Epitaxial Growth Dynamics in Gallium Arsenide

by

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Abstract

The problem of a complete theory describing the far-from-equilibrium statistical mechanics of epitaxial crystal growth remains unsolved. Besides its academic importance, this problem is also interesting from the point of view of device manufacturing. In order to improve on the quality and performance of lateral nanostructures at the lengthscales required by today's technology, a better understanding of the physical mechanisms at play during epitaxial growth and their influence on the evolution of the large-scale morphology is required. In this thesis, we present a study of the morphological evolution of GaAs (001) during molecular beam epitaxy by experimental investigation, theoretical considerations and computational modeling. Experimental observations show that initially rough substrates smooth during growth and annealing towards a steady-state interface roughness, as dictated by kinetic roughening theory. This smoothing indicates that there is no need for a destabilizing step-edge barrier in this material system. In fact, generic surface growth models display a much better agreement with experiments when a weak, negative barrier is used. We also observe that surface features grow laterally, as well as vertically during epitaxy. A growth equation that models smoothing combined with lateral growth is the nonlinear, stochastic Kardar-Parisi-Zhang (KPZ) equation. Simulation fits match the experimentally observed surface morphologies quite well, but we argue that this agreement is coincidental and possibly a result of limited dynamic range in our experimental measurements. In light of these findings, we proceed by developing a coupled growth equations (CGE) model that describes the full morphological evolution of both flat and patterned starting surfaces. The resulting fundamental model consists of two coupled, spatially dependent rate equations that describe the interaction between diffusing adatoms and the surface through physical processes such as adatom diffusion, deposition, and incorporation and detachment at step edges. In the low slope, small amplitude limit, the CGE model reduces to a nonlinear growth equation similar to the KPZ equation. From this, the apparent applicability of the KPZ equation to surface shape evolution is explained. The CGE model is based on fundamental physical processes, and can therefore explain the un-
derlying physics, as well as describe macroscopic pattern evolution during growth.
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>( \alpha )</td>
<td>roughness exponent: ( W_{\text{sat}} \sim L^\alpha ); also adatom-to-adatom incorporation coefficient</td>
</tr>
<tr>
<td>( a_{</td>
<td></td>
</tr>
<tr>
<td>( a_{\perp} )</td>
<td>monolayer height</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscope</td>
</tr>
<tr>
<td>( \beta )</td>
<td>growth exponent: ( W \sim t^\beta ), ( t ) small; also adatom-to-step-edge incorporation coefficient</td>
</tr>
<tr>
<td>BCF</td>
<td>Burton-Cabrera-Frank</td>
</tr>
<tr>
<td>CGE</td>
<td>coupled growth equation</td>
</tr>
<tr>
<td>( d )</td>
<td>spatial dimension index</td>
</tr>
<tr>
<td>( D, D_0 )</td>
<td>diffusion constant, diffusion constant prefactor</td>
</tr>
<tr>
<td>( D^s )</td>
<td>single particle diffusion constant</td>
</tr>
<tr>
<td>( \eta(x,t) )</td>
<td>stochastic, random Gaussian deposition noise</td>
</tr>
<tr>
<td>( E_{\text{act}} )</td>
<td>surface activation energy</td>
</tr>
<tr>
<td>( E_{\text{es}} )</td>
<td>ES potential barrier</td>
</tr>
<tr>
<td>( E_{\text{lat}} )</td>
<td>lateral activation energy</td>
</tr>
<tr>
<td>( E_{\text{sub}} )</td>
<td>substrate binding energy</td>
</tr>
<tr>
<td>ES</td>
<td>Ehrlich-Schwöbel</td>
</tr>
<tr>
<td>EW</td>
<td>Edwards-Wilkinson</td>
</tr>
<tr>
<td>( F )</td>
<td>flux term or growth rate of surface</td>
</tr>
<tr>
<td>( \Gamma_n, \Gamma_c )</td>
<td>(Non-)conservative noise</td>
</tr>
<tr>
<td>( \mathcal{G} )</td>
<td>prefactor in continuum growth equations</td>
</tr>
<tr>
<td>( h )</td>
<td>Planck's constant, surface height</td>
</tr>
<tr>
<td>HE</td>
<td>hydrogen etched</td>
</tr>
</tbody>
</table>
List of Notation

\( \mathcal{H} \) ........ spatial Fourier transform of the surface height, \( h \)
\( j \) ........ net current of surface adatoms
\( \kappa \) ........ coefficient of linear fourth-order term in Mullins' equation
\( k_B \) ....... Boltzmann's constant
\( K \) ........ step edge release rate
KMC ........ kinetic Monte Carlo
KPZ .......... Kardar-Parisi-Zhang
KS .......... Kuramoto-Sivashinsky
\( \lambda \) ....... coefficient of non-linear term in KPZ equation
\( \Lambda_{1,3} \) ........ coefficient of non-linear term in Das Sarma equation
\( \Lambda_{2,2} \) ........ coefficient of non-linear term in Villain equation
\( l \) ........ terrace width
\( l_{es} \) ........ Ehrlich-Schwöbel length
\( l^* \) ........ terrace width for which the adatom current is zero
\( \mu \) ........ chemical potential
MBE ........ molecular beam epitaxy
ML .......... monolayer
\( \nu \) ....... coefficient for surface relaxation term in EW
PSD ........ power spectral density
\( q \) ........ spatial frequency
\( p, P, n \) .... adsorbate particle density; \( also \) lattice site occupation probability
RHEED ........ reflection high energy electron diffraction
\( R_{inc} \) ........ incorporation radius
SOS ........ solid-on-solid
t, \( \Delta t \) .... time, time increment
TD ........ thermally desorbed
\( \tau_{des} \) ........ average time between adatom desorption events
\( \theta_j \) ........ filling of \( j^{th} \) layer
\( W \) ........ interface width given by rms fluctuation
\( (x, y) \) .... surface coordinates
\( z \) ........ dynamic exponent: \( z = \alpha/\beta \)
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¹Deceased.
Chapter 1

Introduction

The shape of the growth surface is a basic property of epitaxial films that contains information about the atomic scale processes which take place during growth by molecular beam epitaxy (MBE). Theoretical investigations have shown that in the long wavelength and small amplitude limit, surface shape evolution during growth can be described by continuum equations whose terms reflect the underlying microscopic processes. The asymptotic scaling behaviour of various possible growth equations has been studied extensively theoretically, with both analytical and numerical methods. Similarly, experimentalists have attempted to verify the theoretically predicted growth exponents and scaling behaviour in real systems. However, experimental studies of scaling are inevitably limited by practical constraints, such as rather small ranges of time and distance, so that accurate measurements of growth exponents are difficult to achieve. As a result, there are few, if any, experimental studies that have been successful in using scaling analysis to show a quantitative match between experimentally grown surfaces and simulated surfaces based on theoretical growth models.

We have investigated the morphology of single crystal semiconductor surfaces during epitaxial growth and attempted a qualitative understanding along with a quantitative model of its evolution. Having such a model is important for many reasons. From a technological point of view, it allows fabrication of lateral nanostructures by epitaxy. It also enables one to predict and control surface structures in devices, and thus to make better materials through better understanding of epitaxial growth. From a theoretical point of view, since there is still no underlying theory for this far-from-equilibrium problem, one can use the large-scale topography in order to understand microscopic atomic processes. Our work aims to relate theoretical efforts in surface morphology modeling to experimental work on the technologically important GaAs (001) surface during homoepitaxial crystal growth on both nominally flat and patterned starting surfaces.

There has been a large amount of research on surface morphology over the last 15 years, and we will use the greater parts of Chapters 2 and 3 to describe some of it. Villain [Vil91] developed a framework for the use of contin-
uum growth models by the means of partial differential equations, where the interface velocity was related to free energy gradients. Venables [VSH84], Bartelt [BE92], and others developed sub-monolayer rate equations that have seen great success for the early stages of growth and nucleation. Cohen [CPP+89] extended the rate equations to account for coalescence of islands on terraces and, thus, enabled the description of multilayer growth. However, morphological information is lacking in a rate equation approach.

Many groups have investigated a variety of spatially dependent continuum and discrete growth models and analysed their scaling behaviour in the hydrodynamic limit. A complete picture of the work done is best obtained by reading the review articles and books by for example Halpin-Healy [HHZ95], Krug [Kru97], Barabasi and Stanley [BS95], and Pimpinelli and Villain [PV98]. Recently, there has been a renewed interest in surface morphology studies due to experimental studies of overgrowth on textured surfaces for quantum wires and distributed feedback laser design [BKT+01, TWY+03].

The nature of the adatom dynamics near step edges has been a theoretical favourite in many studies. It is believed that the descent of adatoms from one terrace to the next ("interlayer transport") is inhibited by an asymmetric potential barrier at the step edges. Villain [Vil91] showed that such a potential barrier (also referred to as the Ehrlich-Schwobel barrier [EH66, SS66]) causes preferential incorporation of adatoms to the ascending step on a terrace, along with reflection off the descending step, and that large-scale mounds would emerge as a result. Pioneering work by Johnson [JOH+94] and Orme [OJS+94, OJL+95] showed that the evolution of GaAs surfaces during growth exhibited the formation of such mounds and they concluded that this destabilizing effect could be attributed to the Ehrlich-Schwobel barrier and that GaAs growth was unstable.

From an experimental point of view, this conclusion came as somewhat of a surprise. Long before theorists started modeling GaAs homoepitaxy, crystal growers had been growing thick buffer layers (on the order of microns) prior to device manufacturing in order to smooth the starting surface. This experimental knowledge indicated the exact opposite of what the potential barrier studies had found: namely that homoepitaxial growth on GaAs (001) was stable and that continued growth would make rough starting surfaces smoother, rather than filled with mounds. The disparity between these two views on the stability of GaAs epitaxy remained for some time.

A stable, smoothing morphological evolution means that the net direction of adatom drift is downhill. This can be achieved in two ways: (1) by letting the step edge barrier be negative, which leads directly to
downhill interlayer transport, or (2) by having a positive Ehrlich-Schwöbel barrier along with other mechanisms that oppose the effects of this destabilizing mechanism. Some such mechanisms have been described in the literature, for example “downhill funneling” [WV90] and “the knock-out effect” [Eva91]. In fact, Šmilauer and Vvedensky [vV93] showed that in order to accurately describe reflective high energy electron diffraction oscillations of GaAs homoepitaxy, a downhill funneling mechanism was required in addition to the positive Ehrlich-Schwöbel barrier [OJS+94]. Krug et al. [KPS93] showed that this combination of opposing mechanisms at the step edge could in some cases lead to a net downhill drift of adatoms. The combined results of Refs. [vV93] and [KPS93] lends additional support to the notion that the evolution of GaAs homoepitaxially grown surfaces is stable. New studies have recently emerged that suggest that the Ehrlich-Schwöbel barrier in GaAs might be small [CCM+98, CC00, IO00] or even negative [BTS04a, BTS+04b].

In this thesis, we approach the problem of surface shape evolution by direct comparison of the morphology of epitaxially grown surfaces with surfaces generated by computer simulation of various growth models. Experimental surface morphologies were measured with atomic force microscopy, which gives atomic resolution in the surface height over a wide range of substrate sizes. We have also tried to match the power spectral densities as a function of time in growth experiments on nominally flat surfaces. We discovered [ABP+00, BRA+01, BRS+02] along with other groups [CCM+98, CC00] that the observed mounding can be explained as being a transient smoothing phenomenon of a rough starting surface, rather than being due to a growth instability inherent in the GaAs surface caused by a positive Ehrlich-Schwöbel barrier. We therefore agree with the view that the morphological evolution of this material system is stable during epitaxial growth. This realization enabled us to model the surface shape evolution with growth equations that contained stable (non-diverging) terms. This modeling, along with accompanying experimental studies is discussed in Chapter 4.

Continuum models are intended to describe surface morphology in the hydrodynamic limit, i.e. for low slopes and small surface roughness amplitudes. The question arises whether our modeling approach will work for lithographically patterned starting surfaces. The answer to this question was made particularly evident in recent work by Kan et al. [KSTEP04b], in which modeling of regrowth on 50 nm deep lithographically defined pits was attempted using conventional continuum growth equations, like the Kardar-Parisi-Zhang (KPZ) equation [KPZ86] and the so-called molecular beam
epitaxy equation\textsuperscript{1} [SGG89]. Kan's calculations showed that several important and very noticeable characteristics of the surface shape evolution were completely missed by attempting to use these equations as a description of real crystal growth. Our analysis of this extended problem led us to formulate a growth model that describes the interaction between adatoms and step edges in the form of a coupled growth equation model [BTS04a, BTS\textsuperscript{+}04b]. This work can be seen in Chapter 5.

The progression of the Chapters is as follows. Due to the extensive body of work related to modeling of epitaxy, we feel that a thorough introduction to the field is appropriate. This appears in the form of a critical review in Chapters 2 and 3. The material in Chapters 4 and 5 is new, and has resulted in a number of publications on growth modeling (see Refs. [ABP\textsuperscript{+}00, BRA\textsuperscript{+}01, BRS\textsuperscript{+}02, BTS04a, BTS\textsuperscript{+}04b, BLST05]) and also the reverse process of etching (see Refs. [SBR\textsuperscript{+}02, STMB04]).

In Chapter 2, we review some basic aspects of adatom diffusion on crystal surfaces and introduce key elements in an approach to a microscopic surface growth model called the "solid-on-solid" model. We also introduce the Burton-Cabrera-Frank (BCF) [BCF51] theory along with the accompanying mathematical framework. We discuss in some detail the potential-energy landscape of the GaAs surface, especially close to the steps, and discuss its effect on macroscopic surface evolution.

A conventional approach to large-scale surface morphology modeling is through the use of continuum growth equations. We describe some common examples of such in Chapter 3, and we also outline the concept of scaling, which is a typical approach used to classify growth models.

We believe that the ultimate test of a model is to try and apply it to the experimental system that it seeks to describe\textsuperscript{2}. This is attempted in Chapter 4, where two surface growth models for MBE are applied and compared in an exhaustive experimental and simulative study. We investigate the dependence of surface evolution on film thickness and temperature. We show that the KPZ equation is successful in describing surface shape evolution of nominally flat starting surfaces in the low amplitude and long wavelength limit, whereas the MBE equation, ironically, is not. We also study the effect

\textsuperscript{1}We use the acronym "MBE" to describe "molecular beam epitaxy". We will also follow literature in referring to this equation as the "MBE equation". We hope that it is clear from the context whether we are referring to the growth technique (MBE) or the growth model (MBE equation).

\textsuperscript{2}This might seem obvious, however, the reader will be surprised to learn that this is not typically done in morphology studies. Quite often, there is not even an image of a surface!
of the starting surface on the surface evolution and show that the As to Ga ratio dictates the anisotropy of the evolving surface features. This study proves to be valuable, in that we learn many things about our particular growth system, and also come to the conclusion that GaAs homoepitaxy is in fact a stable growth system.

We conclude Chapter 4 by noting that conventional asymptotic growth equations leave many questions unanswered. We progress to Chapter 5, where we develop a complete physical model based on the underlying physical processes and mechanisms that take place on the surface during growth and annealing. We show that this new model can describe regrowth experiments on lithographically patterned surfaces, including the complex shape evolution associated with large surface slopes. It can also describe the evolution of the nominally flat surfaces that we studied in Chapter 4. The new model reduces to a nonlinear evolution equation in the low amplitude and long wavelength limit reminiscent of the KPZ equation.

The four appendices describe details of the various mathematical techniques used in this work.
Chapter 2

The crystal growth problem

Before we start the task of modeling surface-shape evolution, we need to describe the phenomena believed to be present at the crystal surface. We will discuss important physical mechanisms that influence the evolution of the surface morphology, both during epitaxial growth and annealing. This Chapter will be historical in nature, and aims to discuss some major ideas that have affected the way we understand the crystal growth problem.

Each square micron of GaAs surface contains approximately 6 million exposed atoms, most of them locked into the 3D crystal lattice and some diffusing freely on the surface, constantly rearranging and working hard to develop macroscopic surface shapes that keep on fascinating surface scientists. Due to the large number of particles involved, the development of complete, atomistic models for surface evolution during growth inevitably results in very calculationally intensive models. Practical models should be computationally tractable, while not jeopardizing their applicability to real surface growth evolution.

We start this Chapter by discussing two common approaches to growth modeling. An old and often quoted theory is the one developed by Burton, Cabrera and Frank (BCF) [BCF51]. It describes the motion of loosely bonded adatoms on a crystal surface consisting of flat terraces separated by atomic step edges. This model was developed over half a century ago, long before any scanning tunneling or atomic force microscopes revealed to us the secrets of the crystal surface. Since then, it has formed the basis for many theoretical models of adatom motion and nucleation on crystal surfaces, such as sub-monolayer rate equations. In this Chapter, we will incorporate many realistic physical processes into the BCF framework, and from that, develop a continuum growth model, thereby showing the strengths and weaknesses of this simple, yet remarkably useful formalism. The other approach that we will cover in this Chapter is the solid-on-solid (SOS) model, in which the stochastic nature of crystal growth is explored.

In the development of both these models, we will pay special attention to the physics of adatoms near step-edges. The variations in the potential landscape near steps is found to have a profound impact on the evolution of
large-scale surface morphology during growth.

2.1 Adatom random walk

The success of molecular beam epitaxy (MBE) as a method for crystal growth is in part due to the clean, high vacuum environment, but also in great part due to the fast diffusion of adatoms on the surface. While growth is done at only about half the melting temperature, which is at 1237°C in the case of GaAs, this is still well above room temperature, and it allows sufficient adatom migration to achieve relatively flat films.

An “adatom” is defined as a single atom, whose only bonds are to the crystal lattice beneath it. It can easily overcome the potential barrier required to jump diffusively from one lattice position to a neighbouring site without desorbing back into the gas phase, since it is still in intimate contact with the surface. This diffusion is Arrhenius activated and allows the adatoms to seek out low-energy sites on the surface. During early stages of growth, when there are fewer steps on the surface, adatoms nucleate dimer-islands along with other adatoms. As the growth progresses, or on surfaces with some initial roughness, the most common way that adatoms minimize their potential energy is by attaching to step edges. Adatoms can also desorb back into the vapour.

The diffusion constant \( D = a_{\parallel}^2 \omega_0 \exp(-E_{\text{act}}/k_BT) \), where \( E_{\text{act}} \) is the energy that must be overcome in order for a diffusion event to occur, \( k_B \) is Boltzmann’s constant, \( T \) is the temperature of the system, \( h \) is Planck’s constant and \( a_{\parallel} \) is the in-plane lattice constant. The attempt frequency \( \omega_0 \) has a weak temperature dependence through the equipartition theorem as \( \omega_0 = 2k_BT/h \).

The simplest models of GaAs growth usually do not make the distinction between atomic and molecular constituents, and an adatom is considered as a representation of a Ga-As complex. A “dimer” (two Ga-As complexes) is considered as part of the surface, although it can diffuse as a unit with a much larger activation energy than that of a single adatom. We will consider dimers as immobile in this thesis. Mobile islands have been treated for example in Refs. [VSH84, LG00, KE00].

We define \( P(x, y, t) \) to be the probability of an adatom occupying a lattice site at position \((x, y)\) at time \( t \). After a diffusional step, we can write...
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\( P(x, y, t + \Delta t) \) as [Zan88]:

\[
P(x, y, t + \Delta t) = \frac{1}{4} \left( P(x + a, y, t) + P(x - a, y, t) + P(x, y + a, t) + P(x, y - a, t) \right)
\]

(2.1)

which can be rewritten as

\[
P(x, y, t + \Delta t) - P(x, y, t)
= \frac{a^2}{4a^2} \left( P(x + a, y, t) - 2P(x, y, t) + P(x - a, y, t) \right) + \frac{a^2}{4a^2} \left( P(x, y + a, t) - 2P(x, y, t) + P(x, y - a, t) \right)
\]

(2.2)

Dividing this equation by \( \Delta t \), we recognise it as a second order finite difference scheme for the heat equation:

\[
\frac{\partial}{\partial t} P(x, y, t) = D^s \nabla^2 P(x, y, t)
\]

(2.3)

where \( D^s = a^2/4\Delta t \) is the diffusion constant of a single particle and \( \partial_t = \partial/\partial t \). In the case of non-interacting adatoms on a surface, Fick's law states that the flux of diffusing adatoms is proportional to the density gradient

\[
j = -D \nabla \rho
\]

(2.4)

where \( \rho = \rho(x, y, t) \) is the adsorbate particle density. Adding the continuity equation

\[
\partial_t \rho = -\nabla \cdot j
\]

(2.5)

we get the diffusion equation (Eq. 2.3) for \( D = D^s \) and \( \rho = P \), which is true when there is no interaction between the adsorbate particles. A further discussion on this can be found in Ref. [Zan88] (p. 375), Ref. [PV98] (p. 112), as well as an in-depth analysis in Ref. [BMT90] (p. 529). We will use \( P \) and \( \rho \) interchangeably throughout this Chapter\(^1\). When these are not interchangable, we will note this explicitly.

\(^1\)In Chapter 5, we will refer to the adatom concentration by the variable name \( n \), so that it should be clear from the context what formalism we are using.
Figure 2.1: Sample of simulated SOS growth on flat starting surface. (a) Perspective view after 1.9 ML growth; (b) top view after 65 ML growth on a 300x300 atom surface; higher layers in lighter shading. Growth parameters were $F=1$ ML/s, $T=500^\circ C$, $E_{sub}=1.25$ eV, $E_{lat}=0.35$ eV and $E_{es}=-0.05$ eV.

2.2 The solid-on-solid model

A widely used method in simulating epitaxial growth is the solid-on-solid model. Its name originates from the fact that it assumes that the smallest particles used in the model land and diffuse on top of other particles, i.e. no overhangs or vacancies are allowed. This means that all the surface atoms are sitting on top of a solid column of atoms, and that the surface can be fully described by a 2D matrix, containing only the height information of the surface atoms. A small area of a typical SOS simulation is depicted in Fig. 2.1. In this Section, we outline the specifications of our particular SOS model.

In the simplest model, the surface atoms are defined on a square lattice with periodic boundary conditions, and individual atoms are deposited randomly around the surface at a rate $F$. Each surface atom is bonded to the substrate directly below it with a bonding potential $E_{sub}$. Atoms with $m$ lateral neighbours feel an additional bonding of $mE_{lat}$, where $m$ ranges from 1 to 4 in a cubic lattice [MG88]. The total activation energy for a surface atom is then $E_{act} = E_{sub} + mE_{lat}$. The surface atoms diffuse at rates dictated by their bond-strength: a weakly bonded atom, such as an adatom, is more likely to move than an atom with many lateral neighbours. An atom with coordination number $m = 4$ is part of a flat surface, and is also allowed to diffuse, although at a much lower rate. We also include an Ehrlich-Schwöbel (ES) barrier, which describes the additional energy barrier that an atom encounters as it approaches a step edge. This barrier is characterized by a potential $E_{es}$. We discuss this barrier in more detail in
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Section 2.4. In this work, unless otherwise noted, we will use a fixed set of parameters in all our SOS simulations, which we will refer to as the standard parameters. These parameters are listed in Table 2.1 and were obtained through optimization and comparison between a wide variety of simulation scenarios, and related experiments, whenever available.

The kinetic Monte Carlo (KMC) algorithm is well suited for simulating the inherent randomness of the SOS dynamics. More details on the KMC approach are outlined in Appendix A. Once the computational method has been established, we can focus on the growth model itself, or the “rule-base” that makes this simulation imitate epitaxial growth as closely as possible. We use a one-component model, which means that the As-atoms are not distinguished from the Ga-atoms. The smallest unit of surface particle is thus a Ga-As complex. This is reasonable, as GaAs epitaxial growth is usually done with excess As present in the growth chamber, which makes the growth Ga-limited. However, the As-overpressure is known to affect the anisotropy in the evolving surface morphology, where surface features are stretched in the [110] direction when the As:Ga ratio decreases [ABP+00]. In our growth experiments, we usually set this ratio to be $> 3$, for which the surface feature anisotropy is minimal. The surface anisotropy could be modeled indirectly by assuming an anisotropic diffusion constant for the Ga-As complex or possibly also an anisotropy in the incorporation dynamics on the surface [Ito01].

The use of a one-component model effectively reduces the crystal structure from a zincblende structure (two face-centered cubic (FCC) crystals intertwined, offset by a quarter lattice spacing in the [111] direction) to a single FCC crystal with a basis representing the Ga-As complex. In our model, this is further simplified to a simple cubic crystal, which can be justified by interpreting each layer in the simulation as a bi-layer, and letting the simulation $(x, y)$ directions be the crystal [110] and [110] directions, respectively, see Fig. 2.2.

We have implemented the restricted SOS model [KK89, RSLP91], in which there can be no double-height steps on the surface. This is a reflection of the fact that a Ga-As complex right at the edge of a step represents a high-energy, and therefore improbable configuration. By restricting the

<table>
<thead>
<tr>
<th>$F$</th>
<th>$E_{sub}$</th>
<th>$E_{lat}$</th>
<th>$E_{es}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 ML/s</td>
<td>1.25 eV</td>
<td>0.35 eV</td>
<td>-0.05 eV</td>
</tr>
</tbody>
</table>

Table 2.1: Standard Parameters used in KMC SOS simulations in this work.
height at the step edge, the FCC lattice of GaAs is more closely simulated. The macroscopic effect is a restriction of the slope to below 45°. We do not consider this to be a limitation of the model’s accuracy, as the next low index planes, (110) and (111), are 45° and 54.7° from the surface normal of the (001) plane. The surfaces investigated experimentally in this thesis have slopes less than ~5° for the randomly rough surfaces described in Chapter 4 and less than ~30° for the patterned surfaces in Chapter 5. Elkinan et al. [EV94] and Politi et al. [PV96] showed that an SOS model without the double-height step restriction leads to infinitely steep sections, due to step-bunching induced by diffusion of adatoms over steps. The double-height restriction is implemented in the following way. Any surface atom with less than 4 lateral neighbours is considered to be a step. Adatoms that land on top of such a step site, either by diffusing or being deposited there, is forced to make another diffusional step until it lands on top of an atom that has 4 lateral neighbours.

