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ALLOY DECOMPOSITION AND SURFACE INSTABILITIES IN THIN FILMS

by

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A thesis submitted in conformity with the requirements
for the degree of Doctor of Philosophy
Graduate Department of Physics
in the
University of Toronto

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ABSTRACT

Alloy decomposition and surface instabilities in thin films

Doctor of Philosophy, 1998

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We theoretically and numerically study the growth of thin alloy layers by slow deposition techniques. We propose microscopic and mesoscopic descriptions of the phenomena, from which composition modulations in the thin film emerge, coupled with surface undulations. We obtain excellent agreement between these two approaches and are able to predict analytically the wavelength of the modulation as a function of the deposition rate and the temperature, which is confirmed numerically. The important non-equilibrium nature of the growth process is shown to lead to the experimentally observed structures, the patterning of the film for device applications is discussed, and we calculate scattering functions that can be compared with experiments. We explore the effects of stress and strain on the composition modulations in lattice-matched films, when phase separation is the driving force for the composition inhomogeneities. It is found that the lamellar structures seen without elastic effects can become dynamically unstable to the formation of hexagonal structures, due to long-ranged elastic interactions. The hexagonal order is found to consist of elastically undeformed droplets of the hard component in an elastically deformed matrix of the soft component. The wavelength of the composition modulation is calculated numerically and is always smaller than the wavelength in the absence of elastic effects. We also discuss the effects of crystal anisotropy in our system. The stability of mismatched alloy layers is studied with emphasis on the non-equilibrium

nature of the growth and the coupling between the surface morphology and the film composition. We consider static and growing films at temperatures and mean compositions inside and outside of the phase diagram miscibility gap. Stability diagrams are presented in terms of the mismatch between the film and the substrate and the growth velocity. It is shown that the experimentally observed difference in stability between tensile and compressed films is due to composition-dependent elastic moduli.

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"Education is an admirable thing. But it is well to remember from time to time that nothing that is worth knowing can be taught."-Oscar Wilde

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À Marie-Josée: ♡

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Chapter 1

INTRODUCTION

Growing good-quality thin solid layers is an important technological process. Many current-day electronic and optical devices operate on length scales of a few hundred atoms, requiring controllable and reproducible techniques to engineer the elements in these devices. A variety of techniques is used to grow thin crystalline layers, with operating conditions ranging from near thermodynamic equilibrium, as in Chemical Vapor Deposition (CVD) and Liquid Phase Epitaxy (LPE), to far from thermodynamic equilibrium as in Molecular Beam Epitaxy (MBE). The essential difference between equilibrium and non-equilibrium processes is that, in the former, there is local thermodynamic equilibrium that is established between the outermost layer in the growing film and the vapor or liquid from which it is growing, while in the latter, no such equilibrium exists since the growth proceeds in a ultrahigh vacuum environment and particles are deposited on the surface through a directed beam. The implication is that CVD and LPE are controlled by processes in the crystallizing phase near the substrate, while kinetics at the solid surface dominate the growth in MBE. Although the work presented in this thesis should be applicable to a variety of growth conditions, we focus on materials grown by MBE for two main reasons, one that simplifies the description of the problem and one that complicates it. The simplification comes from the fact that the gas or liquid phase above the growing film can be neglected, and hence treatment of the solid film itself is sufficient. The analysis is more complex because the calculations must be performed out of equilibrium since the film/vapor or film/liquid equilibrium is absent.

Technologically, MBE is an important procedure used in the growth of a variety of thin films, due to the excellent control of the beam fluxes and growth conditions, and

the ability to simultaneously deposit different elements. Furthermore, MBE can be monitored by in situ methods, making possible the control of the growth process while it is proceeding and allowing detailed studies of dynamical processes at the surface. Examples of applications of MBE include photo-voltaic devices [1], optoelectronic micro-sensors [2], insulator layers [3] and Bragg reflectors [4].

The MBE growth technique is based on the fact that surface diffusion is an activated process. Particles diffuse on the surface and overcome potential energy barriers with probability proportional to $\exp(-\Delta E/k_B T)$, where ΔE is the activation energy and T is the temperature. To successfully grow flat epilayers, the temperature has to be chosen such that atoms have a high probability of finding the minimum energy configuration while having a large sticking coefficient. In practice, this corresponds to a so-called growth window. However, the diffusion process is hindered by the incoming flux of particles. For example, a particle that is not in a minimum energy state can be covered by an incoming particle, and hence its subsequent diffusion is much more difficult and the probability that it finds the energy minimum before being incorporated in the bulk is reduced. The implication of this non-equilibrium growth is that the surface reaches a steady-state where its width is saturated but the surface is not at equilibrium. Experiments therefore require a careful selection of the growth temperature and the deposition rate.

While the simplest way to grow a layer with MBE is to deposit one type of particle (for example Si on Ge), it has now become necessary to grow more complex films made of different atoms. This is because the number of elements is limited, and hence the range of properties available is also limited. Properties intermediate between those of individual elements can be obtained by growing *alloy* layers. The usage that one wants to make of the alloy epilayer dictates the growth conditions. This is because multicomponent crystals exhibit phase transformations with temperature. For example [5], bulk equilibrium conditions show that for SiGe the low temperature phase is two-phase coexistence, followed by the random alloy and then the rhombohedral structure, while for GaAsGe two-phase coexistence is the only phase seen at temperatures lower than the melting temperature. Hence there exists the possibility that the thermodynamically favored phase at the surface of the growing film is

not homogeneous, leading to phase separation of the alloy constituents as the film is growing. This decomposition of the alloy can be detrimental to device performance if the composition is intended to be homogeneous, but if controlled properly, can be used to naturally tailor new device types.

The dynamical process of phase separation can be understood in terms of quenching experiments in bulk systems. There, a mixture of two species is suddenly quenched from the high temperature homogeneous phase to a state in the coexistence region of the phase diagram. The kinetics following the quench to this non-equilibrium state is referred to as phase separation. If the quench is inside the spinodal line, a thermodynamic instability amplifies the fluctuations in the composition and domains of the two phases will form. The domains will be convoluted and their time evolution will proceed by the reduction of the interfacial energy and the motion of interfaces. For quenches in the coexistence region but outside the spinodal line, the formation of domains is a nucleation process, and the domains are droplets. The time evolution proceeds by the growth of the larger droplets at the expense of the smaller droplets. In this thesis, we will be concerned with mean alloy compositions that are inside the spinodal line.

1.1 Experimental observations of phase separation during film growth

Experimentally, phase separation during crystal growth can be divided in two categories [6]: (i) lateral phase separation where the concentration modulation is parallel to the growth plane [7–19] and (ii) vertical phase separation, where the modulation is along the growth direction [20–22]. We review below the experimental findings for these two cases.

1.1.1 Vertical phase separation

Although not as frequent as lateral phase separation, this growth mode occurs in different types of materials. In the case of GaAlAs grown by MBE at 873K on GaAs(110) [20], composition modulations with a wavelength of 15-300 Å spontaneously form during growth, with the modulation perpendicular to the growth plane. Layers grown on

GaAs(100) do not show composition modulations, implying that the substrate miscut is important to generate these compositional patterns. Experiments on InAsSb by MBE [21] also identified the formation of vertical composition patterns, with large variations in the composition. The observed horizontal platelets have a thickness in the range 240-500 Å and a lateral size of 2500-26000 Å, with both dimensions increasing with the growth temperature. Similar self-organized formation of superlattices [22] has also been seen in the II-VI alloy ZnSeTe grown by MBE. Again, the miscut angle is crucial in determining the morphology since layers with a miscut angle less than 2° were compositionally homogeneous.

There are two current views on the formation of these vertical superlattices. Because of the experimental evidence for the importance of the miscut angle, the motion of steps at the surface is seen as the propagator of the composition modulation [23, 24] (the requirements for step-flow growth are discussed in Ref. [25]). The other view that we begin to explore in chapter 5 of this thesis is that bumps form on the surface due to the lattice mismatch between the overlayer and the substrate; the subsequent lateral motion of these islands propagates the composition modulation.

1.1.2 Lateral phase separation

In their paper, McDevitt *et al.* [7] studied phase separation in InGaAs epilayers grown by MBE (with a growth rate of 1 μm/hour) and found that two-dimensional phase separation occurs in the growth plane, leading to a concentration-modulated structure. In the temperature range 670-780 K, they found that the wavelength of the modulation increases with increasing temperature, which they explained with the surface diffusion of As atoms. Work on InGaAs and the related material InGaAsP has also resulted in the observation of lateral composition modulations [12-15], and of a complicated interrelation between the composition profile and the morphology of the growing layer. It was also found that compressively strained layers were morphologically stable while layers under tension were unstable.

In other studies [9, 11], Zn, Se, Mg and ZnS were deposited simultaneously at temperatures around 530 K to grow thin layers (about 1 μm thick) of (100) $\text{Zn}_{1-y}\text{Mg}_y\text{Se}_{1-x}\text{S}_x$ or $\text{Zn Se}_{1-x}\text{S}_x$. These overlayers were used in the fabrication of blue/green laser diodes.

In these systems grown by MBE, phase separation occurs mostly when $x > 0.2$, and a top view of the film shows stripes oriented in the $[01\bar{1}]$ direction. Also, it was observed that the free surface has a modulation consisting of hills and valleys, with a wavelength of the order of 400 Å, comparable to the bulk concentration modulation wavelength; the hills are sulfur-deficient while the valleys are sulfur-rich.

The systems we have discussed so far are ternary and quaternary alloys. Alloy decomposition is also seen during the growth of binary mixtures. For example in Ref. [19], co-deposition of AlGe thin films leads to the formation of Al-rich and Ge-rich domains at the surface. As opposed to the other systems above, the composition is not modulated and resembles the domain morphology seen in bulk phase-separating alloys; furthermore, a depression in the surface profile runs along the interfaces between Al and Ge domains. Important evidence on the coupling between the composition and the surface morphology has recently been obtained for the SiGe alloy [10]. A direct measurement of the composition at the hills and in the valleys showed that the larger atom, Ge, segregates to the hills where the lattice constant is the largest.

The experiments discussed so far use homogeneous growth conditions where the alloy elements are simultaneously deposited on the surface. Lateral composition modulations are also seen [16–18] when AlAs/InAs (and InAs/GaAs) short period superlattices are being grown by alternately depositing AlAs and InAs (or InAs and GaAs). For example, in AlAs/InAs, the system consists of vertical stacks of AlAs and InAs as well as a lateral modulation consisting of In-rich and In-depleted bands correlated with undulations in the shape of the growth front.

As discussed above, the development of the MBE technique has been especially useful in the growth of thin semiconductor films, but also finds applications in the growth of many other materials. Our approach to the problem is to include only the essential physics that gives us phase separation and surface relaxation, and should describe the generic properties of a wide class of materials. For a given alloy, the phase diagram is determined by minimizing the energy of the mixture in different arrangements and then comparing these energies. The structure with the lowest energy at a given temperature and composition is the most stable structure. In the case of semiconductor mixtures the total energy consists of three main contributions

[5]: (i) a volume deformation energy that represents the increase in energy when atoms of different lattice constants are mixed together, (ii) a strain-relief energy associated with the packing of different bond arrangements, and (iii) short-range chemical interactions. There are 3 general classes of semiconductor mixtures that we consider:

(a) Size-matched pseudobinary systems

This category includes materials such as AlAs-GaAs and CdTe-HgTe. For these materials [26–28], the volume deformation and strain-relief energies vanish and a short-range, weakly repulsive interaction is responsible for phase separation at low temperatures.

(b) Size-mismatched binary systems

A typical example is SiGe, where the phase separation is favored both by vanishing strain and chemical energies [29].

(c) Size-mismatched pseudobinary systems

This is similar to case (a), but here the volume deformation energy does not vanish. This contribution scales as $(\Delta a)^2$ where Δa is the difference in the lattice constants of the two compounds. This elastic energy favors the phase separation in mixtures such as GaInP or GaAsSb [26, 28, 30].

In the case of growing thin films, the surface energetics can be very different from the bulk energetics due to strain-relieving relaxation mechanisms and electronically driven reconstructions, leading to important differences between the epitaxial phase diagram and the bulk phase diagram. For example, the appearance of new stable phases and new phase transformations has been predicted [31] and observed experimentally [6]. In this thesis, we focus on *alloys* that show phase separation at low temperatures and homogeneity at high temperatures. Other systems where phase transformations are relevant include ferromagnetic [32], ferroelectric [33], and polymeric [34] films.

1.2 Contents of the thesis

One of the theoretical methods to study MBE is to propose a microscopic Hamiltonian and numerically simulate the system using a Monte Carlo algorithm. This approach is

useful because it permits us to focus on certain microscopic interactions, and see their effect on the surface growth. Recently, Siegert and Plischke [35–37] have simulated MBE using a Solid-on-Solid (SOS) model that allows the surface to relax, but also takes into account the constant deposition of particles from the beam. To simulate MBE with phase separation we have used a SOS model augmented by an Ising model to describe the phase separation. The dynamics at the surface and in the bulk are chosen to satisfy detailed balance in the absence of deposition. We have simulated our model in 1+1 dimensions, relevant to experimental systems where the strain is highly anisotropic, and phase separation occurs only in one preferred direction at the surface. Our Monte Carlo simulations show that, for low deposition rates, a lamellar pattern emerges in the bulk with a modulation parallel to the growth plane (lateral phase separation). The appearance of the composition modulation is due to phase separation at the surface. We also show how the temperature and the deposition rate can be used to tailor the wavelength of the modulation and the microstructure of the film. The effects of the phase separation on the surface morphology create a modulation consisting of steps or grooves at the interface between surface domains, which can be seen in the height-height correlation function and in the surface width. The temperature dependence of the surface width at fixed deposition rate is also presented.

Our Monte Carlo results are presented in chapter 2. In chapter 3, we explain the results of our simulations with a long-wavelength field theory. The system is described by a Ginzburg-Landau-type free energy functional, from which we obtain dynamical equations for the height of the interface and for the concentration. The form of the dynamical equations arises from the conservation laws for material and concentration. The equation for the composition at the growing surface consists of a diffusion term in competition with the constant burial of material in the bulk. This competition leads to concentration modulations at the free surface that propagate in the bulk as the film grows. The lamellar regime is found to occur below a critical deposition rate that depends on the relative concentration of the two species and on the surface mobility. The equations are solved in the steady-state near and far from the onset of instability, with the assumption that the non-Euclidean nonlinearities of the surface

are negligible. In contrast to homoepitaxy, we predict a non self-affine structure of the surface for these bulk morphologies from a consideration of the deterministic equation. The set of dynamical equations is integrated numerically using a Euler discretization scheme, and we present morphologies for different growth rates. These surface and bulk structures are characterized by calculating the height-height and concentration-concentration correlation functions. The wavelength of the concentration modulation is found to be in excellent agreement with our theoretical predictions, as well as with our Monte Carlo simulations of chapter 2.

In chapter 4, we introduce in the long-wavelength theory of chapter 3 elastic effects originating from a difference in the lattice constant and in the elastic moduli of the alloy components. By assuming that mechanical equilibrium is instantaneously satisfied, we derive an effective free energy in terms of the composition of the alloy at the growing surface. It is shown that this effective free energy contains long-range contributions due to the dependence of the lattice constant and the shear modulus on composition. These elastic fields alter drastically the composition modulations seen in the growing films, as droplets of the hard phase can form in a matrix of the soft phase even for equal volume fractions of the two alloy components. We numerically calculate the wavelength of the composition modulations and show that the wavelength of the modulation is reduced by the elastic fields. We also obtain scattering functions relevant to experimental observations in the various growth regimes, which are indicative of the underlying symmetry of the composition modulation. A theoretical derivation of the transition line between the droplet and the lamellar phase is also presented.

Chapter 5 considers the fundamental problem of the stability of alloy layers *mis-matched* to their substrate. In the case of one-component heteroepitaxy (for example Si on Ge), the misfit between the lattice constants creates strain in the overlayer which is eventually relieved by the formation of long-wavelength modulations of the surface profile. For *alloy* layers, the elastic fields generated by the difference in the lattice constant and the difference in the elastic moduli of the alloy components can couple with the elastically induced surface deformations. We show that in the presence of substrate misfit and compositional stresses, static or growing films that undergo surface

spinodal decomposition are always unstable to perturbations around the planar surface. For sufficiently rapid deposition processes, the planar surface can be stabilized due to a suppression of the alloy decomposition. Films grown outside the miscibility gap can become unstable due to the mismatch with the substrate and compositionally generated stresses. We also demonstrate that the instability is independent of the sign of the misfit when the elastic moduli of the alloy constituents are equal, and the existence of a maximum misfit above which the film is always unstable, even at high growth rates. The symmetry under sign reversal of the misfit can be broken by composition-dependent elastic constants.

1.3 A model phase diagram

The phase behavior of binary or pseudo-binary alloy mixtures as a function of temperature and composition can be described on long wavelengths by the introduction of a local continuous field $\phi(\mathbf{r})$, the order parameter. In the case of alloys of type A_xB_{1-x} , $\phi(\mathbf{r})$ is related to the composition x , $\phi = (2x - 1)$, implying that $\phi > 0$ corresponds to an excess of A atoms, while $\phi < 0$ corresponds to an excess of B atoms. $\phi = 0$ represents a compositionally homogeneous alloy.

In principle, the free energy of the alloy can be calculated from the microscopic interactions between the alloy constituents. However, this task is exceedingly difficult and the complexity of the calculations masks the important properties of the phase transition problem. In recent decades, it has been recognized that the essential properties of phase transitions can be obtained from a coarse-grained free energy appropriate to the system under consideration, i.e. that includes the relevant underlying symmetries. For a simple binary or pseudo-binary alloy, the order parameter is the important variable entering the free energy, and a simple expression for the free energy is

$$\mathcal{F}[\phi] = \int d\mathbf{r} \left[f(\phi) + \frac{c}{2} |\nabla\phi|^2 \right]. \quad (1.1)$$

$\mathcal{F}$ is in fact a free-energy *functional* since it depends on the function $\phi(\mathbf{r})$. $f(\phi)$ is a local function of the order parameter and is specific to the particular alloy under consideration, although the critical (in the sense of phase transition) properties of the

Figure 1.1: The local free energy plotted above and below the critical temperature. For $T > T_c$, there is only one minimum corresponding to the homogeneous phase. For $T < T_c$, the free energy has two minima corresponding to A-rich and B-rich phases.

system are independent of the form of $f(\phi)$, as long as it represents the high and low temperature phases. At high temperatures, the entropic contributions to the free energy dominate, and the alloy is perfectly mixed and homogeneous in composition. At low temperatures, the entropic contributions can be neglected, and the internal energy dominates. In the case of atomic interactions that favor phase separation, the alloy components separate from one-another and the equilibrium state consists of the coexistence of A-rich and B-rich phases. The considerations above suggest that, at the critical composition, $f(\phi)$ has a single well at $\phi = 0$ for high temperatures and a double-well structure with minima at ϕ_A and ϕ_B at low temperatures. A simple model for $f(\phi)$ is then

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

where $r \propto T_c - T$ with T_c the critical temperature for the phase transition between the homogeneous phase and the phase-separated phase. Figure 1.1 shows sketches of $f(\phi)$ for values of T above and below T_c , which can be understood in terms of a mean-field analysis of $f(\phi)$. In equilibrium, $\frac{\partial f}{\partial \phi} = 0$ and $\frac{\partial^2 f}{\partial \phi^2} > 0$, leading to the equations

$$-r\phi + u\phi^3 = 0 \quad (1.3)$$

Figure 1.2: Model phase diagram for a binary or pseudo-binary alloy. The coexistence region is inside of the solid line while the spinodal line is denoted by the dotted line.

and

$$-r + 3u\phi^2 > 0. \quad (1.4)$$

Solving the first equation gives $\phi = 0$ or $\phi = \pm\sqrt{\frac{r}{u}}$. Substitution of $\phi = 0$ in the inequality gives $-r > 0$, implying $T > T_c$, while the inequality requires $r > 0$ ($T < T_c$) for $\phi = \pm\sqrt{\frac{r}{u}}$. The value of $f(\phi)$ at the two double-well minima is $-\frac{r^2}{4u}$.

The mean-field considerations are not enough to truly describe the alloy phase behavior, since, to conserve the volume fraction of the two species, a gradient in the order parameter must appear somewhere in the system. Hence the true phase behavior must be computed from $\mathcal{F}[\phi]$ which contains the gradient energy contributions. A sketch of the phase diagram corresponding to $f(\phi)$ in Eq. (1.2) is shown in figure 1.2 as a function of the temperature and the average value of ϕ . The free energy $\mathcal{F}[\phi]$ can be rescaled to dimensionless form $\mathcal{F}[\phi] = \frac{r^2}{u} \left(\frac{\varepsilon}{r}\right)^{d/2} \mathcal{F}[\psi]$ using the transformations

$$\psi = \sqrt{\frac{u}{r}}\phi \quad (1.5)$$

and

$$\mathbf{x} = \sqrt{\frac{r}{c}}\mathbf{r}, \quad (1.6)$$

leading to

$$\mathcal{F}[\psi] = \int d\mathbf{x} \left[-\frac{1}{2}\psi^2 + \frac{1}{4}\psi^4 + \frac{1}{2}|\nabla\psi|^2 \right]. \quad (1.7)$$

In dimensionless form, the high temperature equilibrium state is $\psi = 0$, while the low temperature minima in the free energy are $\psi = \pm 1$. Also, the fluctuations around the average order parameter $\psi = \bar{\psi} + \delta\psi$ describe the inhomogeneities in the system, and the free energy $\mathcal{F}[\delta\psi] = \mathcal{F}[\psi] - \mathcal{F}[\bar{\psi}]$ is

$$\mathcal{F}[\delta\psi] = \int d\mathbf{x} \left[(-\bar{\psi} + \bar{\psi}^3) \delta\psi - \frac{1}{2} (1 - 3\bar{\psi}^2) \delta\psi^2 + \bar{\psi} \delta\psi^3 + \frac{1}{4} \delta\psi^4 + \frac{1}{2} |\nabla \delta\psi|^2 \right]. \quad (1.8)$$

We now discuss what happens as the alloy is brought from the homogeneous phase to the coexistence region of the phase diagram. To do so, we consider the *dynamics* of the order parameter field fluctuations. Because the average composition of the alloy stays fixed during the quenching process, the rate of change of ϕ is related to the divergence of a current

$$\frac{\partial \phi}{\partial t} = -\nabla \cdot \mathbf{J}_\phi. \quad (1.9)$$

The order parameter current can be obtained from the gradient of the chemical potential

$$\mathbf{J}_\phi = -\Gamma_\phi \nabla \mu_\phi, \quad (1.10)$$

where Γ_ϕ is a mobility coefficient. The chemical potential is computed from the free-energy functional as

$$\mu_\phi = \frac{\delta \mathcal{F}}{\delta \phi}, \quad (1.11)$$

leading to the dynamical equation

$$\frac{\partial \phi}{\partial t} = \Gamma_\phi \nabla^2 [-r\phi + u\phi^3 - c\nabla^2 \phi]. \quad (1.12)$$

This equation can be written in dimensionless form using the transformations (1.5), (1.6) and the time rescaling

$$\tau = \left(\frac{\Gamma_\phi r^2}{c} \right) t, \quad (1.13)$$

giving

$$\frac{\partial \psi}{\partial \tau} = \nabla^2 [-\psi + \psi^3 - \nabla^2 \psi]. \quad (1.14)$$

Hence the dynamical equation describing the time evolution of the fluctuations in the

order parameter is

$$\frac{\partial \delta \psi}{\partial \tau} = \nabla^2 \left[\left(-1 + 3\bar{\psi}^2 \right) \delta \psi + 3\bar{\psi} \delta \psi^2 + \delta \psi^3 - \nabla^2 \delta \psi \right]. \quad (1.15)$$

In Fourier space,

$$\delta \psi(\mathbf{x}) = \sum_{\mathbf{q}} \hat{\psi}(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{x}}, \quad (1.16)$$

and a linearization of Eq. (1.15) gives

$$\frac{\partial \hat{\psi}}{\partial \tau} = \Omega(\mathbf{q}, \bar{\psi}) \hat{\psi}, \quad (1.17)$$

with the linear dispersion relation Ω given by

$$\Omega(\mathbf{q}, \bar{\psi}) = \left(1 - 3\bar{\psi}^2 \right) q^2 - q^4. \quad (1.18)$$

At early times, the order parameter fluctuation modes evolve as

$$\hat{\psi}(\mathbf{q}, \tau) = \hat{\psi}(\mathbf{q}, 0) e^{\Omega \tau}, \quad (1.19)$$

implying that the modes with wavenumber in the band $0 < q^2 < 1 - 3\bar{\psi}^2$ will be unstable. The line $1 - 3\bar{\psi}^2 = 0$ is known as the spinodal line, and roughly delimits the regions where the system phase separates by spinodal decomposition and by nucleation and growth. The early time analysis is valid until the order parameter fluctuations reach values where the nonlinear terms in the dynamical equation become comparable in size to the linear terms. When this happens, the order parameter saturates and the system enters the late-time regime, eventually reaching the completely phase-separated state. When the average composition of the alloy is $\bar{\psi} = 0$, the final state has the analytical form $\delta \psi(x) = \tanh\left(\frac{x}{\sqrt{2}}\right)$ since this makes the right-hand side of Eq. (1.15) equal to zero.

