12}$$

## B. Inner expansion

Here, we use the local curvilinear coordinate system defined above. It implies that the Laplacian and the time derivative take the following form:

$$\nabla^2 u = u_{rr} + \nabla^2 r \, u_r + |\nabla s|^2 u_{ss} + \nabla^2 s \, u_s \,, \tag{A.13}$$

and,

$$u_t = u_t + r_t \, u_r + s_t \, u_s \, . \tag{A.14}$$

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

$$u(x, y, t, \epsilon) \equiv U(z, s, t, \epsilon) \tag{A.15}$$

$$= U^{(0)}(z, s, t) + \epsilon U^{(1)}(z, s, t) + \cdots, \qquad (A.16)$$

and,

$$\phi(x, y, t, \epsilon) \equiv \Phi(z, s, t, \epsilon) \tag{A.17}$$

$$= \Phi^{(0)}(z, s, t) + \epsilon \Phi^{(1)}(z, s, t) + \cdots$$
 (A.18)

Now, the equations (A.1) and (A.2) can be written in the following form:

$$\begin{split} \Phi_{zz} + f_{\phi}(\Phi) + \lambda u g_{\phi}(\Phi) + \epsilon \left\{ \Phi_{z} \nabla^{2} r - \alpha \Phi_{z} \dot{r} \right\} \\ + \epsilon^{2} \left\{ \Phi_{ss} |\nabla s|^{2} + \Phi_{s} \nabla^{2} s - \alpha \dot{\Phi} - \alpha \Phi_{s} \dot{s} \right\} = 0 \,, \end{split}$$
(A.19)

and,

$$U_{zz} + \epsilon \left\{ U_z \nabla^2 r + \frac{1}{2} p_z \dot{r} - U_z \dot{r} \right\}$$

$$+ \epsilon^2 \left\{ U_{ss} |\nabla s|^2 + U_s \nabla^2 s + \frac{1}{2} \left( \frac{\partial p}{\partial t} + p_s \dot{s} \right) - \dot{u} - u_s \dot{s} \right\} = 0.$$
(A.20)

Therefore the equations of  $\Phi$  and U to zeroth order in  $\epsilon$  are:

$$\Phi_{zz}^{(0)} + f_{\phi}(\Phi^{(0)}) + \lambda u^{(0)} g_{\phi}(\Phi^{(0)}) = 0, \qquad (A.21)$$

and,

$$U_{zz}^{(0)} = 0. (A.22)$$

To first order in  $\epsilon$ :

$$\Phi_{zz}^{(1)} + f_{\phi\phi}(\Phi^{(0)})\Phi^{(1)} + \lambda u^{(1)}g_{\phi}(\Phi^{(0)}) + \lambda u^{(0)}g_{\phi\phi}(\Phi^{(0)})\Phi^{(1)} + \Phi_z^{(0)}\nabla^2 r - \alpha \Phi_z^{(0)}\dot{r} = 0, \quad (A.23)$$

and,

$$U_{zz}^{(1)} + U_z^{(0)} \nabla^2 r + \frac{1}{2} p_z(\Phi^{(0)}) \dot{r} - U_z^{(0)} \dot{r} = 0.$$
 (A.24)

#### 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

$$U(z,t,\epsilon) = u(\Gamma(t,\epsilon) + \epsilon z, t,\epsilon) , \qquad (A.25)$$

where  $z = (x - \Gamma(t, \epsilon))/\epsilon$  is the scaled coordinate. The right hand side of equation (A.25) can be expanded in a Taylor series in  $\epsilon$ 

$$U(z,t,\epsilon) = \sum_{n=0}^{N} \epsilon^n P_n(z,t) + \epsilon^{N+1} R_N , \qquad (A.26)$$

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.27)

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.27) is of lower order than any of the preceding terms.

The two first matching conditions are

$$U^{(0)}(\pm\infty,t) = P^{0}_{\pm}(\pm\infty,t) = u^{(0)}(\Gamma^{(0)}_{\pm},t), \qquad (A.28)$$

and,

$$U^{(1)}(z,t) = u^{(1)}(\Gamma^{(0)}_{\pm},t) + z \, u^{(0)}_r(\Gamma^{(0)}_{\pm},t) + \Gamma^{(1)}(t) u^{(0)}_r(\Gamma^{(0)}_{\pm},t) \,, \tag{A.29}$$

with  $z \to \pm \infty$ .