Surface reconstruction, where the exposed atoms settle into reduced-potential configurations, is not included in our models. Surface reconstruction is dependent on the substrate temperature, and also on the As2:Ga ratio. The inclusion of this effect could be done at a large computational expense, but would be better handled by a truly atomistic model implemented for example with molecular dynamics, in which surface atoms can be moved off their bulk lattice positions. In this work, we keep the minimum number of mechanisms necessary to be consistent with experiments and remain consistent with generally accepted models of crystal growth.

In spite of the many simplifications that go into our SOS model, the re-
Suits that emerge from this computational tool have proven to be predictive and accurate in describing a wide range of surface dynamics phenomena. If one views the SOS model as a box of Lego-pieces, i.e. not as an accurate description on the small scale, but great at resembling large-scale surface shapes, then one could call this method a computational playground for the surface theorist. In order to explore phenomena that are not readily available through experiment, we will resort to the SOS model, and consider systems with up to about ~1000×1000 atoms and growth times on the order of hours.

2.3 The Burton-Cabrera-Frank model

The fundamental assumptions in the theory of adatom diffusion according to BCF [BCF51] are that the surface consists of flat terraces separated by steps, and that the concentration of adatoms on a terrace is determined fully by the position of the step edges. This means that the re-ordering of the adatom concentration on a terrace is fast compared to the motion of the steps.

A surface that is not perfectly flat can be considered as a collection of steps separated by top and bottom terraces. If the surface average normal is slightly tilted off a low-index crystal orientation, such as (001) or (111), it is called vicinal or stepped. A flat surface that is not vicinal is called singular. Figure 2.3 illustrates a vicinal surface along with some definitions that we will use in the following. With adatoms impinging on the surface at an average rate $F$, the equation that governs their steady-state configuration on a terrace of width $l$ is

$$0 = \partial_t \rho(x, t) = D \nabla^2 \rho(x, t) + \frac{F}{a^d}$$

(BCF equation) (2.6)

where $a^d$ is the $d$-dimensional lattice site area. In the simplest 1D ($d=1$) model, we will assume that the ascending step is perfectly absorbing, which gives us the boundary condition

$$\rho(x = 0) = 0,$$

(Absorbing boundary) (2.7)

On the descending step, we allow drift of adatoms over the step without any additional barrier, which gives us the following condition:

$$-D \nabla \rho(x = l) = \frac{D}{a^d} \rho(x = l)$$

(Zero barrier boundary) (2.8)

\footnote{The units of Eq. 2.6 in $d$ dimensions is: $[\rho] = 1/L^d$, $[D] = L^2/T$, $[F] = 1/T$, where $L$ is length and $T$ is time.}
where the left hand side represents the particle current at the step edge, and at the right hand side we have the number of jump attempts at the step edge.

The breach of symmetry in the boundary conditions is a result of this system being in a nonequilibrium steady-state situation. A simple experimental proof of this fact is that the morphology evolves: without the asymmetric boundary conditions, the net current of adatoms off a terrace would be zero, and the surface shape would remain fixed\(^3\).

The solution to Eq. 2.6 with boundary conditions Eqs. 2.7 and 2.8 is a simple quadratic:

\[
\rho(x) = -\frac{Fx}{2a_D} \left( x - \frac{l(2a_D + l)}{(a_D + l)} \right)
\]  

and is plotted on the diagram in Fig. 2.3.

Fick’s law (Eq. 2.4) will now give us the current of adatoms at the ascending step, \( j_{\text{up}} \), and the descending step, \( j_{\text{down}} \). The destabilizing current \( j_{\text{up}} \) drives adatoms towards the ascending step, and hence make the terrace shorter. On the descending step, \( j_{\text{down}} \) will represent a measure of the number of adatoms that fall over the edge and hence lengthen the terrace in question; such a stabilizing term acts to flatten the overall surface. For the adatom density defined by Eq. 2.9, we get the following expressions for the

\(^3\) Another example of a nonequilibrium steady-state system is that of a gas contained in a cylinder, with the two ends of the cylinder being held at different temperatures. One could here easily obtain a situation where the temperature reached a steady-state. Yet, the pressure of the gas near the two ends of the cylinder will be different, even in the steady-state, due to the fact that the system is in non-equilibrium.
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two contributing currents:

\[
\begin{align*}
J_{up}(l) &= -D\nabla \rho \big|_{x=0} \\
&= -\frac{Fl}{2a_{||}} \frac{(2a_{||} + l)}{(a_{||} + l)} \\
J_{down}(l) &= -D\nabla \rho \big|_{x=l} \\
&= \frac{Fl^2}{2a_{||}(a_{||} + l)}
\end{align*}
\] (2.10) (2.11)

The total current is the sum of these:

\[
J(l) = J_{up}(l) + J_{down}(l)
\]

\[
= -\frac{Fl}{a_{||} + l}
\] (2.12)

This expression is negative for all values of \( l > 0 \). On the surface depicted in Fig. 2.3, where the gradient is negative, this means that the net adatom drift is uphill. Thus, the surface will get rougher as the growth progresses, by building up 3D structures. A net downhill adatom current, on the other hand, will cause an initially rough surface to smooth. In the next Section, we will allow for permeable boundaries at both ends of the terrace, and we will describe in more detail the physics of adatoms traversing step edges, which in the context of surface growth modeling is referred to as “interlayer transport”. The physics determining the permeability of the step edges is crucial in order to understand the surface shape evolution on all interesting length scales. In a recent Nature article, aptly named “Thin-Film Cliffhanger”, Legoally and Zhang [LZ02] write that: “A proper accounting for these barriers in film growth will determine the ultimate quality, reliability and stability of films grown for a great variety of purposes”. We continue by discussing physical mechanisms that favour adatom drift in either of the two directions, uphill or downhill, and the consequences of incorporating such mechanisms into our surface model.

2.4 Interlayer transport

In order to create smoother surfaces from a rough starting surface, the adatoms have to flow downhill, making terraces longer, thereby depleting the top terraces and filling the troughs. There must be physical processes on the surface that allow for the adatoms to jump to terraces above or below the one they are currently on. In this Section, we discuss some important
mechanisms that would influence the nature of interlayer transport, including potential barriers at step edges (Section 2.4.1 and 2.4.2), local relaxation of newly deposited atoms (Section 2.4.3), as well as some of the consequences of having competing mechanisms for interlayer transport (Section 2.4.4). Finally, we discuss some alternative theories (Section 2.5.1).

2.4.1 The Ehrlich-Schwöbel step edge barrier

A naïve rendering of the potential landscape near the step-edge of a 1D cubic lattice is illustrated in Fig. 2.4. On its journey across the surface, a diffusing adatom continually encounters potential energy barriers. Away from steps, this activation energy is caused mostly by the interaction between the adatom and the atoms in the substrate immediately beneath it, characterized by $E_{\text{sub}}$ in Fig. 2.4. Near to an ascending step, the adatom feels added bonding from the lateral bond to the step-atom. It is based on this argument that crystal growth is often described as being a dynamic and reversible process of attachment and detachment of step edge atoms (BCF theory).

In order to descend over a step, the adatom has to overcome a potential barrier that is somewhat larger than that which characterizes a plain diffusion event on a flat surface. The added potential barrier in this naïve picture is the ES barrier of magnitude $E_{\text{es}}$, named after the experimental
observations by Ehrlich and Hudda [EH66]. Some of the consequences of such a barrier were analyzed by Schwöbel and Shipsey [SS66, Sch69]. We also note the lowered activation energy associated with diffusing to the ascending step from the lower terrace. This activation energy towards the step edge is referred to as the “incorporation barrier” [XLT02], and is indicated as $E_{\text{inc}}$ in the figure.

2.4.2 Step-traversal by insertion

Another possibility for step-traversal was suggested by Hansen et al. [HSJN91]. The diffusing adatom approaching the step edge is inserted behind the edge atom, and hence pushes the current edge atom over to the next lattice site. This process is commonly referred to as “insertion” or “the exchange process”. In this case, two atoms are rearranged, instead of just one, as was the case for over-the-edge step-traversal.

Little is known about the microscopies of the ES barrier on a polar semiconductor surface, such as GaAs, including whether step-traversal is over-the-edge or via insertion. Pimpinelli and Villain (p. 94 in [PV98]) indicate that in the case of (100) face of metals, Au favours the insertion mechanism before over-the-edge traversal. Effective medium theory calculations by Stoltze [Sto94] and direct field-ion microscopy observations by Wang and Ehrlich [WE91]) indicate that the opposite is true for Cu, Ag, Ni, Pd and Pt, as well as for (111) facets. $Ab$ $initio$ calculations by Stumpf and Scheffler [SS94] indicate that for aluminium, the insertion mechanism is important, but also predict that for certain orientations of the steps, there is no ES barrier, “in the sense that the potential is maximum at the center of the terrace rather than on the terrace edge” (p. 95 in [PV98]). Itoh et al. [Ito01, IO00] argue a similar point, that polar semiconductors like GaAs might not have an ES barrier at all.

In this thesis, we will not attempt to derive the exact magnitude of this barrier. Instead, we will look at the effects of incorporating such a barrier into analytical models (this Chapter) and computational models (Chapter 4) and compare simulation results of large-scale morphology to experimental data in the form of atomic force microscopy (AFM) images. However, it is important to realize the immediate and very dramatic effect that this barrier has on the morphological evolution of a flat starting surface, even for very small barriers.

As an example, in Fig. 2.5 we show the effect on the large-scale morphology of simulating the surface evolution with an SOS model that incorporates the ES barrier. Part (a) shows that even after a few monolayers of growth,
protrusions (~16 ML high) form when a positive ES barrier of 100 meV is employed; these are the initiators of mound-growth. For comparison, part (b) of the Figure shows the effect of growing over 50 ML on a surface where a negative ES barrier of -100 meV is employed. Only a slight deviation from the ideal layer-by-layer growth mode is observed. It is clear that the ES barrier in the common sense as implemented in part (a) destabilizes the evolution of the surface. On the other hand, a negative ES barrier, as seen implemented in part (b), will result in a roughness evolution that is even less pronounced than in the case of kinetic roughening with a neutral ES barrier.

The physical meaning of a negative ES barrier is that on GaAs (001), step edges are more attractive to adatoms from the top than they are from the bottom. Due to the complex geometry of reconstructed step edges on GaAs (001) it would not be surprising that intuitive arguments for ES barriers based on SOS models and double height steps might give the wrong sign.

In the epitaxial growth experiments done in our laboratory, instabilities like those in Fig. 2.5 (a) have never been observed in GaAs. This important observation could mean one of two things: (1) that the ES barrier is negative,
or (2) that there are other mechanisms on the step edge that counteract and stabilize the destabilizing effects of a positive ES barrier. We discuss two such stabilizing mechanisms in the next Section.

2.4.3 Downhill funneling / knock-out process

The ES barrier is commonly implemented as a positive barrier that impedes downhill drift, and for many growth systems, especially epitaxy of metal films, it is quite clear that this is a correct assumption (see for example work by Michely et al. [MKC+02] and references therein). It was shown in the previous Section that such a mechanism causes an instability. However, as we will show in Chapter 4, the immediate consequences of the ES barrier, namely mounding, is not observed in GaAs growth experiments. Crystal growers had been growing smooth GaAs films years before the ES barrier became a theoretical favourite, and additional mechanisms for interlayer transport were introduced in order to reach agreement between surface growth models and experiments.

The two mechanisms for surface relaxation that we will describe in this Section only occur during growth, i.e. to recently deposited atoms. The first mechanism is that of “downhill funneling”, introduced by Wolf and Villain [WV90]. This mechanism describes the local relaxation that a freshly deposited atom can undergo while dissipating its kinetic energy. It is typically implemented as a search for a highest coordination number site within some distance $L$ of the deposition site. Šmilauer et al. [vV93, vV95] implemented the downhill funneling effect in combination with a positive ES barrier as part of an SOS model in order to describe RHEED oscillations in (001) GaAs homoepitaxy. In their study, the deposited atoms were allowed to relax within a 7×7-atom area of the drop points.

The downhill funneling effect is a smoothing mechanism, just like the inverse ES barrier (i.e. $E_{ss} < 0$, as in Fig. 2.5 (b)), except that it only applies to atoms that have just dropped from the vapour. Including this relaxation mechanism can cancel the effect of a positive ES barrier during growth, and the net current in such a model can be downhill [KPS93]. It should therefore be noted that the combined effect of a positive ES barrier and a relaxation mechanism could equally well be interpreted using a single mechanism, namely a negative ES barrier. We will show this analytically in the framework of BCF in Section 2.5, where a surface relaxation mechanism is explicitly implemented.

Another mechanism for growth induced surface relaxation, often referred to as the “knock-out” [Eva91] process, has an effect on the surface morphol-
ogy similar to that of the downhill funneling mechanism described above: an energetic incoming atom that lands close to a step edge can insert behind one or more of the atoms closest to the step edge, or "knock them out" as the name indicates, much like the "insertion" mechanism described in Section 2.4.1. The overall effect on the surface morphology of the two mechanisms is similar.

2.4.4 Step traps

The potential landscape surrounding a step edge is more complex than the naive diagram in Fig. 2.4 indicates. Some particularly interesting studies were reported by Wang and Ehrlich [WE91, WE93] and Kyuno and Ehrlich [KE00]. Diffusion of iridium atoms on small islands on the (001) plane was imaged by a field-ion microscope, and the adatoms were found to get temporarily trapped on the upper side of the descending step. This lead to the speculation that for certain surfaces, there might be a potential minimum there. Furthermore, the temporarily trapped atoms at the step were more likely to descend over the step than return to the upper terrace. Based on these observations, the potential diagram in Fig. 2.7 was suggested [WE91, WE93, KE00].

The reduced $E_B$ in Fig. 2.7 serves to make traversal across the descending step more attractive, as a return to the upper terrace is through the larger barrier $E_R$ [Mar94]. Markov [Mar96] suggested that an adatom that got stuck in the trap on the upper side of the step could more easily insert and hence effectively incorporate to the lower step that way, even if the barrier for downhill diffusion might be larger than $E_{sub}$ (note that the barrier labelled by $E_B$ here equals $E_{sub} + E_{es}$).

The potential diagram in Fig. 2.7 might have merit for other surfaces, in addition to the metal surfaces studied in [WE91]. Figure 2.8 (b) shows a top-view AFM image of homoepitaxial growth on GaAs. This surface is prepared with a hydrogen etch and was grown at 590°C for 75 minutes at a
growth rate of 1 ML/s with an As:Ga ratio of 3.5. The rich morphology of this image requires further study, but it is tempting to point out that the step edges appear white in several places, an indication of additional height. This might be a real effect and hence indicate that even GaAs steps could have potential traps. The white ridges in the AFM image could also simply be an underdamping effect from the oscillating AFM tip.

Another interesting feature of this surface is the elongated finger-shapes pointing towards the upper right hand corner of the image. The surface is slightly vicinal with an approximate slope of about 0.05° in the [110] direction, the same direction the fingers are pointing. Figure 2.8 (a) illustrates a possible explanation for these fingers-shapes. Using the terminology from Fig. 2.7, we note that if the potential barrier for descent, $E_B$, is larger than the incorporation barrier $E_{inc}$ to the step from the lower terrace, the step front will receive more adatoms from the lower terrace than from the upper terrace. In addition, as the adatom isoconcentration lines (dashed) in Fig. 2.8 (a) indicate, the protruding points on the lower side of the step have a higher chance of being visited by these adatoms and will grow at an average rate $\nu_2$ that will be larger than the growth rate of the receding parts of the step front, $\nu_1$. As a result, the already protruding points of the step front will get bigger, eventually causing the fingering that we observe in Fig. 2.8 (b). This effect has been discussed in the literature (the "Bales-Zangwill instability" [BZ90]), and is qualitatively similar to that of dendritic growth. A nice overview of the Bales-Zangwill instability can be
Figure 2.8: The Bales-Zangwill instability: part (a) illustrates in top-view the mechanism where protruding points on the step front receive more adatoms from the lower terrace, and therefore grow at a faster rate $v_2$ than the receding points that grow at a rate $v_1$; part (b) shows $2 \times 2 \mu m$ AFM image of hydrogen-etched GaAs grown for 75 minutes at $590^\circ C$.

Interestingly, the Bales-Zangwill instability is typically associated with a positive ES barrier that allows more adatoms to approach the step from the lower terrace. However, as we pointed out, this effect is also consistent with a negative ES barrier, as long as the incorporation barrier $E_{inc}$ is more easily overcome than $E_B$. The fingering that we see in Fig. 2.8 (b) might also be explained by an anisotropy in the adatom diffusion constant. We will return to this point in Chapter 4 (p. 65), where we show how the As:Ga ratio affects the degree of anisotropy of the growing surface features. The finger-shaped formations seen in Fig. 2.8 (b) may be explained by the potential-energy landscape of the GaAs surface near the step edges, by the anisotropy caused by the As:Ga ratio, or by a combination of the two effects.

2.5 Interlayer transport in the Burton-Cabrera-Frank model

The interlayer transport mechanisms can be introduced into the BCF framework by altering the boundary conditions. The ES barrier can be introduced
by noting that it changes the probability of diffusion over the step edge:

\[-D \nabla \rho(x = 0) = -\frac{D}{a_\parallel} \rho(x = 0) \quad \text{(Ascending step with ES barrier)} \quad (2.13)\]

\[-D \nabla \rho(x = l) = \frac{D}{l_{es}} \rho(x = l) \quad \text{(Descending step with ES barrier)} \quad (2.14)\]

where the right-hand side of Eq. 2.14 denotes the number of jump attempts at the descending step edge \((\sim D \rho)\) times a relative rate for crossing the ES barrier, expressed as \([PV96]\)

\[l_{es} = a_\parallel e^{E_{es}/k_B T}. \quad (2.15)\]

The ES length \(l_{es}\) is a measure of the bias that the ES barrier introduces to an adatom placed near the step edge: at a length \(a_\parallel\) away from the ascending step edge, the adatom behaves as if it were placed at \(l_{es}\). When the ES barrier is negative, then \(l_{es} < a_\parallel\), and vice versa when the ES barrier is positive. In the event that there is no ES barrier associated with the step edge, then the diffusion probability over the step equals that of a diffusion event on the flat terrace away from the edges \((l_{es} = a_\parallel)\). Solving Eq. 2.6 with the boundary conditions of Eqs. 2.13 and 2.14 gives an adatom current of the form:

\[j(l) = \frac{F l (a_\parallel - l_{es})}{a_\parallel (a_\parallel + l_{es} + l)} \quad (2.16)\]

The details of this calculation can be found in Appendix B.1. By allowing the boundaries to be permeable, we see that the ES barrier fully determines the sign of the adatom current: a positive barrier \((l_{es} > a_\parallel)\) creates an uphill, unstable current and a negative barrier \((l_{es} < a_\parallel)\) creates a downhill, stable current.

Next, we discuss the local relaxation effects from Section 2.4.3. Schinzer et al. [SKR00] incorporated the local relaxation mechanisms described above into the 1D BCF formalism by assuming that "there exists an incorporation radius \([R_{inc}]\) such that all particles arriving close to a downward step within this radius immediately jump down the step edge." This adds to the downhill current, and stabilizes the growth process. Mathematically, little difference can be seen between the effects of the downhill funneling and knock-out mechanisms, and Schinzer's approach can be seen as an implementation of either effect.

In order to incorporate \(R_{inc}\) into the BCF model, we split the terrace into two regions: in region 1 \((x < l - R_{inc})\) the diffusion equation holds
The solution to the adatom concentration on a step where the incorporation radius is included, is depicted in Fig. 2.9. A full derivation can be found in Appendix B.2. The adatom current off the terrace can be written as:

\[
\mathbf{j}(l) = \left(-D\nabla \rho_1(0)\right)_\text{up} + \left(-D\nabla \rho_2(l) + \frac{R_{\text{inc}}F}{a_\parallel}\right)_\text{down}
\]

\[
= \frac{F}{a_\parallel} \times \frac{[l(a_{\parallel} - l_{es}) + R_{\text{inc}}(2l_{es} + R_{\text{inc}})]}{a_\parallel + l_{es} + l}
\]

and we will discuss this expression in the next Section. Notice that the step edge detachment does not enter into the expression for the surface current. This indicates that the steps release adatoms back onto the terrace, independent of the size of the terraces.
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An approximation can be made by noticing that $R_{inc}$ is usually small (on the order of $a_\parallel$), so by assuming that the solution is $\rho_3(x) \approx \rho_1(x)$ in region 2 ($x > l - R_{inc}$), the current expression including the incorporation radius is equal to the current expression without $R_{inc}$, plus a term $FR_{inc}/a_\parallel$. The effect of including an “incorporation radius” is therefore simply an increase in the surface current, which in turn acts to stabilize the surface growth. This can lead to a “magic slope”, that we will describe in the next Section.

2.5.1 The “Magic Slope”

We have plotted the current expression from Eq. 2.18 in Fig. 2.10 for various combinations of $E_{es}$ and $R_{inc}$. For a zero incorporation radius and a positive ES barrier, we see that the current is negative for all values of the terrace width. However, when a positive incorporation radius is included, the curve crosses zero. This happens at a terrace width, $l^*$, that is given by

$$l^* = \frac{R_{inc}(2l_{es} + R_{inc})}{l_{es} - a_\parallel}$$

A positive “magic-length” can only happen when the ES barrier is positive, so that $l_{es} > a_\parallel$. This form for the adatom current is interesting in that it causes the surface to stabilize at a fixed (“magic”) slope: terraces of width $l < l^*$ will get longer by the downhill current and terraces wider than $l^*$ will get shorter through the uphill current. Eventually, all terraces will have a width $l^*$. Note that without the incorporation radius, there is no stable slope. Thus, two opposing mechanisms are necessary for the current to have a zero-point; in this case, in the presence of a stabilizing incorporation radius, the ES barrier must be positive.

“Magic slopes” have not been observed on GaAs, however, they can easily be identified in homoepitaxy of Pt on Pt(111) [MKC+02, KPVC00], where the emergence of pyramid-like mounds occurs from growth on initially flat surfaces, see Fig. 2.11. Similar work on many other metal systems shows similar results, for example Cu(100) [EFFL94, ZW97], Ge(001) [NCH+95], Fe(001) [SPSZ95, TKWR95] and Rh(001) [TWUC96].

The “mounds” in Fig. 2.11 have straight, linear slopes, and for that reason we will refer to them as “pyramids”. These pyramids therefore appear to be inversion-symmetric under $h \rightarrow -h$. However, closer inspection of the images in Fig. 2.11 (c and d) reveals that the top layers of the pyramids are flat and become relatively large before further nucleation of new islands occur on them. On the other hand, the bottoms appear to be sharp or cuspy, a pinning effect that we will discuss further in Section 3.2.2 (p. 31).
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Figure 2.10: Adatom current as function of terrace width. The ES barrier and the incorporation radius is varied. The current crosses zero only in the case when $E_{es} > 0$ and $R_{inc} > 0$, and the zero-current point is indicated: terraces shorter than $l^*$ will grow longer and terraces longer than $l^*$ will shorten.

The inversion symmetry is therefore not complete, even for metal epitaxy and positive ES barriers. These pyramid-shapes differ markedly from the typical mounds that we observe in GaAs homoepitaxy both in shape and temporal evolution [BRA+01, NCC+96].

The "magic slope" has been investigated by, among others, Schinzer et al. [SKR00]. Johnson et al. [JLB+96] did similar work, where a stable-current expression was derived by customizing the surface adatom current. By stabilizing the current, the uncontrollable growth due to the instabilities induced by the ES barrier are avoided. The magic slope therefore serves two purposes: (1) on one hand, it allows pyramid-growth on initially flat surfaces, and (2) it prevents such perturbations in the surface height from diverging.