Chapter 2

MBE IN THE PRESENCE OF PHASE SEPARATION: MONTE CARLO SIMULATIONS

2.1 Introduction

In this chapter, we study a MBE process where two types of particles are deposited simultaneously on a substrate, and where the interatomic potential energy leads to phase separation at the growth temperature and composition [38, 39]. We show, using Monte Carlo simulations of a microscopic model, that the microstructure of the growing film does not correspond to the minimum of the thermodynamic energy, but rather, is a direct consequence of a competition between surface thermodynamics and the constant deposition of particles by the beam. This competition between deposition and phase separation leads to the emergence of a critical deposition rate above which the alloy film is compositionally uniform. Below this critical deposition rate, a lamellar pattern emerges reminiscent of experimental observations of lateral phase separation, and with the modulation wavelength dependent on the temperature and the deposition rate.

2.2 Model

During MBE, evaporation of particles is negligible, and the surface relaxation proceeds through diffusion of material along the surface, due to the much larger surface diffusion coefficient. Typically, overhangs and incorporation of vacancies in the bulk are neglected, and MBE is modeled by SOS models. The investigations of various SOS models have shown that both in 1+1 and 2+1 dimensions, the simplest realistic

discrete model Hamiltonian for MBE is

$$\mathcal{H}_{SOS} = \frac{1}{2} E_{SOS} \sum_{\langle i,j \rangle} |h_i - h_j|^n, \quad (2.1)$$

where h_i is the discrete height at site i and the sum is over nearest-neighbor sites ($E_{SOS} > 0$). The exponent n is related to the so-called Schwoebel barriers [40]: on a vicinal surface of large terraces separated by steps, a particle diffusing on a terrace will be repelled from the downward step, because it has to jump over a potential energy barrier. This barrier is due to a decrease of the coordination number as the particle passes from the upper terrace to the lower terrace. The $n = 1$ model possesses a negative Schwoebel effect producing downhill currents and realistic surface properties. The case $n = 2$ has a special symmetry and is not expected to be realistic. For $n = 4$, there is a positive Schwoebel effect that causes instabilities and the formation of large pyramid-like structures. For these reasons, we have chosen to model the surface relaxation in our problem with $n = 1$. In this case, $\mathcal{H}_{SOS}$ is proportional to the number of broken bonds at the surface and thus has a simple physical origin.

The properties of this model have been studied both in 1+1 ($d = 1$) and 2+1 ($d = 2$) dimensions by Monte Carlo simulations [35] (details of the Monte Carlo algorithm will be given in section 2.2). Most of the surface structural properties can be obtained from the surface structure factor, defined as

$$S_s(\mathbf{k}, t) = \langle \hat{h}(\mathbf{k}, t) \hat{h}(-\mathbf{k}, t) \rangle \quad (2.2)$$

where $\hat{h}(\mathbf{k}, t) = L^{-d/2} \sum_{\mathbf{r}} [h(\mathbf{r}, t) - \bar{h}] e^{i\mathbf{k}\mathbf{r}}$ with $\bar{h}$ the average value of $h(\mathbf{r}, t)$, L the linear system size, and the angular brackets denote an average over independent initial conditions. The surface structure factor follows a simple scaling form

$$S_s(\mathbf{k}, t) = k^{-\delta} s(k^z t), \quad (2.3)$$

with the exponents obeying a hyperscaling relation $\delta = z$, and are equal to 2. Thus during MBE growth, a unique length scale, ξ , emerges and obeys the power law

$$\xi \sim t^{1/z}. \quad (2.4)$$

The width of the interface, W , defined through the relation

$$W^2(L, t) = \left(\frac{L}{a}\right)^{-d} \sum_{\mathbf{r}} \langle [h(\mathbf{r}, t) - \bar{h}]^2 \rangle = a^d \sum_{\mathbf{k}} S_s(\mathbf{k}, t), \quad (2.5)$$

(a is the lattice constant) thus follows a power law in time, $W \sim t^\beta$ with $2\beta = (\delta - d)/z$ until saturation is reached, where $W \sim L^\zeta$ with $\zeta = \frac{1}{2}$ for $d = 1$ and $\zeta = 0$ for $d = 2$. Prior to saturation, $W \sim \xi^\zeta \sim t^{\frac{\zeta}{z}}$ which leads to the relation $\beta = \zeta/z$. The three relations among the exponents lead to ζ as one independent exponent. The above scaling forms imply that the correlation function

$$G_s(\mathbf{r}, t) = \langle [h(\mathbf{r}, t) - h(0, t)]^2 \rangle = r^{2\zeta} g(r/\xi(t)). \quad (2.6)$$

Furthermore it was found that the value of ζ is independent of the deposition rate and of the presence of an equilibrium roughening transition [35].

The above scaling relations and exponents can be reproduced from the Edwards-Wilkinson (EW) equation [41]

$$\partial_t h = \kappa \nabla^2 h + aF + \eta_h, \quad (2.7)$$

where F is the deposition rate and η_h its nonconserved fluctuations with second moment D . Indeed, the structure factor is $S_s(\mathbf{k}, t) = \frac{D}{\kappa k^2} (1 - e^{-2\kappa k^2 t})$, which gives (in the steady-state and in 1+1 dimensions) $W = (D/\kappa)^{1/2} L^{1/2}$.

In the case of multicomponent MBE growth, one needs to include in the model the interactions between different atomic species. The simplest model capable of describing phase separation in a binary alloy is the Ising model

$$\mathcal{H}_{Ising} = -\frac{1}{2} E_{Ising} \sum_{\langle i, j \rangle} \sigma_i \sigma_j, \quad (2.8)$$

where σ_i is a variable equal to ± 1 for an A or B atom respectively, and the sum is over nearest-neighbor pairs. On a two-dimensional square lattice, the Ising model has a phase transition between a high temperature homogeneous phase and a low temperature two-phase region around $T_c \approx 2.26 \frac{E_{Ising}}{k_B}$, k_B being Boltzman's constant. The dynamical evolution of such a system after a quench from a high temperature to a temperature below T_c is governed by an initial instability and the development of domains of local order parameter corresponding to that of the two coexisting phases,

with average size growing as a power law in time with an exponent $\frac{1}{3}$ [42–44]. For MBE, we suppose that the concentration of each atomic type falling on the surface is constant in time, and because of conservation of material, $(\bar{h}L^d)^{-1} \sum_{system} \sigma_i = \text{constant}$. A coarse-grained description of the phase separation in the Ising model in terms of a continuous variable $\psi(\mathbf{x})$ proportional to the local concentration difference of the two species is the Cahn-Hilliard equation [45]:

$$\partial_\tau \psi = \nabla^2(-\psi + \psi^3 - \nabla^2 \psi) + \eta_\psi, \quad (2.9)$$

with η_ψ a conserved thermal noise.

We postulate the full Hamiltonian for MBE with phase separation to be

$$\mathcal{H} = \mathcal{H}_{SOS} + \mathcal{H}_{Ising}. \quad (2.10)$$

There are three parameters entering in our model: E_{Ising}/E_{SOS} , $k_B T/E_{SOS}$ and the deposition rate F . In the following, we have set E_{SOS} to 1 and shall refer to $k_B T/E_{SOS}$ as T , while lengths are rescaled by the lattice constant a .

In the simulations, we start with a one-dimensional flat interface of size L , and the space above the substrate is divided in a square lattice with lattice constant $a = 1$. A site i from 1 to L is chosen randomly, and a particle is deposited at $h_i + 1$. In the case of a "critical" deposition, i.e. $\sum_{system} \sigma_i = 0$, we choose the type of the freshly landed atom randomly to be ± 1 . Then we randomly visit all of the atoms that have been deposited. If the atom lies on the surface, it is allowed to hop to a nearest-neighbor site on the surface (corresponding to processes 1, 3 and 4 in Fig. 2.1) with a transition rate

$$w_{i \rightarrow j} = \exp\left(-\frac{\Delta \mathcal{H}_{i \rightarrow j}}{2T}\right), \quad (2.11)$$

where $\mathcal{H}$ is the Hamiltonian of Eq. (2.10). This choice for the transition rates ensures that detailed balance is satisfied if the deposition rate is set to zero [35]. If the atom lies in the bulk, we randomly choose a nearest-neighbor site and attempt to exchange the two atoms, as process 2 of Fig. 2.1 illustrates (this choice for the bulk dynamics conserves the volume fraction). We do not allow exchanges between surface and bulk atoms, and we assume periodic boundary conditions along the x direction. The deposition rate F is controlled by the number of sweeps through the surface after each

deposition. To model the difference in the diffusion constant on the surface and in the bulk, the number of diffusion attempts (Monte Carlo steps) per deposition event for atoms on the surface is set to n_s while for atoms in the bulk it is n_b . For $n_b < n_s$ the surface diffusion coefficient is larger than the bulk diffusion coefficient. If E_e is the extra activation energy for an atom in the bulk as compared to an atom at the surface, then the ratio $n_b/n_s \sim \exp(-E_e/k_B T)$. In our simulations, we have kept the ratio $n_b/n_s = 0.01$ fixed. The deposition rate F in time units of Monte Carlo steps is $F = 1/n_s$.

Figure 2.1: Monte Carlo moves allowed in the simulations. Processes 1, 3 and 4 are surface diffusions, while process 2 is a bulk exchange.

2.3 Results

We have simulated our model for systems of size $L = 200$, for various values of the Ising and SOS interactions and with different deposition rates and temperatures. Finite size effects were minimal since the compositional domains that formed were much smaller than the system size, as shown in sections 2.3.1 and 2.3.2 below. If $\varepsilon(\sigma_i, \sigma_j)$ represents the interaction energy between nearest-neighbor atoms i and j ,

and if we identify an unoccupied site with $\sigma = 0$, the energies in our model are $\varepsilon(1, 1) = \varepsilon(-1, -1) = -E_{Ising}$, $\varepsilon(1, -1) = \varepsilon(-1, 1) = E_{Ising}$, and $\varepsilon(\pm 1, 0) = E_{SOS}$. In the case where $E_{Ising} > 2E_{SOS}$, processes 3 (detachment from islands) and 4 of Fig. 2.1 will spontaneously occur because they lower the energy, thereby creating very rough surfaces. With our choice for the Hamiltonian (and large E_{Ising}), process 4 will always reduce the energy, independently of the depth of the groove, leading to columnar structures.

2.3.1 Effects of temperature

Fig. 2.2 shows the top 50 layers after deposition of 200 layers for temperatures below the critical temperature, with the deposition rate fixed at $F = 0.01$. We found that if we set the bulk diffusion to zero, the same kind of lamellar patterns appears, implying that the phase separation occurs at the surface. For temperatures above the critical temperature, the atoms are homogeneously mixed, in agreement with annealing experiments [6]. Below T_c , the atoms form domains at the surface that are buried as the film grows. Newly deposited atoms then diffuse along the surface, which now contains concentration gradients, and will tend to stay on top of lamellae that minimize the bonding energy. Iteration of this idea produces stripes that extend from the substrate to the free surface. When the bulk interfaces are straight, they do not decay and are metastable. (In fact, $\psi = \tanh(x/\sqrt{2})$ is a one-dimensional steady-state solution of Eq. (2.9) without thermal noise). For the lamellar bulk configurations where the concentration interfaces are rough, reducing the temperature after the deposition process would quench in the morphology. On the other hand, this roughness could be decreased by the local straightening of the interfaces by the chemical potential gradients as time proceeds, leading to flat interfaces. Which of these two processes is useful in practice depends on the application. For example, in [46], it has been shown that the interface roughness in semiconductor superlattices leads to quantum phase-coherent backscattering which localizes the electrons and increases the magnetoresistance.

As Fig. 2.2 illustrates, the pattern wavelength depends strongly on the temperature. At low temperatures, the diffusion length is small, and the atoms sample the

Figure 2.2: Top 50 layers after deposition of 200 layers for $n_s = 100$, $E_{Ising}=1$ and $T =$ (a) 0.2, (b) 0.5, (c) 1.0 and (d) 1.6. A lateral portion of the $L = 200$ system is shown.

surface only locally and stick. For example, at $T = 0$, a move occurs only if $\Delta\mathcal{H} \leq 0$, i.e. attachment to islands, downward jumps or diffusion on a flat surface. This creates small domains, and an interconnected bulk domain structure. At the top surface, steps form at the domain boundaries, and sometimes arrange themselves in step trains [Fig. 2.2(a)]. As the temperature is increased two effects come into play. First, the increase in the diffusion length causes the lamellar thickness, λ , to increase. Second, surface atoms acquire enough thermal energy to overcome the energy barriers at the surface domain boundaries, and diffuse to the top of stripes of opposite concentration, leading to a larger bulk miscibility than that of the equilibrium mixture. We stress that at low temperatures a newly deposited atom diffuses to the nearest favorable lamellae and stays confined to the top of this stripe. The diffusion length is then only of the order of λ . Because the one-component model leads to self-affine surfaces, the fact that the atoms are confined within λ does not drastically affect the value of the surface width, except for corrections at surface domain boundaries.

The wavelength of the bulk pattern is an important quantity to measure as a function of the temperature. In order to calculate the thickness of the stripes, we have computed the concentration structure factor $S_\sigma(k) = L^{-1} \langle \sigma_k \sigma_{-k} \rangle$ in the direction parallel to the growth plane, 25 sites below the average steady-state height. The peak in $S_\sigma(k)$ represents the modulation period. A measure of the lamellar thickness, λ , can be obtained from twice the first zero of the correlation function $G_\sigma(x) = L^{-1} \sum_k S_\sigma(k) \cos(kx)$. Fig. 2.3 shows the correlation function for the temperatures of Fig. 2.2. The periodic structure is apparent in the oscillations of the correlation function about zero; as the temperature is increased, spatial correlations extend farther along the direction parallel to the growth plane.

The temperature dependence of λ is plotted in Fig. 2.4. As a general trend, λ increases at low temperatures, reaches a maximum and decreases as T_c is approached. This behavior can be explained by considering the motion of interfaces between ordered domains on the surface. The steady-state wavelength is related to the velocity of the moving interfaces times the typical time scale between monolayer completion. The interface velocity (and hence λ) is proportional to the surface tension and the diffusion coefficient. The surface tension is constant at low temperatures and decreases

Figure 2.3: Bulk correlation function $G_\sigma(x)$ in the direction parallel to the growth plane for the parameters of Fig. 2.2.

Figure 2.4: Thickness of the lamellae as a function of temperature for $n_s = 100$. The vertical dashed line corresponds to the critical temperature for the Ising model on a square lattice.

Figure 2.5: Temperature dependence of the surface width. The solid circles are for MBE with phase separation, while the open squares correspond to single-component MBE.

towards zero as the critical point is approached, while the diffusion coefficient should have an Arrhenius form. These two effects conspire to give a maximum in $\lambda(T)$. In addition, the shape of this curve shows a shoulder around $T = 0.6$, which can be associated with the behavior of the surface width, which we discuss next. We find that the width has a non-monotonic temperature dependence, as shown in Fig. 2.5. As the temperature is increased from zero, the width (solid circles) decreases linearly with T , reaches a minimum, and then starts to increase as T^2 . This minimum occurs around the same temperature where $\lambda(T)$ has a shoulder in Fig. 2.4. For comparison, we show in Fig. 2.5 the width (W_{SOS}) when only one kind of atom is deposited. In contrast to multicomponent MBE growth, W_{SOS} increases roughly as T for $T > 0.6$. Our understanding of the temperature dependence of the interface width is as follows: at low temperatures, atoms form thin lamellae, and the energy barriers at the A-B interfaces keep the atoms on top of a favorable stripe (i.e. same type). This creates steps at the lamellar interfaces and gives rise to a width larger than W_{SOS} . Since the number of interfaces decreases with temperature, the width also decreases, and does so faster than W_{SOS} . With the assumption that the system is composed of pure lamellae of thickness λ , the average size of the steps can be evaluated from

$h_i = h_i^{SOS} + \Delta h \delta_{i,n\lambda}$ where n is an index labelling the location of the surface domain interfaces. This gives $\Delta h = \sqrt{\lambda} (W^2 - W_{SOS}^2)^{1/2}$, and from our data points, we find that Δh is of order 1 and decreases in the range $0.2 < T < 0.6$. There are two possible explanations for this: either the size of the steps is temperature dependent, or the effect on the neighbor sites that we have neglected has to be taken into account (this is more important when λ is small). At high temperatures, the atoms can jump over the potential energy barriers at the surface A-B interfaces, leading to a mixing at the top of these stripes, thereby decreasing the surface tension and thus causing the width to increase rapidly with T in Fig. 2.4. This enhanced diffusion at $T > 0.6$ is also responsible for the sudden increase of λ with T .

The high temperature behavior can be explained in terms of a continuum equation that includes both the EW term and the surface tension contribution:

$$\partial_t h = \kappa \nabla^2 h - \Gamma_h \gamma \nabla^4 h + \eta_c + \eta_{nc} \quad (2.12)$$

with η_c a conserved thermal noise with second moment $\langle \eta_c(x, t) \eta_c(x', t') \rangle =$

$-2\Gamma_h k_B T \nabla^2 \delta(x - x') \delta(t - t')$, and η_{nc} a nonconserved beam noise of strength D . In this equation, Γ_h is a kinetic coefficient and γ is the surface stiffness. The steady-state structure factor can be easily calculated, and is given by

$$S_s(k) = \frac{D + \Gamma_h k^2 k_B T}{\kappa k^2 + \Gamma_h \gamma k^4}, \quad (2.13)$$

which reduces to $S_s(k) = \Gamma_h k_B T (\kappa + \Gamma_h \gamma k^2)^{-1}$ in the limit of small D and large T . From this expression, we obtain the surface width

$$W^2 = \frac{\Gamma_h k_B T}{\sqrt{\Gamma_h \gamma \kappa}} \left[\arctan \left(\sqrt{\frac{\Gamma_h \gamma}{\kappa}} \frac{2\pi}{a} \right) - \arctan \left(\sqrt{\frac{\Gamma_h \gamma}{\kappa}} \frac{2\pi}{L} \right) \right]. \quad (2.14)$$

When the system size is large and the lattice constant is small, the surface width becomes $W \sim \left(\frac{\Gamma_h k_B T}{\sqrt{\Gamma_h \gamma \kappa}} \right)^{1/2}$. In the homoepitaxial case, γ is constant and the temperature dependence is buried in κ and Γ_h . In the case of multicomponent epitaxial growth with phase separation, we expect the temperature dependence of κ and Γ_h to remain roughly the same, while γ acquires a temperature dependence due to the diffusion effect discussed earlier. Because γ decreases with temperature, the overall

Figure 2.6: Scaling function for the surface correlation function for temperatures above and below the width minimum. The inset is the scaling function for single-component MBE.

effect is to cause the width to increase faster than in homoepitaxy.

The shape of the surface can be described by computing the surface correlation function $G_s(r)$ as defined in Eq. (2.6). As Fig. 2.6 indicates, the correlation function is qualitatively different for temperatures above and below the minimum in the surface width. For large distances, $r^{-1}G_s(r)$ for $T = 1.0$ and $T = 1.6$ decays as r^{-1} , consistent with the behavior of the one-component SOS model (see inset). However, at small distances, these two functions are not constant. The faster decrease of the height-height correlation function for temperatures above 0.6 is in agreement with the previous statement that thermal fluctuations become important in this regime. Because the interface width is of order 1, the effects of the domain interfaces on the surface shape are not apparent in the surface correlation function or the structure factor, although at low temperatures, extra steps are obviously seen in the configurations, and at high temperatures, grooves and steps are more often seen at those interfaces. To clarify this, we simulated the system at large values of E_{Ising} . As Fig. 2.7 illustrates, grooved states are now more apparent in the configurations. In the case where $E_{Ising} = 1.9$, grooves are found to occur at the surface domain interfaces, with a saturated depth of 3-4 atoms, while the other surface features (roughness) are one atom

Figure 2.7: Time evolution of the structure factor for $E_{Ising} = 4$. Curves from bottom to top correspond to time=20, 30, 40, 60 and 100 monolayers. The peak at $k = 0$ is typical of homoepitaxy, while the peak at nonzero k represents the surface modulation. In the inset, the top configuration is typical of this regime, whereas the bottom configuration shows grooves as seen when $E_{Ising} = 1.9$.

high. For $E_{Ising} = 4$, it becomes energetically favorable under certain conditions for the system to incorporate empty sites between stripes of opposite concentration, creating very thin and deep crevasses. Such large modulations of the surface are now apparent in the surface structure factor (Fig. 2.7). The peak at $k = 0$ represents the usual fluctuations that lead to self-affine surfaces (that is, of the EW form), while the peak at $k \neq 0$ represents the surface modulation. Note that as time increases, the divergence at $k = 0$ overwhelms the modulation peak. As discussed earlier, when the Ising interaction is not as large, the surface saturates rapidly, and the peak in the surface structure factor is not as clear.

The extreme roughness of the surface for large E_{Ising} has been seen experimentally during co-deposition of Al-Ge thin films [19], as discussed in the introduction chapter. In particular, phase separation is found at the surface and in the bulk, with the Al domains forming large mounds of height $0.25 \mu\text{m}$, separated from the Ge by grooves. Whether such deformations of the surface are due to the effects we are reporting here or due to elastic effects remains to be explored.

2.3.2 Effects of the deposition rate

Although the lamellar wavelength can be controlled by appropriately choosing the temperature, this also leads to wandering lamellae at low temperatures or rough lamellar interfaces at high temperatures. One can alternatively control the pattern wavelength by varying the deposition rate. Qualitatively, the effects of the deposition rate are shown in Fig. 2.8, from which it is clear that a decrease in the deposition rate ($F = 1/n_s$) increases λ , since the atoms have a longer time to sample the surface before being covered. Also, at larger rates, the surface roughness increases. In Fig. 2.9, we plot the lamellar thickness as a function of the deposition rate at fixed temperature. Our data are well described by $\lambda \sim F^{-x}$ (where $F \sim 1/n_s$) with $x = 1/3$ for low deposition rates, and $x = 1/4$ for moderate deposition rates. For $1/n_s > 0.1$, the bulk consists of an interconnected structure, suggesting a critical growth rate above which the film is homogeneous. The exponent $x = 1/3$ at low deposition rates is not surprising since the domain size in bulk phase separating alloys grows as $t^{1/3}$. The regime with $x = 1/4$ and the stabilization of the alloy decomposition at high deposition rates

Figure 2.8: Typical configurations for $T = 1.2$ and $n_s =$ (a) 1, (b) 100, (c) 400 and (d) 1000. The top 50 layers and a lateral portion of size 100 of the $L = 200$ systems are shown.