#### 2. Leading order solution

The leading order solutions for U takes the form

$$U^{(0)} = az + b, (A.30)$$

with the matching condition:

$$U^{(0)}(\pm\infty,t) = u^{(0)}(\Gamma^{(0)}_{\pm},t).$$
 (A.31)

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

This implies that:

$$a = 0, \qquad (A.32)$$

and,

$$U^{(0)} = b, (A.33)$$

and the leading order solution for  $\Phi$  takes the form:

$$\Phi_{zz}^{(0)} + f_{\phi}(\Phi^{(0)}) + \lambda b g_{\phi}(\Phi^{(0)}) = 0.$$
(A.34)

with the matching condition:

$$\Phi^{(0)}(\pm \infty) = \phi(\Gamma^{\pm}) = 0 \text{ and } 1.$$
 (A.35)

For further convenience, we define:

$$\Psi(z,t) \equiv \Phi^{(0)}(z,t),$$
 (A.36)

and,

$$h(\Psi) = f_{\phi}(\Phi^{(0)}) + \lambda b g_{\phi}(\Phi^{(0)}) , \qquad (A.37)$$

so that equation (A.34) yields:

$$\Psi_{zz}(z,t) + h(\Psi) = 0.$$
 (A.38)

#### 3. First-order solution

The first-order inner equation for U has the form

$$U_{zz}^{(1)} + \frac{1}{2} p_z(\Psi) \dot{r} = 0.$$
 (A.39)

Integrating once yields:

$$U_z^{(1)} = \frac{1}{2} p(\Psi) v^{(0)} + C_1, \qquad (A.40)$$

where  $v^{(0)} = -\dot{r}$ , and  $C_1$  is a integration constant. The matching condition implies:

$$u_r^{(0)}|_{\pm\Gamma} = \frac{1}{2}p(\pm 1)v^{(0)} + C_1.$$
 (A.41)

Choosing  $p(\phi) = \phi$  results in:

$$\left[u_r^{(0)}\right]_{\pm\Gamma} = \frac{1}{2} v^{(0)} . \tag{A.42}$$

Integrating once more:

$$U^{(1)} = \frac{v^{(0)}}{2}P(z) + C_1 z + C_2, \qquad (A.43)$$

with

$$P(z) = \int_0^z dz' \, p(\Psi) \,, \qquad (A.44)$$

and  $C_2$  being another integration constant, so

$$U^{(1)} = \frac{v^{(0)}}{2} \int_0^z dz' \left[ sgn(z') - p(\Psi) \right] - \frac{v^{(0)}}{2} |z'| + C_1 z' + C_2 \,. \tag{A.45}$$

Using the matching condition:

$$U^{(1)} = u^{(1)}(\Gamma_{\pm}) + z u_r^{(0)}(\Gamma_{\pm}^{(0)}) + \Gamma^{(1)} u_r^{(0)}(\Gamma_{\pm}^{(0)})$$
(A.46)

results in:

$$u^{(1)}|_{\Gamma_{\pm}} = \frac{v^{(0)}}{2} \int_0^\infty dz \left[ sgn(z) - p(\Psi) \right] + C_2 \,. \tag{A.47}$$

The first order inner equation for  $\Phi$  takes the form:

$$\mathcal{L}\Phi^{(1)} = -(\kappa + \alpha v^{(0)})\Psi^{(1)} - \lambda u^{(1)}g_{\phi}(\Psi), \qquad (A.48)$$

where,

$$\mathcal{L} = \frac{\partial^2}{\partial z^2} + h'(\Psi) \,. \tag{A.49}$$

The Fredholm alternative states that the linear inhomogeneous equation (A.48) is only solvable, if the r.h.s is orthogonal to the null space of the adjoint operator  $\mathcal{L}^{\dagger}$ . Because  $\mathcal{L}$  is self adjoint,  $\mathcal{L}^{\dagger}\Phi = 0$  is solved by  $\Psi' = \Phi_z^{(0)}$ , which is the Goldstone mode. This can easily be seen by differentiating equation (A.38). We are left with the following solvability condition:

$$\int_{-\infty}^{\infty} dz \Psi' \left[ (\kappa + \alpha v^{(0)}) \Psi' + \lambda u^{(1)} g(\Psi) \right] = 0, \qquad (A.50)$$

and,

$$(\kappa + \alpha v^{(0)}) \int_{-\infty}^{\infty} dz (\Psi')^2 + \int_{-\infty}^{\infty} dz \lambda u^{(1)} \Psi' g(\Psi) = 0.$$
 (A.51)