2.6 Adatom desorption

It is typically assumed that desorption of adatoms is negligible in the case of GaAs homoepitaxy at standard growth temperatures (~600°C), as the rate of incoming atoms at typical growth fluxes is high enough to bury an adatom before it has a chance to escape back into the vapour. However, when the flux decreases and we anneal the surface, this situation changes. We will
implement desorption in this Section with annealing or low-flux growth in mind and see how it affects the adatom current. We incorporate desorption into the BCF model by

$$D \nabla^2 \rho(x,t) = -\frac{F}{a ||} + \frac{\rho(x,t)}{\tau_{des}}$$  \hspace{1cm} (2.20)$$

where $\tau_{des}$ is the average time between desorption events. We include step edge detachment as before and solve Eq. 2.20 with the boundary conditions defined by Eq. 2.17. However, in order to reduce the complexity of the solution somewhat, we make use of the fact that $R_{inc} \approx a ||$, that is, $R_{inc}$ is small compared to the typical terrace width in the weak surface texture limit. This means that we can approximate $\rho_2$ by $\rho_1$ in region 2 of Fig. 2.9, but still add the downhill funneling to the current term. The expression for
the adatom current is

\[ j(l) = \frac{\left(\Delta^2 - 1\right) \left(l_{es} - a_\parallel\right) \left(\frac{a_\parallel K}{\tau_{des}} - \frac{DF}{a_\parallel}\right)}{(\Delta^2 + 1) \sqrt{\frac{D}{\tau_{des}}} \left(l_{es} + a_\parallel\right) + \left(\Delta^2 - 1\right) \left(\frac{a_\parallel l_{es}}{\tau_{des}} + D\right)} \]  

(2.21)

where

\[ \Delta \equiv e^{l/\sqrt{DF\tau_{des}}} \]  

(2.22)

The details of the calculation can be found in Appendix B.3. The term \((\Delta^2 - 1)\) in Eq. 2.21 is always positive, and hence does not contribute to the overall net direction of the surface adatom current. The denominator in Eq. 2.21 is also always positive. The term \((l_{es} - a_\parallel)\) changes sign with the ES barrier, as before. The last factor in the numerator of Eq. 2.21 is negative for \(\tau_{des} > a_\parallel^2 K/DF\), which it is in the case of GaAs growth, so the expression for the current that we have derived is positive (stable) during growth. However, when the flux goes to zero, and we anneal the surface, desorption could have a destabilizing effect on the surface morphology.

### 2.7 A surface growth model derived in the Burton-Cabrera-Frank framework

Earlier in this Chapter, we derived expressions for the adatom current in the BCF framework (see for example Eqs. 2.12, 2.16, 2.18 and 2.21) of the form

\[ j(l) = \frac{P_a(l)}{Q_b(l)} \]  

(2.23)

where \(P\) and \(Q\) are polynomials in \(l\) of order \(a\) and \(b\), respectively, with prefactors that are determined by the growth parameters \(F\), \(T\), \(E_{es}\), and \(R_{inc}\), but not the diffusion constant \(D\) or the step edge release rate \(K\). Noting that the local surface derivative \(m\) can be written as \(m_\pm = \pm a_\bot / l\) (for \(\nabla h \geq 0\)), we can rewrite \(j(l)\) as \(j(m_\pm)\), and obtain a surface growth equation in terms of the surface derivatives. We Taylor expand \(j(m_\pm)\) in order to get the leading terms in \(m_\pm\). Using the expression Eq. 2.18 for the current, where all the physics of BCF was involved except the adatom desorption, we expand \(j(m_\pm)\) for positive slopes and get

\[ j \left( m_+ = \frac{a_\bot}{l} \right) = \frac{F(a_\parallel - l_{es})}{a_\parallel} + \nu \sum_{i=1}^{\infty} (-1)^{i-1} \left( \frac{a_\parallel + l_{es}}{a_\parallel} \right)^{i-1} m_+^i \]  

(2.24)
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where

\[ \nu = \frac{F}{a^3} \left( a_{\parallel}^2 - l_{es}^2 + R_{inc}(2l_{es} + R_{inc}) \right) \] (2.25)

Replacing \( m_+ \) with \( \nabla h \), we can derive the growth equation directly from this expression as:

\[ \partial_t h = \nabla_x \cdot j(\nabla h) = \nabla^2 h \times \frac{\partial j(\nabla h)}{\partial(\nabla h)} \]

\[ = \nu \nabla^2 h \sum_{i=0}^{\infty} (i+1) \left( -\frac{(a_{\parallel} + l_{es})}{a_{\parallel}} \nabla h \right)^i \] (2.26)

\[ = \frac{\nu \nabla^2 h}{\left( 1 + \frac{(a_{\parallel} + l_{es})}{a_{\parallel}} |\nabla h| \right)^2} \] (2.27)

where in Eq. 2.27 we let \( \nabla h \rightarrow |\nabla h| \) in order to account for the negative slope expansion \( m_- = -a_{\perp}/l \). This closed form equation is valid as long as

\[ |\nabla h| < \frac{a_{\parallel}}{a_{\parallel} + l_{es}} \] (2.28)

Inserting the expression for \( l_{es} \) from Eq. 2.15, we note that the slope restriction for a zero ES barrier is \( \nabla h < 1/2 \), or surfaces less steep than about 26°. A similar form for the growth equation was proposed by Johnson et al. [JOH 94]. In their case, the ES barrier was assumed positive, and the incorporation radius was not considered, so the prefactor \( \nu \) turned out negative. Their growth equation was therefore unstable, and a stabilizing “diffusional” term \(-\kappa \nabla^4 h \) was added, without which the equation would be ill-behaved (see discussion on p. 231 in Ref. [BS95]).

By truncating Eq. 2.26 at \( i = 2 \), a more common form for the continuum growth equations is revealed:

\[ \partial_t h \approx \nu \nabla^2 h + \nu_1 |\nabla h| \nabla^2 h + \nu_2 (\nabla h)^2 \nabla^2 h, \] (2.29)

where

\[ \nu_i = \nu \left( (-1)^i (i+1) \frac{(a_{\parallel} + l_{es})^i}{a_{\parallel}^i} \right), \quad i = 1, 2, 3, ... \] (2.30)

Remarkably, Eq. 2.29 shows that to the lowest order in \( \nabla h \), we have re-derived the Edwards-Wilkinson (EW) equation. A close inspection of the prefactor \( \nu \) (Eq. 2.25) shows that for a zero incorporation radius \( (R_{inc} = 0) \),
the sign of \( \nu \) is completely determined by the ES barrier: a positive barrier makes \( l_{es} > a_0 \) and hence leads to a negative \( \nu \), and vice-versa for a negative barrier. It also shows that when we set the ES barrier to zero, i.e. when interlayer diffusion is unbiased, the presence of the incorporation radius indeed stabilizes the surface, as \( \nu > 0 \) whenever \( R_{inc} > 0 \). The third term of Eq. 2.29 can be recognized from Ref. [SK94], and is equivalent in form to \( \nabla(\nabla h)^3 \).

\[ \text{2.8 Summary} \]

In this Chapter, we reviewed some basic concepts in crystal growth dynamics, including mechanisms that have a strong influence on the evolution of the surface morphology, such as adatom diffusion, the ES barrier and downhill funneling. These mechanisms were introduced into two growth models, specifically the analytical BCF theory and a stochastic SOS model. Through analysis of these models, it was found that a positive ES barrier causes mounding on initially flat surfaces. Conversely, a negative barrier was found to smoothen initially rough surfaces. It was also argued that the combined effect of a positive, destabilizing ES barrier and a surface relaxation mechanism could be equally well explained by a negative ES barrier.

Some consequences of various interlayer transport mechanisms were discussed. As an example, the “magic slope” arose when competing uphill and downhill adatom drift mechanisms were included in the growth model. This was found to give rise to slope-limited pyramid-shapes in the evolving surface morphology. We also discovered that the potential-energy landscape of GaAs near step edges can give rise to finger-shaped protrusions in the direction perpendicular to the step-direction. This effect was also consistent with the ES barrier being negative.

The BCF formalism assumes that the motion of step edges is much slower than diffusion of adatoms between the steps. This way, the adatom concentration on the terraces can be assumed to be in steady-state. Furthermore, it does not include the nucleation of islands on terraces, a limitation that we will investigate further in Chapter 3. Although simple, the BCF theory proves to be a remarkably useful formalism. Based on surface adatom current expressions calculated in this Chapter, we derived a continuum growth equation that to the lowest order coincides with the EW model. This derivation required that the net surface adatom current was downhill.
Chapter 3

Conventional continuum modeling of homoepitaxial growth

A particularly useful approach for modeling the surface morphology during epitaxial growth is to use continuum growth equations of the type that we referred to in Chapter 2 (see for example Eqs. 2.27 and 2.29 of Section 2.7). These equations use a coarse-grained version of the surface, and hence exhibit a lower spatial resolution than for example SOS models. However, their relative calculational simplicity allow them to complete in minutes, rather than hours or days which is the case for microscopic models like SOS. Also, they allow for an understanding of the effects of microscopic mechanisms on the macroscopic morphology. Many books and review articles are available for a more complete introduction to the topic of continuum models, see for example Refs. [Vil91, BS95, HHZ95, PV98] and references therein.

3.1 Continuum growth equations

In a continuum approximation, the discrete nature of the atoms is averaged, and the vertical steps are coarse-grained into a smooth surface, whose slope determines the density of incorporation sites (or steps) as $S \propto \nabla h$. In this approach, the time rate of change in the surface height $h(x, t)$ is expressed in terms of derivatives of $h$ [Vil91, BS95, HHZ95, Kru97, ZL99], of the form

$$\partial_t h \propto \nabla^2 h + \nabla^4 h + (\nabla h)^2 + \nabla^2(\nabla h)^2 + \nabla(\nabla h)^3 + \ldots + F + \eta(x, t)$$

(3.1)

The various terms on the right hand side are preceded by constants (left out of Eq. 3.1) that further reflect the underlying physical processes during growth. The source term $\eta(x, t)$ simulates the random arrival of atoms ("noise") at an average rate $F$. Generally, the noise is assumed to be uncorrelated, with $\langle \eta(x, t)\eta(x', t') \rangle = D\delta(x-x')\delta(t-t')$, where (...) represents an average over possible noise configurations. It is common to write the growth
equations in a moving reference frame, by the transformation \( h \rightarrow h - Ft \), which removes \( F \) from the growth equation. We will adopt this convention here.

In this general growth equation, symmetry arguments account for the absence of certain terms on the right hand side, like the direct dependence on \( h, x, \) and \( t \), as well as \( \nabla^n h \) and \( (\nabla h)^n \) for \( n \) odd. For a more in-depth discussion on symmetry, see for example Ref. [BS95]. Certain symmetries will be broken in some growth systems. For example, sloped parts of the surface grow faster laterally than vertically, causing a \textit{mounding} effect, and this asymmetry in the growth direction is a sign of the presence of nonlinear terms in the growth equations that inherently break the up-down symmetry \( h \rightarrow -h \).

Continuum equations in the context of crystal growth have received much attention in the literature, especially in the last decade. The emphasis has been on the understanding of universality classes of various growth models when applied to perfectly flat starting surfaces. Less effort has been put towards applying such models to actual surface growth experiments, with realistic starting surface shapes. In fact, investigations into various growth equations typically do not even have a figure showing a surface. Obviously, stronger communication between crystal growers and surface theorists will lead to better growth models.

### 3.2 Linear growth equations

The linear part of a growth equation consists of even derivative terms of the form

\[
\partial_t h = \nu \nabla^2 h - \kappa \nabla^4 h + C_6 \nabla^6 h + \ldots + \eta \tag{3.2}
\]

where the equation is written in such a way that positive prefactors \( \nu, \kappa \) and \( C_6 \) lead to a stable growth equation. For small surface slopes (long wavelength surface height perturbations), terms of order 6 and higher are very weak and their impact on the surface evolution harder to verify, and therefore they are often not included. The stability of a linear growth equation can easily be investigated by taking the spatial Fourier transform of the deterministic part of Eq. 3.2:

\[
\mathcal{F}[\partial_t h] = \partial_q \mathcal{H} = (-(iq)^2 \nu - (-iq)^4 \kappa) \mathcal{H} = -(\nu q^2 + \kappa q^4) \mathcal{H} \tag{3.3}
\]
Chapter 3. Conventional continuum modeling of homoepitaxial growth

where $\mathcal{H}(q, t) = \mathcal{H}(q, t)$ and $q$ is the spatial frequency. The straightforward solution is

$$\partial_t \mathcal{H}(q, t) = e^{-(\nu^2 + \kappa q^4)t} \mathcal{H}(q, 0)$$

(3.4)

As long as the prefactors are all positive, the evolution of each Fourier component is stable. If the highest order prefactor (in this case $\kappa$) is negative, then the $q^4$ term dominates, and the higher-order Fourier components of the surface diverge. A special case occurs when the lower order term is unstable, but the higher order term stabilizes it, as is the case in the Kuramoto-Sivashinsky (KS) equation [Kur94, Siv77, SM80]

$$\partial_t h = -\nu \nabla^2 h - \kappa \nabla^4 h + \eta$$

(3.5)

In this case, the lowest order term $-\nu \nabla^2 h$ grows when $\nu > 0$, but is stabilized by the higher order term $-\kappa \nabla^4 h$. This results in the emergence of a fixed wavelength $L_c = 2\pi/q_c$ with spatial frequency $q_c = \sqrt{\nu/2\kappa}$ [PT00]. Higher order analogies can be made. For example, a stable sixth order term can stabilize an unstable fourth order term with a critical $q_c = \sqrt{2\kappa/3C_6}$, or even an unstable second order term $-\nu \nabla^2 h$, with a critical $q_c = (\nu/3C_6)^{1/4}$. The KS equation was used in models of turbulence in chemical reactions and in fluid mechanics. It has been used to describe for instance flame fronts and unstable flow of a viscous fluid on a vertical plane [FBSK04]. Barabási and Stanley [BS95] showed that the KS equation could explain the pattern formation that occur during sputtering. However, it does not apply to the case of GaAs homoepitaxy, since the surface amplitude decays with time and there is no fixed wavelength.

3.2.1 The Edwards-Wilkinson equation

The lowest order linear equation that could be expected to describe surface growth is the EW equation [EW82]:

$$\partial_t h(x, t) = \nu \nabla^2 h(x, t) + \eta(x, t)$$

(3.6)

The linear term can arise from evaporation/condensation dynamics, as suggested by Mullins [Mul59] who described the interaction between a vapour with a constant chemical potential $\mu_v$ and a surface with an average chemical potential $\mu_0 < \mu_v$. In the continuum approximation, $\mu_0$ is determined by the surface tension $\sigma_s$ (free energy per unit surface area). To lowest order, variations about $\mu_0$ are induced by the local surface curvature [Kru97] as

$$\mu(x) = \mu_0 - \sigma_s \nabla^2 h(x)$$

(3.7)
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The incorporation rate can be determined using the ansatz: \( \partial_t h = -\gamma \mu \) for the relaxation, where \( \gamma > 0 \) is the interface mobility. Inserting this expression for \( \mu \) (Eq. 3.7) and subtracting the constant growth rate \( \gamma \mu_0 \) yields the EW equation (Eq. 3.6), with \( \nu = \sigma \gamma \), where \( \nu \) is always positive. The EW equation is stable, and any perturbations on the starting surface will smooth out towards a long-time steady-state level dictated by kinetic roughening, i.e. a balance between the smoothing effects of \( \nabla^2 h \) and the fluctuations due to the growth noise \( \eta \). The deterministic version of the EW equation is easy to solve, and gives a monotonic decay of each Fourier coefficient of the surface according to \( \exp(-\nu q^2 t) \), where \( q = 2\pi/L \) for surface features of lateral size \( L \).

3.2.2 The Ehrlich-Schwöbel barrier in the continuum limit

In an influential paper, Villain [Vil91] argues that the ES barrier can lead to the EW equation. This argument contradicts the results of the simulations that we showed in Figure. 2.5, where the conventional ES barrier caused mounding on a flat starting surface. His argument considers the case of a slightly miscut (vicinal) surface. Intuitively, in the presence of “diffusion bias” (interlayer transport in the uphill direction) caused by the ES barrier at the step edge, a stepped surface with terraces of different lengths would even out, and successive approximations result in the linear smoothing term \( \nu \nabla^2 h \) with \( \nu > 0 \). The argument in Ref. [Vil91] can be summarized as follows: assume an infinite ES barrier at the descending step, and assume a stepped surface where the terraces alternate between being wide and narrow, and where no island nucleation is allowed. The wide terraces will receive more atoms due to their larger areas than the narrow terraces, and all of these atoms will eventually attach to the ascending step. The ascending steps on a wide terrace will therefore move faster than the ascending step on a narrow terrace, thus the terrace widths equalize. This Gedanken-experiment is verified by a 1D calculation in Fig. 3.1, where the artificially created rough and vicinal starting surface straightens out during growth. The growth-mode reached when the terrace widths equalize is called step-flow.

Villain continues his discussion of growth equations by deriving the EW term for growth on a singular surface, but this time the conclusion is that the prefactor \( \nu \) is negative (see Appendix C in Ref. [Vil91]). This contradiction is not resolved in the paper by Villain, although a consensus seems to be that \( \nu \) must be negative due to the commonly accepted destabilizing effect of the ES barrier. Villain estimated that the size of the ES barrier can be no more than a room temperature value of \( k_B T \) (\( \sim 26 \) meV), and at the
time of the paper (1991), “no such instability has been reported, presumably because experimentalists just try to avoid it” so that at common epitaxial growth temperatures (~500-600°C), the effect of the ES barrier is “probably negligible”.

In the following, we will show where it is that Villain’s argument for a positive ES barrier’s stabilizing effect on a vicinal surface breaks down. We already showed in Fig. 2.5 that introducing a positive ES barrier into an SOS simulation triggered instabilities in the evolution of the morphology of a singular, flat starting surface. Fig. 3.2 shows a similar SOS calculation, but this time using a vicinal starting surface. The results indicate that the 1D calculation in Fig. 3.1 must be ignoring important physics. Fig. 3.2 (a) shows a starting surfaces that we evolve in Fig. 3.2 (b) and (c) for ES barriers with opposite sign. The starting surface was created so as to include both large flat terraces where nucleation is likely to occur, as well as steep sections where step-flow is the preferred growth mode. These simulations show that it is a negative ES barrier that stabilizes vicinal surfaces, and not a positive one, in contrast to Villain’s argumentation.

Figure 3.2 (b) shows the evolution of this starting surface using a negative ES barrier. The preferred growth mode is by step-flow, and there is only a minor indication of 2D growth on the wider terraces on top and bottom of this image. The negative ES barrier is stabilizing, and the initially very wide terraces at the top and bottom of the surface have shortened and the shorter terraces in the middle have grown wider.
Figure 3.2: SOS simulations showing the effect of the ES barrier on the surface morphology of a vicinal surface. Figures (a) through (c) show 400x200 atom topographs of (a) the starting surface; (b) 28 ML growth with $E_{es}=-50$ meV and (c) 20 ML growth with $E_{es}=50$ meV ($z$-range 48 ML). Figure (d) shows, from left to right, cross-sections down the middle of the images (a)-(c). Apart from the ES barrier, the standard parameters were used (Table 2.1). The growth temperature was 600°C.

Figure 3.2 (c) shows the corresponding simulation for a positive ES barrier. In this image, there is enhanced nucleation on the wider terraces when compared with the simulation in part (b), as one might expect. What might be surprising here is that large mounds form on the steep parts of the surface. This is in direct disagreement with Villain's 1D thought experiment (Fig. 3.1). The adatom concentration, $n$, on the narrow terraces in the steep regions will increase due to the blockage at the descending steps. This in turn increases the probability of dimer nucleation, which goes as $\sim n^2$. It is evident that even a few occurrences of nucleation on the narrow terraces is enough to destabilize this surface and lead to 3D growth. While it is the 2D effect of nucleation of small dimer-islands that triggers this effect, it is the formation of "advacancies" between the small islands and the step edges of the macroscopic morphology that causes the dramatic 2D to 3D transition. Figure 3.2 (d) shows, from left to right, scanlines down the middle of the images (a)-(c). Again, it is quite clear that a negative ES barrier (middle line) preserves the step-flow growth mode, while the positive ES barrier (right line) causes mounding in the steeper section of the surface.

As the terraces are already narrow, small advacancies (or trenches) will quickly develop when dimers nucleate. A conventional ES barrier inhibits
downhill flow of adatoms, and will therefore prevent adatoms from entering the vacancies. In fact, with a large ES barrier, a single vacancy will fill in at an average rate of $F$. This means that it obeys the statistics of, and evolve similarly to, a surface subject to a random deposition model without surface diffusion. Surface sites away from vacancies are bombarded by the same amount of atoms from the vapour, but also get visited by diffusing adatoms. The added visits from diffusing adatoms allow regular surface sites to fill in at a faster rate than the vacancies, or vice-versa, the vacancies can be seen as pinning centres for the surface height. Recent theoretical work recognizes the instability in step-flow growth on vicinal surfaces due to large, positive ES barrier [RvK96, KK04]. It has also been suggested that the instability on vicinal surfaces is a realization of the Bales-Zangwill mechanism\(^1\), which causes the steps to "meander" [KKK02].

We summarize this Section as follows: (1) a positive ES barrier is destabilizing both to singular (Fig. 2.5) and vicinal surfaces (Fig. 3.2) and cause an obvious emergence of 3D growth. Conversely, a negative ES barrier is stabilizing in both cases, and 3D growth is not observed; (2) Villain’s simple thought experiments [Vil91] in 1D ignore nucleation of dimer islands, and the resulting morphology from his model is in stark contradiction with the 2D analysis done in this Section. Based on the arguments made in this Section, the unstable EW equation ($\partial_t h = -|\nabla|V^2 h/\mu$) is now consistently linked to a positive ES barrier, whether it is applied in growth on vicinal or singular surfaces.

### 3.2.3 Mullins' diffusion

The next possible linear growth term is the diffusion term attributed to Mullins [Mul59]:

$$\partial_t h = -\kappa \nabla^2 (\nabla^2 h) \tag{3.8}$$

or simply $-\kappa \nabla^4 h$. The formulation is based on the mass conservation argument, where it must be possible to write the growth equation as a continuity equation

$$\partial_t h = -\nabla \cdot j \tag{3.9}$$

The current density $j$ is a vector parallel to the average surface direction (and not the local surface). Landau & Lifshitz [LL67] showed that

$$j = \text{Const.} \times \nabla \mu(r,t) \tag{3.10}$$

\(^1\)J. Krug, private communication.
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Equation (3.9) and (3.10), together with the expression in Eq. 3.7 for the chemical potential, lead to Mullins' diffusion term, Eq. 3.8.

An interesting consequence of Mullins' diffusion term is that for certain starting surfaces, namely those with steep sections and hence significant higher-order Fourier components, it causes the initial peak-to-peak amplitude to temporarily overshoot, as indicated by Fig. 3.3. This might seem surprising, as Mullins' equation (3.8) should have its Fourier coefficients decay in a fashion similar to the EW equation, namely as \( \exp(-\kappa q^4 t) \). However, Fig. 3.3 (a) shows the evolution of a square grating surface (at time \( t_0 \)) during growth, according to Mullins' equation. Soon after growth commences, holes are formed close to the sidewalls in the valleys, as well as bumps close to the top of the grating. This causes the early increase in the surface amplitude, labelled \( t_1 \) in Fig. 3.3 (b). As these valley-holes move slowly towards the centre of the valley, they temporarily start to level out, but then superimpose to form one deeper cusp (at time \( t_2 \)), which causes the second rise in the surface amplitude. The bumps on the top of the grating do the same in this symmetric problem. Once the bumps come together, the valley fills monotonically. Interestingly, this form of amplitude overshoot (bimodal, non-monotonic) is observed in a later Chapter (Ch. 5), where the starting surfaces are pre-patterned lithographically with shapes similar to those depicted in Fig. 3.3 (a).

3.3 Nonlinear growth equations

Linear growth equations like Eq. 3.2 are analytically solvable in the deterministic case, but the inclusion of noise or nonlinear terms requires the use of
numerical solution techniques. The complex properties of even the simplest nonlinear growth model, the Kardar-Parisi-Zhang (KPZ) equation \cite{KPZ86}, continue to fascinate researchers, and new publications on this equation itself as well as its applicability to crystal growth occur frequently. In this Section, we describe some of the simplest nonlinear growth terms. The questions we seek to answer include (a) their effects on the surface morphology, and (b) their physical origins.

3.3.1 The Kardar-Parisi-Zhang equation

One of the most studied continuum equations is the KPZ equation \cite{KPZ86, Yak81}:

\[
\frac{\partial h}{\partial t} = \nu \nabla^2 h + \frac{1}{2} (\nabla h)^2 + \eta
\]  

The nonlinear term is an approximation which is often used to model the situation where growth proceeds outward from the local surface normal \cite{BS95, Kru97}, although other interpretations are possible. Villain \cite{Vil91} showed that growth on a stepped surface where desorption was allowed could lead to the KPZ nonlinearity. It has also been shown that the nonlinear term comes out naturally when overhangs and vacancies are allowed in the growth model \cite{Bal98}, for example in models like the ballistic deposition model. Overhangs and vacancies are not observed in MBE, and in GaAs homoepitaxy, neither is desorption. A common objection to the KPZ nonlinearity in the context of MBE is that it does not conserve mass. This is a valid concern in the case of GaAs homoepitaxy, although for the relatively flat surfaces that we treat in this Chapter, the added material due to the KPZ nonlinearity has a minimal influence on the average growth rate.

The nonlinear term also breaks inversion symmetry in the growth direction: positive values of \( \lambda \) cause round mounds on the tops with sharper cusps in the valleys, and vice versa for negative values. Intuitively, one would assume that the mounded shapes are related to the added growth on the sloped parts of the surface, where the incorporation of adatoms to steps takes place, as the steps are in abundance there.