Figure 2.9: Thickness of the lamellae as a function of the deposition rate at $T = 1.2$. The solid (dashed) line has slope $-1/4$ ($-1/3$). The vertical line represents roughly the transition between the lamellar and the disordered regimes.

shows the importance of the deposition rate in determining the microstructure of the growing film.

2.4 Conclusion

In this chapter, we have considered the growth of thin solid films by Molecular Beam Epitaxy. We considered the growth of multicomponent films, where the ground state energy favours phase separation. During the growth process, two phenomena attracted our attention. First, we were interested in surface roughening, whereby the beam fluctuations are transformed into fluctuations of the surface height, typically leading to self-affinity of the surface shape. Second, the growth of correlated domains due to the nature of the chemical potential (phase separation) was considered. The interplay between these two processes was the central theme of this chapter. Our Monte Carlo simulations demonstrated important aspects seen in experimental systems: above a critical temperature, the films are homogeneous; the wavelength of the concentration modulation increases with temperature; phase separation does not occur by bulk diffusion. Furthermore, our data indicate that the width of the free surface is only slightly larger when phase separation is present. The characteristics of the surface were also analyzed using the structure factor and the correlation function. The self-affinity of the surface is destroyed by the concentration gradients, and this was explained by the presence of steps and grooves at the interface between domains.

Chapter 3

FIELD THEORY FOR MBE IN THE PRESENCE OF PHASE SEPARATION

3.1 Introduction

In this chapter, we revisit the systems considered in chapter 2 from a long-wavelength point of view [39,47]. A continuum theory that takes into account the fluctuations of the free surface and the phase separation is formulated. We explain how bulk lamellar patterns develop from a competition between the surface phase separation and the constant burial of surface domains by the incoming beam. The dependence of this concentration wavelength on the deposition rate is in excellent agreement with our simulations in chapter 2. We demonstrate that the free surface is modulated, with a period that is half of the bulk modulation wavelength.

This chapter is divided as follows: in section 3.2 we introduce our model, in section 3.3 we derive the dynamical equations for the surface height and the concentration variable which are studied analytically in section 3.4. Section 3.5 connects our analytical results with typical experimental situations, while section 3.6 presents numerical integrations of the dynamical equations. The conclusions are presented in section 3.7.

3.2 Model

In this section, we propose and study a long wavelength field theory for MBE with

phase separation, by extending the free energy of Ginzburg and Landau to include the fluctuations of the free surface. The height of the surface is represented by a single-valued continuous variable $h(\mathbf{r})$ obtained by coarse-graining the microscopic discrete height. The local concentration of the two species is represented by a continuous order parameter $\phi(\mathbf{r}, z)$ which is proportional to the local difference in the concentrations. If $\phi(\mathbf{r}, z) = \phi_{max}$, the concentration of atoms of type A is zero and the concentration of type B atoms is maximal. Similarly, $\phi(\mathbf{r}, z) = -\phi_{max}$ represents a pure A mixture. For compounds of the form $AB_{1-x}C_x$, $\phi = 0$ corresponds to $x = 1/2$, while $\phi = \phi_{max}$ corresponds to $x = 0$ and $\phi = -\phi_{max}$ corresponds to $x = 1$.

The free-energy functional for our problem consists of two contributions:

$$\mathcal{F}[h, \phi] = \mathcal{F}_S[h] + \mathcal{F}_B[h, \phi], \quad (3.1)$$

where $\mathcal{F}_S$ and $\mathcal{F}_B$ are the surface and bulk free-energy functionals, respectively. We assume that the surface fluctuations are limited by the surface tension, and we write

$$\mathcal{F}_S[h] = \gamma \int d\mathbf{r} \sqrt{g(h)}, \quad (3.2)$$

where $g(h) = 1 + (\nabla h)^2$ and γ is the surface tension. In writing this expression, we did not include a pinning term that describes the equilibrium roughening transition [48] of the crystal surface; in what follows, it can be considered that the equilibrium roughening transition is at $T = 0$. The bulk free energy is given by the modified Ginzburg-Landau functional

$$\mathcal{F}_B[h, \phi] = \int d\mathbf{r} \int_0^{h(\mathbf{r})} dz \left[-\frac{r}{2}\phi^2 + \frac{u}{4}\phi^4 + \frac{c}{2}(\nabla\phi)^2 \right], \quad (3.3)$$

where the conserved order parameter $\phi(\mathbf{r}, z)$ is zero for $z < 0$ and for $z > h(\mathbf{r})$, and the constant r is proportional to $T_c - T$ where T_c is the critical temperature of the binary alloy. Above T_c , the equilibrium state is the homogeneous one with $\phi = 0$, while for $T < T_c$, the local free energy has two stable minima, corresponding to $\phi = \pm\sqrt{\frac{r}{u}}$.

The lower limit in the integral for $\mathcal{F}_B$ represents the substrate on which the particles are being deposited. Here, we assume that the substrate remains flat, and we do not consider surface interactions and contact potentials between the order parameter and the substrate. The upper limit in Eq. (3.3) provides information on the way material

is distributed around the free surface, and compared with the usual Ginzburg-Landau free-energy functional, gives a new mechanism for the system to reduce its energy. The upper limit also provides a coupling between the two variables $h(\mathbf{r})$ and $\phi(\mathbf{r}, z)$.

3.3 Dynamical equations

The dynamics of the model are governed by two local conservation laws, since we are considering the case where the concentration of atoms deposited by the beam remains constant. Because of this, we require

$$\int d\mathbf{r} dz \phi(\mathbf{r}, z, t) = \text{constant} \quad (3.4)$$

which amounts to

$$\frac{\partial \phi}{\partial t} = -\nabla \cdot \mathbf{J}_\phi, \quad (3.5)$$

where $\mathbf{J}_\phi$ is the order parameter current driven by inhomogeneities in the local chemical potential and can be obtained from the free energy functional:

$$\mathbf{J}_\phi = -\Gamma_\phi \nabla \mu_\phi = -\Gamma_\phi \nabla \frac{\delta \mathcal{F}}{\delta \phi}. \quad (3.6)$$

Hence we can write

$$\frac{\partial \phi}{\partial t} = \Gamma_\phi \nabla^2 \mu_\phi + \eta_\phi, \quad (3.7)$$

with Γ_ϕ the mobility and $\eta_\phi(\mathbf{r}, z, t)$ a conserved noise with second moment

$$\langle \eta_\phi(\mathbf{r}, z, t) \eta_\phi(\mathbf{r}', z', t) \rangle = -2\Gamma_\phi k_B T \nabla^2 \delta(\mathbf{r} - \mathbf{r}') \delta(z - z') \delta(t - t'). \quad (3.8)$$

The second conservation law demands that material be conserved. Because the diffusion coefficient is much larger at the surface, we assume that diffusion proceeds along the surface only. Then

$$\frac{\partial h}{\partial t} = \Gamma_h \sqrt{g} \nabla_s^2 \frac{\delta \mathcal{F}}{\delta h} + \Gamma_h \sqrt{g} \nabla \cdot \boldsymbol{\eta}_M, \quad (3.9)$$

where

$$\nabla_s^2 = \frac{1}{\sqrt{g}} \frac{\partial}{\partial x_i} \left[\sqrt{g} \delta_{i,j} - \frac{1}{\sqrt{g}} \frac{\partial h}{\partial x_i} \frac{\partial h}{\partial x_j} \right] \frac{\partial}{\partial x_j}, \quad (3.10)$$

is the Laplace-Beltrami operator (with the Einstein summation convention) that ensures that the surface diffusion is parallel to the free surface. In this equation $\boldsymbol{\eta}_M$ is

a conserved thermal noise current.

When a beam of particles (growth rate v with non-conserved fluctuations η_v) impinges on the surface, Eq. (3.9) has to be modified to

$$\frac{\partial h}{\partial t} = \Gamma_h \sqrt{g} \nabla_s^2 \frac{\delta \mathcal{F}}{\delta h} + \Gamma_h \sqrt{g} \nabla \cdot \boldsymbol{\eta}_M + v + \eta_v, \quad (3.11)$$

where the beam fluctuations are not conserved and satisfy

$$\langle \eta_v(\mathbf{r}, t) \eta_v(\mathbf{r}', t') \rangle = 2D \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'). \quad (3.12)$$

The functional derivatives in Eqs. (3.6) and (3.9) can be shown to be

$$\frac{\delta \mathcal{F}}{\delta h} = -\gamma \nabla \cdot \frac{\nabla h}{\sqrt{g}} + \left[-\frac{r}{2} \phi_s^2 + \frac{u}{4} \phi_s^4 + \frac{c}{2} (\nabla \phi)_s^2 \right] \quad (3.13)$$

and

$$\begin{aligned} \frac{\delta \mathcal{F}}{\delta \phi} = & -r\phi + u\phi^3 - c\nabla^2 \phi + c\delta(z) (-\hat{\mathbf{z}} \cdot \nabla \phi) \\ & + c\delta(z - h) (\hat{\mathbf{n}} \cdot \nabla \phi), \end{aligned} \quad (3.14)$$

where the subscript s represents a function evaluated at the surface (i.e. at the vertical coordinate $h(\mathbf{r})$), and the unit vector $\hat{\mathbf{n}} = \frac{1}{\sqrt{g}} (-\nabla h, 1)$ is normal to the free surface. We can remove the delta function divergences by making the assumption that the surface is in equilibrium with the adjacent bulk layer, implying that $c\hat{\mathbf{z}} \cdot \nabla \phi = 0$ at $z = 0$ and $c\hat{\mathbf{n}} \cdot \nabla \phi = 0$ at $z = h$. Additional boundary conditions can be derived by requiring that no current flow through the surfaces, implying that $c\hat{\mathbf{z}} \cdot \nabla \mu_\phi = 0$ at $z = 0$ and $c\hat{\mathbf{n}} \cdot \nabla \mu_\phi = 0$ at $z = h$. These boundary conditions represent surfaces that do not favor either of the two components; as shown in previous numerical simulations, this corresponds to the case where droplets of both phases are in contact with the surfaces [49].

The relaxation of the surface we have discussed so far occurs through the diffusion of material along the surface, and we have taken the drumhead model to represent the energy cost of the surface deformations. However, it has been shown by Villain [40] that a purely kinetic effect can lead to a contribution that depends on the local curvature of the surface (note that such a contribution also arises when desorption is

important, but we do not consider this case here). Monte Carlo simulations [50] have shown that such a current exists for a variety of growth models, and for small slopes, this current is negative, i.e. downhill. So, to represent this kinetic effect, one needs an added term $\kappa \nabla \cdot \nabla h / \sqrt{g}$ in the equation for h which can also predict the exponents of our Monte Carlo simulations when only one type of particle is deposited. With this, the coupled equations describing the time evolution of h and ϕ are obtained as

$$\begin{aligned} \frac{\partial h}{\partial t} = & \kappa \nabla \cdot \frac{\nabla h}{\sqrt{g}} - \Gamma_h \gamma \sqrt{g} \nabla_s^2 \left[\nabla \cdot \frac{\nabla h}{\sqrt{g}} \right] \\ & + \Gamma_h \sqrt{g} \nabla_s^2 \left[-\frac{r}{2} \phi_s^2 + \frac{u}{4} \phi_s^4 + \frac{c}{2} (\nabla \phi)_s^2 \right] \\ & + \Gamma_h \sqrt{g} \nabla \cdot \boldsymbol{\eta}_M + v + \eta_v, \end{aligned} \quad (3.15)$$

$$\frac{\partial \phi}{\partial t} = \Gamma_\phi \nabla^2 \left[-r\phi + u\phi^3 - c\nabla^2 \phi \right] + \eta_\phi, \quad (3.16)$$

and

$$\begin{aligned} \frac{\partial \phi_s}{\partial t} = & \Gamma_\phi^S \nabla_s^2 \left[-r\phi_s + u\phi_s^3 - c(\nabla^2 \phi)_s \right] \\ & + (v/a)(\phi_0 - \phi_s) + \eta_{\phi_s} + \eta_\phi. \end{aligned} \quad (3.17)$$

We have explicitly written out the dynamical equation for ϕ_s , because it is assumed to evolve through diffusion along the surface only. The mobility at the surface, Γ_ϕ^S , is larger than the bulk mobility, Γ_ϕ , and the noise η_{ϕ_s} in Eq. (3.17) is nonconserved because it represents the fluctuations of the concentration in the beam. The linear term in ϕ_s in Eq. (3.17) coupled to the beam concentration deposition rate, v/a (with a the lattice constant), has been proposed before [51]. This contribution can be obtained as follows: we can write $\phi_s(t + \Delta t) = \phi_s(t) + R\Delta t$, where R represents the amount and concentration of material falling on the surface. R can be expanded around the average value of the order parameter: $R(\phi_s) = R(\phi_0) + (v/a)(\phi_0 - \phi_s)$, which simply states that the order parameter has a tendency to flow towards ϕ_0 .

These three equations must be augmented by the appropriate boundary conditions discussed earlier, implying in particular that the contributions $(\nabla \phi)_s^2$ and $(\nabla^2 \phi)_s$ in

Eqs (3.15) and (3.17) can be taken as $(\nabla\phi_s)^2$ and $\nabla^2\phi_s$. The set of Eqs. (3.15)-(3.17) represents a system of coupled partial differential equations, with Eqs. (3.15) and (3.17) directly coupled, because ϕ_s appears explicitly in the equation for h , and the h dependence enters through the Laplace-Beltrami operator in (3.17). In Eq. (3.16) the bulk order parameter is not explicitly coupled to h , but the coupling comes through the boundary conditions and the spatial derivatives.

The coefficient κ describes the sign of the Schwoebel barriers at step edges. For $\kappa < 0$, there is an instability that has to be controlled by the nonlinearities. However, if $\kappa > 0$, the nonlinear term in Eq. (3.15) proportional to γ is irrelevant on large length scales, and can be neglected [35]. A linearized version of Eq. (3.15) was used in chapter 2, Eq. (2.12), to explain the high temperature results of our Monte Carlo simulations. The expression for the structure factor calculated from this equation appears in Eq. (2.13), showing that in the limit of long wavelengths or low temperatures, the contributions from the surface tension can be neglected. Furthermore, the conserved noise η_M appearing in Eq. (3.15) is irrelevant compared with the non-conserved beam noise η_v , and can also be neglected. After transformation to the comoving reference frame $h \rightarrow h + vt$, we arrive at the equation for h valid on long length scales

$$\frac{\partial h}{\partial t} = \kappa \nabla \cdot \frac{\nabla h}{\sqrt{g}} + \Gamma_h \sqrt{g} \nabla_s^2 \left[-\frac{r}{2} \phi_s^2 + \frac{u}{4} \phi_s^4 + \frac{c}{2} (\nabla \phi)_s^2 \right] + \eta_v. \quad (3.18)$$

In principle, the coefficients κ and Γ_h depend on ϕ and ∇h , but we do not consider such complications. Eq. (3.18) without the contribution from the order parameter is referred to as the Edwards-Wilkinson equation, and leads to a scaling behaviour of the correlation length and the correlation function.

The equations of motion and the boundary conditions may be rescaled, using the transformations

$$\mathbf{x} = \left(\frac{r}{c} \right)^{1/2} \mathbf{r}, \quad (3.19)$$

$$\tau = \left(\frac{\Gamma_\phi r^2}{c} \right) t, \quad (3.20)$$

and

$$\psi(\mathbf{x}, \tau) = \left(\frac{u}{r}\right)^{1/2} \phi(\mathbf{r}, t). \quad (3.21)$$

To be consistent with the length rescaling we also make the transformation $\left(\frac{r}{c}\right)^{1/2} z \rightarrow z$. The boundary conditions become

$$\hat{\mathbf{z}} \cdot \nabla \psi = 0, \quad \hat{\mathbf{z}} \cdot \nabla \mu_\psi = 0, \quad \text{for } z = 0,$$

$$\hat{\mathbf{n}} \cdot \nabla \psi = 0, \quad \hat{\mathbf{n}} \cdot \nabla \mu_\psi = 0, \quad \text{for } z = h.$$

The equations of motion in terms of the dimensionless parameters are

$$\frac{\partial \psi}{\partial \tau} = \nabla^2 [-\psi + \psi^3 - \nabla^2 \psi] + \sqrt{\epsilon_\psi} \eta_\psi, \quad (3.22)$$

$$\begin{aligned} \frac{\partial \psi_s}{\partial \tau} &= \frac{\Gamma_\phi^S}{\Gamma_\phi} \nabla_s^2 [-\psi_s + \psi_s^3 - (\nabla^2 \psi)_s] \\ &\quad + V(\psi_0 - \psi_s) + \sqrt{\epsilon_{\psi_s}} \eta_{\psi_s} \end{aligned} \quad (3.23)$$

and

$$\frac{\partial h}{\partial \tau} = \alpha \nabla^2 h + \beta \sqrt{g} \nabla_s^2 \left[-\frac{\psi_s^2}{2} + \frac{\psi_s^4}{4} + \frac{(\nabla \psi)_s^2}{2} \right] + \sqrt{\epsilon_h} \eta_h, \quad (3.24)$$

where we have defined

$$\alpha = \frac{\kappa}{\Gamma_\phi r}, \quad \beta = \frac{\Gamma_h r}{\Gamma_\phi u} \left(\frac{r}{c}\right)^{1/2}, \quad V = \left(\frac{c}{\Gamma_\phi r^2}\right) v/a,$$

$$\epsilon_\psi = \frac{k_B T u}{r^2} \left(\frac{r}{c}\right)^{d/2}, \quad \epsilon_h = \frac{D}{\Gamma_\phi r} \left(\frac{r}{c}\right)^{(d-1)/2}, \quad \epsilon_{\psi_s} = \frac{A u}{r^2} \left(\frac{r}{c}\right)^{d/2}. \quad (3.25)$$

The rescaled noises have the correlations in the new system $\langle \eta_h(\mathbf{x}, t) \eta_h(\mathbf{x}', t) \rangle = 2\delta(\mathbf{x} - \mathbf{x}')\delta(\tau - \tau')$, $\langle \eta_\psi(\mathbf{x}, z, t) \eta_\psi(\mathbf{x}', z, t) \rangle = -2\nabla^2 \delta(\mathbf{x} - \mathbf{x}')\delta(z - z')\delta(\tau - \tau')$ and $\langle \eta_{\psi_s}(\mathbf{x}, t) \eta_{\psi_s}(\mathbf{x}', t) \rangle = 2\delta(\mathbf{x} - \mathbf{x}')\delta(\tau - \tau')$.

3.4 Analytical results

3.4.1 Linear stability analysis

At early times of the deposition, the system is homogeneously mixed and we can

expand ψ_s as $\psi_s = \psi_0 + \delta\psi_s$, where ψ_0 is the average value of ψ_s in the beam. The dispersion relation for $\delta\psi_s$ is then $\Omega(q) = \frac{\Gamma_\phi^S}{\Gamma_\phi} q^2 (1 - 3\psi_0^2 - q^2) - V$, which is positive in the band of wavevectors $q_-^2 < q^2 < q_+^2$ where $2q_\pm^2 = (1 - 3\psi_0^2) \pm \sqrt{(1 - 3\psi_0^2)^2 - 4V \frac{\Gamma_\phi}{\Gamma_\phi^S}}$, if

$$V < V_c = \frac{1}{4} \left(\frac{\Gamma_\phi^S}{\Gamma_\phi} \right) (1 - 3\psi_0^2)^2. \quad (3.26)$$

Hence, for values of V below V_c , there is an instability that causes fluctuations in ψ_s to be amplified. The expression for the critical deposition rate, V_c , shows that the morphology of the thin film is controlled by three parameters: the deposition rate V , the concentration ψ_0 and the temperature (in Γ_ϕ^S). These results are in agreement with our Monte Carlo simulations, where $\psi_0 = 0$. The maximally unstable wavenumber $q_m^2 = (1 - 3\psi_0^2)/2$ is where the dispersion relation reaches its maximum, and $\Omega(q_m) = V_c - V$. Figure 3.1 shows the q dependence of the dispersion relation when $\psi_0 = 0$.

Figure 3.1: The dispersion relation $\Omega(q)$ in the case of equal volume fractions of the two components. The curves from top to bottom correspond to $\frac{\Gamma_\phi^S}{\Gamma_\phi} V = 0.01, 0.2$ and 0.3 .

The stability of the surface to fluctuations around its mean position can be considered by keeping the lowest order terms in h and $\delta\psi_s$ in Eq. (3.24). With the Fourier

expansion $h(\mathbf{x}) = \sum_{\mathbf{k}} h_{\mathbf{k}}(\tau) e^{i\mathbf{k} \cdot \mathbf{x}}$ we get

$$h_{\mathbf{q}}(\tau) = h_{\mathbf{q}}(0) e^{-\alpha q^2 \tau} + \beta \sum_{\mathbf{k}} f(k, q) \delta \psi_s^{\mathbf{k}}(0) \delta \psi_s^{\mathbf{q}-\mathbf{k}}(0) (e^{(\Omega(\mathbf{k}) + \Omega(\mathbf{q}-\mathbf{k}))\tau} - 1), \quad (3.27)$$

with $f(k, q)$ a polynomial function in k and q . To find the maximally unstable wavenumber for h , we first maximize $\Omega(k) + \Omega(q - k)$ with respect to k keeping q fixed, giving us $k_m^h(q) = q/2$. With this value for $k_m^h(q)$, the effective dispersion relation that amplifies the order parameter fluctuations in $h_{\mathbf{q}}$ is $2\Omega(q/2)$, with a maximally unstable mode at $q = 2q_m$. Hence the surface is most unstable at half the order parameter wavenumber, and as we shall see below, this produces grooves at the surface domain boundaries.

The effects of the non-Euclidian nature of the surface on the dispersion relation $\Omega(q)$ can be naively considered by assuming that $|\nabla h| = \text{constant} \gg 1$, leading to a critical growth rate that is decreased by a factor of $(\nabla h)^2$, and implying that the surface diffusion is slower in regions where $|\nabla h|$ is significant. We stress that such an effect is geometrical in nature, representing the extra length on the surface that diffusing atoms have to cover in order to create domains of a given projected size on the $\hat{\mathbf{z}}$ plane.

Eq. (3.24) can be considered in the case when the beam fluctuations and the nonlinearities are negligible, and we can look for steady state solutions, i.e. $\partial_\tau h = 0$. This gives

$$h = \frac{\beta}{\alpha} \left[\frac{\psi_s^2}{2} - \frac{\psi_s^4}{4} - \frac{(\nabla \psi_s)^2}{2} \right] + C \quad (3.28)$$

where C is a constant that ensures that the average value of h , $\bar{h} = 0$. In the steady-state, the surface order parameter has to satisfy (V has been rescaled as compared to Eq. (3.23) by a factor of $\frac{\Gamma_\phi^S}{\Gamma_\phi}$, and we take $\psi_0 = 0$)

$$0 = -\partial_x^2(\psi_s - \psi_s^3 + \partial_x^2 \psi_s) - V \psi_s, \quad (3.29)$$

which is equivalent to the steady-state of a dynamical Langevin equation for block copolymers [52]. In particular, for $\psi_0 = 0$, the dispersion relation is always positive for $V < 1/4$, and formation of domains occurs. We show below that two regimes can be identified: (i) weak segregation regime, where the system has lamellae with wavelength $\lambda^{-4} = V + \mathcal{O}(\epsilon^4)$ with $\epsilon^2 = 1/4 - V$ (ii) strong segregation regime, where

$\lambda \sim V^{-1/3} + \mathcal{O}(1)$. Note also that $\epsilon^2 = \Omega(q_m)$.

In their paper [51], Atzmon *et al.* correctly identified the instability and the critical growth rate. However, using an analogy with eutectic solidification from the liquid phase, they predicted that the wavelength of the modulation decreases algebraically with the deposition rate with an exponent $2/5$. As they pointed out, the flaw in their argument is that in the case of MBE, the system is not free to select the growth velocity, a direct consequence of the absence of thermodynamic equilibrium between the film and the phase above it. Dimensional analysis was also used to predict another exponent of $1/2$. The treatment below rigourously calculates the relationship between the wavelength of the modulation and the deposition rate, which can be extended to any order of accuracy in our expansion parameters.