Replacing  $u^{(1)}$  by equation (A.45) and defining:

$$I = \int_{-\infty}^{\infty} dz (\Psi')^2 , \qquad (A.52)$$

we obtain:

$$(\kappa + \alpha v^{(0)})I = -\lambda \int_{-\infty}^{\infty} dz \left[ \frac{v^{(0)}}{2} P(z) + C_1 z + C_2 \right] \Psi' g(\Psi) .$$
 (A.53)

In the case that  $f(\Phi)$  is an odd function of  $\Phi$ , *i.e.*,  $f(-\Phi) = -f(\Phi)$ ,  $\Psi'$  will be an even in z. Then, if  $g(\Phi)$  is even function of z, the integral:

$$\int_{-\infty}^{\infty} dz \Psi' g(\Psi) C_1 z = 0. \qquad (A.54)$$

Rewriting equation (A.53) determines  $C_2$  to be:

$$C_2 = -\frac{1}{J} \left[ \frac{v^{(0)}}{2} K + \frac{\kappa + \alpha v^{(0)}}{\lambda} I \right], \qquad (A.55)$$

where

$$J = \int_{-\infty}^{\infty} dz \,\Psi'(z) \,g(\Psi) \,, \tag{A.56}$$

and,

$$K = \int_{-\infty}^{\infty} dz \,\Psi'(z) \,g(\Psi) \int_{0}^{z} dz' \,p(\Psi) \,. \tag{A.57}$$

Hence,  $u^{(1)}$  at the interface is given by:

$$u^{(1)}|_{\pm} = -\frac{I}{\lambda J} \kappa - \left(\frac{K + JF}{2J} + \frac{\alpha I}{\lambda J}\right) v^{(0)} . \tag{A.58}$$

where,

$$F = \int_0^{\pm \infty} dz \left( p(\Psi) - sgnz \right). \tag{A.59}$$

This is the generalized Gibbs-Thomson condition in which the kinetic coefficient  $\beta$  is given by:

$$\beta = \frac{\alpha I}{\lambda J} \left[ 1 + \lambda \frac{K + JF}{2 \alpha I} \right] . \tag{A.60}$$
## A.2 Solution of elastic equations

Many problems related to elasticity reduce to solving partial differential equations with fixed boundary values. In the case of the Grinfeld instability, we are dealing with a semi-infinite, isotropic, uni-axially stressed solid which is in contact with its own melt or vapor. The interface between the solid and the liquid is free. Since the elastic equations (5.2) are linear, it is useful to decompose the free interface into Fourier modes:

$$h(x) = h_0 \sin qx \,. \tag{A.61}$$

The condition of mechanical equilibrium provides us, in two-dimensions, with two partial differential equations:

$$\frac{\partial \sigma_{xx}}{\partial x} + \frac{\partial \sigma_{xz}}{\partial z} = 0, \qquad (A.62)$$

$$\frac{\partial \sigma_{zx}}{\partial x} + \frac{\partial \sigma_{zz}}{\partial z} = 0.$$
 (A.63)

A general solution for the stresses are given by:

$$\sigma_{xx}(x,z) = \partial_z \Psi_x(x,z), \qquad (A.64)$$

$$\sigma_{xz}(x,z) = -\partial_x \Psi_x(x,z) , \qquad (A.65)$$

$$\sigma_{zx}(x,z) = -\partial_z \Psi_z(x,z), \qquad (A.66)$$

and,

$$\sigma_{zz}(x,z) = \partial_x \Psi_z(x,z) . \tag{A.67}$$

Since the stress tensor is symmetric,  $\sigma_{xz} = \sigma_{zx}$ , an additional constraint is imposed on  $\Psi_x$  and  $\Psi_z$ :

$$\partial_x \Psi_x(x,z) = \partial_z \Psi_z(x,z),$$
 (A.68)

which is solved by:

$$\Psi_{\boldsymbol{x}}(\boldsymbol{x},\boldsymbol{z}) = \partial_{\boldsymbol{z}}\chi(\boldsymbol{x},\boldsymbol{z}), \qquad (A.69)$$

$$\Psi_z(x,z) = \partial_x \chi(x,z) . \tag{A.70}$$

Hence, the stress field can be derived from only one scalar field  $\chi$ , which is called the Airy stress function:

$$\sigma_{xx}(x,z) = \partial_{zz}^2 \chi(x,z) , \qquad (A.71)$$

$$\sigma_{xz}(x,z) = -\partial_{xz}^2 \chi(x,z) , \qquad (A.72)$$

$$\sigma_{zz}(x,z) = \partial_{xx}^2 \chi(x,z) . \tag{A.73}$$

and,

and,

Since the free interface has a sinusoidal profile, the following Ansatz for  $\chi$  is justified:

$$\chi(x, z) = \Phi(z) \exp(iqx) . \tag{A.74}$$

Hence, the stress fields have a functional dependence as follows:

$$\sigma_{xx}(x,z) = \Phi''(z) \exp(iqx), \qquad (A.75)$$

$$\sigma_{xz}(x,z) = -i q \Phi'(z) \exp(iqx) , \qquad (A.76)$$

and,

where the prime means differentiation with respect to z. Now, only  $\Phi(z)$  has to be determined, which is a function of z only. To do so, we take the divergence of the Lamé equation (5.8) and obtain:

 $\sigma_{zz}(x,z) = -q^2 \Phi(z) \exp(iqx) \,,$ 

$$\nabla^2 (\nabla \cdot \vec{u}) = 0. \tag{A.78}$$

Using Hooke's law (5.5), we obtain an expression for the stress field:

$$\nabla^2 \sigma_{ll} = 0. \tag{A.79}$$

Replacing  $\sigma_{ll}$  by equation (A.75) and equation (A.77) results in an ordinary differential equation of fourth order for  $\Phi(z)$ :

$$\left(\frac{d^2}{dz^2} - q^2\right) \left[\Phi''(z) - q^2 \Phi(z)\right] = 0.$$
 (A.80)

Its solution is given by:

$$\Phi(z) = (a_1 + b_1 z)e^{qz} + (a_2 + b_2 z)e^{-qz}, \qquad (A.81)$$

where  $a_1, b_1, a_2$  and  $b_2$  are constants which have to be determined by the boundary conditions. Since the stress field should vanish at  $(x, z \to -\infty)$ , it follows that  $a_2 = 0$  and  $b_2 = 0$ .

Hence,  $\chi(x, z)$  is then:

$$\chi(x,z) = \frac{\sigma_0 z^2}{2} + (a_1 + b_1 z) \sin(qx) e^{qz}, \qquad (A.82)$$

(A.77)

(A.85)



Figure A.1: Sketch of local coordinate system at the liquid-solid interface.

where we have used only the sine part.

Now, the stress field can be determined:

$$\sigma_{xx}(x,z) = \sigma_0 + q \, [2b + q(a+bz)] \sin(qx) e^{qz} , \qquad (A.83)$$

$$\sigma_{zz}(x,z) = -\left[q^2(a+bz) + bq\right] \cos(qx) e^{qz},$$
(A.84)  
$$\sigma_{zz}(x,z) = -q^2 \left[a + bz\right] \sin(qx) e^{qz},$$
(A.85)

and.

where we have dropped the index 1. Now we must determine the two constants a and b from the boundary conditions (5.24), (5.25) and (5.26):

$$\sigma_{nn} = 0, \qquad (A.86)$$

$$\sigma_{nt} = 0. \tag{A.87}$$

First, we have to express the stress tensor in the local coordinate system of the interface, which is given by the normal  $\vec{n}$  and tangential  $\vec{t}$  of the interface:

$$\vec{n} = \begin{pmatrix} \sin \theta \\ \cos \theta \end{pmatrix}, \qquad (A.88)$$

and,

$$\vec{t} = \begin{pmatrix} -\cos\theta\\ \sin\theta \end{pmatrix}, \tag{A.89}$$

where  $\theta$  is the angle between the normal  $\vec{n}$  and the z-axis as shown in figure A.1.

Since the stress field is a tensor of rank two, it is transformed as:

$$\begin{pmatrix} \sigma_{nn} & \sigma_{tn} \\ \sigma_{nt} & \sigma_{tt} \end{pmatrix} = \begin{pmatrix} \sin\theta & \cos\theta \\ -\cos\theta & \sin\theta \end{pmatrix} \cdot \begin{pmatrix} \sigma_{xx} & \sigma_{zx} \\ \sigma_{xz} & \sigma_{zz} \end{pmatrix} \cdot \begin{pmatrix} \sin\theta & -\cos\theta \\ \cos\theta & \sin\theta \end{pmatrix}$$
(A.90)