In the case of homoepitaxy on GaAs (001), the presence of a second order linear term means that there is a downhill current of adatoms, caused for example by a negative ES barrier, as we discussed in Section 3.2.2. Even if the ES barrier is positive, the nonlinear term is capable of balancing the instability introduced by a negative EW term (\( \nu < 0 \)) \cite{KPS93}, but it is not known whether weaker nonlinearities that conserve mass (i.e. \( \nabla^2 (\nabla h)^2 \)) have this ability \cite{SKJ+92}.
3.3.2 The molecular beam epitaxy equation

Under typical GaAs MBE growth conditions, atoms arriving at the surface undergo significant diffusion before incorporating at favourable sites. If the sticking coefficient is unity, then the growth rate is determined solely by the flux and not by the surface shape. Therefore, nonconservative terms should not be present in the growth equation. To this end, the MBE equation has been formulated \[\text{SGG89, WV90, LS91, Sar93, SK94, BS95, Kru97}\]

\[
\frac{\partial h}{\partial t} = -\kappa \nabla^4 h - \frac{\Delta}{2} \nabla^2 (\nabla h)^2 + \eta
\] (3.12)

where \(\eta\) may be either nonconservative flux noise like we described in Section 3.1, or conservative diffusive noise with correlation function [Kru97]

\[
\langle \eta(x, t)\eta(x', t') \rangle = D_c \nabla^2 \delta(x - x') \delta(t - t').
\]

The fourth order linear term is the same as Mullins' diffusion term [Kru97, Mul57]. The fourth-order nonlinear term is generally believed to be generated by a nonequilibrium surface chemical potential induced by the deposition flux [Kru97]. In this case, one expects the chemical potential to be an even expansion of \(\nabla h\), of the type \(\mu(x) \propto (\nabla h)^2 + (\nabla h)^4 + \ldots\), instead of the linear form in Eq. 3.7. A discussion on this expansion can be found in Ref. [Kru97], pp.245-252. This term can also be attributed to a slope dependent adatom concentration [Vil91]. For a highly symmetric orientation, Villain proposed an adatom concentration dependency of the form \(\rho = \rho_0 + \rho_1 (\nabla h)^2\), from which the nonlinear term emerges through the application of Fick's Law, Eq. 2.4, and a continuity equation, like Eq. 3.9 [Vil91]. We will refer to the fourth-order nonlinearity as the "Villain-term".

3.3.3 Conservative Kardar-Parisi-Zhang equation

A conservative version of the KPZ equation can be generated by modifying the nonlinear term. To achieve this, we first note that when the growth proceeds outward from the surface normal at a constant rate \(\lambda\), the growth rate can be projected onto the vertical direction, leading to

\[
\partial_t h = \lambda \sqrt{1 + (\nabla h)^2} \approx \lambda \left[1 + \frac{1}{2} (\nabla h)^2\right]
\] (3.13)

demonstrating the link between normal growth and the KPZ term. The approximation is valid for \(|\nabla h| \ll 1\). For a rough surface of side length \(L\), Eq. (3.13) leads to the addition of a total volume:

\[
\delta V = \delta t \int_0^L \int_0^L \lambda \sqrt{1 + (\nabla h)^2} d^2x
\]

\[
= \lambda \delta t L^2 \left\langle \sqrt{1 + (\nabla h)^2} \right\rangle
\] (3.14)
in an infinitesimal time $\delta t$, where $\langle \ldots \rangle$ represents an averaging over the surface. On a perfectly flat surface with the same dimensions, the total volume added is simply $\delta V_0 = \lambda \delta t L^2$. A conservative growth equation is obtained by normalizing the volume added, then subtracting the growth rate. This is achieved through the substitution

$$\frac{\lambda}{2} (\nabla h)^2 \to \lambda \left[ \frac{\delta V_0}{\delta V} \sqrt{1 + (\nabla h)^2} - 1 \right]$$

where we have used the approximation in Eq. (3.13). Physically, in the case of GaAs growth discussed here, the correction describes the situation where the density of mobile atoms on the surface adjusts itself such that the net incorporation rate balances the arrival rate of atoms from the growth flux. The resulting equation is non-local and is difficult to investigate using standard analytical techniques, so we have simulated the behavior numerically. One could also analyze the KPZ equation in its original form (Eq. 3.11) by viewing it as a lowest order approximation to an actual, conservative term. Our particular treatment results in a non-local equation, which might very well belong to a different universality class than the KPZ equation itself (see Section 3.5).

### 3.3.4 The Das Sarma equation

The last term that we will discuss is the conservative, nonlinear term $\Lambda_{1,3} \nabla (\nabla h)^3 = 3\Lambda_{1,3} (\nabla h)^2 \nabla^2 h$. Das Sarma and Kotlyar [SK94] discovered that in the absence of the EW term $\nabla^2 h$, this term will dominate the asymptotic, long-time scaling behaviour of a general growth equation of the type

$$\partial_t h = -\kappa \nabla^4 h + \frac{\Lambda_{2,2}}{2} \nabla^2 (\nabla h)^2 + \Lambda_{1,3} \nabla (\nabla h)^3 + \eta$$

(3.16)

We have already covered the first two terms on the right hand side, so in Fig. 3.4 we show the effect of the third term $\Lambda_{1,3} \nabla (\nabla h)^3$ on a square starting surface, with $\Lambda_{1,3} > 0$. We see that this term ensures smooth surface evolution: in the case that the EW term $\nu \nabla^2 h$ is zero, the surface still smooths. No physical mechanism is known to generate this term in the absence of the $\nabla^2 h$ term [LS91].

\footnote{See Section 3.6.}
3.4 Effect of growth equation terms on surface shape evolution

An educational way of looking at the various linear and nonlinear growth terms is to evolve them one time step and see what effect they have on the surface evolution. In order to achieve this, we have included the often-used illustration [BS95, SK94] depicted in Fig. 3.5. In part (a), a typical surface segment is shown. Parts (b) to (f) show the various growth terms discussed in this Section when applied to the surface in (a). The nonlinear KPZ term in (b) adds to the steepest parts of the surface, but it is always positive, and hence nonconservative. The EW term in (c) smooths the surface by removing material from points and adding it to kinks. The Das Sarma term in (f) is seen to act similarly to the EW term, but at a slightly shorter length scale, or higher spatial frequency, as expected from the higher-order of derivatives present in this term. Mullins' term in (d), with a negative pre-factor, adds material to kinks by drawing from nearby regions. The Villain term in (e) conservatively draws adatoms from kinks and points and adds it to the steeper parts of the surface.

3.5 Universality classes

The different kinds of growth processes, as represented by the different growth equations, can be characterized by their universality class. Associated with each universality class is a set of exponents $\alpha$ (roughness exponent), $\beta$ (growth exponent), and $z = \alpha/\beta$ (dynamic exponent), describing the scaling properties of the surface. These scaling parameters were introduced in the previous Section. We give a quick overview of the theory of scaling in this Section [Bal98].
The interface width, $W$, of a continuous surface is defined by

$$W^2 = \frac{1}{L} \int_L dx \left( h(x) - \bar{h} \right)^2$$  \hspace{1cm} (3.17)

where $\bar{h}$ is the average height of the surface, and equals $Ft$. This quantity gives us a statistical measurement of the surface roughness. Many studies of thin film growth are based on the dynamic scaling behaviour of the surface statistics that depends on the various surface relaxation and roughening processes [FV85, FV91]. By plotting the interface width as a function of time, two distinct regions are observed: at times less than some 'crossover' time $t_x$, $W$ increases as a power of time [BS95]:

$$W(L, t) \sim t^\beta, \hspace{1cm} [t \ll t_x]$$  \hspace{1cm} (3.18)

where $\beta$ characterizes the time-dependence of the growth dynamics. This interface width continues to increase until a certain value is reached: $W$ saturates according to

$$W_{sat}(L) \sim L^\alpha, \hspace{1cm} [t \gg t_x]$$  \hspace{1cm} (3.19)

The crossover time depends on the system size as

$$t_x \sim L^z, \hspace{1cm} [t \sim t_x]$$  \hspace{1cm} (3.20)
Table 3.1: Critical exponents associated with various growth equations in (2+1) dimensions. The second column indicates whether the noise is conservative (C), or nonconservative (N).

<table>
<thead>
<tr>
<th>Equation</th>
<th>Noise</th>
<th>( \alpha )</th>
<th>( \beta )</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>EW</td>
<td>N</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>KPZ</td>
<td>N</td>
<td>0.385</td>
<td>0.24</td>
<td>1.58</td>
</tr>
<tr>
<td>MBE</td>
<td>N</td>
<td>0.667</td>
<td>0.2</td>
<td>3.333</td>
</tr>
<tr>
<td>MBE</td>
<td>C</td>
<td>0</td>
<td>0</td>
<td>4</td>
</tr>
</tbody>
</table>

The three parameters, \( \alpha \), \( \beta \) and \( z \) are dependent on one another, and they can be extracted from a given system by normalizing \( W \) and \( t \) [FV85]. We obtain the relation

\[
\frac{W(L,t)}{W_{\text{sat}}(L)} \sim f \left( \frac{t}{t_x} \right) \tag{3.21}
\]

Substituting from above we find that for an initially smooth surface, the interface width scales according to the so called Family-Vicsek scaling relation [BS95, FV85, FA85]:

\[
W(L,t) = L^\alpha f \left( \frac{t}{L^{\alpha/\beta}} \right) \tag{3.22a}
\]

\[
f(x \ll 1) \sim x^\beta \tag{3.22b}
\]

\[
f(x \gg 1) \rightarrow \text{constant} \tag{3.22c}
\]

By plotting this relationship, we see that systems of different sizes \( L \) will collapse onto one curve. Solving for \( z \) around \( t = t_x \) we get

\[
z = \frac{\alpha}{\beta} \tag{3.23}
\]

This scaling law links the three exponents, and is valid for any growth system that follows the Family-Vicsek scaling relation. Table 3.1 summarizes the known exponents for some of the growth equations [BS95].

Experimental measurements of the surface shape can be used to extract the growth exponents, thereby giving an indication of the particular equation governing the surface evolution. One useful measure is the power spectral density (PSD), defined by

\[
\text{PSD}(q,t) = [\mathcal{H}(q,t)]^2 \tag{3.24}
\]
where \( \mathcal{H}(q, t) \) is the Fourier transform of \( h(x, t) \) at spatial frequency \( q \). After a long period of growth the PSD is expected to approach an asymptotic form determined by the critical exponents of the growth equation. In \((2+1)\) dimensions the asymptotic form is

\[
\text{PSD}(t \to \infty) \sim q^{-2(1+\alpha)}
\]

(3.25)

where \( q = |q| \), and the overall amplitude depends on both the strength of the noise and the coefficients in the growth equation. For finite growth times, the asymptote will be observed only for \( q \) larger than some cutoff value \( q_c \sim t^{-1/\alpha} \).

Neither the PSD nor the interface width \( W \) contain any phase information. This means that \( W \) does not distinguish between a surface that has mounds in the up-direction from one that has them in the down-direction. In Fig. 3.5, we showed that certain terms in a general growth equation expansion attribute to a breach in the inversion symmetry for the surface height, \( h \). The prefactor of such terms determines whether the mounds point up or down. This means that the sign of the prefactors for the nonlinear terms cannot be determined by analyzing the interface width or PSD alone.

### 3.6 Power counting and relevance of terms

By scaling the growth equation in question, we can determine the relevance of the various terms in the long-time, long-wavelength limit ("the hydrodynamic limit"). We scale the relevant variables according to the following transformation:

\[
\tilde{h} = b^\alpha h(bx, bt)
\]

(3.26)

In the new coordinates, the interface velocity can be written as:

\[
\partial_t \tilde{h} = b^\alpha \partial_t h
\]

(3.27)

The EW term scales as:

\[
\nabla^2 \tilde{h} = b^{\alpha-2} \nabla^2 h
\]

(3.28)

We can therefore write the scaled EW equation (3.6) as:

\[

\begin{align*}
\nu b^{\alpha-2} \partial_t h &= \nu b^{\alpha-2} \nabla^2 h + b^{-(d+z)/2} \eta \\
\downarrow \\
\partial_t h &= \nu b^{2-2} \nabla^2 h + b^{(z-d)/2-\alpha} \eta
\end{align*}
\]

(3.29)

(3.30)
where a derivation of the scaling of the noise-term in Eq. 3.29 can be found in Refs. [BS95, Kru97]. Dynamical scaling invariance requires that Eq. 3.30 can be written as the original equation we started with, the EW equation. This is obtained by "counting the powers" in Eq. 3.30. In order to regain the EW equation, the prefactor for the $\nabla^2 h$ term must equal $\nu$, which can be achieved when $z = 2$. Substituting this value into the prefactor for the noise-term gives the general scaling relation for the EW equation:

$$\text{EW scaling : } \begin{cases} z = 2 \\ \alpha = \frac{2-d}{2} \\ \beta = \frac{2-d}{4} \end{cases} \quad (3.31)$$

In order to see the relevance of the nonlinear term with respect to the linear term in the KPZ equation, we scale it:

$$(\nabla h)^2 = b^{2(\alpha - 1)}(\nabla h)^2 \quad (3.32)$$

Inserting (3.32) into (3.29), and using the results for the scaling parameters $(\alpha, \beta, z)$ from the linear case (Eq. (3.31)), we arrive at

$$\lambda = b^\alpha \lambda = b^{(2-d)/2} \lambda \quad (3.33)$$

This means that the KPZ nonlinearity is relevant as long as the prefactor amplifies during scaling, i.e. as long as in Eq. 3.33 we have $b^{(2-d)/2} > 1$. This creates the condition that $d < 2$, and we refer to this as the "critical dimension" for the KPZ equation.

By applying power counting to the KPZ equation, we have learned that the nonlinear term is irrelevant in the hydro-dynamic limit for the practical case $d = 2$. There is, however, a situation where power counting does not give a fully reliable answer, namely in the strong coupling regime. This occurs when the prefactor, $\lambda$, exceeds some critical value. It has been shown that for the KPZ equation, such a situation occurs whenever $\lambda h_0/\nu > 1$, where $h_0$ is proportional to the amplitude of the largest perturbation in the surface height [NB96, NK96]. It is not clear at present whether strong coupling applies to other nonlinear interface models [Kru97].

The various growth terms considered in this Chapter scale as follows:

- EW : \[ \nabla^2 h \rightarrow b^{\alpha-2} \nabla^2 h \]
- Mullins : \[ \nabla^4 h \rightarrow b^{\alpha-4} \nabla^4 h \]
- KPZ : \[ (\nabla h)^2 \rightarrow b^{2\alpha-2} (\nabla h)^2 \]
- Villain : \[ \nabla^2 (\nabla h)^2 \rightarrow b^{2\alpha-4} \nabla^2 (\nabla h)^2 \]
- Das Sarma : \[ \nabla (\nabla h)^3 \rightarrow b^{3\alpha-4} \nabla (\nabla h)^3 \] \quad (3.34)
From these relationships, it can be seen that the Mullins term is irrelevant when compared to the EW term, because

\[ \nabla^4 \tilde{h} : \nabla^2 \tilde{h} \sim b^{-2} \]  

(3.35)

This means that a completely linear growth equation scales according to the parameters determined in (3.31), i.e. the EW scaling parameters. We also see that the KPZ term dominates the Villain term (\( \sim b^2 \)), and the Das Sarma term dominates both the Mullins term (\( \sim b^{2\alpha} \)) and the Villain term (\( \sim b^3 \)), as indicated in Section 3.3.4. In the absence of the EW term then, the Das Sarma equation (3.16) scales according to the term \( \nabla (\nabla h)^3 \) in the hydro-dynamic limit.

It might appear as if the order of the linear term must be equal or smaller than the order of the nonlinear term in a growth equation in order to agree with scaling arguments. This is not always the case, as was shown by Golubović et al. [GB91], who investigated the following equation:

\[ \partial_t h = -\kappa \nabla^4 h + \frac{\lambda}{2} (\nabla h)^2 + \eta \]  

(3.36)

It was found that the nonlinear term was relevant for \( d < 8 \). However, as the nonlinear KPZ term is nonconservative, it must always be accompanied by an evaporation/condensation term proportional to \( \nabla^2 h \) [Kru97].
Chapter 4

Epitaxial growth experiments on GaAs (001)

Theoretical analysis of different growth mechanisms yields different continuum equations [Vil91, BS95, HHZ95, Kru97], so determining the equation that best fits the experimental data can provide valuable insight into the dominant physical processes involved in the growth. As an example, the presence of an ES barrier [EH66, SS66], which inhibits downward diffusion of mobile atoms at step edges, leads to a lowest order growth equation \( \partial_t h \propto -\nabla^2 h \). This equation is unstable, and a small initial perturbation in \( h \) will grow with time. This seems like a suitable mathematical description of mounding, and it has been interpreted that way by several groups [OJS+94, JOH+94, HOW+94, AHD+00]. In these references, countering mechanisms were introduced into the growth models in order to limit the growth and extent of the mounds. We discussed some of these mechanisms in Chapter 2.

In this Chapter, we will investigate mounding and large-scale morphology of GaAs by looking into the the low-amplitude, long-wavelength limit of homoepitaxial growth. We put two continuum models to the ultimate test by comparing their predictions to the real world of epitaxial growth. This is done by growing thin films on top of GaAs substrates with various starting surfaces, at different temperatures and for different thickness films. We then compare the surfaces and power spectra obtained from AFM images of the experimental surfaces and the corresponding images from the growth simulations based on the KPZ equation and the MBE equation\(^1\). The epitaxy experiments that we report in this Chapter were performed in great part by

Martin Adamcyk, with some aid from Ben Ruck, Tom Tiedje and myself. Further experimental details beyond those outlined here can be found in Martin Adamcyk's thesis [Ada02].

4.1 Simulations

The critical exponents given in Table 3.1 for the different growth equations are difficult to determine experimentally, due to a limited dynamic range accessible during growth. Furthermore, for real systems the morphology of the starting surface may also affect the scaling properties of the system at finite growth times. During this transient regime, measurements of the scaling exponents may not reveal the universality class. Instead, it is desirable to compare the measured surfaces to simulations of the different growth equations.

We have discretized the continuum growth Eq. 3.11 (KPZ equation) including the modification described by Eq. 3.15, as well as Eq. 3.12 (MBE equation). Numerical instabilities restrict the range of parameters which can be used in typical finite difference implementations of the nonlinear terms [NB96]. Therefore, we have used a novel, more stable implementation based on the normal growth approximation to the KPZ term (Eq. 3.13). The algorithm translates all points on the surface outwards along the normal by a constant amount, thereby providing an excellent way to approximate the \((\nabla h)^2\) term. Details of the implementation of this term and the other terms in the growth equation are provided in Appendix C.

Nonconservative noise is included in the simulations by adding an amount \(\Gamma_n \sigma_n \sqrt{2 \Delta t U(t)}\) to each point on the surface at each time step [BS95], where \(\sigma_n^2 = 2D/(\Delta x)^2\), \(\Delta x\) is the spacing between the lattice points in the simulation, \(\Delta t\) is the simulation time step, \(U(t)\) is a random number uniformly distributed between \(-0.5\) and \(0.5\), and \(\Gamma_n\) is a dimensionless fitting parameter. For flux noise, one expects \(\Gamma_n = 1\), and \(D = Fa_\perp a_\parallel^2\) in our units [BS95], where \(F\) is the flux in nm/s, \(a_\parallel\) is the in-plane atomic spacing of 0.4 nm and \(a_\perp\) is the GaAs monolayer height of 0.28 nm.

Conservative noise can also arise during the growth process due to thermal fluctuations in the binding site of surface atoms. We have implemented an algorithm to approximate conservative noise in the following way. At each time step, we add/remove an amount \(\Gamma_c \sigma_c \sqrt{12 U(t)}\) from each point on the surface and transfer exactly this amount to one of the nearest neighbor sites. This is repeated for each of the four nearest neighbors, using periodic boundary conditions. The coefficient \(\sigma_c = \sqrt{\Delta t/(\Delta x)^4}\) ensures that
the amplitude of the PSD generated by the simulations does not change if we vary the lattice spacing $\Delta x$ or time step $\Delta t$. $\Gamma_c$ is a fitting parameter with dimensions $\text{nm}^3/s^{1/2}$ that adjusts the overall noise level to optimize the match between the simulations and experimental data. Generally, $\Gamma_c$ is expected to increase as either the number of mobile atoms or the individual adatom diffusion constant increases, by increasing the growth rate $F$ or the growth temperature $T$, respectively. Although other, more detailed implementations of conservative noise are certainly possible, our algorithm is adequate for testing the continuum growth equations.

We have simulated the KPZ and the MBE equations numerically in order to generate the PSD at a range of different times, using a flat surface as the initial condition. The fourth order MBE equation was simulated using both conservative and nonconservative noise. In all cases the critical exponents extracted from the PSDs agree within uncertainty with the values given in Table 3.1, confirming the accuracy of our numerical schemes.

### 4.2 Experimental method

All samples in this study were prepared on [001] oriented GaAs substrates in a VG-V80H MBE chamber equipped with solid source effusion cells for both group III and group V elements. The growth rate, determined by the Ga flux, was kept constant at around $1 \mu\text{m/hr}$ during each run. A valved cracker was used as the As source, under conditions which give almost entirely As\textsubscript{2} as the group V flux. The group V to group III beam equivalent pressure (BEP) flux ratios were estimated from measurements made with an ion gauge placed in front of the samples. The substrate temperature was monitored by optical bandgap thermometry [Joh95, JLT93, JT97] throughout the growth, with an absolute accuracy of about $\pm 5^\circ\text{C}$. Prior to loading into the MBE chamber, the substrates were exposed to ultraviolet light and ozone to remove carbon contaminants. The resulting surface oxide was removed in-situ, either by thermal evaporation at $600^\circ\text{C}$ under an As\textsubscript{2} overpressure, or by an atomic hydrogen etch. The hydrogen used in the etch was cracked with a W filament placed in front of the sample. During the etch the substrate was nominally set to $150^\circ\text{C}$, but radiation from the W filament caused the temperature to rise somewhat above this value. Details of the parameters associated with each sample can be found in Table 4.1.

During growth, the surface roughness was monitored by elastic light scattering. Light from a chopped Hg arc lamp was incident through a quartz viewport onto the growing sample. The surface roughness diffusely
Table 4.1: Summary of growth parameters for the samples described in the text. \( T_{\text{sub}} \) is the substrate temperature and V:III is the Ga to As flux ratio (BEP) during growth. The oxide removal method is either thermal desorption (TD) or hydrogen etch (HE).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_{\text{sub}} ) (°C)</th>
<th>Growth Time (mins.)</th>
<th>V:III</th>
<th>Surface Prep.</th>
</tr>
</thead>
<tbody>
<tr>
<td>730 T0</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>TD</td>
</tr>
<tr>
<td>744 H1</td>
<td>595</td>
<td>75</td>
<td>6.5</td>
<td>HE</td>
</tr>
<tr>
<td>755 T4</td>
<td>550</td>
<td>75</td>
<td>2.9</td>
<td>TD</td>
</tr>
<tr>
<td>769 H0</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>HE</td>
</tr>
<tr>
<td>776 H2</td>
<td>552</td>
<td>10</td>
<td>5.5</td>
<td>HE</td>
</tr>
<tr>
<td>780 H3</td>
<td>553</td>
<td>37.5</td>
<td>6.5</td>
<td>HE</td>
</tr>
<tr>
<td>836 T6</td>
<td>600</td>
<td>69</td>
<td>8.3</td>
<td>TD</td>
</tr>
<tr>
<td>838 T2</td>
<td>550</td>
<td>37.5</td>
<td>7.8</td>
<td>TD</td>
</tr>
<tr>
<td>839 T1</td>
<td>550</td>
<td>10</td>
<td>8.3</td>
<td>TD</td>
</tr>
<tr>
<td>841 T3</td>
<td>550</td>
<td>150</td>
<td>8.4</td>
<td>TD</td>
</tr>
<tr>
<td>852 T5</td>
<td>550</td>
<td>3</td>
<td>8.5</td>
<td>TD</td>
</tr>
<tr>
<td>899 H5</td>
<td>550</td>
<td>30</td>
<td>1.0</td>
<td>HE</td>
</tr>
<tr>
<td>912 H4</td>
<td>550</td>
<td>30</td>
<td>3.0</td>
<td>HE</td>
</tr>
</tbody>
</table>

scatters some of the incident light out of the chamber through two additional viewports, where it is detected by photomultiplier tubes fitted with wavelength selective filters. The chamber geometry, and the wavelength of light monitored, allows us to measure the roughness at spatial frequencies of 16 and 41 \( \mu \text{m}^{-1} \), corresponding to length scales of 393 and 153 nm, respectively. It can be shown that the measured light scattering signal is proportional to the PSD of the surface at the spatial frequency monitored [ABP+00, CJZ77, CJZ79]. The scattering vectors for the two signals are 22.5° apart in the plane of the wafer, so the roughness is probed along slightly different crystallographic directions on the film surface.

AFM images were obtained from the samples soon after removal from UHV, using a Digital Instruments Multimode Scanning Probe Microscope. Scans ranging from \( 1 \times 1 \mu \text{m}^2 \) to \( 100 \times 100 \mu \text{m}^2 \) were taken in tapping mode using Si tips with approximate tip radius 30 nm [Pin99]. Therefore, we can obtain reliable data up to spatial frequencies of at least 100 \( \mu \text{m}^{-1} \) before tip convolution effects become significant.
4.3 Results and analysis

4.3.1 Growth on thermally desorbed substrates

Time dependence

Figure 4.1 shows a GaAs surface immediately prior to growth, after thermal cleaning of the surface oxide. The thermal desorption process produces a surface covered with pits, with the largest pits separated by a characteristic distance of around 1 μm, and having a maximum depth of around 40 nm. Figure 4.2 shows a set of AFM scans from samples grown for different times at 550°C on thermally cleaned substrates, using a similar As₂ flux for each growth. Each of the grown surfaces is covered with mounds elongated along the [110] crystal axis, and separated by sharp V-grooves. The mounds have a characteristic separation similar to that of the pits on the starting surface, strongly suggesting that they are a remnant of the initial condition.