We start by showing how the steady-state equation (3.29) can be obtained from the relaxational dynamics of a free energy-like function. We write

$$0 = \partial_x^2 \left[-\psi_s + \psi_s^3 - \partial_x^2 \psi_s - \frac{1}{\partial_x^2} V \psi_s \right] \quad (3.30)$$

where the operator $1/\partial_x^2$ is the inverse of the one-dimensional Laplacian ∂_x^2 . The function $C(x) \equiv -\psi_s + \psi_s^3 - \partial_x^2 \psi_s - \frac{1}{\partial_x^2} V \psi_s$ is the solution of the Laplace equation (3.30), and can be written as $\frac{\delta \mathcal{L}\{\psi_s\}}{\delta \psi_s(x)}$ with $\mathcal{L}\{\psi_s\} = \mathcal{L}_{sr}\{\psi_s\} + \mathcal{L}_{lr}\{\psi_s\}$. Here, $\mathcal{L}_{sr}\{\psi_s\}$ is a short-range interaction free energy functional, while $\mathcal{L}_{lr}\{\psi_s\}$ is a long-range contribution. We have

$$\mathcal{L}_{sr}\{\psi_s\} = \int dx \left[-\frac{\psi_s^2}{2} + \frac{\psi_s^4}{4} + \frac{(\partial_x \psi_s)^2}{2} \right] \quad (3.31)$$

and

$$\frac{\delta \mathcal{L}_{lr}\{\psi_s\}}{\delta \psi_s(x)} = -V \frac{1}{\partial_x^2} \psi_s(x). \quad (3.32)$$

To obtain $\mathcal{L}_{lr}\{\psi_s\}$, we proceed as follows:

$$\frac{\delta \mathcal{L}_{lr}\{\psi_s\}}{\delta \psi_s(x)} = -V \int dx' \frac{1}{\partial_{x'}^2} \psi_s(x') \delta(x - x'), \quad (3.33)$$

and after two integrations by parts, we get

$$\frac{\delta \mathcal{L}_{lr}\{\psi_s\}}{\delta \psi_s(x)} = -V \int dx' \psi_s(x') \frac{1}{\partial_{x'}^2} \delta(x - x'). \quad (3.34)$$

Now define $G(x - x') = \partial_{x'}^{-2} \delta(x - x')$ and integrate over ψ_s to obtain

$$\mathcal{L}_{tr} \{\psi_s\} = -\frac{V}{2} \int \int dx dx' \psi_s(x) G(x - x') \psi_s(x'). \quad (3.35)$$

3.4.2 weak segregation regime

Near the onset of instability, the amplitude of the order parameter is small, and we expect that the first few modes in a Fourier expansion will give reliable results. In this region, we expand in terms of a small parameter ϵ defined by $\epsilon^2 = V_c - V$ where V_c is the value of V at the critical point and equals $1/4$. For $\psi(x) = \psi(-x)$, we write

$$\psi(x) = \sum_{n=1}^{\infty} \epsilon^n A_n(k) \cos(nkx) \quad (3.36)$$

with $k = k_0 + \epsilon k_1 + \mathcal{O}(\epsilon^2)$ and solve Eq. (3.29) order by order in ϵ . The constant V must also be expanded: $V = V_c - \epsilon^2$. To first order we find $k_0 = 1/\sqrt{2}$, while the second order equation gives $A_2 = 0$. The third order equation provides solutions for A_1 and A_3 :

$$A_1^2 = \frac{8}{3}(1 - 2k_1^2); \quad A_3 = \frac{9}{128} A_1^3, \quad (3.37)$$

while the next order correction vanishes so that the order parameter is accurate to $\mathcal{O}(\epsilon^5)$.

To find the wavenumber in the steady-state we minimize $\mathcal{L}\{\psi_s\}$, since Eq. (3.29) can be obtained in full from the dynamics

$$\partial_\tau \psi = -\nabla^2 \frac{\delta \mathcal{L}\{\psi\}}{\delta \psi}. \quad (3.38)$$

In a one-dimensional formulation, we can write the free energy density as [53]

$$\begin{aligned} \frac{\mathcal{L}}{\lambda} = & \frac{4}{\lambda} \int_0^{\lambda/4} \left[-\frac{\psi(x)^2}{2} + \frac{\psi(x)^4}{4} + \frac{1}{2} |\partial_x \psi(x)|^2 \right] dx \\ & - \frac{V}{2\lambda} \int_0^{\lambda/2} \int_0^{\lambda/2} \psi(x) |x - x'| \psi(x') dx dx', \end{aligned} \quad (3.39)$$

and substituting the expression for the order parameter, we find

$$\frac{\mathcal{L}}{\lambda} = \frac{\epsilon^2 A_1^2}{4} (k^2 - 1) + \frac{\epsilon^2 V A_1^2}{4k^2} + \frac{3\epsilon^4 A_1^4}{32} + \mathcal{O}(\epsilon^6). \quad (3.40)$$

Minimizing this expression with respect to k we find that the steady-state wavelength

is

$$\lambda_{ss} = \frac{2\pi}{k_{ss}} = V^{-1/4} + \mathcal{O}(\epsilon^4). \quad (3.41)$$

With the first harmonic for the order parameter, h is given by

$$h = \frac{\beta}{\alpha} \left[\frac{A_q^2 \cos^2(qx)}{2} - \frac{A_q^4 \cos^4(qx)}{4} - \frac{A_q^2 q^2}{2} \sin^2(qx) \right] + \frac{\beta A_q^2}{32\alpha} (8q^2 - 8 - 3A_q^2). \quad (3.42)$$

Figure 3.2 shows the surface morphology according to Eq. (3.42) with $q = 1.2$ (this corresponds to a lamellae thickness of about 2.5). Notice that at the location of the order parameter interfaces, the interface has grooves of size proportional to $(\beta/\alpha) \epsilon^2$. The physical principle behind the formation of these dips is simply the decrease of interfacial energy when atoms move from the point of contact between the two phases to the top of the lamellae. Expression (3.42) can be rewritten as

$$h = \frac{\beta}{\alpha} \left[\frac{A_q^2}{8} (2 - A_q^2 + 2q^2) \cos(2qx) - \frac{A_q^4}{32} \cos(4qx) \right], \quad (3.43)$$

and therefore, the Fourier coefficients in the expansion $h = \sum_k \hat{h}_k \cos(kx)$ are

$$\hat{h}_k = \frac{\beta}{\alpha} \left(\frac{A_q^2 (2 - A_q^2 + 2q^2)}{8} \right) \delta_{k,2q} - \frac{\beta}{\alpha} \left(\frac{A_q^4}{32} \right) \delta_{k,4q}, \quad (3.44)$$

implying that the surface structure factor is

$$S_s(k) = \langle \hat{h}_k \hat{h}_{-k} \rangle = \left\langle \frac{\beta^2}{\alpha^2} \left(\frac{A_q^2 (2 - A_q^2 + 2q^2)}{8} \right)^2 \delta_{k,2q} + \frac{\beta^2}{\alpha^2} \left(\frac{A_q^4}{32} \right)^2 \delta_{k,4q} \right\rangle. \quad (3.45)$$

This expression for the structure factor shows peaks at $k = 2q$ and at $k = 4q$. At $k = 2q$, the height of the peak $\sim (\frac{\beta}{\alpha} \epsilon^2)$. The broadening of the peaks will come from the average over the noise.

3.4.3 strong segregation regime

When the deposition rate is small, the interfaces between the order parameter domains are sharp, the lamellar thickness is large, and the system can be divided in two regions [52]. The inner region is of thickness unity around the interface, and the order parameter varies rapidly in this region. The outer region is characterized by nearly constant values of ψ_s , and the direction normal to the interface is rescaled as

$X = \epsilon x$, with $\epsilon \sim \lambda^{-1}$. We have

$$0 = \epsilon^2 \partial_X^2 [-\psi_s + \psi_s^3 - \epsilon^2 \partial_X^2 \psi_s] - V \psi_s, \quad (3.46)$$

and since far from the interface $\psi_s = \pm 1$ and $\partial_x^2 \psi_s = 0$, V must be of $\mathcal{O}(\epsilon^3)$. With the rescaling $B = \epsilon^{-3} V$ the equation in the outer region becomes

$$0 = \partial_X^2 [-\psi_s + \psi_s^3 - \epsilon^2 \partial_X^2 \psi_s] - \epsilon B \psi_s, \quad (3.47)$$

which can be solved to first order in ϵ to give

$$\psi_s^{outer}(X) = \pm \left[1 + \frac{\epsilon}{4} B X \left(X \mp \frac{1}{2} \right) \right] + \mathcal{O}(\epsilon^2). \quad (3.48)$$

In the interfacial region, the equation is

$$0 = \partial_x^2 [-\psi_s + \psi_s^3 - \partial_x^2 \psi_s] - \epsilon^3 B \psi_s, \quad (3.49)$$

yielding a solution

$$\psi_s^{inner}(x) = \tanh(x/\sqrt{2}) + \mathcal{O}(\epsilon^2). \quad (3.50)$$

The steady-state wavelength is calculated by minimizing the free energy density $\mathcal{L} \{ \psi_s^{inner}, \psi_s^{outer} \} / \lambda$ with respect to λ . To $\mathcal{O}(\epsilon^2)$, the free energy density is

$$\frac{\mathcal{L}}{\lambda} = \frac{4\sqrt{2}}{3\lambda} + \frac{\lambda^2 V}{96}, \quad (3.51)$$

giving to leading order

$$\lambda_{ss} = \left(\frac{V}{64\sqrt{2}} \right)^{-1/3}. \quad (3.52)$$

With the relations for the order parameter in the inner and outer regions, we can calculate the profile of the free surface using Eq. (3.28). We find that

$$h^{outer}(X) = constant + \mathcal{O}(\epsilon^2) \quad (3.53)$$

$$\begin{aligned} h^{inner}(x) &= \frac{\beta}{\alpha} \left[\tanh^2(x/\sqrt{2}) - \frac{1}{2} \tanh^4(x/\sqrt{2}) \right] \\ &\quad + C + \mathcal{O}(\epsilon^2), \end{aligned} \quad (3.54)$$

where C ensures that the average value of h is zero. The profile for h consists of the inner solution matched to the outer solution, and this is repeated every period of the modulation. This is shown in Fig. 3.2 in the case when the lamellae thickness is large

(>50). Note that far from onset, $|\nabla h|$ is of $\mathcal{O}(\frac{\beta}{\alpha})$, and this quantity controls the importance of the nonlinearities in ∇h that we have neglected.

Figure 3.2: Steady-state deterministic height profiles far from onset (top) and near onset (bottom). The top curve corresponds to a concentration wavelength $\lambda > 50$, and the bottom curve is for $\lambda = 5$. The vertical scale in the figure is arbitrary.

3.5 Connection with experiments

In this section, we give order-of-magnitude estimates for the quantities we have calculated and compare with typical experiments. Let us start by considering the critical growth velocity: in dimensional form, we have (see Eqs (3.25) and (3.26))

$$v_c = \frac{1}{4} \frac{\Gamma_\phi^S r^2 a}{c} \left(1 - 3 \frac{u}{r} \phi_0^2\right)^2. \quad (3.55)$$

The constants r and u have units of energy/volume while c has units of $\text{length}^2 \times \text{energy/volume}$. The ratio c/r is of order ξ_0^2 , with ξ_0 a microscopic length describing the thickness of interfaces, while far below T_c , $\frac{u}{r}$ is of order 1; this gives a critical growth velocity $v_c \sim \Gamma_\phi^S r a / \xi_0^2$. This can be related to the surface diffusion constant using the relation $\Gamma_\phi^S = \frac{V_0 D}{k_B T}$, where V_0 is the atomic volume. For example [54], the diffusion coefficient for Si on Si has an Arrhenius form $D = D_0 e^{\frac{-E_m}{k_B T}}$ with D_0 in the range $10^{-9} \text{ m}^2/\text{s}$ and $E_m = 0.6 \text{ eV}$. Taking this as a representative value

and assuming a critical temperature of 1000K, the critical growth velocity is about $1 \mu\text{m/s}$ at 700K, which is 3-4 orders of magnitude larger than typical MBE growth rates.

The selected wavelength depends on the distance from the onset of instability. Near onset, the dimensional form is (Eqs (3.25) and (3.41))

$$\lambda = \left(\frac{\Gamma_{\phi}^S c}{v/a} \right)^{1/4}, \quad (3.56)$$

which is of order ξ_0 , independently of our estimate for v_c . This makes physical sense, because near onset, the pattern amplitude and wavelength are very small, the latter corresponding to a few angstroms in a real system.

Far from onset, we have

$$\lambda = \left(\frac{64\sqrt{2}\Gamma_{\phi}^S \sqrt{rc}}{v/a} \right)^{1/3} \quad (3.57)$$

which is of order $10^{-11}v^{-1/3}$. Typical experiments with $v \approx 1 \text{ \AA/s}$ would then yield λ in the range of 400 $\text{\AA}$.

Order-of-magnitude estimates can also be obtained for the grooves in the surface associated with the phase separation. Far from onset, the grooves have a scaled size $\Delta h = \beta/\alpha$, giving in dimensional form

$$\Delta h = \frac{\Gamma_h r^2}{\kappa u}. \quad (3.58)$$

Well below the critical temperature, the energy scales in r , u and Γ_h are the same and cancel. We can say that $\Gamma_h \sim \Gamma_{\phi}^S a$, while $\kappa \sim (v/a)l^2$ implying that $\Delta h \sim (\Gamma_{\phi}^S r^2) a^2 / v l^2 u$ where l represents the typical distance between steps on the surface, which depends on the surface roughness and has to be evaluated in the groove. For $l \approx 10 \text{ \AA}$, we find that Δh is a few lattice constants.

3.6 Numerical results

The equations of motion (3.22), (3.23) and (3.24) are discretized both in space and time using an Euler method. Growth occurs in the positive z direction and we consider only one lateral dimension x . The substrate is located at $z=0$, while the

order parameter is defined at the points of a lattice (with spacing Δx), from $z=\Delta x/2$ to $z_{max}(x, t)=\text{int}(h(x, t)/\Delta x)$. The boundary conditions are satisfied by taking

$$\psi_s(x, -\Delta x/2, t) = \psi_s(x, \Delta x/2, t), \quad (3.59)$$

$$\partial_x h(x, t) \partial_x \psi_s(x, t) = \partial_z \psi_s(x, t), \quad (3.60)$$

$$\mu(x, -\Delta x/2, t) = \mu(x, \Delta x/2, t), \quad (3.61)$$

and

$$\partial_x h(x, t) \partial_x \mu_s(x, t) = \partial_z \mu_s(x, t). \quad (3.62)$$

The time derivative is

$$\partial_t f(x, z, t) = \frac{1}{\Delta t} [f(x, z, t + \Delta t) - f(x, z, t)], \quad (3.63)$$

and the spatial derivatives are discretized to

$$\partial_x f(x, z, t) = \frac{1}{2\Delta x} [f(x + \Delta x, z, t) - f(x - \Delta x, z, t)], \quad (3.64)$$

while the Laplacian in the x, z coordinate system is

$$\begin{aligned} \nabla^2 f(x, z, t) = & \frac{1}{(\Delta x)^2} [f(x + \Delta x, z, t) + f(x - \Delta x, z, t) \\ & + f(x, z + \Delta x, t) + f(x, z - \Delta x, t) \\ & - 4f(x, z, t)]. \end{aligned} \quad (3.65)$$

In order to implement the boundary conditions at the substrate, we generate an order parameter and chemical potential at $z = -\Delta x/2$. This is then used to integrate the equations for the order parameter at $z = \Delta x/2$. At the free surface, we use a backwards version of the spatial derivative, which gives us $\psi(x, z_{max})$ and $\mu(x, z_{max})$ as a function of $\psi_s(x)$ and $\mu_s(x)$ according to equations (3.60) and (3.62). The nonconserved noise is generated with a Gaussian random number generator, while the conserved noise is obtained from

$$\begin{aligned} \eta_{\psi_s}(x, z, t) = & r1(x + \Delta x/2, z, t) - r1(x - \Delta x/2, z, t) \\ & + r2(x, z + \Delta x/2, t) - r2(x, z - \Delta x/2, t), \end{aligned} \quad (3.66)$$

where the noise current $j=(r1, r2)$ can be thought of as lying on the bonds between

the order parameter sites. Because $\hat{\mathbf{n}} \cdot \mathbf{j} = 0$ at the boundaries, $r_2(x, \Delta x/2, t) = 0$, and $\partial_x h(x, t)r_1(x, z_{\max}(x) + \Delta x/2, t) = r_2(x, z_{\max}(x), t)$. Figure 3.3 illustrates our scheme.

Figure 3.3: The figure represents the discretized system used for the numerical integration.

Figure 3.4 shows configurations far and near the onset of instability in the case where $\frac{\Gamma_\phi}{\Gamma_S} = 0.01$, $\alpha = 1$, $\beta = 0.1$, $\epsilon_\psi = 0.001$, $\epsilon_{\psi_s} = 0.01$ and $\epsilon_h = 0.01$. The constant V was set as $0.25v$, where v is the velocity at which the free surface is growing. The time and space mesh were chosen to be $\Delta x = 1.1$ and $\Delta t = 0.2$, such that artificial bifurcations in the set of equations were avoided (the systems were of lateral size $L = 220$). Soon after the deposition starts, the linear dynamics hold, and the system is characterized by the amplification of the fluctuations by the instability, leading to segregation into two phases. This early time regime is governed by the maximally unstable mode, $k_m = 1/\sqrt{2}$, which corresponds to the location of the maximum in the dispersion relation $\Omega(k)$. The end of the linear regime is characterized by the saturation of the order parameter to its steady-state value due to the nonlinearities, accompanied by the formation of well defined domain boundaries. The time scale to reach the end of the linear regime is $\tau_m \sim \Omega(k_m)^{-1}$. Once in the nonlinear regime, the dynamical evolution proceeds to decrease the selected wavenumber from k_m to k_{ss} . This occurs through the collision and merging of lamellae. In the case of block

Figure 3.4: Configurations as well as h and ψ_s in the steady-state obtained from numerical integration. The left panels are simulation results in the far from onset regime and the right panels are results from the near onset regime. The top portion of lateral size 100 and vertical size 50 of the full system is shown. The average value of h is 400.

copolymers [52], the time dependence of the wavenumber follows the relation

$$k(t, V) = k_{ss}(V) g(tV), \quad (3.67)$$

where the scaling function $g(x) \sim x^{-1/3}$ for small x relative to the end of the linear regime, and $g(x) \sim \text{constant}$ for large x . This relation is expected to hold in our case, not too close to onset.

Of particular interest in Fig. 3.4 is the one-to-one correspondence between surface domain boundaries (i.e. $\psi_s = 0$) and grooves in the surface. Fluctuations of h around the periodic profile have two origins: noise in the beam strength and in the beam concentration. This can be demonstrated by computing the surface structure factor

$S_s(k)$, which is shown in the inset to Fig. 3.5, where two peaks in $S_s(k)$ can be identified. Near $k = 0$, there is a peak that decays as k^{-2} , signalling the

Figure 3.5: The steady-state wavelength of the concentration modulation as a function of the deposition rate. The solid (dashed) line represents the expansions near (far from) onset. The points correspond to numerical integration results. In the inset, the surface structure factor in the near onset regime is shown.

presence of the Villain contribution in the growth equation. The width of this peak is controlled by the strength of the beam fluctuations (ε_h) and the Schoewbel barriers (α). The second peak at non-zero wavevector represents the surface modulation. We find that the location of the peak is at twice the wavenumber corresponding to the peak in the bulk order parameter structure factor. The broadening of this peak is due to the strength of the concentration fluctuations in the incoming beam (ε_{ψ_s}). The early time evolution of the surface shape is characterized by the (deterministic) linear dynamics with the instability coming from the same dispersion relation as for the order parameter. As time proceeds, the surface shape follows the same dynamical evolution as the order parameter at half the wavenumber: formation of the grooves, saturation of the groove depth and crossover to $2k_{ss}$. There are also other time scales that correspond to the time evolution of the surface roughness (the $k = 0$ peak in the surface structure factor). The solution of Eq. (3.24) for $\beta = 0$ and including the

fluctuations gives for the surface structure factor

$$S_s(k, t) = \frac{\epsilon_h}{\alpha k^2} \left(1 - e^{-\alpha k^2 \tau} \right). \quad (3.68)$$

At early times, $S_s(k, t) = \epsilon_h \tau$, which represents an uncorrelated process, while for all times, the correlation length is $\xi(\tau) = \sqrt{\alpha \tau}$ until it reaches the system size. Three dynamical regimes can be identified from the behavior of the surface width, W : (i) early times corresponding to $W \sim \tau^{1/2}$, (ii) intermediate times where $W \sim \tau^{1/4}$ and (iii) saturated regime with $W \sim L^{1/2}$.

We calculated the bulk modulation wavelength from the first moment k_1 of the structure factor $S_\psi(k) = \langle \psi(k) \psi(-k) \rangle$,

$$k_1 = \frac{\int k S_\psi(k) dk}{\int S_\psi(k) dk}. \quad (3.69)$$

In order to judge if the steady-state is reached, two quantities have to be monitored: the width of the surface determines if the surface is saturated, and the selected length scale for the bulk morphology must also be stationary. The time scale for the selected wavenumber to reach its steady-state value depends on the deposition rate as $t^* \approx 100V$ [52], which means that the number of layers deposited has to be equal to $h^* = 400$, independently of the growth velocity. Results were averaged over 4 independent runs near onset, and one run was performed far from onset. As Fig. 3.5 illustrates, the numerical results for k_1 are in excellent agreement with the near and far from onset expansions.

3.7 Conclusion

In this chapter, we introduced an order parameter describing the extent of the phase separation, and proposed a free energy functional that includes the fluctuations of the free surface. The time evolution of our model was dictated by two conservation laws, one for material and one for the order parameter. We showed that the constant bombardment of the surface by the beam tends to bury the phase-separated domains in the bulk, where they are frozen. This permits control of the morphology of the bulk, since above a critical deposition rate, the film is homogeneously mixed, while below this threshold, a reproducible compositionally modulated pattern emerges. We

calculated the order parameter profile near and far from the critical growth rate, and obtained expressions for the thickness of the lamellae in excellent agreement with our Monte Carlo results. In this theoretical framework, the modulation of the surface emerges, with grooves at the interface between domains.

To accurately represent real systems, the effects of strain between the components and between the substrate and the growing film would have to be included. Such effects will be discussed in the following chapters.

Chapter 4

ELASTIC EFFECTS AND PHASE SEGREGATION IN LATTICE MATCHED ALLOY FILMS

4.1 Introduction

In Chapters 2 and 3, we considered phase separation during MBE in the absence of elastic effects, and found that a lamellar pattern emerges from phase separation occurring at the surface. It was shown that the concentration modulation arises from a competition between the phase separation and the constant deposition of material on the surface. Our work, however, did not consider the important contributions originating from elastic fields. Such effects have been shown [55] to alter drastically the morphology of domains in *bulk* phase-separating systems, leading to very slow growth of the domain size with time. In particular, even for equal volume fractions of the two components, the soft phase was found to wrap around the hard phase, thereby creating hard droplets in a soft matrix.

A similar approach to the one we propose here was introduced by Ipatova *et al.* [56] and considered from an *equilibrium* perspective. As we have shown in Chapter 3, the concentration modulations in the bulk of the thin film are *not* equilibrium morphologies, and the inherent dynamical or non-equilibrium nature of the problem is crucial in explaining the morphologies which are seen experimentally. The present chapter considers the following idealized experimental situation: 1) two atomic species are de-

posited simultaneously on a substrate held at a temperature within the coexistence region of the binary alloy phase diagram; 2) the diffusion proceeds along the surface only; 3) the volume fractions of the two components are equal; 4) surface fluctuations and surface instabilities are neglected.