Hence  $\sigma_{nn}$ ,  $\sigma_{nt}$  and  $\sigma_{tt}$  are:

$$\sigma_{nn} = \sigma_{xx} \sin^2 \theta + 2\sigma_{xz} \sin \theta \cos \theta + \sigma_{zz} \cos^2 \theta, \qquad (A.91)$$

$$\sigma_{nt} = (\sigma_{zz} - \sigma_{xx}) \sin \theta \cos \theta + \sigma_{xz} (\sin^2 \theta - \cos^2 \theta), \qquad (A.92)$$

and,

$$\sigma_{tt} = \sigma_{xx} \cos^2 \theta - 2\sigma_{xz} \sin \theta \cos \theta + \sigma_{zz} \sin^2 \theta.$$
 (A.93)

In addition, we have:

$$\tan \theta = \frac{\sin \theta}{\cos \theta} = \frac{\partial h}{\partial x} = h_0 q \, \cos(qx) \,. \tag{A.94}$$

Hence:

$$\sin \theta = h_0 q \, \cos(qx) \cos \theta \,. \tag{A.95}$$

Inserting equation (A.95) in equation (A.91) and equation (A.92), and using the boundary conditions (A.86) and (A.87), we can eliminate  $\sigma_{zz}$ , and are left with:

$$\sigma_{xz} \left[ 1 - 3 h_0^2 q^2 \cos^2(qx) \right] - \sigma_{xx} \left[ 1 + h_0^2 q^2 \cos^2(qx) \right] h_0 q \cos(qx) = 0.$$
 (A.96)

At the interface,  $z = h_0 \sin(qx)$ ,  $\sigma_{xx}$  and  $\sigma_{xz}$  are given by:

b

$$\sigma_{xx} = \sigma_0 + q \left[ 2 b + q \left( a + b h_0 \sin(qx) \right) \right] \sin(qx) \exp(h_0 q \sin(qx)) , \quad (A.97)$$

and, 
$$\sigma_{xz} = -\left[bq + q^2(a + bh_0\sin(qx))\right]\cos(qx)\exp(h_0q\sin(qx))$$
 (A.98)

Considering only terms up to order  $q^2$ :

$$\sigma_{xx} = \sigma_0 + \left[ 2 \, b \, q + 2 \, b \, h_0 q^2 \sin(qx) + a \, q^2 + b \, h_0 \, q^2 \sin(qx) \right] \sin(qx) \,, \quad (A.99)$$

and,

d, 
$$\sigma_{xz} = -b q - b h_0 q^2 \sin(qx) - a q^2 - b h_0 q^2 \sin(qx)$$
. (A.100)

Substituting equation (A.99) and equation (A.100) in equation (A.96), and considering terms only up to second order in q, we obtain:

$$\sigma_0 h_0 q - b q + 4 b h_0 q^2 \sin(qx) + a q^2 \sin(qx) + O(q^3) = 0.$$
 (A.101)

Hence,

$$a = -4 b h_0 = 4 \sigma_0 h_0^2, \qquad (A.102)$$

and,

$$= -\sigma_0 h_0 . \tag{A.103}$$

Since we are only interested in contributions up to linear order in  $h_0$ :

$$a = 0. \tag{A.104}$$

The stress fields  $\sigma_{xx}$ ,  $\sigma_{xz}$  and  $\sigma_{zz}$  are now completely determined:

$$\sigma_{xx}(x,z) = \sigma_0 \left[ 1 - q \, h_0(2 + qz) \, \sin(qx) \, e^{qz} \right] \,, \tag{A.105}$$

$$\sigma_{xz}(x,z) = \sigma_0 q h_0 [1+q z] \cos(qx) e^{qz}, \qquad (A.106)$$

$$\sigma_{zz}(x,z) = \sigma_0 q^2 h_0 z \sin(qx) e^{qz} .$$
 (A.107)

Since

$$\sigma_{tt} = \left[\sigma_{xx} + h_0^2 q^2 \sigma_{zz} \cos^2 qx + 2 h_0 q \sigma_{xz} \cos qx\right] \cos^2 \theta, \qquad (A.108)$$

we can substitute equation (A.105), equation (A.106), and equation (A.107) for the stress fields. Keeping only terms up to first order in  $h_0q$ , we obtain:

$$\sigma_{tt}(x,z) = \sigma_0 \left[ 1 - h_0 q \left( 2 + qz \right) \sin(qx) e^{qz} \right] + O((h_0 q)^2) , \qquad (A.109)$$

and at the interface:

$$\sigma_{tt} = \sigma_0 \left[ 1 - 2 q h_0 \sin(qx) \right] + O((h_0 q)^2) \,. \tag{A.110}$$

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