The root-mean-square (RMS) roughness of the surfaces shown in Figs. 4.1 and 4.2 decreases steadily with time during growth, progressing through 4.9 nm, 1.0 nm, 0.7 nm, and 0.5 nm after 0, 10, 37.5, and 150 minutes of deposition, respectively. This smoothing is inconsistent with the idea of unstable growth [OJS+94, JOH+94], in which the mounds would be ex-
Figure 4.2: AFM images from thermally desorbed samples grown under nominally identical conditions, but for different times. (a) 10 minutes growth (sample T1, z-range 11 nm). (b) 37.5 minutes growth (sample T2, z-range 7 nm). (c) 150 minutes growth (sample T3, z-range 5 nm). The arrows point along the [110] direction, and the image size was 10 x 10 \( \mu \text{m}^2 \).
expected to increase in amplitude as time progresses. A careful comparison of Figs. 4.2 (a)–(c) shows also that the number of mounds decreases as the surface smooths, while the lateral length scale of the remaining mounds increases. This is consistent with the behavior expected from the second order nonlinear term in the KPZ equation (Eqs. 3.11 and 3.15); the mounds grow outward in time such that the larger mounds absorb the smaller ones.

If a single continuum equation is to be used to describe the surface evolution, then the equation must be capable of reproducing the morphology after a range of different growth times. The persistence of V-grooves on the surface suggests that a nonlinear equation, such as the KPZ or MBE equations, is the correct choice. Figure 4.3 shows two surfaces simulated using the KPZ equation with parameters $\nu_x = 10 \text{ nm}^2/\text{s}$, $\nu_y = 1 \text{ nm}^2/\text{s}$, and $\lambda_x = \lambda_y = 12 \text{ nm}/\text{s}$, where the subscripts $x$ and $y$ correspond to the [1\bar{1}0] and [\bar{1}10] directions, respectively. Nonconservative noise was included in each of the simulations with strength $\Gamma_n = 10$, considerably larger than the value $\Gamma_n = 1$ expected from the random arrival of atoms from the flux (see Section 4.1). Figure 4.4 shows two surfaces simulated using the MBE equation with parameters $\kappa_x = 3 \times 10^5 \text{ nm}^4/\text{s}$, $\kappa_y = 10^5 \text{ nm}^4/\text{s}$, $\Lambda_x = 10^6 \text{ nm}^3/\text{s}$, and $\Lambda_y = 10^5 \text{ nm}^3/\text{s}$. Conservative noise was added to these simulations with strength $\Gamma_c = 100 \text{ nm}^3/\text{s}^{1/2}$. In both cases the simulations
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Figure 4.4: 10 × 10 μm² simulations generated using the fourth order molecular beam epitaxy equation with growth times of (a) 10 minutes (z-range 14 nm), and (b) 37.5 minutes (z-range 11 nm). The arrows point along the [110] direction. The fourth order equation also produces a mounded surface, although the depth of the cusps between the mounds is greater than on the real surfaces. A comparison between these images and the real surfaces shown in Fig. 4.2 (a) and (b), are not as favourable as the KPZ simulations shown in Fig. 4.3 were.

are performed on a 256×256 grid, using an AFM scan of the desorbed wafer as the initial condition.

For both sets of simulations the times match the shortest two growth times in Fig. 4.2 (10 and 37.5 minutes), and the coefficients have been adjusted to provide the best possible agreement with the experimental data, as determined by visual inspection. Note that the coefficients used for the KPZ simulations are slightly different to those used in Ref. [BRA+01] to model a 75 minute growth. This is due to slight variations in the surface morphology caused by the higher As₂ overpressure used during the growth of the present samples. Without the nonlinear terms both growth equations generate inversion symmetric surfaces [Vil91, BS95, HHZ95, Kru97], whereas with our inclusion of the nonlinear terms both equations cause the etch pits on the starting surface to develop into mounds separated by V-grooves, in agreement with the experimental surface morphology. However, while the surfaces generated by the KPZ equation have similar roughness to the real surfaces at all length scales, the MBE equation generates less smoothing of the largest features than is seen in the experiment. Modifying the parameters of the MBE equation to enhance smoothing of the deepest
pits causes the smaller mounds to be less prominent than those on the real surface.

Figure 4.5 (a) shows the PSDs of a thermally desorbed substrate (sample T0), a sample grown for 10 minutes (sample T1), and a sample grown for 150 minutes (sample T3), measured along the [110] direction. Figure 4.5 (b) shows the PSD from the same surfaces measured along the [110] direction. PSDs calculated from AFM scans ranging in size from $1 \times 1 \mu m^2$ to $100 \times 100 \mu m^2$ were combined to generate these Figures. The PSD shrinks rapidly as a function of time during growth, until it reaches a saturated level for spatial frequencies greater than a crossover frequency $q_c$ (indicated by the vertical dashed lines). The crossover frequency decreases monotonically as a function of growth time, going from around 36 $\mu m^{-1}$ to around 9 $\mu m^{-1}$ ([110] direction), or from around 60 $\mu m^{-1}$ to around 17 $\mu m^{-1}$ ([110] direction) after 10 and 150 minutes growth respectively. In the saturated region ($q > q_c$) the PSD is well described by a power law, with slope close to $-2$, and a magnitude which is the same for all samples grown under similar conditions. The peak in the PSD of the thermally desorbed surface, located at around 4 $\mu m^{-1}$, moves gradually towards lower spatial frequencies during growth as the average size and spacing of the mounds increases.

The solid lines on Fig. 4.5 show the PSDs obtained from simulations using the conservative form of the KPZ equation (Eq. 3.11 with the correction in Eq. 3.15). Figure 4.6 shows the PSD of the same samples shown in Fig. 4.5, but in this case the solid lines are PSDs obtained from simulations using the MBE equation.

The simulation times match the experimental data, and the parameters are the same as those used to generate the images shown in Figs. 4.3 and 4.4. As above, the PSDs are generated from a combination of simulated surfaces of different sizes. In the saturated region $q > q_c$ the magnitude of the PSD is determined by both the coefficients in the growth equation and the strength of the noise included in the simulations. The values of the parameters $\Gamma_n$ (KPZ equation) and $\Gamma_c$ (MBE equation) quoted above were determined by matching the simulated and measured PSDs in the saturated region at high spatial frequencies.

The KPZ simulations in Fig. 4.5 are in excellent agreement with the experimental data over the entire $q$ range. For $q > q_c$ the MBE equation with conservative noise predicts the correct slope on the log–log plot (Fig. 4.6). However, unlike the KPZ equation, it does not predict the time dependence of the cutoff frequency, and for $q < q_c$ it tends to predict a slope steeper than the experimental data. Very little smoothing takes place at the lowest spatial frequencies in the MBE equation simulations, whereas the experimental data
Figure 4.5: PSD after different growth times on thermally cleaned substrates, measured along (a) the [110] direction, and (b) the [110] direction. The symbols represent the experimental data. The solid lines, representing 10 and 150 minute simulations generated with the KPZ equation, are in excellent agreement with the experimental data. The vertical dashed lines indicate the cutoff frequencies $q_c$ at 10 and 150 minutes (right to left).
Figure 4.6: PSD of the same samples shown in Fig. 4.5, measured along (a) the [110] direction, and (b) the [110] direction. The solid lines are from 10 and 150 minute simulations generated with the MBE equation. The simulated PSD has a stronger $q$ dependence than the PSD of the grown films. The vertical dashed lines indicate the cutoff frequencies $q_c$ at 10 and 150 minutes (right to left).
clearly show a decrease corresponding to filling in of the thermal desorb pits.

The time dependence of the surface roughness can also be monitored by elastic light scattering. Figure 4.7 shows the measured light scattering signal at spatial frequencies of 16 and 41 \( \mu \text{m}^{-1} \) during the thermal cleaning and subsequent growth of sample T4. The thermal desorption of the surface oxide at 600°C, which takes place at around 10 minutes in the Figure, is accompanied by a rapid increase in the scattered light intensity at both spatial frequencies, caused by the appearance of the desorption pits seen in Fig. 4.1. The sample is maintained at 600°C for several minutes to complete the oxide removal, during which time the surface smooths considerably at 41 \( \mu \text{m}^{-1} \) but stays approximately constant at 16 \( \mu \text{m}^{-1} \), corresponding to the annealing of some short scale features. The sample is brought down to growth temperature (550°C) after 23 minutes, and growth begins at a time of 31 minutes. The surface immediately begins to smooth at both length
scales, until a background level is reached after about 10 minutes of growth.

The light scattering data indicate that, during growth, the surface smooths at a rate which is approximately independent of the probed length scale. In fact, the data are well described by an exponential decay with time constants $\tau_{16}$ and $\tau_{41}$ both equal to around 3 minutes. An exponential decay would be expected from purely linear equations such as the EW equation or the fourth order linear term in the MBE equation. However, the EW equation predicts the characteristic smoothing times to be in the ratio $\tau_{41}/\tau_{16} = (16/41)^3$, and the linear MBE equation predicts the ratio $(16/41)^4$, both inconsistent with the observed ratio.

The predicted smoothing rates of nonlinear equations, such as the KPZ equation, are harder to determine analytically, but for a given starting surface they can be determined from simulations. The inset in Fig. 4.7 shows the measured light scattering signal during growth and the scattering signal calculated from simulations using the KPZ equation. The agreement between the calculated and measured data is quite reasonable, as the only parameter in the calculation is the initial amplitude. All other parameters were taken to be identical to those employed in Ref. [BRA+01] to fit the AFM images from this sample, namely $\nu_x = 10$ nm$^2$/s, $\nu_y = 1$ nm$^2$/s, $\lambda_x = \lambda_y = 5$ nm/s, and $\Gamma_n = 10$. Most notably, the calculated time constant is only weakly $q$ dependent (much less so than for simulations based on the linear growth equations), and is within a factor of two of both of the measured values.

During the growth of this sample, the plane of incidence of the Hg lamp was at 45° to the [110] and [110] axes. The 16 $\mu$m$^{-1}$ signal is measured in the plane of incidence, while the 41 $\mu$m$^{-1}$ signal is measured at an angle 22.5° out of the plane of incidence, rotated towards the [110] direction. Therefore, the 16 $\mu$m$^{-1}$ signal measures the roughness along a direction closer to the [110] axis, where the value of $\nu$ is largest, than the 41 $\mu$m$^{-1}$ signal, which measures along a direction with a smaller value for $\nu$. This partially offsets the expected faster smoothing rate at 41 $\mu$m$^{-1}$. More importantly, the nonlinear KPZ term has a large effect on the smoothing rate early in the growth when the surface is at its roughest. The nonlinear term tends to favor a weaker $q$ dependence in the smoothing rate than the linear term in the growth equation. Further simulations have shown that this weak sensitivity to length scale cannot be reproduced by the MBE equation.

Finally, in Figure 4.8 (a) we show a series of scan lines from AFM images of samples grown at 550° C. From bottom to top the cross sections come from the thermally desorbed starting surface, and samples grown for 3, 10, 37.5, and 150 minutes (samples T0, T5, T1, T2, and T3, respectively). The
Figure 4.8: Scan lines along the [110] direction from (a) measured AFM images, (b) the corresponding KPZ simulations, (c) MBE equation simulations, and (d) EW equation simulations. From bottom to top the curves correspond to growth times of 0, 3, 10, 37.5, and 150 minutes. The lines in (a) are from five separate samples, whereas the scan lines in (b), (c), and (d) are taken at the same position in the evolving simulations. Scans are offset for clarity.
scan lines are taken along the [110] direction and are offset by 15 nm for clarity. Figure 4.8 (b) shows scan lines from the KPZ simulations, where the different lines are extracted at the same times as those in Fig. 4.8 (a). Figure 4.8 (c) shows a similar set of scan lines from the MBE equation simulations. The initial condition for the simulations is the thermally desorbed surface (sample T0). These lines are all taken from the same position on the surface as the simulation progressed. It is clear that while the KPZ simulations are in excellent agreement with the real surfaces at all times and length scales, the MBE equation does not correctly predict the rate at which the deepest pits fill in. This, again, indicates that the rate of change of the surface morphology during growth of this material system is only weakly dependent.

In Fig. 4.8 (d) we also include a series of scan lines extracted from a simulation using the EW equation with \( \nu_x = 20 \text{nm}^2/\text{s}, \nu_y = 5 \text{nm}^2/\text{s}, \) and \( \Gamma_n = 10 \) (i.e., the KPZ equation with \( \lambda_x = \lambda_y = 0 \text{nm/s} \)). As before, the parameters have been selected to optimise the similarity between the simulated and real surfaces. Although we obtain reasonable agreement with the real data after long growth times, the large features associated with the desorption pits clearly smooth too slowly in the EW simulation. Furthermore, the cusp-like features reproduced in the KPZ simulations become rounded in the purely linear simulation, demonstrating the importance of the nonlinear KPZ term.

**Temperature dependence**

Figure 4.9 (a) shows an AFM scan from sample T6, grown for 69 minutes at 600°C on a thermally desorbed substrate. The surface still shows large scale mound-like features related to the initial roughness. However, the V-grooves between the mounds are not apparent, and the surface is much more inversion symmetric than the samples grown at 550°C.

To simulate the 600°C growth, we have scaled the linear coefficients in the KPZ equation by a factor of three relative to their values at 550°C. This is the ratio that would be expected if the linear term represents a thermally activated process with activation energy of around 0.7 eV. Using values for the nonlinear coefficients of \( \lambda_x = \lambda_y = 5 \text{nm/s} \), and \( \Gamma_n = 10 \) results in the simulation shown in Fig. 4.9 (b). As above, the KPZ simulation generates an excellent likeness of the experimental data. The increase of the linear relative to the nonlinear coefficients enhances the anisotropy of the surface structure, and at the same time reduces the inversion asymmetry. Overall, the grown surface is smoother at 600°C than at 550°C.
4.3.2 Growth on hydrogen etched substrates

Kinetic roughening

Figure 4.10 (a) shows an AFM image of a substrate from which the surface oxide has been removed by hydrogen etching. Unlike the thermal desorption process, the hydrogen etch leaves a relatively smooth surface, with an RMS roughness of less than 0.2 nm in this sample. Figure 4.10 (b) shows an AFM image from sample H1, grown for 75 minutes at 595°C on a hydrogen etched substrate. The surface remains relatively smooth, with RMS roughness equal to 0.2 nm. The large amplitude mounds seen on the thermally desorbed samples are absent in this case, but the roughness does appear to be correlated over larger length scales than on the initial substrate. A 75 minute growth simulation generated using the KPZ equation with parameters $\nu_x = 30 \text{ nm}^2/\text{s}$, $\nu_y = 3 \text{ nm}^2/\text{s}$, $\lambda_x = \lambda_y = 5 \text{ nm/s}$, and $\Gamma_n = 10$, is shown in Fig. 4.10 (c), where the hydrogen etched surface was used as the initial condition. These parameters, which are the same as those used above to successfully model the growth at 600°C on thermally desorbed substrates, provide an excellent likeness of the grown surface.

Because the starting surface is almost flat, we can investigate the kinetic
Figure 4.10: AFM images of GaAs surfaces which have had the surface oxide removed by hydrogen etching: (a) Starting surface (sample H0, z-range 1.8 nm); (b) 75 minutes growth at 595°C (sample H1, z-range 1.2 nm); and (c) KPZ simulation using sample in (a) as initial condition (z-range 1.1 nm). The parameters are the same as those used to simulate the growth on thermally desorbed substrates at 600°C. The arrows point along the [110] direction, and the image size was 5 x 5 \( \mu \text{m}^2 \).
Figure 4.11: PSD of samples grown on hydrogen etched substrates, measured along (a) the [110] direction, and (b) the [110] direction. The growth times are 10 minutes and 37.5 minutes for samples H2 and H3, respectively. The solid lines are from simulations generated with the KPZ equation, using the same parameters used to model the growth on thermally desorbed substrates. The vertical dashed lines in (b) indicate the cutoff frequencies $q_c$ at 10 and 37.5 minutes (right to left).
roughening of the films grown on hydrogen etched substrates. The PSD of two such films, grown at 550°C for 10 and 37.5 minutes, are shown in Figures 4.11 (a) and (b) (samples H2 and H3 respectively). The PSD of the starting surface, not shown in the figure, lies slightly below the PSDs of the grown films, and has a sharper roll-off at high spatial frequencies. In the [110] direction, the PSD of the grown films follows a power law with exponent approximately $-2$ over the entire $q$ range. The amplitude of the PSD in this direction is independent of time, indicating that a saturated roughness has been reached. In the [110] direction the PSD also follows a power law with exponent $-2$, but only for spatial frequencies greater than a cutoff frequency $q_c$ of about $20 \mu m^{-1}$ after 10 minutes growth, and about $10 \mu m^{-1}$ after 37.5 minutes growth (indicated by the vertical dashed lines on the Figure). Below the cutoff frequency the PSD is approximately independent of $q$, and has an amplitude which increases with time. This behavior is exactly what is expected from kinetic roughening; correlations develop at longer and longer length scales as time progresses, leading to a saturation in the PSD which shifts to smaller and smaller spatial frequencies. The PSD saturates more quickly along the [110] axis due to the more rapid smoothing rate in this direction.

The solid lines on Figs. 4.11 (a) and (b) show simulated PSDs generated with the KPZ equation using the same parameters used to generate the simulated PSDs in Figs. 4.5 (a) and (b), but with a hydrogen etched starting surface. The simulations are in excellent agreement with the measured data. Most notably, the slope and amplitude of the saturated PSDs are reproduced, and the position of the cutoff frequency $q_c$ is in good agreement with the data. Therefore, we conclude that the modified KPZ equation describes the growth on both smooth and rough initial surfaces.

The exponent of the power law describing both the measured and the simulated PSDs is close to $-2$ in both directions. This is in agreement with the exponents measured on the thermally desorbed surfaces, although it is somewhat surprising, as it differs from the KPZ prediction of $-2.8$. We return to this point in Section 4.4, below.

**Dependence on As overpressure**

The anisotropy of the surface structure is sensitive to the As$_2$ overpressure during growth. This is demonstrated in Figure 4.12 which shows three high resolution AFM scans from samples grown at 550°C on hydrogen etched substrates under varying As$_2$ flux, (samples H3 (a), H4 (b), and H5 (c)). Well defined atomic steps are visible in all three images. At a group V to group III
Figure 4.12: AFM images illustrating the effect of reducing the $\text{As}_2$ overpressure. (a) $V:III$ ratio = 6.5 (sample H3), (b) $V:III$ ratio = 3.0 (sample H4), and (c) $V:III$ ratio = 1.0 (sample H5). The gray scale in all images are 2.4 nm, and the surface features are elongated along the [110] direction (along the arrow), and the image sizes were $2 \times 2 \mu \text{m}^2$. The 2D PSD of each image is included as insets, with spatial frequencies ranging from $-300$ to $300 \mu \text{m}^{-1}$ in each direction.
flux ratio of 6.5 [Fig. 4.12 (a)] the surface is covered with islands which show a moderate amount of elongation along the [110] direction, as demonstrated by the relatively isotropic two dimensional PSD shown in the inset. As the V:III ratio is decreased to 3.0 [Fig. 4.12 (b)] the anisotropy increases, and the PSD becomes much more elongated. In terms of the continuum growth equations this corresponds to an enhancement in the anisotropy of the coefficients. Physically, the elongation results from an anisotropic mobility of the adatoms, and possibly also an anisotropy in the incorporation dynamics on the surface [Ito01]. Once the V:III ratio approaches unity [Fig. 4.12 (c)] the surface structure changes considerably, possibly due to an imminent change in the reconstruction from 2 x 4 to 2 x 2. The surface is now covered by terraces that are almost continuous along the [110] direction, each with a characteristic width of around 80 nm. This length scale is reflected in the PSD, which now shows two peaks on either side of the origin perpendicular to the direction of elongation.

The GaAs surfaces described in Refs. [JOH+94, OJS+94, HOW+94], on which mounds were attributed to unstable growth, also show a large degree of anisotropy. This indicates that they were grown under an effectively lower As overpressure (As$_4$ was used as the source) than most of the samples displayed here. It is therefore interesting to consider whether an appreciable Ehrlich-Schwöbel barrier may emerge in the [110] direction in conditions of low As flux. This could explain the length scale that we observe emerging in Fig. 4.12 (c), and is consistent with the flat tops that we observed in Pt growth in Fig. 2.11. The extensions of surface features in the [110] direction indicates that the ES barrier in this direction remains negative, or at least relatively unaffected by the As overpressure.

4.4 Discussion

Our simulations show that both the KPZ and the MBE equations can qualitatively reproduce the mounds on the surface, and clearly prove that mounds can emerge as a transient shape during smoothing, rather than as a manifestation of unstable growth. Quantitatively, only the KPZ equation is able to reproduce the PSD of the surfaces. This is because the measured PSD smooths at a rate which is fairly insensitive to the length scale being probed. The stronger spatial frequency dependence inherent in the higher order MBE equation makes it difficult to reproduce the relatively $q$ independent decrease in the measured PSD (see Figs. 4.5 and 4.6). While the KPZ simulations provide the better fits to the experimental surface evolution, it should be
mentioned that the values of \( \lambda \) required in the simulations are considerably larger than the growth rate of around 0.3 nm/s. Thus, the nonlinear KPZ term cannot be accounted for by simply assuming the surface grows outward along the surface normal.

Our interpretation of the terms in the KPZ equation also provides a natural explanation for the excess noise in the KPZ simulations. The noise represents fluctuations in the density of adatoms at a given point on the surface. The fluctuations associated with adatom incorporation and dissociation from step edges can be much larger than the fluctuations in the arrival rate of adatoms from the flux. Furthermore, due to the existence of the 2\( \times \)4 surface reconstruction, it may not be favorable for Ga adatoms to incorporate individually [Ito01]. Instead, the basic unit which must be added to the surface may consist of several Ga atoms, enough to recreate a unit cell of the 2\( \times \)4 reconstruction, for example. In this case the coefficient of the noise correlation function will be modified from \( D = F a_{\perp} a_{\parallel}^2 \) to \( D = n F a_{\perp} a_{\parallel}^2 \), where \( n \) is the number of Ga atoms forming the basic incorporation unit. Therefore the value \( \Gamma_n = 10 \) used in the KPZ simulations is physically possible.

We now comment on the power law observed in the PSD at high spatial frequencies. Despite the importance of the nonlinear terms for reproducing the surface morphology, the PSD tends to display the power law exponent expected for the purely linear equations (i.e. \(-2\)). This should not be taken as indicating a disagreement with the theoretical predictions. Instead, it simply indicates that we are in a transient regime in which the relatively large linear terms are dominating the nonlinear terms at short length scales [NB96]. The small surface roughness at short length scales means that the nonlinear term can be neglected in this regime. This conclusion is supported by numerical simulations of the KPZ equation. For example, using the isotropic parameters \( \nu = 5 \text{ nm}^2/\text{s}, \lambda = 5 \text{ nm/s}, \) and \( \Gamma_n = 10 \) the simulations exhibit a power law exponent of \(-2\) in the PSD even after 1000 minutes of growth on a flat 10\( \times \)10 \( \mu \text{m}^2 \) substrate. However, using the parameters \( \nu = 0.01 \text{ nm}^2/\text{s}, \lambda = 5 \text{ nm/s}, \) and \( \Gamma_n = 10, \) an exponent of \(-2.8\) is observed for times greater than about 60 minutes, consistent with the expected value \( 2(1 - \alpha) = 2.76 \) as obtained from Eq. 3.25.

4.5 Summary

Based on our comparison of experimental data with simulations of two popular continuum growth equations, we conclude that the evolution of the sur-
face morphology of MBE grown GaAs is well described by the KPZ equation with a stable linear term. By contrast, the MBE equation fails to reproduce the measured surface morphology of the grown films.

These results lead us to the following interpretation of the dominant smoothing mechanism during film growth. The surface is covered by mobile adatoms which diffuse randomly on the surface, forming an effective vapor phase. Incorporation of these adatoms takes place preferentially at sites on the surface with positive curvature, as described by a second order, linear growth equation. Nonlinear corrections to the incorporation rate are observed to be important. We attribute these corrections to the preferred incorporation of adatoms to the sloped parts of the surface, where the steps are in abundance. The breach of inversion symmetry in the growth direction, as indicated by the transient mounds separated by cusps, is well approximated by the KPZ nonlinearity, although we speculate that this second-order term is a lowest order approximation to a conservative nonlinear term of higher order. We will return to this important point in Chapter 5.

In MBE growth, the incorporation process must necessarily be of a conservative nature, i.e. the growth rate should not depend on the surface shape. To account for this fact we have made a correction to the KPZ equation. It is important to point out that, due to the rather small slopes on even the thermally desorbed substrates, this modification has only a minor effect on the morphology of the simulated surfaces. Therefore, the simulations although conservative are essentially indistinguishable from simulations of the unmodified KPZ equation.

For a given growth condition, a single set of parameters successfully describes growth on surfaces that are initially rough or smooth. Regardless of initial condition, after long growth times the surface tends towards a steady-state roughness level determined by the interplay between the smoothing rate and random noise in the system, as predicted by kinetic roughening theory. We have found that increasing the temperature or As overpressure leads to smoother surfaces, implying increased values for the coefficients of the smoothing terms in the KPZ equation. Increasing the As overpressure also reduces the anisotropy of the surface morphology.