This chapter is divided as follows: In Sec.4.2, we introduce our Ginzburg-Landau free-energy functional and dynamical equations that describe the time evolution of concentration fluctuations. In Sec. 4.3, we present results of numerical integrations of the dynamical equations while Sec. 4.4 gives a conclusion to our work. Results presented in this chapter have also been published elsewhere [57].

4.2 Model

In this section, we start by deriving the free-energy functional for a bulk binary mixture, taking into account the elastic effects. We then obtain dynamical equations that describe the time evolution of the composition in thin solid films grown by MBE.

4.2.1 Free-energy functional

Our derivation of the free-energy functional follows the procedure of Onuki [58] and is also presented for a more complex situation in Ref. [59]. We introduce a continuous variable $\phi(\mathbf{r})$, with $\mathbf{r}$ a two-dimensional vector in the (flat) plane of the growing surface, that represents the extent of the phase segregation. The order parameter $\phi(\mathbf{r})$ is proportional to the concentration difference between the two species at local position $\mathbf{r}$. A second variable $\mathbf{u}(\mathbf{r})$, the displacement vector, represents the displacement from the local equilibrium position due to elastic deformations. For single-component cubic crystals in d dimensions [60], the elastic free-energy functional can be written as

$$\mathcal{F}_{el}[\mathbf{u}] = \int d\mathbf{r} \left[\frac{1}{2}K (\nabla \cdot \mathbf{u})^2 + M \sum_{i,j} \left(\mu_{ij} - \frac{\delta_{ij}}{d} \nabla \cdot \mathbf{u} \right)^2 + \frac{1}{2}B \sum_i \mu_{ii}^2 + \alpha \phi \nabla \cdot \mathbf{u} \right], \quad (4.1)$$

with the last term added to describe the change of local lattice constant, a , with composition. The strain tensor is $\mu_{ij} = \frac{1}{2}(\nabla_j u_i + \nabla_i u_j)$. The constants K , M and B are related to the elastic moduli in the Voigt notation as $M = C_{44}$, $K = C_{12} + \frac{2}{d}C_{44}$

and $B = C_{11} - C_{12} - 2C_{44}$. The degree of anisotropy of the crystal is represented by the parameter $\xi = B/M$, which is considered a small quantity in the present work.

In the case of binary systems, the free-energy functional has to be augmented to describe the miscible and immiscible regions of the phase diagram. For this purpose, the essential characteristics of the system can be obtained from the Ginzburg-Landau free-energy functional

$$\mathcal{F}_{GL}[\phi] = \int d\mathbf{r} \left[-\frac{r'}{2}\phi^2 + \frac{u}{4}\phi^4 + \frac{c}{2}(\nabla\phi)^2 \right], \quad (4.2)$$

where r' is proportional to the temperature difference $T_c - T$, with T_c the critical point *without* elastic fields. The total free-energy functional $\mathcal{F}[\phi, \mathbf{u}]$ is just the sum of $\mathcal{F}_{GL}$ and $\mathcal{F}_{el}$. To make a connection with real systems, we note that in the homogeneous phase ($\phi = \text{constant}$) of a d -dimensional system, the stress is $\sigma_{ij} = \alpha\phi\delta_{ij}$, implying that the constant α can be obtained from $\ln a = -\frac{\alpha\phi}{dK}$. Thus, slow local variations in ϕ and K can lead to slow local variations in the lattice constant a .

To take into account the change in the elastic moduli with composition, we expand the moduli to first order in the concentration variable ϕ :

$$\begin{aligned} M &= M_0 + M_1\phi \\ K &= K_0 + K_1\phi \\ B &= B_1, \end{aligned} \quad (4.3)$$

and assume that the coefficients M_1, K_1 and B_1 are small, implying $\xi = B_1/M_0$. Because the time scale to reach positional order is much smaller than the diffusion time, we make the assumption that mechanical equilibrium is instantaneously achieved, in order to adjust to a given spatial distribution of ϕ . This provides a way to obtain the displacement variable $\mathbf{u}$ as a function of ϕ , leading to effective long-ranged contributions to the free-energy functional. As shown in Appendix A, substitution of the resulting expression for $\mathbf{u}$ in $\mathcal{F}_{el}$ yields an effective free-energy functional that is a function of ϕ only:

$$\mathcal{F}_{el}[\phi] = \int d\mathbf{r} \left[-\frac{\alpha^2}{2C}\phi^2 + \frac{\alpha^2\xi M_0}{2C_0^2}\phi^2 + f_E + f_\xi \right], \quad (4.4)$$

with the free energy densities f_E and f_ξ given by

$$f_E = \frac{M_1 \alpha^2}{C_0^2} \phi \sum_{i,j} \left(\nabla_i \nabla_j W - \frac{\delta_{ij}}{d} \phi \right)^2 \quad (4.5)$$

and

$$f_\xi = -\frac{\alpha^2 \xi M_0}{2C_0^2} \sum_{i \neq j} (\nabla_i \nabla_j W)^2, \quad (4.6)$$

and the constant $C = K + 2M_0 - 2M_0/d$ (this definition for C absorbs the contribution coming from K_1). Also, W is related to ϕ through the solution of Eq. (A.8), and gives the nonlocal nature to the free-energy functional. We now discuss the different contributions to the free-energy functional. The contributions proportional to ϕ^2 in Eq. (4.4) simply renormalize the ϕ^2 coefficient in $\mathcal{F}_{GL}$, which changes the critical temperature by a constant factor (the critical point occurs when the coefficient of ϕ^2 is zero). Hence, we define r as $r = r' + \frac{\alpha^2}{2C} - \frac{\alpha^2 \xi M_0}{2C_0^2}$. The contribution f_E corresponds to a long-ranged interaction leading to shape deformations of precipitates in a matrix [55]. f_E is proportional to M_1 , which means that the difference in the shear moduli between the two components is essential to obtain this contribution. The cubic anisotropy term f_ξ leads to spinodal decomposition along the soft directions [01] and [10], creating elongated domains [61] in the absence of external stresses.

The free-energy functional may again be rescaled to dimensionless form as in chapter 3, using the transformations $\mathbf{x} = (r/c)^{1/2} \mathbf{r}$ and $\psi(\mathbf{x}, t) = (u/r)^{1/2} \phi(\mathbf{r}, t)$. With this, we obtain

$$\mathcal{F}[\psi] = \int d\mathbf{x} \left[-\frac{\psi^2}{2} + \frac{\psi^4}{4} + \frac{(\nabla \psi)^2}{2} + g_E \psi Q_E + g_\xi Q_\xi \right], \quad (4.7)$$

with $g_E = \frac{M_1 \alpha^2}{C_0^2 \sqrt{ru}}$, $g_\xi = -\frac{\alpha^2 M_0 \xi}{2C_0^2 u}$ and the functions Q_E and Q_ξ defined as

$$Q_E = \sum_{i,j} \left[\nabla_i \nabla_j W - \frac{\delta_{ij}}{d} \psi \right]^2 \quad (4.8)$$

and

$$Q_\xi = \sum_{i \neq j} (\nabla_i \nabla_j W)^2. \quad (4.9)$$

The rescaled function W satisfies $\nabla_{\mathbf{x}}^2 W = \psi$. Note that the elastic term destroys the symmetry between the two phases, implying that the equilibrium value of ψ is no

longer ± 1 .

4.2.2 Dynamical equations

The time evolution of the alloy thin film is initiated by the simultaneous deposition of the two components on a flat substrate. The interactions with the substrate are neglected, as well as fluctuations in the free surface. Because the surface diffusion coefficient is much larger than the bulk diffusion coefficient, we assume that all of the atomic motions occur at the free surface. Also, the coupling between the surface layer and the bulk is neglected. Hence, the system is modelled as a two-dimensional flat square, with periodic boundary conditions, representing the top view of a three-dimensional thin film. Because the bulk diffusion is not included, a vertical cross-section of the thin film can be obtained through the history of the surface layer.

The diffusion in the surface plane is governed by inhomogeneities in the chemical potential and by the requirement that the average concentration must be fixed, as discussed in chapter 3. The constant deposition of material on the surface tends to draw the value of $\phi(\mathbf{x})$ towards the average concentration in the incoming beam (we take this average to be zero in the following, which is equivalent to the deposition of a symmetric 50-50 mixture). The time evolution of ϕ is

$$\frac{\partial \phi}{\partial t} = \Gamma_\phi \nabla^2 \frac{\delta \mathcal{F}}{\delta \phi} - (v/a)\phi, \quad (4.10)$$

where Γ_ϕ is a kinetic coefficient and the growth velocity v is proportional to the deposition rate. With the time rescaling $\tau = (\Gamma_\phi r^2/c) t$, the time evolution of the dimensionless variable ψ is

$$\begin{aligned} \frac{\partial \psi}{\partial \tau} = & \nabla^2 (-\psi + \psi^3 - \nabla^2 \psi + g_E Q_E) + 2g_E \sum_{i,j} \nabla_i \nabla_j \psi \left[\nabla_i \nabla_j W - \frac{1}{2} \delta_{ij} \psi \right] \\ & + g_\xi \sum_{i \neq j} \nabla_i^2 \nabla_j^2 W - V\psi, \end{aligned} \quad (4.11)$$

with $V = (cv/a) / (\Gamma_\phi r^2)$. We will refer to the important parameter V as the deposition rate. In this equation, we have neglected fluctuations in the order parameter coming from thermal and beam noise, which we incorporate as initial conditions on ψ . In the absence of a deposition process ($V = 0$), various cases have been studied. For $g_E = g_\xi = 0$, a quench from an initial homogeneous state to a point in the coex-

istence region of the phase diagram leads to formation of domains that grow in time as $\tau^{1/3}$ [45]. When only the anisotropic contribution is present ($g_E = 0, g_\xi \neq 0$), the dispersion relation has a maximum value along the [01] or [10] directions, leading to needle-like domains [62] with the longer direction oriented in [01] or [10]. In the presence of the elastic interaction only ($g_E \neq 0, g_\xi = 0$) [55], the elastic energy slows the domain growth, with a saturation of the average domain size at late times. The system consists of ellipsoidal hard domains in a soft percolated matrix (the saturated hard domain size scales as $1/g_E$). Finally, the presence of both the elastic term and the anisotropy creates saturated hard cuboidal domains in the soft matrix [63]. In the case of alloy growth by MBE without elastic effects ($g_E = 0, g_\xi = 0$), the deposition rate V is a crucial parameter in determining the stability of the alloy to phase segregation. As we found in chapter 3, if the deposition rate $V < 1/4$, lamellar patterns appear with a V -dependent modulation wavelength; if $V > 1/4$, the constant burial of surface domains by the incoming beam suppresses the phase separation, and the thin film is homogeneously mixed [47]. In this chapter, we concentrate on the case where $V < 1/4$ and study the elastic and anisotropic effects on the time evolution and the steady-state of the system.

4.3 Results

The Langevin equation [Eq. (4.11)] was discretized in space and time using a finite-difference scheme, and integrated using the Euler method. The results reported here correspond to simulations on a 128x128 square grid with periodic boundary conditions. We believe that finite size effects were minimal since the selected wavelength of the modulation in the steady-state is much smaller than the system size. The mesh size and time step were chosen as $\Delta x = 1.25$ and $\Delta t = 0.1$. A discrete, isotropic form for the Laplacian was used [52], while the field W was obtained using Fourier transform methods. The initial state of the system consisted of a random distribution of ψ in the range $(-0.1, 0.1)$. Due to the length and size of the simulations, averages were taken over one to four initial conditions. For the deposition rate $V > 1/4$, the initial homogeneous state is stable. The onset of thermodynamic instability for $V < 1/4$ leads to phase segregation. Hence, in what follows, we take $V < 1/4$ and study the

effects of g_E and g_ξ . We start with results for $g_E = g_\xi = 0$, establishing basic results and a basis for comparison.

4.3.1 Isotropic growing film without elastic fields

This case corresponds to MBE growth at deposition rate V with no elastic or anisotropic effects. Figure 4.1 shows configurations for the field ψ at different times. On the

Figure 4.1: The left column shows the concentration field in the near onset regime when $g_E = 0$ and $V = 0.24$. The right column is for $g_E = 0$ and $V = 0.001$ (far from onset). Times from top to bottom are $\tau = 100, 1500$, and 10000 . Black: $\psi > 0$, White: $\psi < 0$. In this and other figures, systems are of size 128×128 .

left, the parameter $V = 0.24$, close to the onset of instability at $V = 1/4$, and the wavelength of the pattern is close to the maximally unstable wavelength, $\lambda = 2\sqrt{2}\pi$. This regime will be referred to as the near-onset regime. The right column is for $V = 0.001$ (far from onset regime). There, the wavelength of the modulation is much

larger than in the near-onset regime, and the value of the order parameter changes from +1 to -1. The differences between the two regimes is also shown in Fig. 4.2, where the circularly averaged structure factor

$$S_\psi(k) = \langle |\psi(k)|^2 \rangle, \quad (4.12)$$

and the profile of the order parameter along a horizontal cross-section are plotted. Initially, the order parameter grows exponentially in time, with segregation in two

Figure 4.2: The left (right) column shows the structure factor and the order parameter along a horizontal cut at $\tau = 10000$ for the near onset (far from onset) regime. The times for the structure factor correspond to those in Fig. 4.1.

phases. The initial maximally unstable wavenumber is $k \approx 1/\sqrt{2}$, which then decreases to attain its steady-state value. At the same time, stripes form and orient themselves locally. Once k is saturated, the ordering proceeds through the elimination of defects. In the near-onset regime, the wavelength of the modulation can be calculated [47] to be $\lambda \sim V^{-1/4}$, while far from onset, $\lambda \sim V^{-1/3}$. Furthermore, the appearance of the lamellar patterns can be explained by appropriately constructing

an effective free-energy functional such that $\frac{\partial \psi}{\partial \tau} = \nabla^2 \frac{\delta F_{eff}}{\delta \psi}$. The effective free-energy functional contribution due to V is repulsively long-ranged, which competes with the attractive short range interaction. Near onset, the amplitude of the modulations (proportional to the concentration difference in a real alloy) is small and scales as $\sqrt{1/4 - V}$; the single-mode approximation is excellent very close to onset. For small values of V , the order parameter is equal to ± 1 within the bulk of the domains, which are separated by thin interfacial regions; the number of modes needed to describe the profile increases as V decreases.

A vertical cross-section of the thin film can be considered if one makes a correspondence between the time scale for diffusion and the velocity at which the free surface is growing. Figure 4.3 shows a cross-section corresponding to a horizontal cut in Fig. 4.1 (the correspondence between the surface height and time has been chosen to show details). Note that the appearance of the cross-sectional configurations depends on the direction chosen, which is in agreement with Transmission Electron Microscopy experiments [9]. After deposition of a few monolayers (bottom configuration) clear vertical structures appear in the thin film. At late times, the wavelength of the modulation is saturated, and the top layers of the alloy film consist of vertical columns of alternating concentration. To better characterize the appearance of the cross-section, we calculated the average wavenumber as a function of time (or film thickness) from the first moment of the structure factor

$$k_1 = \frac{\int_0^\infty k S_\psi(k) dk}{\int_0^\infty S_\psi(k) dk}. \quad (4.13)$$

Figure 4.4 shows k_1 as a function of time for the near-onset and the far-from-onset regimes. Near-onset, k_1 saturates rapidly to a value ≈ 0.7 , while for small V , the wavenumber decreases over a wide time scale. In fact, Yeung and Desai [52] have shown that not too close to onset, the wavenumber satisfies the scaling form $k(t, V) = k_\infty(V)g(tV)$, with $k_\infty(V)$ the steady-state wavenumber. The function $g(x) \sim x^{-1/3}$ for small x , and $g(x) \sim \text{constant}$ for large x . The inset in Fig. 4.4 shows the rescaled function $g(tV)$. It also shows that the data in the figure correspond to the crossover regime of the function $g(x)$.

Figure 4.3: A vertical cross-section of the thin film taken along the x direction. The bottom configuration shows the bottom portion of the thin film (early times of the deposition corresponding to $0 < \tau < 100$), while the top configuration corresponds to the top portion of the thin film (late times of the deposition corresponding to $1400 < \tau < 1500$). The lateral size of the system is 128 and the vertical scale is chosen to show details.

4.3.2 Isotropic growing film with elastic fields

When $g_E \neq 0$, we expect that the competition between the long-range interaction and the saturation of the domain size due to the elastic effects will lead to new ordered structures. Figure 4.5 shows the time evolution of the concentration field near the onset of instability ($V = 0.24$) for $g_E = 0.05$ (left column) and $g_E = 0.5$ (right column). In these figures, the locations of the grid points were corrected for the displacement $\mathbf{u}$. For the smallest value of g_E , the system orders in a lamellar phase very similar to the case $g_E = 0$. Differences between Fig. 4.1 and Fig. 4.5 can be seen where crystalline defects are present. For $g_E = 0.5$, droplets of the hard phase form in a soft matrix and order themselves to create an hexagonal pattern (the distribution of droplet sizes is sharp). The appearance of the hexagonal phase here is special because for $g_E = 0$, the lamellar phase is always seen if the volume fraction

Figure 4.4: The wavenumber as a function of time in the near onset (open circles) and the far from onset regimes (solid circles), corresponding to Fig. 4.1. Note that the wavenumber is divided by the steady-state wavenumber k_∞ . The scaled function $g(tV)$ is shown in the inset.

of the two components is the same. Because of conservation of material, there is a relation between the value of the order parameter in the phases and the area occupied by the droplets. For the hexagonal and the lamellar order, the fraction of the area occupied by the hard droplets is $-\psi_s/\Delta\psi$, with ψ_s the order parameter in the soft phase and $\Delta\psi = \psi_h - \psi_s$. Further characterization of the film surface can be found in Fig. 4.6, where the structure factor and the order parameter are plotted. The order parameter profile shows clearly the difference in the saturation value of the concentration field in the hard and the soft phases. Peaks in the scattering intensities describe the crystalline ordering, with the position of the first peak at $k = \frac{2\pi}{\lambda}$ for the lamellar phase (λ is the wavelength of the order parameter modulation) and at $k = \frac{4\pi}{\sqrt{3}D}$ for the hexagonal phase (D is the distance between the centre of neighboring droplets).

To describe the elastic deformation of the system, we computed the function Q_E .

Figure 4.5: The left column shows the concentration field in the near-onset regime when $g_E = 0.05$ and $V = 0.24$. The right column is for $g_E = 0.5$ and $V = 0.24$. Times from top to bottom are $\tau = 100, 1500$ and 10000 .

The grey-scale contour plot of Fig. 4.7 corresponds to the last configuration for the lamellar phase in Fig. 4.5. Both the hard phase ($\psi > 0$) and the soft phase ($\psi < 0$) show elastic deformations, while the interfaces between the two phases are not deformed. In this regime $\Delta\psi$ is small and the elastic interactions do not alter drastically the final configurations. In fact, if we assume that the order parameter is given by $\psi(x) = \psi_0 \cos(kx)$, then $Q_E = \frac{1}{2}\psi_0^2 \cos^2(kx)$, which is in excellent agreement with Fig. 4.7. For larger values of g_E , the function Q_E (Fig. 4.8) shows that the soft phase wraps the hard phase in such a way as to minimize the deformation of the hard phase, thereby creating droplets. The long-ranged effect of the deposition rate then orders the droplets in the hexagonal array. Q_E takes its maximum value in the thinner regions of the soft phase, which appear six times around a droplet. We note that

Figure 4.6: The structure factor and the order parameter along a horizontal cut at $\tau = 10000$ in the near-onset regime. Left column: $g_E = 0.05$. Right column: $g_E = 0.5$. The times for the structure factor correspond to those in Fig. 4.5.

transmission electron microscopy measurements are sensitive to fluctuations of the local lattice parameter [12]. Hence, our pictures can give a correspondence with such measurements.

Far from the onset of instability (i.e. for a slow deposition process), $\Delta\psi$ is at its maximum, and domains of the two phases are separated by sharp interfaces. Because f_E is proportional to $\Delta\psi$, it becomes more important in this regime. As Fig. 4.9 illustrates, the final state of the deposition process consists of deformed droplets, even for $g_E = 0.05$. For this smaller g_E value, the time evolution of the system proceeds through the formation of an interconnected network which then breaks up. Long stripes become unstable and pinch away to form droplets. In Fig. 4.10, we show the structure factor and the order parameter profile.

For $g_E = 0.5$, droplets form quickly, due to the larger elastic energy. The far from onset steady-state consists of deformed droplets with flattened interfaces between

Figure 4.7: Grey scale plot of the degree of deformation Q_E for the last lamellar configuration of Fig. 4.5. Black represents $Q_E = 0$, while white represents $Q_E = 0.014$.

neighbor droplets. Also, the size distribution is not as sharply peaked as compared to the near onset results. Figure 4.10 shows that the structure factor possesses a strong peak around $k = 0.55$ and a secondary peak at $k = 1$, still representative of the underlying hexagonal structure. However, the two peaks are broadened by the distortions in the lattice order and the size of the droplets. The flattening of the sides of droplets is due to shape changes of the hard domains from spheres to plates in order to minimize the elastic energy. This is shown in Fig. 4.11, where it can be seen that Q_E is zero inside the hard domains, while the soft phase has its maximum elastic energy in the thin regions separating the hard domains. Such shape adjustments of the hard domains have been studied by Onuki and Nishimori [64] where they showed that for bulk phase separation in the presence of elastic misfits, hard precipitates are deformed in order to cancel the elastic field produced by nearby precipitates.

It is very instructive to consider the time evolution towards the droplet phase by looking at the function Q_E . As can be seen in Fig. 4.12, the initial elastic deforma-

Figure 4.8: Grey scale plot of the degree of deformation Q_E for the last hexagonal configuration of Fig. 4.5. Black represents $Q_E = 0$, while white represents $Q_E = 0.1$.

tion is similar to the near onset regime: deformed stripes separated by undeformed interfaces. As time proceeds, the value of the order parameter difference increases and the elastic contribution becomes more important. The contribution to the energy coming from deformations inside hard domains become too costly, leading to a bending of straight interfaces to produce droplets. The instability of straight interfaces (and of the lamellar phase) can be understood as follows [62]: in the far from onset regime, we suppose that we have a straight interface separating two uniaxially deformed regions. The interface is located at $x = 0$, and the order parameter goes to $\psi_{\pm}$ far from the interface. We allow for fluctuations in the order parameter around the interface profile $\psi = \psi_0(x) + \psi'_0(x) \sum_k \delta_k(t) e^{iky}$ and calculate the change in the free energy to $\mathcal{O}(\delta_k^2)$. We find that

$$\delta F_{el} \propto \sum_k \left[lk^2 + \frac{1}{2} g_E (\Delta\psi)^2 s k - \frac{bV}{k} \right] |\delta_k|^2, \quad (4.14)$$

where s is the average of the strain in the two phases and l and b are positive constants

Figure 4.9: The left column shows the concentration field in the far from onset regime for $g_E = 0.05$ and $V = 0.001$. The right column is for $g_E = 0.5$ and $V = 0.1$. Times from top to bottom are $\tau = 5000, 15000$ and 100000 in the left panels and $\tau = 100, 1500$ and 10000 in the right panels.

that depend on the form of $\psi_0(x)$. The time dependence of δ_k is given by the equation

$$\frac{\partial \delta_k}{\partial t} = -Dk^2 \left[lk + \frac{1}{2}g_E (\Delta\psi)^2 s + \frac{bV}{k^2} \right] \delta_k, \quad (4.15)$$

implying that the interface is unstable when $lk + \frac{1}{2}g_E (\Delta\psi)^2 s + \frac{bV}{k^2} < 0$. This last result means that the lamellar phase becomes unstable when

$$V < \left(\frac{g_E (\Delta\psi)^2 s}{4b^{1/3}l^{2/3}} \right)^3, \quad (4.16)$$

i.e. the threshold value for $V \sim g_E^3$. For values of V close to onset, the above analysis is no longer valid, and a single mode approximation shows that the critical line has negative second derivative, and eventually meets with the far from onset line. To appropriately calculate the "non-equilibrium steady-state phase diagram", considera-

Figure 4.10: The left column shows the structure factor and the order parameter along a horizontal cut at $\tau = 100000$ for the left column, and at $\tau = 10000$ for the right column, in the far from onset regime. Left column: $g_E = 0.05$. Right column: $g_E = 0.5$. The times for the structure factor correspond to those in Fig. 4.9.

tion of more than one mode is essential, as well as the possibility of phase coexistence. Such calculations have not been carried out.