Our experimental studies lead us to draw new conclusions as to the stability of the GaAs (001) surface during epitaxial growth. While commonly believed to be unstable, as first reported by Johnson [JOH+94] and Orme [OJS+94], we find that the long-time behaviour shows the opposite: GaAs (001) homoepitaxy is stable and the observed mounds are simply transient remnants of the starting surface roughness. Since the mounds are no longer a result of an instability, there is no need for a strong, positive ES
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... barrier to explain the long-time surface morphology evolution. In fact, modeling the surface evolution with the KPZ model showed that the net adatom drift in this growth system must be downhill.

It remains an unresolved issue how one can relate the KPZ coefficients $\nu$ and $\lambda$ to real physical parameters, like $F$, $T$ and the As overpressure, as well as physical processes, such as step edge incorporation and detachment, and nucleation. While it is clear that the EW parameter $\nu$ is dependent on growth chamber temperature, growth rate and the ES barrier, it is unclear exactly how it is related to the underlying physics.

We also have concerns about the origin of the growth terms themselves. For example, the linear EW term $\nabla^2 h$ has been associated with either an evaporation/condensation mechanism, or an inverse ES effect. Since these processes may occur simultaneously and independently, can their effects be expressed mathematically as multiplicative effects, or additive effects? And while we are fairly confident about the existence and origin of the linear EW term, what is the underlying mechanisms causing the nonlinear KPZ term, and is it at all valid in the context of MBE growth? If not valid, then why does it do such a good job at simulating the evolution of GaAs surface morphology?

In Chapter 2, we discussed surface growth mainly from the point of view of the diffusing adatoms on flat terraces separated by steps. In Chapter 3, we discussed surface morphology directly in terms of the surface height itself and through terms that depend on it through spatial derivatives of various linear and nonlinear orders. We showed in this Chapter how to apply continuum equations in order to model surface growth. In the next Chapter, we will try and motivate a formulation that describes the interplay between the adatoms and the surface, and hence combines the approaches from these previous Chapters. We arrive at a surface growth model that includes physically based, continuum, morphological terms, and we put this model to test by applying it to the evolution of flat and patterned surfaces.
Chapter 5

Modeling of growth on patterned surfaces

We showed in Chapter 4 that the KPZ equation adequately describes the evolution of GaAs (001) surfaces during epitaxial growth for nominally flat starting surfaces, where the roughness induced by common surface preparation techniques is relatively small, and the local surface slopes do not exceed a few degrees. We also showed that in spite of its applicability to GaAs homoepitaxy, the KPZ equation faces some theoretical problems surrounding the interpretation and validity of the nonlinear term.

In this Chapter we investigate patterned surfaces, with lithographically textured large-scale features like gratings and pits. Such surfaces are interesting from the point of view of device manufacturing, but conventional continuum equations derived in the low slope approximation fail to describe their evolution. We describe experiments where large scale gratings are prepared, epitaxy is performed and the evolution of the shape of the gratings is closely investigated with AFM. The epitaxy-regrowth experiments, as well as the grating preparation, were done by Jens Schmid and is described in detail in his Ph.D. thesis [Sch04].

We show that the KPZ equation breaks down for the large slope surfaces, and develop a coupled equation continuum model that explains the complex surface shapes observed in these regrowth experiments. This model describes the dependence of the surface morphology on film thickness and growth temperature in terms of a few simple atomic scale processes including adatom diffusion, step edge attachment and detachment, and a net downhill migration of surface adatoms. The continuum model reduces to a nonlinear

equation reminiscent of the KPZ equation in the long wavelength limit, with a smoothing rate that is dependent on the growth rate, the magnitude of the ES barrier, and temperature.

5.1 Introduction

The problem of the time evolution of the shape of crystal surfaces has a long history dating back to Mullins and Herring who considered relaxation during annealing above the roughening temperature [PV98]. More recently, shape relaxation below the roughening temperature has been studied extensively [DP97, EAC+00, SRF03]. Below the roughening temperature the problem is complicated by the need to keep track of the dynamics of atomic steps and the fact that the surface free energy of crystal facets is singular. Biasiol et al. [BGLK02] have extended the theory of shape relaxation below the roughening temperature to include the effects of atom deposition, and use this theory to explain the self limiting V-grooves observed in organo-metallic chemical vapour deposition growth on corrugated GaAs substrates. In this Chapter, we present a new continuum model which we use to interpret measurements of the shape of corrugated (001) GaAs surfaces under growth conditions which do not produce faceting. Facets are not present in our experiments due to atomic scale roughness associated with atom deposition in the island growth mode, and the fact that the surface topography is sufficiently weak that the surface slope does not reach the low energy [111] facets. We show that this model reproduces the surface morphology that develops during MBE regrowth on 1D surface gratings.

5.2 Conventional modeling of weak surface texture

The nonlinear term in KPZ is associated with growth along the outward normal, as in chemical vapour deposition. In this case, which is not obviously applicable in MBE, $\lambda$ should be equal to the growth rate $F$. Also, the value for $\lambda$ needed to simulate the experimental results is almost two orders of magnitude larger than $F$ (see Ref. [BRS+02] and Chapter 4). This raises the question as to the physical origin of the non-linear term in the context of MBE growth. The KPZ nonlinearity is non-conservative, whereas MBE growth is conservative with a growth rate that is independent of the surface shape. In practice, for the low surface slopes where KPZ is applicable, the change in growth rate associated with the non-linear term is very
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Figure 5.1: Light scattering during growth corresponding to surface power spectral density at 41 \( \mu \text{m}^{-1} \) showing the effect of atom deposition on the smoothing rate. The sample roughens during a temperature ramp to remove the surface oxide at about 5 minutes in the figure, which is followed by relatively fast smoothing during a high temperature (620\(^\circ\)C) anneal for about 7 minutes, and then slower smoothing during annealing at growth temperature (550\(^\circ\)C).

small. Although the KPZ nonlinearity gives a good approximation to the surface shape, its physical origin is obscure in the case of MBE growth. One would prefer to have a model that can be derived from underlying physical phenomena.

In addition, the KPZ description with constant coefficients is not consistent with experiments which show that the smoothing rate depends on the growth rate. For example, in Fig. 5.1 we show the scattered light intensity from a GaAs surface during an interruption in growth on a randomly textured substrate. The intensity of scattered light is proportional to the power spectral density of the surface topography at a spatial frequency \( q \) determined by the optical wavelength and geometrical factors [BRS+02]. In this case \( q=41 \mu \text{m}^{-1} \), corresponding to a lateral surface length-scale of about 150 nm. For low amplitude surface textures, in the KPZ model the surface should smooth exponentially with a characteristic rate given by \( \nu q^2 \) where \( q \) is the spatial frequency of the surface roughness [PV98]. As shown in the
Figure 5.2: AFM images of (a) a sample quenched (fast cooled) after 69 minutes of growth at 600°C and (b) a sample annealed for 15 minutes at growth temperature 595°C after 40 minutes of growth.

The inset of Fig. 5.1, the smoothing rate responds immediately to changes in the growth flux; it is faster during deposition and slower during annealing, suggesting that \( \nu \) is flux dependent. This continued smoothing of the surface in the absence of an atom flux indicates that the physical mechanisms at play on the surface favor a net downhill migration of surface adatoms, even when the flux of atoms is turned off. This suggests that if there are two competing mechanisms including a positive ES barrier that the stabilizing mechanism that creates the downhill flow is not associated with energetic adatoms deposited from the vapor such as step edge knockout or downhill funneling.

To summarize, the KPZ equation provides an accurate description of the surface morphology under certain restricted conditions (constant growth rate, low surface slope and long wavelength surface structures). In addition, the physical origin of the non-linearity in KPZ is unclear in the case of MBE growth. Therefore, we would like to develop a new continuum model based on a few simple physical processes that describes the surface morphology over a broader range of conditions than the KPZ equation, and that can be compared with experimental data.

To illustrate the physical processes involved in the epitaxial growth process and to motivate the new model, we compare atomic force microscope
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(AFM) images of a growth surface which is fast cooled after growth is terminated (quenched) with one that has been annealed (see Fig. 5.2 (a) and (b)). In this Figure and in Fig. 5.1, the As:Ga flux ratio was 10:1. The quenched sample (a) is covered with small islands, whereas the annealed sample (b) has broad terraces with few islands. The small islands must coalesce into the step edges during annealing. The kinetic barrier to the adatom coalescence into the step edges, causes the growth process to be non-local. This means that the growth rate at one location will be affected by the morphology at another location in contrast to KPZ, for which the growth rate only depends on the local surface slope and curvature. This is a problem not only for KPZ but also for alternative growth equations such as the MBE equation [PV98]. Physically, a high density of steps at one location that absorb adatoms will affect the adatom density and hence the growth rate at another nearby location. We hope to have motivated the necessity for a model that includes the diffusion of adatoms. We proceed by discussing an approach that describes the concentration of islands of all sizes and that has been a popular description of nucleation during the early stages of growth.

5.3 Sub-monolayer rate equations

Sub-monolayer rate equations (SMREs) describe the nucleation and growth of 2D islands on an initially flat surface through mean-field concentrations \( n_s \) of islands of size \( s \). The source of adatoms is as usual through a flux term \( F \). The total number of islands with \( s \) atoms in them is \( N_s = n_s \times A \), where \( A = L^2 \) is the substrate area. If only, adatoms are mobile on the surface, then islands with \( s \) atoms can form either by the attachment of an adatom to an island of size \((s-1)\), or by the detachment of an adatom from an island of size \((s+1)\). The reverse processes reduce \( n_s \), and the total nucleation rate of islands of size \( s \) can conveniently be described by

\[
\frac{dn_s}{dt} = Dn_1 (n_{s-1} - n_s) - K (n_s - n_{s+1})
\]  \hspace{1cm} (5.1)

where \( D \) is the diffusion constant and \( K \) is the detachment rate of an atom from an island. The concentrations \( n_s \) for various values of \( s \) are coupled: \( n_{s-1} \) decreases when hit by an adatom that increases \( n_s \). The coupling leads to the following set of self-consistent SMREs [BE92, Kru97, KKv00, vS16,
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Figure 5.3: Evolution of sub-monolayer rate equations (Eqs. 5.2) for $E_{sub} = 1.3$ eV, $mE_{lat} = 0.9$ eV, $T = 600^\circ$C, $F = 1$ ML/s and $\sigma_s = \gamma_s = 1$ for all $s$. Growth with (solid lines) and without (dashed lines) detachment is shown, and the growth times are indicated.

$vS17, Vve00, GRG^{+}01, Ven87, BC94, RZv94$:

\[
\frac{dn_1}{dt} = F - Dn_1(2\sigma_1 n_1 - \Sigma_{s \geq 2} \sigma_s n_s) + K(2\gamma_2 n_2 + \Sigma_{s \geq 3} \gamma_s n_s) \tag{5.2a}
\]

\[
\frac{dn_s}{dt} = D n_1(\sigma_{s-1} n_{s-1} - \sigma_s n_s) - K(\gamma_s n_s - \gamma_{s+1} n_{s+1}), \quad s = 2, 3, \ldots \tag{5.2b}
\]

where $\sigma_s$ is the “capture coefficient” [VSH84] for islands of size $s$, and are related to the size, stability and spatial distribution of islands. $\gamma_s$ is a corresponding “release coefficient” from a step edge. All concentrations $n_s$ have the initial value of 0. An example of the evolution of theses SMREs are shown in Fig. 5.3. We see that the average size of islands grows as more material is deposited on the surface, as well as their total count.

The success and applicability of SMREs is well documented for a variety of growth systems, as evidenced by the large amount of literature on the subject (see earlier references in this Section). We have introduced these equations here for completeness, but we do not intend any further investigation into their current format, as we are mainly concerned with growth of surfaces that span several layers. The SMREs are limited to low coverages.
(less than $\sim 20\%$) on flat starting surfaces, as coalescence of islands is unac­
counted for in its formalism. We now address the question of how to extend
this formalism to account for coalescence within the layer and multilayer
growth.

5.4 Multilayer mean-field models

In order to extend the rate equation approach to a multilayer description, we
choose to express the filling of each layer rather than the densities of each
island size in each layer. We denote the filling of the $j^{th}$ layer above the
substrate by $\theta_j \in [0,1]$. The index $j = 0$ denotes the substrate, for which
$\theta_0(t = 0) = 1$, and a flat starting surface is described by $\{ \forall j, j > 0, \theta_j(t = 0) = 0 \}$. As with the SMREs in the previous Section, this formulation does
not take into account the morphology of the growing surface. Also, the
incoming atoms are considered to incorporate directly into the growing film,
so there is no explicit variable for the adatom concentration. A multilayer
description in $\theta$ couples the growth of all active (that is non-empty and
non-full) layers on the surface.

5.4.1 “Birth-death” models and diffusive growth

In one extreme case, layers fill in at a rate proportional to their exposed area,
and several layers will be active at any given time. This is called nondiffusive
or Poisson growth. In this limit, all atoms that land in a layer incorporate
to the ascending step edge. The filling of successive layers according to this
model can be described by

$$\theta_j = F(\theta_{j-1} - \theta_j)$$  \hspace{1cm} (5.3)

This is a birth-death (BD) model [WGJ76] “since the growth of an unfilled
layer is rapid, while the growth of a nearly completed layer is slow” [CPP+89].
Nondiffusive growth refers to an experimental scenario where the adatom
diffusion is low. This could be caused by either a strong binding energy
between the adatom and the surface, or by the presence of a high growth
flux that prevents the adatoms from diffusing before they are hit by another
incoming atom from the vapour. In a simple model, such as the one de­
scribed by Eq. 5.3 where no morphology is specified, it can also be used to
describe a strong ES barrier at the step edge.
The solutions for the first two layers are

\[ \theta_1 = 1 - e^{-Ft} \]
\[ \theta_2 = 1 - e^{-Ft} - Fte^{-Ft} \]

and the general solution for the \( j^{th} \) layer can be written as:

\[ \theta_j = 1 - e^{-Ft} \sum_{n=0}^{j} \frac{(Ft)^n}{n!} \]

where the sum, incidentally, is the Taylor series expansion of \( e^{Ft} \), truncated after the \( j^{th} \) term. The evolution of the first few layers according to this expression is shown in Fig. 5.4. The leftmost line in that plot is the filling of the first layer, the second line from the left is the second layer, and so forth.

In the other extreme, each layer fills in completely before the next layer is started, a model often referred to as layer-by-layer growth. The filling of the active layer is then simply \( \theta = Ft \). This extreme corresponds to the case where the temperature is high, the growth flux low or the ES barrier is strongly negative. This makes the descending step not only transparent, but attractive, since all atoms that land on a higher terrace funnel down to the lowest terrace on the surface.

Nondiffusive and layer-by-layer growth represent two extremes for layer-filling during epitaxial growth. In Figure 5.5 we show the layer filling according to SOS simulations, using the standard parameters. In part (a), low-temperature growth is simulated, and in part (b), the temperature is set to 625°C, close to that typically used in GaAs growth. The insets show the actual surface after some 5 seconds of growth. Both simulations show a layer-filling behaviour that is very close to that found in the layer-by-layer growth model.
5.4.2 Evolution of the step density

In Section 5.3, the early stages of growth within one monolayer was described as an evolution of islands of all sizes. Earlier in this section, all the islands in a given layer were summed into a single parameter as the filling of that layer, \( \theta_j \). If we for the time being assume that the surface grows like the layers of a circular wedding-cake, then we can define the number of steps within one layer as being equal to the length of the perimeter of the island, \( S_j = 2\pi r_j \), where \( r_j = \sqrt{\theta_j/\pi} \) is the radius of the (single) island that has incorporated on the \( j \)th layer. We then get that \( S_j \propto \sqrt{\theta_j} \).

As the islands grow, coalescence of islands become a factor, and we can eventually expect that the step density will decrease as the filling exceeds \(~0.5\) and proceeds towards a full layer: \( S_j \propto (1 - \sqrt{\theta_j}) \). A formula that incorporates both the initial and later filling of a layer was proposed by Cohen [CPP+89]:

\[
S_j \propto \theta_j^p(\theta_{j-1} - \theta_j)^q
\]

where \((p, q) \in [0.5, 1]\). This expression was then used in a model that encapsulates the basics of a multi-layer mean-field description [CPP+89]:

\[
\dot{\theta}_j = F [(\theta_{j-1} - \theta_j)(1 - \alpha_{j-1}) + (\theta_j - \theta_{j+1})\alpha_j]
\]

where \((\theta_{j-1} - \theta_j)\) can be recognized as the area of the \( j \)th terrace, and \( \alpha_j \)
describes a perimeter effect that we define by:

\[
\alpha_j = \frac{A S_j}{S_j + S_{j+1}}
\]  

(5.9)

where \( A \) is a constant that determines the degree of interlayer transport present in the model.

### 5.4.3 Reflection high energy electron diffraction oscillations

Reflection high-energy electron diffraction (RHEED) is a popular technique used in MBE for measuring surface roughness as well as reconstructions on the growing surface. The occurrence of intensity oscillations of specular RHEED has been linked to the layer-by-layer filling of monolayers during growth \([\text{SJS}^+92, \text{SJE}^+93]\). Experimentally, it was found that as initial surface roughness smoothed out, and the surface entered a layer-by-layer growth mode, the specular intensity would oscillate with a frequency that appeared similar to the growth rate, \( F \).

It has been shown that the intensity variations of the specular amplitude of the RHEED signal follows \([\text{CPP}^+89]\):

\[
I \propto \sum_{j=0}^{m} (\theta_j - \theta_{j+1})^2.
\]

(5.10)

where \( m \) represents the index for the uppermost level with a non-zero filling. This expression is based on the notion that the step-edges scatters the RHEED signal and hence reduces its specular intensity. Several groups have used the relationship in Eq. 5.10 in order to study RHEED oscillations, and also the transition to step-flow growth which occurs at high temperatures and low Ga fluxes \([\text{NDJZ85, SVW}^+92, \text{VC90}]\).

We illustrate the relationship between the layer-filling and the intensity oscillations calculated from Eq. 5.10 in Figure 5.6. In part (a), we show the layer-filling from an SOS simulation using the standard parameters. The intensity oscillations in (b) are very similar to typical experimental findings for RHEED oscillations. As the growth is stopped at 19.4 s in the figure, the intensity slowly increases, an effect typically referred to in the literature as "step-recovery". We saw this effect in Figure 5.2.

Closer inspection of the signal Fig. 5.6 (b) indicates that at 15 seconds, less than 15 full oscillations are completed. The frequency of these intensity oscillations is often associated with the completion time of a layer, and hence is used to calibrate the growth rate: one oscillation per monolayer deposited.
If this were the case, then the signal should oscillate with a frequency of 1 Hz, which it clearly does not. For smooth growth, as indicated here, the oscillation frequency of the diffracted intensity is close, but not identical to the growth rate $F$. This is because as the surface is subjected to kinetic roughening, several layers are active at any given time. Therefore, a phase-lag is introduced into the layer-completion time, with the effect of decreasing the oscillation frequency of the specular RHEED intensity.

Recently, an alternate explanation for RHEED oscillations has been suggested [BDP98]. In this model, the oscillations are believed to be caused by an interference effect in elastic multiple scattering of electrons between the top and bottom of the reconstructed adlayers. The decreased RHEED oscillation frequency is consistent with this idea. In fact, there is no inconsistency between the two models: in one case, the RHEED intensity is linked to the step-density, and in the other it is linked to the layer-filling. We showed in Eq. 5.7 that the step-density $S$ is linked to the layer-filling $\theta$, and we speculate that the two explanations for RHEED oscillations are ultimately different formulations of the same idea.

In these last two sections, we have introduced some mean-field models that were shown to be useful in simple comparisons with experimental observations, such as the specular RHEED oscillations. We showed how attachment and detachment could be incorporated in a simple fashion. The obvious weakness in the mean-field models is their lack of spatial information. This makes it difficult to use them for modeling of growth on vicinal
substrates, or on surfaces with some pre-defined roughness. This will be the topic of the next Section, where we will derive a growth equation from first principles of statistical motion of adatoms on a surface filled with available incorporation sites.

5.5 Coupled growth equations model

The growth phenomena discussed in the previous sections can be explained in a natural way if we extend the growth model to include the adatom dynamics explicitly with two 1D coupled growth equations (CGE)\(^2\):

\[
\text{CGE: } \partial_t n + \nabla \cdot \mathbf{j} = F - a_\parallel^{-1} \partial_t (a_\perp h) \quad (5.11a)
\]

\[
\partial_t (a_\perp h) = \alpha D n^2 + \beta D n S - a_\parallel KS \quad (5.11b)
\]

Eq. 5.11a is a continuity equation for the adatom density \(n(x,t)\) (in units of \(\text{nm}^{-1}\)) with source and sink terms, while Eq. 5.11b describes the time dependence of the surface height \(h(x,t)\) (in nm), which depends on the dimer nucleation rate and the net adatom attachment rate at steps. The constants are defined as follows: \(F\) - deposition rate from the vapor (in \(1/\text{nm-s}\)), \(D\) - adatom diffusion coefficient (in \(\text{nm}^2/\text{s}\)), \(S(x,t)\) - density of steps (in \(1/\text{nm}\)), \(K\) - rate of thermal detachment of atoms from step edges into the adatom phase (in \(1/\text{s}\)), \(\alpha\) and \(\beta\) are the incorporation coefficients for an adatom to another adatom or a step edge site, respectively. The lattice parameters are \(a_\parallel\) (in-plane) and \(a_\perp\) in the growth direction. An adatom is defined as a diffusing unit on the surface, which could be a Ga atom or a Ga-As complex. Equations 5.11a and 5.11b are continuum equations in the sense that the variables, namely the surface height, adatom density and step density are macroscopic quantities averaged over a number of atomic units. In Eq. 5.11b, any adatom that attaches to a step edge is assumed to have incorporated into the film. We also define:

\[
\mathbf{j} = -D(a_\perp^{-1} \zeta n \nabla h + \nabla n) \quad (5.12a)
\]

\[
S = \sqrt{S_0^2 + (a_\perp^{-1} \nabla h)^2} \quad (5.12b)
\]

where in Eq. 5.12a, \(\mathbf{j}\) is the surface current of adatoms and \(\zeta\) is a proportionality constant which describes the net directional drift of adatoms. A

\(^2\)Related coupled equations have been used earlier to describe growth on faceted surfaces [KNT+94, BKT+01, HIWK90]. In this work the adatom incorporation rate was dependent on the crystal facet orientation.
positive value for $\zeta$ gives a net downhill adatom current, consistent with the
surface smoothing that is observed experimentally for GaAs (001) [CC00,
CCM+98, BRS+02]. At this point the form for the surface current in
Eq. 5.12a can be regarded as a hypothesis, motivated by the success of
the second order linear term in the KPZ equation in fitting the GaAs sur-
face morphology in the limit of low surface slopes [BRA+01]. The second
term in Eq. 5.12a represents adatom diffusion.

Equation 5.12b is a physically plausible expression for the dependence of
the rms step density on the surface slope. In this equation $S_0$ is the random
step density on a flat surface due to growth related phenomena such as island
nucleation and thermally induced disorder. This step density will depend on
temperature, growth rate, arsenic flux and on time, if the growth rate is not
constant (see Fig. 5.2 (a) and (b)) [BJK+03]. If the random step density is
not too large, one can define a random local slope associated with the local
configuration of the steps. In the presence of a macroscopic topography
the random local slope associated with $S_0$ adds to the macroscopic slope
$\nabla h$. If the two slopes are uncorrelated then the rms step density is given
by Eq. 5.12b. In general there may be correlations between $S_0$ and $\nabla h$.
Nevertheless, one might expect this expression for the step density to be
relatively insensitive to correlations, as it has the correct limiting behavior
for large and small surface slopes. Therefore one could also regard Eq. 5.12b
as a convenient interpolation formula.

In the limit that $\nabla h < S_0$ there will be numerous up and down steps
(i.e. small islands) between successive net upward (or net downward) steps
associated with the macroscopic surface slope. The net downward flux associ-
ated with the step edge ES barriers or other mechanisms which drive the
flow of adatoms downhill will depend on the macroscopic average surface
slope. For example, a monolayer island located on a terrace on a vicinal
surface, will not cause a net macroscopic downhill flux of adatoms, even in
the presence of ES barriers as the down flow on one side of the island will
balance the down flow in the opposite direction on the other side. For this
reason the adatom current in Eq. 5.12a is proportional to the macroscopic
surface slope $\nabla h$.