The wavelength of the concentration modulation in the steady-state as a function of the deposition rate is plotted in Fig. 4.13. In the absence of elastic interactions, $k_{ss} \sim V^{1/4}$ near $V = 1/4$, while $k_{ss} \sim V^{1/3}$ for small V . When elastic interactions are present, the near onset relation still holds, but the far from onset behavior is different. For small V , the elastic effects are responsible for the appearance of droplets, which decreases the wavelength and increases the wavenumber. Thus, at fixed deposition rate, the wavenumber increases with g_E .

4.3.3 Anisotropic growing film with elastic fields

In this section, we discuss how the cubic anisotropy alters the findings of the previous sections. Figure 4.14 shows order parameter and Q_E configurations for $V = 0.24$,

Figure 4.11: The elastic deformation, Q_E , for a portion of the last droplet configuration in Fig. 4.9.

$g_E = 0.05$ and $g_\xi = 0.1$ (see Figs. 4.1 and 4.5 for comparison). The phase segregation occurs preferentially along the $[01]$ and $[10]$ directions, leading eventually to a perfectly ordered lamellar structure (not shown in the figure). Interestingly, the stripes have bubbles and necks, which are mostly found at the boundaries between different stripe orientations for the latest time shown. These bubbles are due to the elastic energy, as can be seen in the grey scale plots of Q_E . Within the ordered lamellar regions, the deformation is inside the stripes, which are separated by undeformed interfaces. The competition between stripe orientations at boundaries creates *deformed* elastic droplets, thereby creating the bulges seen in the concentration field. Far from the onset of instability (Fig. 4.15) the droplets are now cuboids with their flat sides oriented along $[01]$ or $[10]$ (compare with Fig. 4.9).

4.4 Discussion

Our results show a number of interesting competing effects during the growth of multi-

Figure 4.12: Time evolution of Q_E in the far from onset regime for $g_E = 0.05$. The straight lamellar interfaces become unstable and bend to form droplets. Panels from left to right correspond to time=100, 500, 1500 and 100000.

component films. First, there is a competition between the phase separation and the constant deposition of material on the surface, leading to the formation of lamellar structures in the absence of elasticity. These lamellar structures appear below a certain threshold deposition rate, while above this threshold, the film is homogeneously mixed. The deposition of material can be viewed as a *non-local repulsive* interaction of the form $-V \int d\mathbf{r} d\mathbf{r}' \psi(\mathbf{r}) G(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}')$ with $\nabla^2 G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$. Because this contribution is quadratic in ψ , it changes the linear dispersion relation. When elastic fields are introduced with first order dependence of the elastic moduli on concentration, there appears another long range interaction due to the difference in the shear moduli between the two phases (f_E). This interaction is cubic in ψ and is of the form $g_E \sum_{i,j} \int \int \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' \psi(\mathbf{r}) G_{ij}(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') G_{ij}(\mathbf{r}', \mathbf{r}'') \psi(\mathbf{r}'')$. It does not contribute to the linear dispersion relation; its effects are purely nonlinear. This can be seen in Fig. 4.9 where upon entering the nonlinear regime the stripes pinch away, fold and form droplets. Calculations have shown that the interaction between two hard spherical precipitates in a soft matrix is *repulsively long-range* and is mediated by the elastic fields [65]. However [64], other authors have argued that this interaction vanishes when the hard precipitates undergo shape changes from spheres to ellipsoids. As seen in our simulations, the hard precipitates do have a vanishing shear energy. This is not to say that the long-range elastic interaction vanishes in general, because deformations of the soft phase to accommodate the shape changes must also be taken into account. Although nothing can be said about f_E in terms of the full free energy ex-

Figure 4.13: Steady-state wavenumber as a function of the deposition rate. The lines are the near onset expansion (solid) and the far from onset expansion (dashed) for $g_E = 0.0$.

pression, we believe that f_E leads to long-range repulsive interactions between the precipitates.

For film growth, the presence of f_E is in competition with both the phase separation and the deposition process. As seen in our simulation results, this leads to a competition between steady-state lamellar phases and steady-state droplet phases. For deposition rates near the threshold for instability, the long range elastic interaction creates the droplets; the long range interaction due to the deposition then orders these droplets in an hexagonal array. Hence, the well ordered hexagonal state is due to *both* long range interactions. This means that if predictions for the selected wave number of the patterns are to be made, they should depend on the two parameters V and g_E .

4.5 Conclusion

To summarize, we have studied the growth by MBE of a thin solid layer composed

Figure 4.14: The left column shows the concentration field and the right column is Q_E for the system with cubic anisotropy, in the near onset regime. $V = 0.24$, $g_E = 0.05$ and $g_\xi = 0.1$. Times from top to bottom are 50, 500 and 2000.

of two different atomic types. The constant deposition of material competes with the phase segregation to produce modulated structures. Elastic effects due to a difference between the elastic moduli and the lattice constants of the two components and crystal anisotropy were shown to modify the dynamical evolution and the steady-state reached by the system. The elastic effects are directly responsible for the appearance of droplets of the hard phase in a soft matrix, while the crystal anisotropy favors spinodal decomposition along the soft directions, aligning the stripes or forming cuboidal droplets.

Figure 4.15: The left panel shows the concentration field and the right panel is Q_E for the system with cubic anisotropy, in the far from onset regime. $V = 0.001$, $g_E = 0.05$ and $g_\xi = 0.1$. The snapshots were taken at time= 10000.

Chapter 5

STABILITY OF MISMATCHED ALLOY FILMS

5.1 Introduction

In recent years, it has been recognized that the effects of a substrate misfit on the surface of a single component film lead to an instability of the planar surface. This instability is responsible for the formation of mounds or islands where elastic relaxation occurs at the peaks, in competition with the extra surface energy. Such instabilities have been observed experimentally [66–68] and predicted theoretically [69–71] by several authors. For alloy layers, the lattice constant and the elastic moduli of the two components can be different, and an interesting coupling arises between the misfit stress and the stress generated by composition inhomogeneities, as shown by Guyer and Voorhees [72]. These authors however, considered the surface composition to be in equilibrium with a vapor, a strong approximation that neglects the dynamics of phase segregation. Another approach has been proposed by Tersoff [73] based on a step-flow growth model. Experiments correlating the compositional and surface profiles have been recently presented as discussed in chapter 1.

In this chapter, we present results of a linear analysis of the joint morphological/compositional stability of alloy layers [74]. We consider the case where the alloy inhomogeneities are initially induced by thermodynamics alone (the alloy is immiscible at the growth temperature and composition), and the case where the alloy is grown outside of the miscibility gap. Furthermore, the full nonequilibrium nature of

the dynamics of phase separation and surface diffusion are taken into account, leading to results that are very different from those in [72]. In particular, we find that the stability is independent of the sign of the misfit when the elastic moduli of the alloy components are equal, and that alloy decomposition is always accompanied by a surface instability. In Sec. 5.2, we introduce the continuum model for the alloy thin film, and in Sec. 5.3, we describe the linear stability analysis. Equations (5.38) and (5.39) form one of the central results in this chapter. Results are presented for a static film in Sec. 5.4 and for a growing film in Sec. 5.5. The effects of a composition-dependent Young's modulus are discussed in Sec. 5.6 and the conclusions are summarised in Sec. 5.7.

5.2 Model

The substrate is a semi-infinite isotropic solid occupying the space $z < 0$, and the film is in the region $0 < z \leq h(x, y, t)$. The film is composed of two species, corresponding to a binary or pseudo-binary alloy, with both species simultaneously deposited by a directed beam. The instantaneous average composition of the alloy film is the same as the composition in the beam, which remains constant in time. The surface $z = 0$ separating the substrate from the film is assumed to remain flat and coherent. Furthermore, the interactions of the film with the substrate are symmetric for the components of the film, and are assumed not to affect the surface energy. A neutral substrate has been shown to produce droplets of both phases of the film in contact with the substrate [39]. An essential ingredient in our model is that diffusion of material proceeds along the surface only, since bulk diffusion coefficients are typically much smaller than surface diffusion coefficients. The neglect of bulk diffusion means that the composition profile in the z direction can be obtained from the history of the composition at the surface. In this section, the elastic constants (Young's modulus E , shear modulus M and Poisson ratio ν) of the substrate and of the film are assumed to be equal and independent of the composition.

As before, the composition of the film is described by a continuous variable $\phi(\mathbf{r})$ proportional to the local composition difference of the two constituents. The important effects in heteroepitaxy arise because the lattice constants of the film components

are different: the lattice constant of the film, a_f , depends on ϕ through the relation $\ln a_f = \eta\phi$, defining the solute expansion coefficient $\eta = (\partial a_f / \partial \phi) / a_f$. The misfit between the substrate and the film is $\varepsilon = (a_f - a_s) / a_s$, (a_s is the lattice constant of the substrate); $\varepsilon > 0$ implies that the film is compressively strained.

The free energy of the system consists of 3 parts: a contribution from the elastic energy, a contribution due to the thermodynamics of the binary alloy and a term that represents the surface energy. The total free-energy functional is written as

$$\mathcal{F}[\phi, \mathbf{u}, h] = \mathcal{F}_{el}[\phi, \mathbf{u}, h] + \mathcal{F}_{GL}[\phi, h] + \mathcal{F}_s[h], \quad (5.1)$$

where $\mathcal{F}_{el}$ is the elastic free-energy functional, $\mathcal{F}_{GL}$ is the Ginzburg-Landau free-energy functional that represents the thermodynamics and $\mathcal{F}_s$ is the surface free-energy functional. Here $\mathbf{u}(\mathbf{r})$ is the displacement vector representing displacements from the local equilibrium position and is related to the strain tensor through $\mu_{ij} = (\nabla_i u_j + \nabla_j u_i) / 2$, with the indices i and j equal to x, y or z . Because the elastic fields will cause deformations to extend into the substrate, the elastic term has to be calculated over the whole system:

$$\mathcal{F}_{el}[\phi, \mathbf{u}, h] = \frac{1}{2} \int_{-\infty}^h d^3r S_{ijkl} \sigma_{ij} \sigma_{kl}, \quad (5.2)$$

with S_{ijkl} the elastic compliance tensor and σ_{ij} the stress tensor. For isotropic bodies, $S_{ijkl} = \delta_{ik}\delta_{jl} (1 + \nu) / E - \delta_{ij}\delta_{kl} \nu / E$ (δ_{ij} is the Kronecker delta). The essential properties of the binary compound phase behavior is again captured by the Ginzburg-Landau energy

$$\mathcal{F}_{GL}[\phi, h] = \int_0^h d^3r \left[-\frac{r'}{2} \phi^2 + \frac{u}{4} \phi^4 + \frac{c}{2} |\nabla \phi|^2 \right]. \quad (5.3)$$

The last contribution in the total free-energy functional is the surface energy

$$\mathcal{F}_s[h] = \gamma \int d^2r \sqrt{g}, \quad (5.4)$$

with γ the surface tension and $g = 1 + |\nabla h|^2$ is the determinant of the surface metric. Here we consider simplified cases where the surface tension is isotropic and independent of the composition or the displacement vector.

The boundary conditions for the system are as follows. For MBE growth, the pressure above the film is negligible; hence the total force on a mass element on the

surface is zero. This implies that

$$\sigma_{ij}^f n_j = 0 \text{ at } z = h, \quad (5.5)$$

with the unit vector $\mathbf{n} = (-\nabla h, 1) / \sqrt{g}$ oriented towards the half space of positive z direction. Because the plane $z = 0$ remains flat and coherent, the displacement vector and the stress tensor must be continuous there, implying that

$$\sigma_{zi}^f = \sigma_{zi}^s \text{ and } \mathbf{u}^f = \mathbf{u}^s \text{ at } z = 0. \quad (5.6)$$

Also, we require the displacement vector within the substrate to vanish far from the film/substrate interface: $\mathbf{u}^s \rightarrow 0$ as $z \rightarrow -\infty$. Since $\phi = 0$ for $z \leq 0$, the boundary condition on the composition is $\phi = 0$ at $z = 0$.

To describe the time evolution of the film, dynamical equations for the fields $\mathbf{u}$, h and ϕ must be provided. These equations must represent the deposition process under consideration. For MBE, evaporation of particles from the film surface is neglected, and a constant amount of material is deposited per unit time. Hence, in a reference frame moving with the average surface position, the surface diffusion process must conserve the total amount of material. The material current at the surface is proportional to the gradient in the chemical potential

$$\mathbf{J}_h = -\Gamma_h \nabla \frac{\delta \mathcal{F}}{\delta h}, \quad (5.7)$$

where Γ_h is a kinetic coefficient. Because material is conserved, the time derivative of h is related to the divergence of the current, and h evolves as

$$\partial_t h = \Gamma_h \sqrt{g} \nabla_s^2 \frac{\delta \mathcal{F}}{\delta h} + v, \quad (5.8)$$

where ∇_s^2 is the Laplace-Beltrami operator that ensures diffusion parallel to the surface, and v is the growth velocity.

The concentration field *at the surface* $\phi(x, y, t) = \phi(x, y, h(x, y), t)$ evolves in a similar manner,

$$\partial_t \phi = \Gamma_\phi \nabla_s^2 \frac{\delta \mathcal{F}}{\delta \phi} - (v/a)\phi. \quad (5.9)$$

The very important last term in this equation represents the constant deposition of material of average composition equal to 0. Since diffusion is neglected in the bulk,

$\phi_b(x, y, z, t) = \phi(x, y, t = z/v)$. The last evolution equation that has to be specified is for the field $\mathbf{u}$. Since diffusion is a much slower process than local lattice rearrangements, the displacement vector can be taken to instantaneously satisfy mechanical equilibrium,

$$\nabla_j \sigma_{ij} = 0. \quad (5.10)$$

These equations can be recast in terms of $\mathbf{u}$ once the stress tensor is specified. This will be described in the next section.

5.3 Linear stability analysis

The linear stability analysis aims at calculating the growth rate of perturbations in the surface profile and in the concentration field. The procedure we describe here is similar to other calculations [75, 76]. The reference state around which perturbations occur must be specified. The basic state for the surface consists of a planar growth front moving at a velocity v for the growing film, and of fixed thickness $\bar{h}$ for the static film. The substrate is unstrained and of lattice constant a_s , $\bar{\mathbf{u}}^s = 0$, while the film is stressed in the x and y directions, such that the lattice constant in these directions is a_s . Since this is the reference state, $\bar{u}_x = \bar{u}_y = 0$. Of course, the stress in the lateral directions will cause Poisson relaxation in the z direction, such that the compression $\nabla \cdot \bar{\mathbf{u}} = \bar{\mu}_{zz}$ is uniform, $\bar{u}_z = \bar{\mu}_{zz}z$, with the constant $\bar{\mu}_{zz} = [(1 + \nu) / (1 - \nu)] \varepsilon$. The stress in the lateral directions is then $\bar{\sigma} = -2M\bar{\mu}_{zz}$. We take the composition $\bar{\phi}$ of the initial state to be uniform and equal to zero. The general stress tensor, in the presence of the misfit ε and compositional stresses, then reads [72, 76]

$$\sigma_{ij} = 2M \left[\frac{\nu}{1 - 2\nu} \mu_{il} \delta_{ij} + \mu_{ij} - \frac{1 + \nu}{1 - 2\nu} (\varepsilon + \eta\phi) \delta_{ij} \right]. \quad (5.11)$$

Substitution of this expression for the stress tensor in Eq. (5.10) leads to the mechanical equilibrium equations

$$\nabla_i \nabla \cdot \mathbf{u} + (1 - 2\nu) \nabla^2 u_i - 2(1 + \nu) \eta \nabla_i \phi = 0. \quad (5.12)$$

The stability is studied by considering small perturbations around the basic state: a general variable ξ is expanded in a two-dimensional Fourier series as $\xi = \bar{\xi} + \sum_{\mathbf{q}} \hat{\xi}(\mathbf{q}, z, t) e^{i(q_x x + q_y y)}$ (the Fourier coefficients for the height variable are independent

of z). The functional derivative in Eq. (5.8), when computed, becomes the free-energy density evaluated at the surface. Hence, for the purpose of calculating $\partial_t \hat{h}$, the free-energy density has to be computed to $\mathcal{O}(\hat{\xi})$. To this order, the Ginzburg-Landau free energy does not contribute, and we have the order $\hat{\xi}$ elastic energy, $\hat{\mathcal{E}}$, as

$$\hat{\mathcal{E}} = \bar{\sigma} \left(\hat{\mu}_{xx} + \hat{\mu}_{yy} - 2\eta\hat{\phi} \right). \quad (5.13)$$

For the dynamical equation for ϕ , the free-energy density must be computed to second order in the perturbations. Because of the mechanical equilibrium condition, the displacement vector can be obtained as a function of h and ϕ . The second order correction to the elastic energy, $\tilde{\mathcal{E}} \sim \mathcal{O}(\hat{\xi}^2)$, is

$$\tilde{\mathcal{E}} = S_{ijkl} \hat{\sigma}_{ij} \hat{\sigma}_{kl}. \quad (5.14)$$

5.3.1 solutions of the mechanical equilibrium equations

The mechanical equilibrium equations are already linear and are, in the film,

$$(1 - 2\nu) (\partial_z^2 - q^2) \hat{u}_x + iq_x [iq_x \hat{u}_x + iq_y \hat{u}_y + \partial_z \hat{u}_z - 2(1 + \nu) \eta \hat{\phi}] = 0, \quad (5.15)$$

$$(1 - 2\nu) (\partial_z^2 - q^2) \hat{u}_y + iq_y [iq_x \hat{u}_x + iq_y \hat{u}_y + \partial_z \hat{u}_z - 2(1 + \nu) \eta \hat{\phi}] = 0, \quad (5.16)$$

$$(1 - 2\nu) (\partial_z^2 - q^2) \hat{u}_z + \partial_z [iq_x \hat{u}_x + iq_y \hat{u}_y + \partial_z \hat{u}_z - 2(1 + \nu) \eta \hat{\phi}] = 0, \quad (5.17)$$

to first order. This is a set of coupled inhomogeneous second order differential equations, with the inhomogeneity due to the concentration field. The homogeneous equations were derived by Spencer *et al.* [75], while Guyer and Voorhees [76] obtained the full inhomogeneous set of equations. In the substrate, the displacements satisfy the homogeneous equations. The general solution to the inhomogeneous set is a linear combination of the solutions to the homogeneous problem added to the particular solution. The particular solution can easily be derived by taking an extra divergence in Eq. (5.12), leading to

$$u_i = \left(\frac{1 + \nu}{1 - \nu} \right) \eta \nabla_i W, \quad (5.18)$$

where W is defined through the relation

$$\nabla^2 W = \phi. \quad (5.19)$$

In the substrate, the displacements are

$$\begin{bmatrix} \hat{u}_x^s \\ \hat{u}_y^s \\ \hat{u}_z^s \end{bmatrix} = \begin{bmatrix} u_x^0 \\ u_y^0 \\ u_z^0 \end{bmatrix} e^{qz} - \begin{bmatrix} iq_x/q \\ iq_y/q \\ 1 \end{bmatrix} B z e^{qz}, \quad (5.20)$$

where $B = [1/(3 - 4\nu)] (iq_x u_x^0 + iq_y u_y^0 + q u_z^0)$, and where we have used the condition that $\mathbf{u}^s$ vanishes far from the film/substrate boundary. In the film, we have

$$\begin{aligned} \begin{bmatrix} \hat{u}_x^f \\ \hat{u}_y^f \\ \hat{u}_z^f \end{bmatrix} &= \begin{bmatrix} \alpha_x \\ \alpha_y \\ \alpha_z \end{bmatrix} \cosh(qz) + \begin{bmatrix} \beta_x \\ \beta_y \\ \beta_z \end{bmatrix} \sinh(qz) - \begin{bmatrix} C iq_x/q \\ C iq_y/q \\ D \end{bmatrix} z \sinh(qz) \\ &\quad - \begin{bmatrix} D iq_x/q \\ D iq_y/q \\ C \end{bmatrix} z \cosh(qz) + \left(\frac{1 + \nu}{1 - \nu} \right) \eta \begin{bmatrix} iq_x \hat{W} \\ iq_y \hat{W} \\ \partial_z \hat{W} \end{bmatrix}. \end{aligned} \quad (5.21)$$

In this last equation, C and D are defined as $C = [1/(3 - 4\nu)] (iq_x \alpha_x + iq_y \alpha_y + q \beta_z)$ and $D = [1/(3 - 4\nu)] (iq_x \beta_x + iq_y \beta_y + q \alpha_z)$. The above relations for the displacements in the film and in the substrate contain 9 coefficients that have to be fixed using the boundary conditions. To $\mathcal{O}(\hat{\xi})$, the boundary conditions are, at $z = h$,

$$\hat{\sigma}_{xz} = iq_x \bar{\sigma} \hat{h}, \quad \hat{\sigma}_{yz} = iq_y \bar{\sigma} \hat{h} \text{ and } \hat{\sigma}_{zz} = 0. \quad (5.22)$$

At $z = 0$ to this order,

$$\hat{\sigma}_{zi}^f = \hat{\sigma}_{zi}^s \text{ and } \hat{\mathbf{u}}^f = \hat{\mathbf{u}}^s. \quad (5.23)$$

The linearized boundary condition on ϕ is $\hat{\phi} = 0$ at $z = 0$, since we consider the alloy to be in the region $z > 0$.

With these boundary conditions, we find that $u_i^0 = \alpha_i = \beta_i$, which implies that $C = D = B$. For the energy calculation it is sufficient to specify C , as well as the relations between α_z and C :

$$C = A \left[-\frac{q \hat{h} \bar{\sigma}}{2M} + \eta \left(\frac{1 + \nu}{1 - \nu} \right) (q \partial_z \hat{W} - \partial_z^2 \hat{W} + \hat{\phi}) \Big|_{z=\hat{h}} \right], \quad (5.24)$$

$$q \alpha_z = C (2 - 2\nu + q \bar{h}) + A \left(\frac{q \hat{h} \bar{\sigma}}{M} - 2\eta \left(\frac{1 + \nu}{1 - \nu} \right) q \partial_z \hat{W} \Big|_{z=\hat{h}} \right), \quad (5.25)$$

where $A = [\cosh(q \bar{h}) + \sinh(q \bar{h})]^{-1}$.

5.3.2 calculation of the energy

The energy can now be calculated to second order in the perturbations from Eqs. (5.13) and (5.14) :

$$\widehat{\mathcal{E}} = \frac{E\varepsilon}{1-\nu} \left[-2\varepsilon(1+\nu)q\hat{h} - 2\eta \left((1+\nu)q\partial_z\hat{W} - (1+\nu)\partial_z^2\hat{W} + \nu\hat{\phi} \right) \Big|_{z=\bar{h}} \right] \quad (5.26)$$

and

$$\begin{aligned} \widetilde{\mathcal{E}} = & \frac{E}{(1-2\nu)(1+\nu)} \left[(1-2\nu)\eta^2\hat{\phi}^2 \left(\frac{1+\nu}{1-\nu} \right) + 2\varepsilon \left(\frac{1+\nu}{1-\nu} \right) q\hat{h}(1-2\nu)(1+\nu)\eta\hat{\phi} \right. \\ & + 2(1-2\nu)\eta^2 \left(\frac{1+\nu}{1-\nu} \right)^2 \hat{\phi} \left[q\partial_z\hat{W} - \partial_z^2\hat{W} \right] \Big|_{z=\bar{h}} \\ & + 2(1-2\nu)(1-\nu)\eta^2 \left(\frac{1+\nu}{1-\nu} \right)^2 \left[q\partial_z\hat{W} - \partial_z^2\hat{W} \right]^2 \Big|_{z=\bar{h}} \\ & \left. + 8(1-2\nu)(1+\nu)\varepsilon \left(\frac{1+\nu}{1-\nu} \right) q\hat{h}\eta \left[q\partial_z\hat{W} - \partial_z^2\hat{W} \right] \Big|_{z=\bar{h}} \right]. \quad (5.27) \end{aligned}$$

In this equation for $\widetilde{\mathcal{E}}$, we have dropped terms of the form $\hat{h}^2$ because they do not contribute to the chemical potential for ϕ .

To obtain the function $\hat{W}$, we proceed as follows. We are interested in the early time regime where the fields grow exponentially in time, i.e. $\hat{\phi} = \hat{\phi}_0 e^{\Omega t}$ and $\hat{h} = \hat{h}_0 e^{\Omega t}$. This means that in the bulk of the film, $\hat{\phi}_b = \hat{\phi}_0 e^{\Omega z/\nu}$, which gives, by Eq. (5.19),

$$\hat{W} = \frac{v^2 \hat{\phi}_0}{\Omega^2 - (qv)^2} e^{\Omega z/\nu}. \quad (5.28)$$

In particular, at the surface, $z = vt$, and $\hat{W} = v^2 \hat{\phi} / (\Omega^2 - (qv)^2)$, which implies that $\widehat{\mathcal{E}}$ and $\widetilde{\mathcal{E}}$ can be calculated in terms of $\hat{h}$ and $\hat{\phi}$ only. For completeness, we write these expressions here:

$$\widehat{\mathcal{E}} = \frac{E\varepsilon}{1-\nu} \left[-2\varepsilon(1+\nu)q\hat{h} - 2\eta\hat{\phi} \left(\frac{\nu qv - \Omega}{qv + \Omega} \right) \right] \quad (5.29)$$

and

$$\begin{aligned} \widetilde{\mathcal{E}} = & \frac{E}{1-\nu} \left[\eta^2 \hat{\phi}^2 \left(1 - 2 \left(\frac{1+\nu}{1-\nu} \right) \Omega \left(\frac{\nu\Omega + qv}{(\Omega + qv)^2} \right) \right) \right. \\ & \left. - 2(1+\nu)\varepsilon\eta q\hat{h}\hat{\phi} \left(\frac{3\Omega - qv}{\Omega + qv} \right) \right]. \quad (5.30) \end{aligned}$$

5.3.3 linearized dynamical equations

The dynamical equations for $\hat{h}$ and $\hat{\phi}$ are obtained from Eqs. (5.8) and (5.9). In Fourier space, they read

$$\partial_t \hat{h} = -\Gamma_h q^2 \left[-2E\varepsilon^2 \frac{1+\nu}{1-\nu} q \hat{h} - \frac{2E}{1-\nu} \varepsilon \eta \left(\frac{\nu q v - \Omega}{q v + \Omega} \right) \hat{\phi} + \gamma q^2 \hat{h} \right] \quad (5.31)$$

and

$$\begin{aligned} \partial_t \hat{\phi} = & -\Gamma_\phi q^2 \left(-r' + c q^2 + \frac{2E}{1-\nu} \eta^2 \right) \hat{\phi} \\ & -\Gamma_\phi q^2 \frac{4E}{1-\nu} \left[-\frac{1+\nu}{1-\nu} \left(\frac{\Omega}{\Omega + q v} \right) + (1+\nu) \left(\frac{\Omega}{\Omega + q v} \right)^2 \right] \eta^2 \hat{\phi} \\ & +\Gamma_\phi q^3 2E \frac{1+\nu}{1-\nu} \left(\frac{3\Omega - q v}{\Omega + q v} \right) \varepsilon \eta \hat{h} - (v/a) \hat{\phi}. \end{aligned} \quad (5.32)$$

It can be seen from these equations that the two variables are coupled due to the elastic effects. In Eq. (5.32), the term $(2E/(1-\nu)) \eta^2 \hat{\phi}$ simply renormalizes the coefficient r' and was first calculated by Cahn [77] in the case of a bulk binary mixture. Experimentally, only the renormalized value for r' is accessible, and we therefore introduce a new coefficient $r = r' - 2E\eta^2/(1-\nu)$, which is proportional to $T_c^{eff} - T$, and we consider the cases where T is above and below T_c^{eff} .

The dynamical equations can be rescaled using typical length and time scales. We take the typical width of interfaces between domains as the length scale, and make the transformation $\mathbf{x} = (|r|/c)^{1/2} \mathbf{r}$ and $k = (c/|r|)^{1/2} q$. The time scale is then related to the surface diffusion constant Γ_ϕ , leading to the rescaling $\tau = (\Gamma_\phi r^2/c) t$. We also introduce new parameters ε^* , η^* and γ^* defined as

$$\varepsilon^* = \left[\frac{2E}{|r|} \left(\frac{1+\nu}{1-\nu} \right) \right]^{1/2} \varepsilon, \quad (5.33)$$

$$\eta^* = \left[\frac{2E}{|r|} \left(\frac{1+\nu}{1-\nu} \right) \right]^{1/2} \eta \quad (5.34)$$

and

$$\gamma^* = (c|r|)^{-1/2} \gamma. \quad (5.35)$$

Furthermore, the growth parameter is also rescaled,

$$V = \left(\Gamma_\phi \frac{r^2}{c} \right)^{-1} v/a, \quad (5.36)$$

while the dimensionless dispersion is

$$\sigma = \left(\Gamma_\phi \frac{r^2}{c} \right)^{-1} \Omega. \quad (5.37)$$

For most semiconductor materials, the Poisson ratio varies around a value of 1/4. For this value of ν , the dimensionless dynamical equations are ($\hat{h}$ has also been rescaled)

$$\partial_\tau \hat{h} = -k^2 \left[-\varepsilon^{*2} k \hat{h} - \frac{1}{5} \varepsilon^* \eta^* \left(\frac{kV - 4\sigma}{kV + \sigma} \right) \hat{\phi} + \gamma^* k^2 \hat{h} \right] \quad (5.38)$$

and

$$\begin{aligned} \partial_\tau \hat{\phi} = & -k^2 \left[\pm 1 + k^2 + \frac{V}{k^2} - \frac{2}{3} \eta^{*2} \sigma \frac{\sigma + 4kV}{(\sigma + kV)^2} \right] \hat{\phi} \\ & + k^3 \varepsilon^* \eta^* \left(\frac{3\sigma - kV}{\sigma + kV} \right) \hat{h}. \end{aligned} \quad (5.39)$$

In Eq. (5.39) [and Eqs (5.40), (5.42), (5.44), (5.45) and (5.46) below], the top sign is taken if the alloy is above the critical temperature and the bottom sign applies if the alloy is below the critical temperature. Immediate important conclusions can be drawn from these equations. In a general case where none of the parameters vanish, the morphological and compositional degrees of freedom are always coupled. Thus, if one of the variables is unstable, then the other will also be unstable. Therefore, decomposition of the alloy will always be accompanied by a surface instability, and the planar surface can be stabilized only if spinodal decomposition is suppressed. In the same way, if a misfit drives a surface instability, it will induce phase separation at the surface. In general, for $T < T_c$, both the instability due to the misfit and the thermodynamic instability of the alloy are present, and the system evolves with a single dispersion relation which is a combination of the two instabilities. The second important conclusion is concerned with the signs of the misfit ε^* and of the solute expansion coefficient η^* . It can be seen in Eqs. (5.38) and (5.39) that ε^* and η^* appear only in the combinations ε^{*2} , η^{*2} and $\varepsilon^* \eta^*$, implying that the only possible dependence on the signs of ε^* and η^* would be from the $\varepsilon^* \eta^*$ terms, i.e., the *coupling* terms in

the equations. Consider for instance the term proportional to $\hat{\phi}$ in Eq. (5.38). To replace the fluctuation in $\hat{\phi}$ by a function of $\hat{h}$, one has to first (simultaneously) solve Eq. (5.39), giving $\hat{\phi} \sim \varepsilon^* \eta^* \hat{h}$ which is then substituted back in Eq. (5.38), yielding an effective contribution which is proportional to $(\varepsilon^* \eta^*)^2$. Hence, the stability is *independent* of the sign of the misfit or the expansion coefficient.

To solve for the dispersion relation, we let $\hat{h} = \hat{h}_0 e^{\sigma \tau}$, $\hat{\phi} = \hat{\phi}_0 e^{\sigma \tau}$ and require that the determinant of the matrix formed by the equations for $\hat{h}_0$ and $\hat{\phi}_0$ be equal to zero. We find that σ satisfies the quartic equation

$$0 = \left[(\sigma + k^2 (k^2 \pm 1) + V) (\sigma + kV)^2 - \frac{2}{3} \eta^{*2} k^2 \sigma (\sigma + 4kV) \right] [\sigma + \gamma^* k^4 - \varepsilon^{*2} k^3] + \frac{1}{5} k^5 (\varepsilon^* \eta^*)^2 (3\sigma - kV) (4\sigma - kV). \quad (5.40)$$

It can now easily be seen that σ does not depend on the sign of ε^* or η^* . In general, there exist four complex solutions to Eq. (5.40). The real part of σ determines the stability of the system, while the presence of a nonzero imaginary part for σ is responsible for oscillations. Here, we are only interested in the stability of the system, and concentrate on the real part of σ . When the analytical solutions for σ are complicated we proceed numerically, and for a given value of k , we calculate the real part of the each of the four solutions, and denote the largest of these four values as σ . Hence, below when we indicate $\sigma > 0$, we mean that the real part of at least one of the four roots is positive, leading to an instability, and σ represents the most unstable dispersion. When ε^* or η^* vanishes, the dynamical equations for h and ϕ decouple, and each variable evolves with its own dispersion relation, which we denote as σ_ϕ and σ_h .

5.4 Results for static films

In the case of a static film of fixed average height, the expression for $\hat{W}$ in Eq. (5.28) is no longer valid. In principle, Eq. (5.19) has to be solved for a composition given by a delta function in $z - h$. However, a simpler argument is as follows: if we assume that $\hat{\phi}_b = \hat{\phi}_s e^{-\lambda(z-h)}$ where $\hat{\phi}_s$ is the value of the order parameter at the surface, then $\hat{W}$ is easily calculated. Substitution of the expression for $\hat{W}$ in the elastic energy Eq.

(5.27) and taking the limit $\lambda \gg q$ yields the same result as setting *the growth velocity* V to zero. The expression for $\hat{\phi}_b$ above is similar in spirit to the calculations of Glas for an equilibrium static film [78]. Various scenarios are possible depending on the values of ε^* and η^* .

When both ε^* and η^* are zero (i.e. a film perfectly matched to the substrate and with the lattice constant independent of composition), the dynamical equations decouple and there are 2 non-trivial solutions for σ . For the height variable,

$$\sigma_h = -\gamma^* k^4, \quad (5.41)$$

which is always negative, leading to a stable planar surface. For the compositional degree of freedom, we have

$$\sigma_\phi = -k^4 \mp k^2, \quad (5.42)$$

which is positive in the band of wave vectors $0 < k < 1$ for $T < T_c$, and is always negative for $T > T_c$. When $T < T_c$, σ_ϕ is the usual expression for spinodal decomposition of a symmetric binary alloy, and in the absence of nonlinear elastic effects, complete phase separation of the two components results. The most unstable wave vector is $k_m^\phi = 1/\sqrt{2}$, and $\sigma_\phi(k_m^\phi) = 1/4$. We plot σ_h and σ_ϕ in Fig. 5.1(a) for $T < T_c$.

When only the substrate misfit is present ($\varepsilon^* \neq 0$, $\eta^* = 0$), the equations are still decoupled, and we recover the result of Asaro and Tiller [69] for the surface dispersion,

$$\sigma_h = \varepsilon^{*2} k^3 - \gamma^* k^4. \quad (5.43)$$

The misfit induces a surface instability, since σ_h is positive in the region $0 < k < \varepsilon^{*2}/\gamma^*$, with the maximum in the dispersion at $k_m^h = (3/4) \varepsilon^{*2}/\gamma^*$, and $\sigma_h(k_m^h) = (27/256) \varepsilon^{*8}/\gamma^{*3}$. The dispersion for ϕ is the same as Eq. (5.42) (see Fig. 5.1(b)).

In the absence of a misfit but in the presence of a nonzero solute expansion coefficient ($\varepsilon^* = 0$, $\eta^* \neq 0$), the two variables are decoupled and the surface is always stable, since its dispersion is given by Eq. (5.41). For the composition, the dispersion is given by

$$\sigma_\phi = -k^4 + k^2 \left(\mp 1 + \frac{2}{3} \eta^{*2} \right). \quad (5.44)$$

Below T_c , the dispersion is now positive in $0 < k < \sqrt{1 + (2/3) \eta^{*2}}$, with a maxi-

Figure 5.1: Dispersion relations when the morphological and compositional degrees of freedom decouple. The solid lines represent the dispersion for ϕ when $T < T_c$, while the dotted lines are for h . The parameter $\gamma^* = 1$. In panel (a), $\varepsilon^* = \eta^* = 0$. In panel (b), $\eta^* = 0$, and the dotted curves from bottom to top are for $\varepsilon^* = 1, 1.25$ and 1.5 . In panel (c), $\varepsilon^* = 0$, and the solid lines from bottom to top correspond to $\eta^* = 0, 0.5$ and 1 .

mum at $k_m^\phi = (1/\sqrt{2}) (1 + (2/3) \eta^{*2})^{1/2}$. The value of the dispersion relation at the maximum is increased to $\sigma_\phi(k_m^\phi) = (1/4) (1 + (2/3) \eta^{*2})^2$, implying that the contribution due to η^{*2} increases the instability to phase separation as well as the value of the most unstable wave vector [Fig. 5.1(c)]. Above T_c , the elastic fields can induce a decomposition of the alloy since σ_ϕ can become positive if $\eta^{*2} > 3/2$. The extra term $(2/3) \eta^{*2}$ in Eq. (5.44) originates from the elastic fields generated by composition inhomogeneities at the surface that are constrained by the boundary condition on the stress tensor at the surface, and corresponds to the 3rd and 4th terms proportional to η^{*2} in Eq. (5.27).

The most interesting case for a static film corresponds to a compositionally stressed film on a mismatched substrate, because the dynamical equations are coupled due to the terms proportional to $\varepsilon^* \eta^*$. Because the variables are coupled, the dispersion relation describes the stability of both variables simultaneously. We first describe the results for $T < T_c$. In Fig. 5.2, we plot the maximum of the real part of the dispersion

Figure 5.2: Dispersion relation for the static film when h and ϕ are coupled for $T < T_c$. The misfit $\varepsilon^* = 0.75$ and $\eta^* = 3.2, 3.5, 4$ and 4.5 from bottom to top.

relations for a fixed value of ε^* but for different values of η^* . As can be seen in this figure, σ is always positive in a band of wave vectors and has two peaks: the first peak at lower k is due to η^* , while the second peak is due to the misfit ε^* . As η^* is increased, the value of σ at the first peak increases and the peak location moves to larger k . Eventually, for very large η^* (not shown in the figure), the first peak is so strong that only one peak is apparent. Except for a special case, one of the peaks will be larger than the other, and the most unstable wave vector will come from that peak. In the special case where the two peaks have the same height, the surface becomes most unstable at two wave vectors simultaneously.

When the temperature is above the critical temperature, there is a region of stability that appears in the $\varepsilon^* - \eta^*$ diagram, as shown in Fig. 5.3. It can be seen that if η^* or ε^* is too large then the coupled system is always unstable. The shape of the stability diagram implies that if the misfit is moderate, the system can be stabilized due to the elastic fields generated by the composition; if the value of η^* is not large enough, the amplitude of the compositional stresses will not be sufficient to control the instability due to the misfit. The results of the stability analysis for the static film are summarized in Table 5.1.

Figure 5.3: Stability diagram for the static film grown above the critical temperature. A joint instability occurs in the unstable region and a joint stability occurs in the stable region. The surface constant $\gamma^* = 1$.

Temperature	ε^*	η^*	surface	alloy
$T < T_c$	0	0	stable	unstable
	0	$\neq 0$	stable	unstable
	$\neq 0$	0	unstable	unstable
	$\neq 0$	$\neq 0$	joint instability	joint instability
$T > T_c$	0	0	stable	stable
	0	$\neq 0$	stable	stable if $\eta < \eta_c$
	$\neq 0$	0	unstable	stable
	$\neq 0$	$\neq 0$	see Fig. 5.3	see Fig. 5.3

Table 5.1: Summary of the stability results for the static film.

In their study, Guyer and Voorhees [76] find that for the static film, compositional strain plays no role in the instability. This is because, in their model, composition decouples from the elastic field and implies $\partial_t \phi = 0$. We believe that by appropriately including the non-equilibrium evolution of ϕ we have captured the missing ingredient to make the understanding of the problem more consistent. Glas [78] has recently calculated the equilibrium stability (in the sense of thermodynamics) of an alloy in a planar half-space whose surface is allowed to deviate from planarity. There, it is found that the state that minimizes the energy consists of a joint modulation of the composition and of the free surface, even if the alloy is stable against decomposition in bulk form. The dynamical analysis presented in the present paper suggests that the equilibrium state may not always be kinetically accessible since there exists combinations of the misfit, the solute expansion coefficient and the temperature for which stabilization occurs.

5.5 Results for growing films

When the film is growing, the growth parameter V becomes important in determining the stability. Again, when $\varepsilon^* = 0$ or $\eta^* = 0$, the dynamical equations for h and ϕ decouple and each variable has its own dispersion relation; in the general case where both ε^* and η^* are non-zero, the variables are coupled and their time evolution is governed by the same dispersion relation.

To establish basic results, we start by describing a perfectly matched film with constituents of the same size ($\varepsilon^* = \eta^* = 0$). Here, the surface is always stable, since there are no compositionally generated stresses and no misfit. The dispersion relation for h is given by Eq. (5.41). Because there is a competition between the constant deposition of material of fixed average composition and the formation of phase separated domains at the surface, the growth rate V can be used to stabilize the homogeneous mixture. This can be seen in the dispersion relation for ϕ , which reads

$$\sigma_\phi = -k^4 \mp k^2 - V. \quad (5.45)$$

For the positive sign, the dispersion relation is positive in the band $1 - \sqrt{1 - 4V} < 2k^2 < 1 + \sqrt{1 - 4V}$, provided that the growth rate $V < 1/4$. Hence, if $V > 1/4$, the

Figure 5.4: Dispersion relation for ϕ in the case of the uncoupled growing film when $T < T_c$. In (a), we plot the dispersion relation when $\eta^* = \varepsilon^* = 0$ for (bottom to top) $V = 0.5, 0.25$ and 0.1 . In (b), $\eta^* = 1, \varepsilon^* = 0$ and the curves from bottom to top correspond to $V = 1, 0.5$ and 0.1 .

constant deposition is too strong for the phase separation, and the alloy is stabilized against decomposition. This implies that there exists a critical growth rate V_c above which the film will be homogeneous in composition. As shown in chapter 4, when the growth parameter is below $1/4$, a top view of the system shows lamellar or droplet concentration patterns in the steady-state. We plot σ_ϕ in Fig. 5.4(a). When the negative sign is taken in Eq. (5.45), the alloy is always stable against decomposition.

If the film is mismatched but $\eta^* = 0$, the surface is unstable due to the Asaro and Tiller instability [69] and its dispersion is given by Eq. (5.43), while the composition is unaffected by the misfit and Eq. (5.45) is still valid. The most unstable wave vectors are in general different for the instabilities in h and ϕ , which means that at early times, the size of concentration domains will be uncorrelated to the size of surface perturbations.

The surface of a matched film ($\varepsilon^* = 0$) in the presence of both the deposition process and the compositional stresses is always stable, since $\sigma_h = -\gamma^* k^4$. The stability around the average composition is described by the solutions to a cubic equation

Figure 5.5: Critical growth rate as a function of the solute expansion coefficient for (a) $T < T_c$ and (b) $T > T_c$. For $V > V_c$ the system is stable.

in σ_ϕ ,

$$\left[\sigma_\phi + k^2(k^2 \pm 1) + V \right] (\sigma_\phi + kV)^2 - \frac{2}{3} k^2 \eta^{*2} \sigma_\phi (\sigma_\phi + 4kV) = 0. \quad (5.46)$$

In Fig. 5.4(b), we plot σ_ϕ as a function of k for different values of V and η^* for temperatures inside of the miscibility gap. As can be seen in this figure, the band of wave vectors where σ_ϕ is positive decreases in size as V is increased. For V large enough, σ_ϕ is always negative, implying that the homogeneous alloy is stable. The critical growth rate introduced earlier now depends on η^* as shown in Fig. 5.5. As an indication, we find that for $T < T_c$, V_c increases roughly as η^{*2} over the range plotted [Fig. 5.5 (a)]. For temperatures outside of the miscibility gap, there is a range of η^* , $0 < \eta^* < 1$ where the alloy is stable at any growth rate [Fig. 5.5 (b)]. Note that when $\varepsilon^* = 0$ and $\eta^* = 0$ the alloy is always stable against decomposition (see Eq. (5.45)). If $\eta^* > 1$ and $T > T_c$, alloy decomposition occurs at low growth rates and is suppressed at high growth rates, as shown in Fig. 5.5 (b).

For most situations, none of the parameters vanish, and the two variables are always coupled. In Fig. 5.6, we plot σ as a function of the wave vector amplitude for various combinations of the parameters ε^* , η^* and V for $T < T_c$. In Fig. 5.6(a), we

Figure 5.6: Dispersion relation for the growing film when h and ϕ are coupled when $T < T_c$. (a) $\varepsilon^* = 0.1$, $\eta^* = 0.5$. From bottom to top: $V = 0.6, 0.34$ and 0.25 . (b) $\varepsilon^* = 0.1$, $V = 0.34$. From bottom to top: $\eta^* = 0.25, 0.5$ and 0.75 . (c) $\eta^* = 0.5$, $V = 0.4$. From bottom to top: $\varepsilon^* = 0.1, 0.5$ and 1 .

Figure 5.7: Stability diagram for the growing film when $\gamma^* = 1$ and for composition independent elastic moduli when $T < T_c$. The dashed (solid) lines are for $\eta^* = 0.5$ ($\eta^* = 1$). The vertical solid and dashed lines overlap for $V > 1.06$. The inset shows the dispersion relation for different values of the misfit and the growth rate for $\eta^* = 0.5$. Bottom to top: $(\varepsilon^*, V) = (0.1, 0.5)$, $(0.1, 0.2)$ and $(0.3, 0.5)$. The stability diagram can be interpreted for $T > T_c$ if the threshold growth rate is taken from Fig. 5.5.

plot σ for fixed values of ε^* and η^* but for different growth velocities, showing that as V is increased, σ becomes negative for all k when $V > V_c$. Note however, that the location of the maximum does not change much with V . If V and ε^* are fixed while η^* is increased [Fig. 5.6(b)], the coupled system goes from stable to unstable, and the location of the maximum increases with η^* as discussed in previous cases. The effects of the misfit ε^* on the stability are shown in Fig. 5.6(c). There is a maximum value for ε^* , $\varepsilon_{\max}^*$ above which the system is unstable. Below this maximum misfit, the deposition is strong enough to control the compositional gradients generated by the intrinsic phase separation and by the surface instability, but as the misfit is increased the instability driven by ε^* becomes stronger than the deposition. The value of $\varepsilon_{\max}^*$ depends only on the surface tension γ^* : $\varepsilon_{\max}^* \sim \gamma^{*1/2}$. In Fig. 5.7, we plot a stability diagram for the coupled system, showing the stable and unstable regions. The shape of the stability diagram is generic for the alloy grown either above or below the critical

Temperature	ε^*	η^*	surface	alloy
$T < T_c$	0	0	stable	stable if $V > V_c$
	0	$\neq 0$	stable	stable if $V > V_c(\eta)$
	$\neq 0$	0	unstable	stable if $V > V_c$
	$\neq 0$	$\neq 0$	see Fig. 5.7	see Fig. 5.7
$T > T_c$	0	0	stable	stable
	0	$\neq 0$	stable	stable if $V > V_c(\eta)$
	$\neq 0$	0	unstable	stable
	$\neq 0$	$\neq 0$	see Fig. 5.7	see Fig. 5.7

Table 5.2: Summary of the stability results for the growing film.

temperature since we find that the maximum misfit is independent of whether T is above or below T_c and the critical velocity boundary is horizontal in both cases. The stability diagram can be interpreted for any value of the temperature if the value of the threshold velocity is taken from Fig. 5.5. A summary of our results is presented in Table 5.2.