The simple picture of a surface consisting of flat terraces separated by
atomic steps, can be expected to provide a good description of the surface
as long as the surface slope does not reach the next low index crystal planes,
namely (110) and (111). These planes are 45° and 54.7° from the surface
normal, and are beyond the range of surface slopes that we have explored
experimentally (less than $\sim 30^\circ$).
5.5.1 Notes on the solution of the coupled growth equation model

Only a few partial differential equations (PDEs) can be solved analytically, and only the simplest ones at that, and it is common to solve more complex PDEs with numerical approximation techniques, for example by the finite difference approach. The CGE model consists of two coupled, nonlinear, stiff partial differential equations, to which no analytical solution exists. In this Section, we show how we would approach the solution of a simple PDE using numerical methods, and outline the extension to the solution of the CGE model with all its complexities. We recall the Taylor formula for a general function \( f(x) \):

\[
f(x \pm \Delta x) = f(x) \pm \Delta xf'(x) + \frac{\Delta x^2}{2!} f''(x) + \ldots 
\]

We can easily verify the following approximations:

\[
f'(x) = \frac{f(x + \Delta x) - f(x - \Delta x)}{2\Delta x} + O(\Delta x) \tag{5.14}
\]
\[
f''(x) = \frac{f(x + \Delta x) - 2f(x) + f(x - \Delta x)}{\Delta x^2} + O(\Delta x^2) \tag{5.15}
\]

where \( O(\cdot) \) indicates the order of the truncation error of the approximation scheme. Applying these techniques, we can write the space-discretized version of the heat equation as

\[
\partial_t f = \nabla^2 f(x, t)
\]

\[
\downarrow
\]

\[
\partial_t f_i \simeq \frac{1}{\Delta x^2} (f_{i+1} - 2f_i + f_{i-1}) \tag{5.16}
\]

where \( f_i = f(i\Delta x) \). All of the quantities on the right hand side are now known, and we are left with a set of coupled ordinary differential equations (ODEs), one for each spatial grid point, \( x = i\Delta x \).

A further complication inherent in the CGE model and its underlying physics is the great spread in timescales of interest: while the diffusion of adatoms operates on the order of microseconds, the evolution of the large scale morphology of the surface is on the order of minutes to hours. This translates directly to the mathematical nature of the CGE model in that it is a stiff model, and more sophisticated techniques are required in order to solve their time evolution in a reasonable amount of calculation time.

To shed some light on this issue, consider the adatom diffusion term that occurs by combining Eqs. 5.11a and 5.12a: \( \partial_t n = D\nabla^2 n \), commonly referred
to as the heat equation. The maximum time step that the conventional forward Euler time stepping scheme will allow for this equation is \(\Delta t_{\text{max}} = \Delta x^2/2D\). The diffusion parameter \(D\) can easily be on the order of \(10^5 \text{nm}^2/\text{s}\) or more. With a grid spacing of typically 10 nm, that gives a max time step of less than a millisecond. Comparing this result to for example the EW equation, which has the same functional form as the heat equation, but a prefactor no larger than \(\nu \approx 10 \text{nm}^2/\text{s}\), we can easily get a time step on the order of tens of seconds. The presence of the adatom diffusion term in the CGE model therefore requires more advanced time-stepping algorithms.

We chose to use Matlab's implementation [SR97, SRK99] of the “Livermore Solver for Ordinary Differential and Algebraic equations” (LSODA) [RH93], one of nine solvers in ODEPACK [Hin83], which is freely available from the Lawrence Livermore National Laboratories website\(^3\). LSODA’s strength lies in its adaptive time-stepping abilities, and hence its abilities to solve stiff ODEs. By combining the use of LSODA with the decoupling of the spatial grid points that we did in Eq. 5.16, the solution of the CGE model was straight forward, and would typically be completed in a few seconds using Matlab on a typical desktop computer.

### 5.6 Coupled equations in the asymptotic limit

Before we go on to calculating the evolution of large scale surface shapes according to our CGE model, we will try and reduce it to a single continuum growth equation. The first and simplest case assumes no adatom nucleation, \(n^2 \approx 0\). This approximation should not affect our calculations very strongly, as we aim to describe the morphology of epitaxial growth on surfaces with large slopes, such that the incorporation of adatoms into the film is mainly mediated through the large amount of steps on the surface, rather than the nucleation of dimer islands. Also, one should keep in mind that although the CGE model is fully deterministic in its current format, there will still be incorporation of adatoms to small scale surface structures through the thermally generated background steps, represented by the variable \(S_0\).

The typical choice of initial condition for the adatom concentration is \(n(x, 0) = 0\). As soon as the growth begins, the adatom concentration quickly builds to a constant level that only varies slightly in time and space, \(n(x, t > 0) \approx \bar{n} + \delta n\). For a sufficiently small variation \(\delta n\), we can make the approximation \(\partial_t n \approx \partial_t \bar{n} = 0\). For low amplitudes and long wavelengths,

\(^3\)The Center for Applied Scientific Computing provides free of charge Alan Hindmarsh’s ODEPACK at http://www.llnl.gov/CASC/odepack/
the large-scale surface morphology is weak, or \( \nabla h < S_0 \), so we also assume that the spatial variation of \( n \) is small. In this case, \( \nabla n \sim \nabla^2 n \sim 0 \), and of course \( S \simeq S_0 \). Furthermore, we assume for now that the product \( n \nabla^2 h \) is small. We incorporate these simplifications into Eqs. 5.11, 5.12 and get

\[
0 = F - a_{\parallel}^{-1} \partial_t (a_{\perp}^{-1} h) \\
= F - a_{\parallel}^{-1} (\beta D \bar{n} S_0 - a_{\parallel} K S_0)
\]

\[
\n \downarrow
\]

\[
\bar{n} = \frac{a_{\parallel}}{\beta DS_0} (F + K S_0) \tag{5.17}
\]

In this case, we can reduce Eqs. 5.11a, 5.11b to

\[
a_{\parallel}^{-1} \partial_t (a_{\perp}^{-1} h) = F + D a_{\perp}^{-1} \zeta \bar{n} \nabla^2 h
\]

\[
\downarrow
\]

\[
\partial_t h = a_{\parallel} a_{\perp} F + \nu \nabla^2 h \tag{5.18}
\]

where

\[
\nu = \frac{a_{\parallel}^2 \zeta}{\beta} \left( \frac{F}{S_0} + K \right) \tag{5.19}
\]

This reproduces the EW equation, and we see the explicit dependency of the linear smoothing coefficient \( \nu \) on the deposition rate and the downhill drift parameter \( \zeta \). In addition, it shows that in the absence of growth \( (F = 0) \) the linear smoothing term is independent of the background step density \( S_0 \). This agrees with the light scattering data in Fig. 5.1, which shows that the smoothing rate is relatively constant during a growth interruption even though the AFM images in Fig. 5.2 indicate that the step density drops dramatically during annealing. We showed in Chapter 4 that the presence of the EW term was well justified experimentally.

We would now like to extend our analysis to include the next higher order terms in the surface gradients. We use a perturbation method devised by Bayo Lau\(^4\), similar to that used in quantum mechanics [Sch68]. Writing the adatom concentration as

\[
n = n_0 + \varepsilon n_1 + \varepsilon^2 n_2 + \ldots \tag{5.20}
\]

we look for a growth equation in \( h \) from the perturbation

\[
\partial_t h = \partial_t (h_0 + \varepsilon h_1 + \ldots) \tag{5.21}
\]

\(^4\)This work was performed as part of a summer term project investigating analytical and numerical aspects of the CGE equations. His report "Brief Report on Coupled Growth Equation Investigation" is available on request.
We insert the expression for $n$ from Eq. 5.20 into Eq. 5.11b and get:

$$\partial_t(a_{\perp}^{-1}h) = (\alpha Dn_0^2 + \beta Dn_0 S - a_{\parallel} KS) + \varepsilon (Dn_1(2\alpha n_0 + \beta S)) + \ldots$$

(5.22)

We now insert the formulation for the surface current (Eq. 5.12a) into Eq. 5.11a, while letting $\partial_t n \rightarrow 0$, and find that:

$$\partial_t(a_{\perp}^{-1}h) = a_{\parallel}(F + a_{\perp}^{-1} D\nabla^2 h) + \sum_{i=1}^{\infty} \varepsilon^i G n_{i-1}$$

(5.23)

where the operator $G$ is defined as

$$G \triangleq a_{\parallel} D(a_{\perp}^{-1} \nabla h \nabla + \nabla^2)$$

(5.24)

We get $n_i$ from equating the $i$th order terms in $\varepsilon$ from Eqs. 5.22 and 5.23. To the zeroth order, this perturbation method gives the following expression for $n_0$:

$$0 = \alpha Dn_0^2 + D(\beta S - a_{\parallel} a_{\perp}^{-1} \nabla^2 h)n_0 - a_{\parallel}(F + KS)
\uparrow
n_0 \approx \frac{S_0 \beta}{2\alpha} \left( \sqrt{1 + \frac{4\alpha a_{\parallel}(F + KS_0)}{\beta^2 DS_0^2}} - 1 \right) \triangleq \frac{S_0 \alpha}{2\beta}(\Gamma - 1)$$

(5.25)

When $\beta^2 DS_0^2 \gg 2\alpha a_{\parallel}(F + KS_0)$, which is the limit in which nucleation of dimer islands is not important, $n_0$ reduces to the expression for $\bar{n}$ as defined in Eq. 5.17.

We proceed to the first order in the perturbation approach. From Eqs. 5.21 and 5.23 we see that $\partial_t h_1$ can be obtained from $a_{\perp} G n_0$. After a little bit of algebra, we arrive at the following expansion

$$\partial_t h_1 = -\frac{\Lambda_{2,2}}{2} \nabla^2(\nabla^2 h)^2 - \kappa \nabla^4 h + \Lambda_{1,3} \nabla(\nabla h)^3 + O(\nabla^i(\nabla h)^j)$$

(5.26)

where $i$ and $j$ are integers and their sum exceeds 4. The prefactor for the Villain term is defined by

$$\Lambda_{2,2} = D \left( \frac{1}{4} - 1 \right) \left( a_{\parallel} \zeta^2 - (1 + \frac{1}{4}) \frac{\beta}{S_0} \right) - 2 \left( 1 + \frac{1}{4} \right) \frac{a_{\parallel} K}{\beta S_0 \Gamma}$$

(5.27)

where $\Gamma$ was defined in Eq. 5.25. We can also here use the approximation that $\beta DS_0^2 \gg 2a_{\parallel}(F + KS_0)$ (ignoring dimer nucleation), and thereby find a simpler expression for the Villain prefactor:

$$\Lambda_{2,2} = \frac{a_{\parallel}}{\beta S_0} \left( \frac{F}{S_0^2} - \frac{a_{\parallel} \zeta^2}{\beta} \left( \frac{F}{S_0} + K \right) \right)$$

(5.28)
The sign of this prefactor changes when the growth flux goes to zero. The prefactor for the Mullins term $\nabla^4 h$ is

$$\kappa = \frac{a^2 D \zeta}{2} \left( \frac{1}{\Gamma} - 1 \right)$$

which is negative for typical values of $D, \zeta$ and $\Gamma$ (see Table 5.1 in Section 5.7.1). This means that its contribution in the growth equation is a destabilizing one. Therefore, we cannot attribute this term to the diffusion of surface adatoms, like Mullins did. We speculate that by further expanding the CGE model, higher order terms will emerge that stabilizes this term. We discussed such a scenario in Section 3.2 with respect to the KS equation.

We see that the Das Sarma term $\nabla (\nabla h)^3$ also emerges from the perturbation method, and we showed in Section 3.6 that this term was dominant in the absence of the EW term $\nabla^2 h$ in the hydrodynamic limit. We have not attempted to work out the prefactor $\Lambda_{1,3}$, and further analytical investigation is required into the nature of this term, as well as higher order terms.

The lowest order nonlinear growth equation that emerges from the perturbation of the CGE model is therefore

$$\partial_t h = a_y a_\perp F + \nu \nabla^2 h - \frac{\Lambda_{2,2}}{2} \nabla^2 (\nabla h)^2$$

where all the prefactors are positive under typical growth conditions, except at high $T$ and low $F$, where $\Lambda_{2,2}$ is found to change sign. It should be pointed out explicitly that in Eq. 5.30, we have dropped the terms of order $\varepsilon^2$, as well as terms from $h_1$ that contained higher order derivatives, like $\nabla^4 (\nabla h)^2$ and the like. We notice immediately that the adatom current proportionality factor $\zeta$ is multiplicative in the linear term, so that in the case of a zero ES barrier, there is no linear smoothing during growth. The Villain term, however, still contributes in the case of a net zero adatom current.

In Fig. 5.7 we compare a simulation of Eq. 5.30 to a homoepitaxy experiment. In the experiment, the surface was prepared with a 10 minute $O_2$ UV treatment, and followed by a thermal desorption at $620^\circ C$. A buffer layer was then grown at $T = 550^\circ C$ for 90 minutes, yielding a 1.2 $\mu m$ thick film. The simulation only includes the first two terms in Eq. 5.30, and the parameters used were $\nu_x = 10 nm^2/s$, $\nu_y = 1 nm^2/s$ and $\Lambda_{2,2,x} = \Lambda_{2,2,y} = 10^6 nm^3/s$. Like the simulations performed in Chapter 4, the added growth noise used in these simulations was non-conservative. Fig. 5.7 (a) shows the surface after growth, with the typical weakly elongated
mounds along the [110] direction. Part (b) shows the corresponding simulated surface for an initial condition similar to that shown in Fig. 4.2 (a). The length scale of the mounds is in good agreement with the surface in (a). Part (c) shows the PSD along the [110] direction, and again excellent agreement is found between the experimental results and the simulation.

Our work in Chapter 4 and Ref. [BRS+02], showed that surface shape comparisons, as well as comparisons of the power spectra from the KPZ simulations and experimental data showed excellent agreement. However, in
Fig. 5.7 we see that by replacing the KPZ nonlinearity with the Villain nonlinearity, the resulting simulated surface shapes and PSDs also show good agreement with experimental results. We conclude that the KPZ and the Villain nonlinearities have similar effects on the surface shape. Fig. 3.5 (b) and (e) showed that the effects of the terms \((\nabla h)^2\) and \(-\nabla^2(\nabla h)^2\) on the surface evolution are very similar.

We conclude that the spatial frequency range accessible to us experimentally is not large enough to allow us to distinguish the two different nonlinear terms in the growth equation. If we compare the magnitude for these two nonlinear terms at the dominant spatial frequency in Fig. 5.7 (c) (approximately \(4 \mu m\)), we find that they are approximately equal. This can be done by considering the two nonlinear terms in Fourier space. The fourth order nonlinearity becomes:

\[
\mathcal{F} \left[ -\frac{\Lambda_{2,2}}{2} \nabla^2(\nabla h)^2 \right] = -\frac{\Lambda_{2,2}}{2} (-i\mathbf{q})^2 \mathcal{F} [(\nabla h)^2] \tag{5.31}
\]

Comparing this result to the Fourier transform of the KPZ nonlinearity, \(\mathcal{F}[(\lambda_{KPZ}/2)(\nabla h)^2]\), we arrive at:

\[
q^2 \Lambda_{2,2} = \lambda_{KPZ} \tag{5.32}
\]

Substituting in values for the dominant spatial frequency along with the parameters used for the simulations in Figure 5.7, we get:

\[
q_{max}^2 \Lambda_{2,2} = (4 \mu m)^2 \times (10^6 \text{ nm}^3/s) = 16 \text{ nm/s} \tag{5.33}
\]

which compares well to the value used for \(\lambda_{KPZ}\) under similar growth conditions in Chapter 4 (see Figure 4.3), namely \(12 \text{ nm/s}\).

This shows that the magnitude of the KPZ nonlinearity obtained from the KPZ fits to experimental data is similar to the magnitude of the Villain nonlinearity inferred from the parameters used in the coupled growth equations. Although the \(q\)-dependence of the two nonlinearities is different, the range of spatial frequencies accessible experimentally is too small to distinguish them. This result provides a natural explanation for why \(\lambda \neq F\) in the KPZ fits, as discussed earlier. The nonlinearity is not due to growth along the surface normal but rather to the more complex growth process discussed by Eqs. 5.11a and 5.11b.

While the randomly roughened substrates that we investigated in Chapter 4 show clear sign of nonlinear shape evolution, they are not rough enough for the nonlinear term to dominate the growth equation. When the nonlinear term is dominant, the surface is said to be in the strong coupling regime [NB96].
In order to explore the relative importance of the nonlinear term, we have performed 2D KMC simulations using the SOS model with standard parameters on a 1D sinusoidal starting surfaces with varying pitch and amplitude (see Fig. 5.8). In part (a), a pitch of 600 atoms was used, and the initial peak-to-peak amplitude was 8 atoms. This corresponds to a steepest surface slope of 2.4°. This surface is found to evolve linearly, with each successive growth scanline being very similar to the starting shape on the bottom, but with a slowly decaying amplitude. Part (b) shows the evolution of a similar...
surface with half the pitch, and hence a steepest surface slope of 4.8°. We see that this is steep enough to warrant nonlinear surface shape evolution, and that the successive growth scanlines evolve into rounded mounds separated by cusps, a growth behaviour typical of the KPZ equation. The fact that a shorter pitch at the same amplitude leads to more nonlinear growth suggests that the Villain nonlinearity is operative. In the case of the KPZ equation, the linear and nonlinear terms have the same \( q \)-dependence.

Fig. 5.8 (c) shows a taller grating, with a 16 atom peak-to-peak amplitude, and a steepest slope of 9.5°. The surface shape evolution is definitely nonlinear, but does not exhibit KPZ behaviour until the uppermost scanline after 90 ML growth, where the amplitude has been sufficiently reduced. The transient surface shapes after 30 and 60 MLs have mounds and cusps, like those we see in (b), but in addition, the sidewalls have positive curvatures, something the KPZ equation cannot produce. We speculate that the Villain nonlinearity is required in order to model such behaviour. In part (d), we show the dependence of the smoothing rate on the spatial frequency of the grating for low aspect ratio surfaces, like the one displayed in (a). It is seen to vary as \( q^{-2} \), close to the \( q^2 \) dependency expected for the linear EW equation.

In the next Section, we will perform regrowth on patterned substrates in the form of 1D gratings with a characteristic spatial frequency of \( q \sim 4 \mu m^{-1} \), corresponding to pitches in the low micron range. These surfaces are found to evolve unmistakeably in a strong nonlinear fashion.

5.7 Evolution of patterned surface gratings

5.7.1 Film thickness evolution

Growth on substrates with larger amplitude surface slopes, up to \( \sim 30° \), show complex surface shapes before evolving into parabolic mounds, as shown in Fig. 5.9 (a). At intermediate times, the valleys are V-shaped with concave rather than convex sidewalls and distinct shoulders near the top of the sidewalls. Note the absence of (001) facets which are predicted theoretically for annealing below the roughening temperature in the absence of deposition [SRF03]. Equations 5.11 and 5.12 can be solved in seconds with a finite difference scheme and a coupled differential-algebraic system solver, and a 1D solution is shown in Fig. 5.9 (b) with parameters adjusted to match the experimental data in Fig. 5.9 (a) (see Table 5.1 for parameters). The agreement with the experimental surface shapes is striking. In particular, the model reproduces the inverted "Gothic window" shape of the valley for
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Figure 5.9: Film thickness dependence: (a) AFM scan lines for regrowth on 100 nm deep gratings oriented perpendicular to the [110] direction (substrate temperature was 580°C, $F = 1$ ML/s and the As:Ga pressure was 3:1); (b) Scan lines from CGE calculation; (c) Scan lines from 2D KMC simulation of 10 nm high grating structure, where one $\Delta t$ equals 5.6 ML of growth. All offsets arbitrary.

the 600 nm growth and the KPZ-like cusps in the 2600 nm growth where the grating amplitude has reduced significantly.

A continuum model cannot include the microscopic details of the atomic scale phenomena, such as the geometrical configuration of the step edges. We therefore compare the continuum model described by Eqs. 5.11 and 5.12 with KMC simulations of the SOS model outlined in Ch. 2, using the standard parameters and a negative ES barrier. KMC simulations produce a random step distribution automatically due to the statistical nature of the model. In KMC, the binding energy for an atom at a step edge depends on how many neighbors it has ($\sim mE_{lat}$), whereas in the CGE continuum model a single average value is used for the step edge binding energy.

SOS simulations of MBE growth by KMC are limited by available com-
puting power to small scale structures, and become intractable for realistic, high temperature growth scenarios where 2D systems have sides up to microns and growth times on the order of hours. In Fig. 5.9 (c), we show a KMC simulation for a surface grating that is a fraction of the size of the experimental structures. The simulated grating profiles in Fig. 5.9 (c) were obtained by projecting 2D KMC simulations onto a line at each time point by taking the average elevation perpendicular to the scan line. The agreement with the experimental shapes is excellent, reproducing all of the main features, except they are on a smaller size scale. The substrate and lateral binding energies are similar to values reported earlier in the interpretation of reflection high energy electron diffraction (RHEED) data [Joy03, SVW+92] and compatible with the fitting parameters found in the continuum model. Kratzer et al. [KMS98] found from density-functional theory calculations that the diffusional barriers are anisotropic, with $D_{[110]} = (0.1 \text{ cm}^2/\text{s}) \exp[-1.5 \text{ eV}/k_B T]$ and $D_{[110]} = (0.07 \text{ cm}^2/\text{s}) \exp[-1.2 \text{ eV}/k_B T]$, i.e. faster diffusion along the [110] direction.

It is plausible that similar shapes could be obtained for the larger size scales relevant to the experiments by scaling the parameters appropriately. In the case of the CGE model (Eqs. 5.11, 5.12) we find that the parameters can indeed be scaled to yield similar surface shapes at different length scales (see Appendix D).

### 5.7.2 Temperature evolution

In Fig. 5.10 (a), we show the dependence of the surface topography on growth temperature, for a fixed layer thickness together with (b) the simulated surface topography using Eqs. 5.11 and 5.12 and parameters as outlined.

---

**Table 5.1: Parameter table for CGE calculations.** The gratings in Fig. 5.9 (b) are $\perp [110]$ and in Fig. 5.10 (b) $\perp [110]$. The numerical values for $\alpha$ match those of $\beta$ in our simulations.

<table>
<thead>
<tr>
<th>Figure</th>
<th>$F$ (ML/s)</th>
<th>$T$ (°C)</th>
<th>$D/10^5$ (nm$^2$/s)</th>
<th>$K$ (1/s)</th>
<th>$S_0$ (1/nm)</th>
<th>$\beta/10^{-4}$</th>
<th>$\zeta/10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.9 (B)</td>
<td>1.0</td>
<td>580</td>
<td>2.5</td>
<td>4.3</td>
<td>0.07</td>
<td>3.3</td>
<td>1.4</td>
</tr>
<tr>
<td>5.10 (B)</td>
<td>0.8</td>
<td>420</td>
<td>0.04</td>
<td>0.004</td>
<td>0.49</td>
<td>6.6</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500</td>
<td>0.4</td>
<td>0.2</td>
<td>0.38</td>
<td>1.6</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>550</td>
<td>1.3</td>
<td>1.4</td>
<td>0.19</td>
<td>0.4</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>610</td>
<td>4.6</td>
<td>12</td>
<td>0.03</td>
<td>13</td>
<td>1.1</td>
</tr>
</tbody>
</table>
in Table 5.1. The experimental data is obtained from growths on 100 nm deep gratings oriented perpendicular to [110]. This is the faster diffusion direction in this material system [BRS+02]. The anisotropy in the diffusion depends on the As2/Ga ratio during growth, which was equal to three for the data shown in Figs. 5.9 and 5.10. This observation is consistent with the values used for the downhill drift parameter in our calculations, where the best fits were obtained using a larger $\zeta$ when the gratings were oriented perpendicular to [110] (Fig. 5.10 (b)) than for gratings perpendicular to the [110] direction (Fig. 5.9 (b)). There is some uncontrolled variation in the pitch and depth of the gratings in the experimental data in Fig. 5.10 (a). With that in mind, we see that the CGE model reproduces the main features in the temperature dependent data, namely the small secondary mound in the valley at 420°C and 500°C, the KPZ-like cusp at 550°C and the inverse Gothic window shape for the valleys at 610°C. The shoulders at the edges of the ridges at 610°C are also reproduced by the model, although they are
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not as sharp as in the experimental data.

The parameters used in these calculations are based on the same energies used in the KMC simulations in Fig. 5.9 (c). The diffusion constant is related to the substrate binding energy by

\[
D = a_n^2 (2kT/h) \exp \left( -E_{sub}/kT \right)
\]

The step edge detachment rate is calculated from

\[
K = D x \exp \left( -\tilde{m} E_{lat}/kT \right),
\]

where \( \tilde{m} \) is an average number of neighbors for atoms at a step edge which we set equal to 2.5. The declining value of \( S_0 \) with temperature is reasonable under growth conditions; one might also expect \( \zeta \) to decrease weakly with temperature. Satisfactory fits to the data were also obtained with a larger activation energy for \( D \) (1.8 eV rather than 1.25 eV) together with a smaller prefactor and somewhat different (yet still physically reasonable) temperature dependences for the other parameters. Experimental and theoretical work suggests that the activation energy for \( D \) is in the 1.2-2.0 eV range [SVW’92, Joy03, YLB’99, KPS02].

5.7.3 Transient amplitude overshoot

In a pair of recent publications, Kan et al. [KSTEP04b] and Shah et al. [SGL’03] (see also Refs. [BTS04a, KSTEP04a]) investigated the shape evolution of patterned GaAs surfaces during epitaxial growth. The starting shapes in their studies consisted of circular holes or pits ~50 nm deep, ordered in a square array across the surface. Using the diameter of the holes as a control parameter, homoepitaxial regrowth experiments were then performed on the patterned surfaces and the grown surfaces were imaged at various growth times with AFM. The diameter of the holes was equal to one half their centre-to-centre spacing.