From a step-flow growth model, Tersoff [73] concluded that alloy decomposition can never stabilize a growing mismatched surface, independently of the sign of the misfit. Our work indicates that stabilization is possible by appropriately choosing the growth rate, since the constant deposition of material competes with the alloy decomposition. Furthermore, the results for the static films presented in this chapter follow naturally from our general model for the growing alloy by taking the limit of zero growth rate, in contrast to the step-flow model [73] which is inapplicable as $V \rightarrow 0$.

5.6 Composition dependent Young's modulus

In this section, we extend the calculations above to include a linear dependence of Young's modulus on the order parameter. We write $E = E_0 + E_1\phi$ and assume that the shear modulus is constant, $M = M_0$. Taking E and M as the two independent elastic moduli, the Poisson ratio is $\nu = \nu_0 + \nu_1\phi$ with $\nu_0 = (E_0 - 2M_0) / (2M_0)$ and

$\nu_1 = (E_1/E_0)(1 + \nu_0)$. The first order stress tensor is

$$\hat{\sigma}_{ij} = 2M_0 \left[\left(\frac{\nu_0}{1 - 2\nu_0} \right) \hat{\mu}_{il} \delta_{ij} + \hat{\mu}_{ij} - \frac{1 + \nu_0}{1 - 2\nu_0} \theta \hat{\phi} \delta_{ij} \right], \quad (5.47)$$

with $\theta = \eta + 2(E_1/E_0)\varepsilon/(1 - \nu_0)$ a new effective solute expansion coefficient. The elastic energy is now

$$\hat{\mathcal{E}} = \bar{\sigma} \left\{ \hat{\mu}_{xx} + \hat{\mu}_{yy} - 2[\eta - (E_1/E_0)\varepsilon/(1 - \nu_0)] \hat{\phi} \right\} \quad (5.48)$$

and

$$\tilde{\mathcal{E}} = \bar{S}_{ijkl} \hat{\sigma}_{ij} \hat{\sigma}_{kl} + \hat{S}_{ijkl} \bar{\sigma}_{ij} \hat{\sigma}_{kl}. \quad (5.49)$$

Elimination of the displacement vector through the mechanical equilibrium equations leads to (to first order in E_1)

$$\hat{\mathcal{E}} = \frac{E_0 \varepsilon}{1 - \nu_0} \left[-2\varepsilon(1 + \nu_0) q \hat{h} - 2 \left(\theta \left(\frac{\nu_0 q v - \Omega}{q v + \Omega} \right) - \frac{E_1}{E_0} \frac{\varepsilon}{1 - \nu_0} \right) \hat{\phi} \right] \quad (5.50)$$

and

$$\begin{aligned} \tilde{\mathcal{E}} = & \frac{E_0}{1 - \nu_0} \left\{ \left(\eta^2 + 4\varepsilon \eta \frac{E_1}{E_0} \right) \left[1 - 2 \left(\frac{1 + \nu_0}{1 - \nu_0} \right) \Omega \left(\frac{\nu \Omega + q v}{(\Omega + q v)^2} \right) \right] \hat{\phi}^2 \right. \\ & + \frac{4\varepsilon \eta}{1 - \nu_0} \frac{E_1}{E_0} \left(\frac{\nu_0 q v - \Omega}{q v + \Omega} \right) \hat{\phi}^2 \\ & + q \hat{h} \hat{\phi} \left[\left(-2\varepsilon \eta (1 + \nu_0) - 4\varepsilon^2 \frac{E_1}{E_0} \frac{1 + \nu_0}{1 - \nu_0} \right) \left(\frac{3\Omega - q v}{\Omega + q v} \right) \right. \\ & \left. \left. + 4\varepsilon^2 \frac{E_1}{E_0} \frac{1 + \nu_0}{1 - \nu_0} \right] \right\} \quad (5.51) \end{aligned}$$

For $\nu_0 = 1/4$, the rescaled dynamical equations are ($E_1^* = E_1/E_0$ and $T < T_c$)

$$\partial_\tau \hat{h} = -k^2 \left\{ -\varepsilon^{*2} k \hat{h} - \left[\frac{1}{5} \varepsilon^* \eta^* \left(\frac{kV - 4\sigma}{kV + \sigma} \right) + \frac{2}{5} E_1^* \varepsilon^{*2} \left(\frac{3kV - 2\sigma}{kV + \sigma} \right) \right] \hat{\phi} + \gamma^* k^2 \hat{h} \right\} \quad (5.52)$$

and

$$\begin{aligned} \partial_\tau \hat{\phi} = & -k^2 \left[-1 + k^2 + \frac{V}{k^2} - \frac{2}{3} (\eta^{*2} + 4\varepsilon^* \eta^* E_1^*) \sigma \frac{\sigma + 4kV}{(\sigma + kV)^2} \right. \\ & \left. + \frac{32}{15} \varepsilon^* \eta^* E_1^* \left(\frac{kV - \sigma}{kV + \sigma} \right) \right] \hat{\phi} \\ & + k^3 \left[\left(\varepsilon^* \eta^* + \frac{8}{3} E_1^* \varepsilon^{*2} \right) \left(\frac{3\sigma - kV}{\sigma + kV} \right) - \frac{8}{3} E_1^* \varepsilon^{*2} \right] \hat{h}. \quad (5.53) \end{aligned}$$

It can be seen in these equations that the composition dependence of E introduces

Figure 5.8: Stability diagram for the growing film when $\gamma^* = 1$ with a composition dependent Young's modulus ($E_1^* = 1$, $\eta^* = 0.5$ and $T < T_c$).

non-trivial dynamical terms and a dependence on the sign of the misfit ε^* . The dependence on the sign of ε^* can be understood as follows: for example, a film under compression with $\eta^* > 0$ would be less unstable for $E_1^* < 0$ since the larger atoms are easier to compress. It can also be noted that even in the absence of η^* the variables are coupled due to the terms in E_1^* . The new stability diagram for the growing film is presented in Fig. 5.8, showing that the maximum misfit is still present and the asymmetry when the sign of the misfit is reversed.

5.7 Conclusion

In this chapter, we have shown that a proper description of static or growing solid films requires considerations of the non-equilibrium nature of the surface diffusion. We obtained coupled dynamical equations for the local composition of the alloy and for the surface profile. The most important conclusion in our work is that, in general, the composition and surface height variables are coupled, implying that a film with a stable (unstable) planar surface is also stable (unstable) against decomposition of the alloy. Another important conclusion is the fact that the stability is independent of the

sign of the mismatch between the film and the substrate when the elastic moduli are independent of composition. This symmetry can be broken if the Young's modulus of the alloy constituents depends on composition. A planar film with the appearance of modulations perpendicular to the growth direction can be obtained if the film is perfectly matched to the substrate. For the unstable surfaces, our calculations suggest that the mode with the most unstable wavenumber will grow faster. However, this does not necessarily mean that a film of arbitrary thickness will show modulations of wavenumber q_m . In fact, nonlinear effects become important on a thickness scale $V\sigma_m^{-1}$, where a possible crossover from q_m to a steady-state wavenumber can occur. Of course, the large stress concentrations at this point may also lead to the formation of dislocations.

Chapter 6

SUMMARY

The order of the chapters in this thesis represents a chronological evolution in our understanding of composition modulations during film growth. The earliest work presented in this thesis (chapter 2) is concerned with simple Monte Carlo simulations of binary alloys grown from directed beams. One of the goals in this research was to try to verify the claim that surface phase separation is sufficient and necessary to explain the experimental observations of composition modulations. To test this claim and to get a feel for the kind of behavior that these systems exhibit, we performed Monte Carlo simulations of simplified interaction potentials (i.e. no elastic fields); these interaction potentials are enough however to produce a phase transition between a homogeneous phase and a phase-separated state. Hence, the combination of a surface temperature below the critical point for phase separation and of negligible bulk diffusion enabled us to study *surface*-induced spinodal decomposition in equiatomic alloys, and its competition with the incoming atomic beam. The experimentally observed lamellar composition modulations were reproduced in our simulations, as well as the temperature dependence of the modulation wavelength. It is also suggested that the deposition rate is an important parameter that controls the wavelength and the amplitude of the compositional patterns. Furthermore, the simplified model showed important nontrivial properties, such as the unusual temperature dependence of the surface width and the appearance of surface modulations, both of which are related to the compositional effects. The results of this chapter established two main themes

of this thesis: (i) the coupling between the surface morphology and the composition, and (ii) the competition between the constant deposition of particles and the phase separation, and hence, the importance of the deposition rate in controlling the film microstructure.

The next approach to the problem was to analyze the deposition process using a long-wavelength description. The point was to propose non-equilibrium equations for the dynamical evolution of the composition field and of the surface morphology, and verify theoretically and numerically if this coarse-grained model has the same universal properties as the Monte Carlo model of chapter 2. For this purpose, only the essential properties (surface phase separation, surface tension and deposition) were included in the continuum model, leading to excellent agreement with the Monte Carlo results. In particular, a critical deposition rate emerged below which the system is unstable, and above which the system is stable against spinodal decomposition. In the unstable regime, the alloy film was shown to reach a steady-state consisting of compositional lamellar patterns coupled with a modulation of the surface profile. Analytical calculations demonstrated that the constant deposition of material can be regarded as a long-range interaction; this long-range interaction competes with the short-range chemical interaction favoring phase separation, leading to the formation of morphologically/compositionally patterned films. Also, the wavelength of the modulation was obtained as a function of the deposition rate, in good agreement with the results of chapter 2. Expressions for the modulation wavelength in terms of material parameters were also provided, and yielded values in the range observed experimentally. Hence, this basic model is suited to describe real systems, and gives results very similar to the (more) microscopic Solid-on-Solid model. Since elastic effects are easier to incorporate in a long-wavelength theory, the continuum model of chapter 3 served as the basis for the work presented in chapters 4 and 5.

In nearly all alloys, the lattice constants and the elastic constants of the alloy elements are different, causing displacements of the atoms around their equilibrium position when the different atomic species are mixed to form the alloy. In our continuum model, these effects were taken into account by using linear elasticity theory, and constitute the next level of complexity added to the problem. The emphasis was

to consider the effects of elastic fields generated by the composition, and therefore, the fluctuations of the surface were neglected. This approximation implies that the alloy layer is exactly matched to the substrate, thereby suppressing the formation of long-wavelength surface deformations due to the film/substrate mismatch, and that the beam is of very good quality so that the fluctuations in the local deposition rate are negligible. The relevant time scales are therefore the diffusion of material at the surface and the equilibration of the elastic displacements around the local lattice positions. Since the latter is much smaller than the former, we assumed that mechanical equilibrium is instantaneously satisfied in order to adjust to the composition variations. This enabled us to eliminate the displacement in favor of the composition, leading to an effective long-range contribution to the free energy. This new contribution turned out to be crucial in determining the composition pattern in the late stages of growth. In particular, a new droplet phase appeared due to the elastic contribution to the energy.

As stated above, the lamellar patterns seen in the absence of elastic fields originate from the competition between the short-range chemical interaction and the long-range effect of the deposition process. With the inclusion of the elastic fields due to composition inhomogeneities, there is now a competition between the short-range chemical interactions and *two* long-range forces, the deposition and the elastic effects. Hence, the deposition rate is no longer sufficient to predict the type and the wavelength of the patterns formed, since the strength of the elastic fields must also be considered. The wavelength of the modulation was computed from numerical simulations and compared to the results from chapter 3, and it was found that the elastic fields always decrease the wavelength for a given deposition rate. The major conclusion from chapter 4 is that the elastic fields can drastically alter the composition morphology in the long-time limit. The essential properties to see these changes are composition-dependent lattice constants and shear moduli.

The studies presented in chapters 2, 3 and 4 were mainly concerned with the long-time behavior of growing films, i.e. when the composition and surface fields have reached a steady-state. Two assumptions related to the earlier time behavior were implicit in these studies: (i) the alloy is unstable against decomposition at the growth

temperature and composition and (ii) the surface of the homogeneous alloy film is stable against long-wavelength fluctuations. The first assumption implies that the alloy is always grown inside of the miscibility gap and that the surface deformations do not affect this characteristic. The most important implication of the second assumption is that there is no misfit between the film and the substrate, preventing the spontaneous formation of islands at the surface. Chapter 5 of this thesis considered the stability of the alloy layer against simultaneous surface deformations and composition fluctuations from a non-equilibrium perspective. The results of the stability analysis support the assumptions made in the previous chapters, namely that the composition and the surface morphology are decoupled in the early stages of growth of *matched* films. The important new findings were that in the presence of misfit, there is a joint stability/instability of the layer against simultaneous decomposition and surface deformations. Hence, a film grown *outside* of the miscibility gap can still decompose due to the elastic fields created by the misfit between the film and the substrate. The work presented in chapter 5 also suggests a very intuitive explanation of the experimentally observed asymmetry in the stability of tensile and compressed films, based on the difference in the elastic constants of the alloy elements.

In conclusion, we presented in this thesis important new theoretical results related to the epitaxial growth of alloy films by non-equilibrium deposition techniques. The contributions in this thesis have been formulated in order to include the generic properties of modern device materials, and should be applicable to a variety of growth methods and compounds. Both the fundamental physical principles and implications for material processing were discussed.

Extensions of the work presented in this thesis are numerous. A direct extension of the results of chapter 5 would be a study of the nonlinear and steady-state behaviors of the joint alloy decomposition and surface deformation. The important question is to determine when the composition and the morphology propagate as standing waves or travelling waves on the surface, in terms of material and growth parameters. This would shed light on the experimental observation of lateral and vertical phase separation in experiments, since the lateral motion of islands on the surface can create vertical separation, while a standing wave propagation would give lateral phase

separation.

Another outstanding issue is the simultaneous alloy decomposition and atomic ordering observed during the growth of many alloys [79]. The interest in this problem is three-fold: (i) the mechanisms responsible for the propagation of order must be identified, and the relationships between ordering, composition and morphology must be established, consistent with experimental observations; (ii) the stability of the layer against simultaneous ordering, decomposition and surface deformations has to be considered; (iii) the long-time evolution of the growing film in terms of morphology, ordering and the appearance of microscopic or macroscopic phase separation is of interest.

In terms of device applications, one of the important issues is the behavior of dislocations. In some devices, the growing layer must remain strained, and the appearance of dislocations has to be prevented, while for other applications, the strain must be relieved by the introduction of dislocations. Hence, the nucleation, propagation and distribution of dislocations in relation with the composition of alloy films is a very interesting research area. The effects of dislocations on the composition modulations and vice versa are possible extensions of the work in this thesis [80].

Finally, this thesis was mainly concerned with growth processes far from equilibrium, as in MBE. Many other growth processes are used to grow thin films, such as LPE and CVD, and appropriate modifications of the theory in this thesis could be used to predict which growth method is preferable to obtain particular alloy properties.

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Appendix A

Derivation of the effective free-energy functional

In this appendix to chapter 4, we show how the displacement vector can be obtained in terms of the order parameter using the mechanical equilibrium condition, and derive the effective free-energy functional as a function of ϕ only. Note that our model for thin film growth is strictly two-dimensional, and therefore, we do not put restrictions on the stress components in the normal direction at the free surface. We start with the expression for the stress tensor

$$\sigma_{ij} = \frac{\delta \mathcal{F}}{\delta \mu_{ij}} = [\alpha \phi + K \nabla \cdot \mathbf{u} + B \mu_{ii}] \delta_{ij} + 2M \left(\mu_{ij} - \frac{\delta_{ij}}{d} \nabla \cdot \mathbf{u} \right). \quad (\text{A.1})$$

(Note that repeated indices do not imply summations and that in the anisotropy term $B \mu_{ii}$, the repeated index i is not summed). The mechanical equilibrium condition is

$$\sum_j \nabla_j \sigma_{ij} = \nabla_i [\alpha \phi + K \nabla \cdot \mathbf{u}] + B \nabla_i \mu_{ii} + 2M \sum_j \nabla_j \left(\mu_{ij} - \frac{\delta_{ij}}{d} \nabla \cdot \mathbf{u} \right) = 0, \quad (\text{A.2})$$

which can be written as

$$(K + M - 2M/d) \nabla_i \nabla \cdot \mathbf{u} + B \nabla_i^2 u_i + M \nabla^2 u_i + \alpha \nabla_i \phi = 0. \quad (\text{A.3})$$

The goal of our scheme is to calculate u_i in terms of ϕ to *first order* in K_1 , M_1 and B_1 . To do so, we write $\mathbf{u} = \mathbf{u}^0 + \mathbf{u}^1$, where $\mathbf{u}^1$ is of $\mathcal{O}(K_1, M_1, B_1)$. To zeroth order in the coefficients M_1 , K_1 and B_1 , we have

$$(K_0 + M_0 - 2M_0/d) \nabla \nabla \cdot \mathbf{u}^0 + M_0 \nabla^2 \mathbf{u}^0 + \alpha \nabla \phi = 0, \quad (\text{A.4})$$

which can be solved for $\nabla \cdot \mathbf{u}^0$ by taking an extra divergence:

$$\nabla^2 \nabla \cdot \mathbf{u}^0 = -\frac{\alpha}{C_0} \nabla^2 \phi, \quad (\text{A.5})$$

with the definition $C_0 = K_0 + 2M_0(1 - 1/d)$. The general solution of this Poisson equation consists of a linear combination of the particular solution and the solution to the Laplace equation. Because of the periodic boundary conditions, the compression $\nabla \cdot \mathbf{u}^0$ and its first derivative are continuous at the boundaries, implying that the solution to the Laplace equation is zero everywhere. Hence, the solution for $\nabla \cdot \mathbf{u}^0$ is

$$\nabla \cdot \mathbf{u}^0 = -\frac{\alpha}{C_0} \phi. \quad (\text{A.6})$$

Substitution of this expression for $\nabla \cdot \mathbf{u}^0$ in Eq. (A.4) gives

$$u_i^0 = -\frac{\alpha}{C_0} \nabla_i W \quad (\text{A.7})$$

where W is obtained from

$$\nabla^2 W = \phi. \quad (\text{A.8})$$

To this lowest order, substitution into Eq. (4.1) leads to $\mathcal{F}_{el}[\phi] = \int d\mathbf{x} f_0$ with

$$f_0 = -\frac{\alpha^2}{2C_0} \phi^2 \quad (\text{A.9})$$

(integration by parts is necessary to obtain this result). We now proceed to calculate the corrections $\mathbf{u}^1$ due to the anisotropy and the difference in elastic moduli between the two phases. We separately calculate these corrections in order to make the derivations more transparent.

Corrections due to the anisotropy

To first order in B_1 , $\mathbf{u}^1$ satisfies the equation

$$(K_0 + M_0 - 2M_0/d) \nabla_i \nabla \cdot \mathbf{u}^1 + B_1 \nabla_i^2 u_i^0 + M_0 \nabla^2 u_i^1 = 0, \quad (\text{A.10})$$

with a solution

$$\nabla \cdot \mathbf{u}^1 = \frac{\alpha \xi M_0}{C_0^2} \phi - \frac{\alpha \xi M_0}{C_0^2} \frac{1}{\nabla^2} \sum_{i \neq j} \nabla_i^2 \nabla_j^2 \frac{1}{\nabla^2} \phi. \quad (\text{A.11})$$

In this last equation, the operator $\frac{1}{\nabla^2}$ represents the inverse laplacian. Substitution of Eq. (A.11) in Eq. (A.10) leads to

$$u_i^1 = \frac{\alpha \xi M_0}{C_0^2} \nabla_i \frac{1}{\nabla^2} \phi - \frac{\alpha \xi M_0}{C_0^2} \nabla_i \frac{1}{\nabla^4} \sum_{i \neq j} \nabla_i^2 \nabla_j^2 \frac{1}{\nabla^2} \phi, \quad (\text{A.12})$$

which is clearly first order in the anisotropy ξ . With the displacement vector determined as a function of ϕ , we can substitute it back in the elastic free-energy functional and obtain an effective free-energy functional in terms of ϕ only. We write the free-energy density as $f_{el} = f_0 + f_\xi$, with f_ξ of $\mathcal{O}(\xi)$. To calculate f_ξ , notice that

mechanical equilibrium requires $\frac{\delta \mathcal{F}}{\delta u_i} = 0$, implying that

$$f_\xi = \frac{1}{2} B_1 \sum_i \mu_{ii}^2 = \frac{\alpha^2 \xi M_0}{2C_0^2} \phi^2 - \frac{\alpha^2 \xi M_0}{2C_0^2} \sum_{i \neq j} (\nabla_i \nabla_j W)^2. \quad (\text{A.13})$$

Corrections due to the difference in the bulk moduli

In this case, $\mathbf{u}^1$ is of $\mathcal{O}(K_1)$ and is a solution of

$$(K_0 + M_0 - 2M_0/d) \nabla_i \nabla \cdot \mathbf{u}^1 + M_0 \nabla^2 u_i^1 + K_1 \phi \nabla_i \nabla \cdot \mathbf{u}^0 = 0. \quad (\text{A.14})$$

Again, taking the divergence of this equation yields

$$\nabla \cdot \mathbf{u}^1 = \frac{\alpha K_1}{C_0^2} \phi^2 \quad (\text{A.15})$$

and

$$u_i^1 = \frac{\alpha K_1}{C_0^2} \nabla_i \frac{1}{\nabla^2} \phi^2. \quad (\text{A.16})$$

The correction to the elastic energy is

$$f_{K_1} = \frac{1}{2} K_1 \phi (\nabla \cdot \mathbf{u}^0)^2 = \frac{1}{2} \frac{\alpha^2 K_1}{C_0^2} \phi^3. \quad (\text{A.17})$$

In the main text, we combine f_0 and f_{K_1} , and use the quadratic form $-\alpha \phi^2/2C$ with $C = K + 2M_0(1 - 1/d)$.

Corrections due to the difference in the shear moduli

Here, $\mathbf{u}^1 \sim \mathcal{O}(M_1)$ satisfies

$$(K_0 + M_0 - 2M_0/d) \nabla_i \nabla \cdot \mathbf{u}^1 + M_0 \nabla^2 u_i^1 + M_1 \phi \nabla^2 u_i^0 + M_1 \nabla_i \nabla \cdot \mathbf{u}^0 = 0, \quad (\text{A.18})$$

which gives

$$\nabla \cdot \mathbf{u}^1 = \frac{2\alpha M_1}{C_0^2} \frac{1}{\nabla^2} \nabla_i \nabla_j \left[\phi \left(\nabla_i \nabla_j W - \frac{\delta_{ij}}{d} \phi \right) \right] \quad (\text{A.19})$$

and

$$u_i^1 = \frac{2\alpha M_1}{C_0^2} \nabla_i \frac{1}{\nabla^4} \nabla_i \nabla_j \left[\phi \left(\nabla_i \nabla_j W - \frac{\delta_{ij}}{d} \phi \right) \right]. \quad (\text{A.20})$$

The contribution to the elastic energy of order M_1 is

$$f_{M_1} = M_1 \phi \sum_{i,j} \left(\mu_{ij}^0 - \frac{\delta_{ij}}{d} \nabla \cdot \mathbf{u}^0 \right)^2 = \frac{M_1 \alpha^2}{C_0^2} \phi \sum_{i,j} \left(\nabla_i \nabla_j W - \frac{\delta_{ij}}{d} \phi \right)^2. \quad (\text{A.21})$$