Kan and Shah observed that the peak-to-valley amplitude of their patterned surfaces underwent a non-monotonic decay: the amplitude of the surfaces with pits larger than about 1 \( \mu \)m diameter would first increase before declining, whereas the amplitude of the smaller diameter holes would decrease immediately upon commencement of growth. This effect is also present in our regrowth experiments on 1D gratings. For example in Fig. 5.9 (a) the data shows that the surface peak-to-valley amplitude has increased after 200 and 600 nm film growth, but has decreased again at longer growth times. Figure 5.10 (a) shows the same effect, where the data shows an increase in the surface peak-to-valley amplitude, except possibly in the case of growth at 620°C, where the amplitude is about the same as the starting surface.

In Fig. 5.11 we show the temporal evolution of the peak-to-valley amplitude of a 1D grating according to the CGE model at T=580°C, with
parameters as outlined in Table 5.1. Cross-sectional linescans from this calculation were shown in Fig. 5.9 (b). The sidewalls of the starting surface are set to 30° in order to match the experimental starting surfaces. The measured values for the amplitudes of the experimental gratings from Fig. 5.9 (a) are also plotted in Fig. 5.11, and found to follow the trend of the calculation very well. It is interesting to note that a stable model, with a net-downhill drift of adatoms can create a characteristic of unstable growth, namely the peak-to-valley amplitude overshoot.

In Figure 5.12, we investigate the full amplitude overshoot dependence on growth time and pit diameter. Part (b) shows the systematic experimental investigation done in Refs. [KSTEP04b, SGL+03], where the pit diameter, and hence the pit spacing, was varied in the range 700 nm to 8 μm. The different lines reflect the peak-to-valley amplitudes for different pit diameters at four different growth times, as indicated in the legend. These data values were digitized from the original Fig. 2 (a) of Ref. [KSTEP04b]. The experimental uncertainties in these measurements were not reported. As the growth time increases, we find that the maximum amplitude overshoot occurs for larger diameter holes. Figure 5.12 (a) shows the corresponding curves calculated from the CGE model, as originally published in Ref. [BTS04a]. The starting surfaces are indicated in the lowest curve in the inset in Fig. 5.12 (a). We tried to match the starting shapes of Kan’s
Chapter 5. Modeling of growth on patterned surfaces

Figure 5.12: Peak-to-valley amplitude evolution for corrugated surfaces: (a) 1D calculations based on CGE model, and the inset shows actual surface evolution; (b) experimental data from regrowth on pitted starting surface (from Kan et al. [KSTEP04b]).

pits, with a fixed sidewall slope of 30°. The remaining curves in the inset show the evolution of a typical grating according to our calculations. The parameters used in the CGE calculation were again the same as those used for the calculation of Fig. 5.9 (b). The agreement between Kan’s data and our calculations are very good.

The surface profiles shown in the inset of Fig. 5.12 (a) suggest an explanation for the non-monotonic decrease in surface amplitude. The sidewalls expand laterally, which means that they grow faster vertically than the ridge tops and valleys. This is due to adatom attachment at the high density of steps on the sidewalls. As the width of the valley shrinks, the adatoms in the valley have a higher probability of migrating to the sidewalls than the adatoms that are deposited on top of the ridges which are now wider. This means the ridge tops grow faster than the valley bottoms, leading to a net increase in peak amplitude, as observed experimentally by Kan et al.

An attempt was made in Ref. [KSTEP04b] at modelling the evolution
of these patterned surfaces using conventional continuum growth equations, including the KPZ and the MBE equations, without success: neither the surface shape evolution nor the amplitude evolution could be reproduced. In fact, according to numerical calculations in Ref. [KSTEP04b] using the KPZ and the MBE equations, the amplitude evolution of their simulated surfaces was monotonically decreasing without the initial overshoot. Kan et al. concluded that none of the growth equations investigated could successfully describe the surface evolution of GaAs during epitaxial growth. The continuum growth equations considered by Kan are asymptotic models, applicable for long times and low surface slopes (\( \nabla h \ll 1 \)), and therefore it is not surprising that these models do not fit the relatively large amplitude surface topography studied experimentally by Kan and Shah.

We showed in Section 5.6 that the nonlinear term that applies to our growth system is in fact \( \nabla^2 (\nabla h)^2 \). Both the KPZ equation and our reduced growth equation (5.30) produce very similar surface shape evolutions in the low amplitude limit. This is evident when comparing simulations based on the KPZ model (Figs. 4.3 and 4.5) and the CGE model (Fig. 5.7 (b) and (c)) to experimental AFM images (Figs. 4.2 and 5.7 (a), respectively). Our growth experiments and accompanying KPZ simulations in Chapter 4 and Ref. [BRS+02] provide sound experimental and computational evidence that KPZ provides an accurate description of the low amplitude surface morphological evolution for GaAs. As is seen in Figs. 5.9, 5.10 and 5.11, the full CGE model does a very good job at reproducing the surface shape evolution of large-scale, patterned surfaces, like Kan's pits and our gratings. It is also evident from the scanlines of the longer growth time gratings in Fig. 5.9 (a,b,c) that all of the experimental data, and calculations based on the CGE model and KMC simulations produce surface shapes that resemble typical KPZ mounds in the low amplitude limit.

## 5.8 Summary

Our analysis in Chapter 4 lead us to investigate the smoothing behaviour of randomly patterned surfaces closer. Light scattering experiments along with AFM images showed that the smoothing rate of the surface roughness must be dependent on the deposition rate \( F \), and hence also the adatom concentration, \( n \).

A coupled growth equation model was devised, incorporating the interplay between the adatom concentration and the surface height. In this model, the adatoms were deposited, and were allowed to diffuse, attach and
detach at steps, as well as nucleate with other adatoms. The step density was modeled by a simple spatially varying interpolation formula. A net adatom current factor, $\zeta$, was also included, and calculations showed that this the net direction of the adatom current was downhill.

Using a perturbation method, we reduced the coupled growth equations to a simple, nonlinear growth equation:

$$\partial_t h = a_{||} a_{\perp} F + \nu \nabla^2 h - \frac{\lambda_{\alpha \beta}}{2} \nabla^2 (\nabla h)^2$$

(5.34)

When applying this formula to the randomly patterned surfaces that we investigated in Chapter 4, they were found to evolve in a fashion very similar to the simulations based on the KPZ model. The prefactors in Eq. 5.34, given by Eqs. 5.19 and 5.28, were found to depend on the growth flux, the ES parameter $\zeta$, the thermally generated steps, as well as the step edge release rate, $K$. SOS simulations supported the findings that it is the Villain nonlinearity that is operative during growth, and not the KPZ nonlinearity.

The coupled growth equation model explains the replication of lithographically patterned surfaces very well, both as a function of film thickness and growth temperature. Unexpected support for our model came in the form of an excellent match with published, yet unexplained data describing the peak-to-valley amplitude overshoot for a pitted surface during epitaxial growth.

In conclusion, we have shown that the complex surface shapes which develop during epitaxial regrowth on patterned (001) GaAs substrates can be explained by the dynamics of the deposited adatoms, including step edge attachment and detachment, adatom diffusion, and a stable, downhill adatom drift. Although we attribute the downhill drift to a negative Ehrlich-Schwöbel barrier we cannot rule out the possibility that this effect is caused by some other mechanism, or a combination of other mechanisms, as discussed in Chapter 2. Our analysis has been specific to GaAs, and all experiments are done on GaAs, however, the concepts are generic and should be applicable to other material systems.
Chapter 6

Conclusion

GaAs is a technologically important material system used to make devices such as microwave integrated circuits, light-emitting diodes and laser diodes. It is a model system for epitaxial studies, since its physical and electronic properties are generally well understood. Something that is not well understood, however, is the evolving surface morphology of epitaxially grown films, and this has been the concern of this thesis. We expect that an understanding of this basic property of growing films and the underlying microscopic mechanisms that govern it will become increasingly important as device dimensions continue to shrink. Examples of this are found in the design and fabrication of distributed feedback lasers and photonic crystals, where lateral shape control is crucial.

In Chapter 2, we described some of the basic concepts related to adatom dynamics on crystal surfaces, and we introduced the Burton-Cabrera-Frank theory. We showed that interlayer transport of adatoms between the different terraces was an important factor in determining the overall evolution of the surface morphology during growth and annealing. If the net direction of adatoms is uphill, then the growth is unstable, and mounds will form due to nucleation of new dimer-islands on top of currently existing islands. However, if the adatoms trickle downhill, then the growth is stable, and rough surfaces will smooth during epitaxial growth. In this case, we were able to derive the stable Edwards-Wilkinson (EW) equation.

A commonly discussed mechanism that governs interlayer transport is the Ehrlich-Schwöbel (ES) step edge barrier. This barrier inhibits adatom diffusion over steps, and is a destabilizing mechanism that effectively introduces an uphill current of adatoms. An example of a stabilizing mechanism is downhill funneling, where newly deposited atoms relax into a low energy position upon impact.

We showed that it is the net direction of the adatom current that determines the long-time outcome of a growth. If, for example, the ES barrier is the stronger step edge mechanism, then large-scale roughness in the form of mounds will grow unabatedly. No such tendencies in the evolving surface morphology were observed experimentally. The next possibility is that
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the destabilizing effects are balanced by the smoothing effects and that at a given "magic slope", the net adatom current is zero. This results in pyramid-shapes on the growth surface, a result also not observed in experiments of GaAs homoepitaxy. The final possibility is that the smoothing mechanisms are stronger than the destabilizing mechanism for terraces of any width. In this case, rough surfaces will smooth until they are balanced by an rms interface width determined by kinetic roughening. This option is consistent with all our experimental observations.

Several groups have modeled GaAs homoepitaxy using a positive ES barrier. In these studies a stabilizing mechanism such as downhill funneling was required in order to get agreement between simulation results and reflective high energy electron diffraction intensity oscillations. We found that all of our experimental results could be reproduced to high accuracy using only one mechanism, namely an inverse (negative) ES barrier. Although similar results could have been obtained by a combination of a positive ES barrier and a stronger downhill funneling, we believe that the continued smoothing of the surface after growth is ended indicates that the ES barrier is indeed negative. This is because the local relaxation mechanisms, such as downhill funneling, are associated with growth only.

Based on these findings, we challenged the notion that the experimentally observed mounds in GaAs form due to a positive ES barrier, and that epitaxy on this growth system is unstable. In Chapter 4, we reported homoepitaxial growth experiments on GaAs (001) that showed that it was the surface preparation technique that caused the observed mounding. A common procedure prior to growth on GaAs is to thermally desorb the native oxide from the surface. This leaves a rough, pitted surface, with pits as deep as 40 nm. These pits, in conjunction with the nonlinear growth that is observed in this material system, causes the surface to go through a mounded stage as it smooths. This is therefore a transient smoothing phenomenon, and not an instability caused by a physical mechanism on an initially flat starting surface. When preparing the samples with a hydrogen-etch technique, a much smoother starting surface was obtained, and in this case, no mounding was observed during growth.

We implemented a solid-on-solid model and simulated growth on singular and vicinal surfaces using both a positive and a negative value for the ES barrier. As expected, a simulation of growth on the singular surface showed an increasingly rough surface as growth progressed when a positive ES barrier was used. On the vicinal starting surface, however, our findings contradicted those by Villain [Vil91]. We found that a positive barrier had a destabilizing effect on the surface morphology also here and that large
Chapter 6. Conclusion

ounds formed on the steep sections of the random starting surface. Again, a negative ES barrier equalized the terrace widths. These results are also consistent with the stable EW equation.

We also showed that the surface morphological evolution of both the thermally desorbed and the hydrogen-etched starting surfaces were well modelled by the Kardar-Parisi-Zhang (KPZ) equation, but not by the molecular beam epitaxy (MBE) equation. The second order linear term in the KPZ equation describes the net downhill diffusion of adatoms across step edges. A problem with the KPZ nonlinearity is that it does not conserve mass, which is a nonphysical scenario in MBE growth. Another issue with the nonlinear term is that it cannot be a manifestation of growth along the surface normal, because the prefactor $\lambda$ should equal the growth rate $F$ and in our simulations the value of $\lambda$ that matches the data was on the order of $50F$. We also questioned how one could relate the KPZ coefficients $\nu$ and $\lambda$ to real physical parameters, like $F$, $T$ and the As overpressure, as well as microscopic physical mechanisms on the surface.

We have presented a new formulation for surface growth based on two coupled partial differential equations (CGE). In this model, we took into account the spatial and temporal evolution of both the adatom concentration and the surface height. We expect this model to be applicable to other material systems, as well. The new model was found to be a good description of the evolution of randomly textured, nearly flat surfaces as well as lithographically patterned surfaces. For low surface slopes, the new model reduces to a KPZ-like equation, except with a fourth order, conservative nonlinear term. The similarity between the results obtained with the CGE model and the KPZ model confirmed that the two conservative and nonconservative nonlinear terms behave very similarly for the relevant experimental parameters. The CGE model was also able to predict the complex shape evolution of lithographically patterned gratings with sidewalls as steep as $30^\circ$. This is well beyond the range which asymptotic continuum growth equations such as the KPZ are applicable. The model was also able to reproduce the temporal evolution of the peak-to-valley amplitude reported recently by another group in regrowth on lithographically patterned GaAs surfaces. It is clear that the model accounts well for relatively disparate scenarios designed independently by different groups. This said, there is still much to be learned about the fundamental physical mechanisms that are at play during epitaxial growth, not only in GaAs, but also in other material systems.

We observed experimentally several interesting features that were not included in our modeling. Specifically, these were the surface feature anisotropy
associated with the As:Ga ratio used during growth and the fingering perpendicular to the step direction, believed to be a manifestation of the Bales-Zangwill instability.

We have developed a model that reproduces the surface shape evolution of GaAs (001) during epitaxial growth. One of the reasons for our success is that we have continuously attempted to match experimental results to the findings obtained by simulations. Continued investigation into this problem will have positive consequences for our fundamental understanding of the semiconductor surface. It will also benefit the device manufacturer, as an increased refinement is required in design on short length-scales.
Appendix A

The kinetic Monte Carlo algorithm
in solid-on-solid models

The kinetic Monte Carlo (KMC) algorithm is particularly well suited for the simulation of epitaxial growth. This algorithm is applicable to externally driven systems and is based on the work by Metropolis et al. [MRRT53] on equilibrium systems. Events on the surface, like diffusion and step edge detachment, are picked randomly from a distribution weighted by their rate of occurrence. This approach is best illustrated by a simple example. Imagine a system where only two events are possible (events 1 and 2) and one of these events are twice as likely to occur as the other: \( P(1) = 2P(2) \). In other words, \( P(1) = 2/3 \) and \( P(2) = 1/3 \), since the sum of the probabilities must equal 1. According to the KMC algorithm, one would now pick a random number, \( r \), from a uniform distribution between 0 and 1. If \( r < 2/3 \), event 1 is chosen and the system is updated. Otherwise, one proceeds with event 2. From the central limit theorem, we know that as the total number of events \( N \) increase, the number of type 1 events \( N_1 \) approaches \( P(1)N \).

The use of the KMC algorithm for implementation of an SOS model is well documented [JOH+94, vV93, Var02, NB99].

Our system is a 2D surface specified in an \( L \times L \) matrix \( \mathbf{H} \) with periodic boundaries, where the matrix entries describe the surface height at the \((i,j)\)th lattice site. During every step of the growth, we keep track of the number of sites \( N_m \) that have a surface atom surrounded by \( m \) lateral neighbouring atoms. In the SOS model that we introduced in Chapter 2, we use a cubic lattice, and only the nearest neighbours are accounted for \((m \in \{0,4\})\). The microscopic process in our system include deposition and diffusion, as well as detachment from any surface-site. This makes for a total of 6 different types of events that can take place: deposition at rate \( F \) (in ML/s), as well as diffusion of atoms with \( m \) neighbours at rates \( k_m \). These rates follow Arrhenius behaviour, and are calculated accordingly to
Appendix A. The kinetic Monte Carlo algorithm in solid-on-solid models

\[ k_m = \nu_0 \exp[-\beta E_{act}], \]

with an activation energy \( E_{act} = E_{sub} + m E_{lat} \), where \( E_{sub} \) is the binding energy to the substrate and \( E_{lat} \) is the lateral binding energy. The prefactor \( \nu_0 \) used in this work is derived from the equipartition theorem: \( \nu_0 = 2kT/h \), where \( h \) is Planck's constant. Deposition is assumed uniform across the surface. The KMC algorithm repeats and time is incremented [MG88, Wil89] until the desired growth time is reached. Due to the temperature dependence of the rates \( k_m \), the high-temperature simulations will require the calculation of more events than a lower-temperature growth in order to get to a certain film-thickness.

We outline the KMC approach according to Vardavas [Var02].

Step I. The first step is to calculate the total rate of activity on the surface based on the possible physical microscopic processes that can take place:

\[ \mathcal{R}_{tot} = FL^2 + \sum_{m=0}^{4} k_m N_m \]  \hspace{1cm} (A.1)

This allows us to associate a probability for a deposition event \( P(dep) \) and the diffusion events \( P(m) \):

\[ P(dep) = \frac{FL^2}{\mathcal{R}_{tot}} \]  \hspace{1cm} (A.2a)
\[ P(m) = \frac{k_m N_m}{\mathcal{R}_{tot}} \]  \hspace{1cm} (A.2b)

We continue by calculating the cumulative probabilities:

\[ C_0 = 0, \quad C_{m+1} = C_m + P(m), \quad m \in \{0,4\} \]  \hspace{1cm} (A.3)

A random number is now generated from a uniform distribution \( r_1[0,1) \) and an \( m \)-event is chosen if:

\[ C_m \leq r_1[0,1) < C_{m+1} \]  \hspace{1cm} (A.4)

A deposition event is chosen if \( r_1[0,1) \geq C_5 \).

Step II. Picking the type of event to execute is the easy part in KMC; finding a site to which we can apply that given transition is harder. In the case that a deposition event is chosen, a site \((i,j)\) is chosen randomly, and the surface height is incremented by 1 atomic unit at that site:

\[ H(i,j) \rightarrow H(i,j) + 1 \]  \hspace{1cm} (A.5)
When the chosen event is not deposition, but rather the diffusion of a surface atom with $m$ neighbours, we need to find an atom that is in such a configuration. Searching randomly around the surface matrix for such an atom can be done, but at a high computational cost. The reason for this is twofold: first, the atoms with the fewest neighbours are the ones that are most likely to diffuse, and secondly, the fast-diffusing atoms are scarce, as they most likely diffuse step edges in a relatively short time, where they are less likely to detach and continue diffusing.

Our approach to finding these rare atoms involves updating 4 binary trees $T_m$ ($m \in \{0, 3\}$) containing the coordinates of all atoms that have $m$ neighbours. Given an event $m$, an appropriate set of coordinates is then randomly chosen out of the binary tree $T_m$. For the atoms that have 4 neighbours, a corresponding matrix $N$ was used, where the $(i, j)^{th}$ entry contains a “1” if that site has 4 neighbours, and a “0” otherwise. This proved to be the most cost-effective approach for our particular growth system, where even the very rough or textured surfaces were found to have an abundance of 4-neighbour atoms. This way, an average of less than two searches were required in order to find the appropriate coordinates. Now that we know what atom to hop, we randomly choose a site $(i', j')$ which is within one jump of $(i, j)$ in the x- or y-direction only, and update $H$ as follows:

$$H(i, j) \rightarrow H(i, j) - 1 \quad (A.6a)$$

$$H(i', j') \rightarrow H(i', j') + 1 \quad (A.6b)$$

After the hop or deposition event has been performed, and the surface matrix has been updated, the quantities $N$, $T_m$ and $N$ must be updated.

Step III. The last step in the KMC algorithm is to increment the time, $\Delta t_{\text{event}}$. In KMC, the time-step is not constant, as the microscopic events are independent of time, and follow a negative
Appendix A. The kinetic Monte Carlo algorithm in solid-on-solid models

exponential distribution. It can therefore be shown that the time interval between successive events over the whole system also follows a negative exponential distribution with parameter $R_{\text{tot}}$. By producing another random variable $r_2 \sim [0, 1)$, we can produce a time increment as follows:

$$\Delta t_{\text{event}} = \frac{\log [r_2 [0, 1)]}{R_{\text{tot}}}$$ (A.7)

Time can also be calculated by dividing the total coverage $\theta$ on the surface by the growth rate, $t = \theta / F$, however, this approach will only increment the time whenever there is a deposition event.
Appendix B

Details of the Burton-Cabrera-Frank calculations

In Chapter 2, we introduced the BCF model for adatom density on vicinal surfaces. In this Appendix, we show some of the details of the calculations that were left out of that Chapter.

B.1 Boundaries with Ehrlich-Schwöbel barriers

When there is no desorption of adatoms back into the vapour, the adatom density in 1D obeys

\[ D \nabla^2 \rho = -F/a \parallel \]  

(B.1)

whose solution regardless of boundary conditions is

\[ \rho(x) = -\frac{Fx^2}{2a\parallel D} + c_1 x + c_2 \]  

(B.2)

where \( c_1 \) and \( c_2 \) are constants to be determined from the boundary conditions.

Including the ES barrier can be done by the following boundary conditions (Eqns. 2.13 and 2.14):

\[ x = 0 : \quad -D \nabla \rho = -\frac{D}{a} \rho, \quad \text{(Ascending step with ES barrier)} \]  

(B.3)

\[ x = l : \quad -D \nabla \rho = \frac{D}{l_{ES}} \rho. \quad \text{(Descending step with ES barrier)} \]  

(B.4)

Solving for \((c_1,c_2)\) gives

\[ c_1 = \frac{Fl}{2a\parallel D} \frac{(l + 2l_{ES})}{(l + a\parallel + l_{ES})} \]  

(B.5)

\[ c_2 = a\parallel c_1 \]  

(B.6)
so that
\[ \rho(x) = \frac{F x^2}{2a_\parallel D} + \frac{F l}{a_\parallel D} \frac{(x + a_\parallel)(2l_{ES} + l)}{(l + a_\parallel + l_{ES})} \] (B.7)

and the adatom current is
\[ j = -D(\nabla \rho(0) + \nabla \rho(l)) \] (B.8)
\[ = -2Dc_1 + \frac{F l}{a_\parallel} \] (B.9)
\[ = \frac{F l (a_\parallel - l_{ES})}{a_\parallel (a_\parallel + l_{ES} + l)} \] (B.10)

which is the result of Eqn. 2.16.

### B.2 Downhill funneling, Ehrlich-Schwöbel barriers and detachment

Eqn. B.2 still holds in zone 1 of Fig. 2.9 for \( \rho = \rho_1 \), but in zone 2 we let \( F \to 0 \) in the BCF equation, with the result that the adatom density in that region becomes
\[ \rho_2(x) = c_3 x + c_4 \] (B.11)

The boundary conditions (Eqns. 2.17) are repeated here
\[ x = 0 : \quad -D \nabla \rho_1 = K - \frac{D}{a_\parallel} \rho_1 \] (B.12a)
\[ x = l - R_{inc} : \quad \begin{cases} \rho_1 = \rho_2 \\ \nabla \rho_1 = \nabla \rho_2 \end{cases} \] (B.12b)
\[ x = l : \quad -D \nabla \rho = \frac{D}{l_{ES}} \rho - K \frac{a_\parallel}{l_{ES}} \] (B.12c)

which gives the following values for the \( c_1 \) and \( c_4 \):
\[ c_1 = \frac{F}{2a_\parallel D} \frac{(l - R_{inc})(2l_{ES} + l + R_{inc})}{(a_\parallel + l_{ES} + l)} \] (B.13)
\[ c_4 = \frac{a_\parallel K}{D} + \frac{F}{2a_\parallel D} \frac{(l - R_{inc})(l_{ES} + l)(l + 2a_\parallel - R_{inc})}{(a_\parallel + l_{ES} + l)} \] (B.14)

and \( c_2 \) and \( c_3 \) can be expressed as
\[ c_2 = a_\parallel c_1 + \frac{a_\parallel K}{D} \] (B.15)
\[ c_3 = c_1 - \frac{F}{a_\parallel D} (l - R_{inc}) \] (B.16)
Appendix B. Details of the Burton-Cabrera-Frank calculations

The adatom current is then

\[ j = -D (\nabla \rho_1(0) + \nabla \rho_2(l)) + \frac{FR_{\text{inc}}}{a_\parallel} \]  
\[ = -D(c_1 + c_3) + \frac{FR_{\text{inc}}}{a_\parallel} \]  
\[ = \frac{F}{a_\parallel} \left[ l(a_\parallel - l_{ES}) + R_{\text{inc}}(2l_{ES} + R_{\text{inc}}) \right] \]

which is Eqn. 2.18.

B.3 Downhill funneling, Ehrlich-Schwöbel barriers, detachment and desorption

When desorption is introduced we have to apply Eq. 2.20. The solution for the adatom density \( \rho(x) \) is

\[ \rho(x) = c_1 \exp \left( \frac{x}{\sqrt{D\tau_{\text{des}}}} \right) + c_2 \exp \left( -\frac{x}{\sqrt{D\tau_{\text{des}}}} \right) + \frac{\tau_{\text{des}}F}{a_\parallel} \]

where

\[ c_1 = y(a_\parallel^2 K - D\tau_{\text{des}}F)(a_\parallel \Delta + l_{ES} - y + \Delta y)/\Gamma \]  
\[ c_2 = \Delta y(a_\parallel^2 K - D\tau_{\text{des}}F)(a_\parallel + \Delta l_{ES} - y + \Delta y)/\Gamma \]  

and

\[ \Gamma = a_\parallel D \left[ (\Delta^2 + 1)y(l_{ES} + a_\parallel) + (\Delta^2 - 1)(y^2 + a_\parallel l_{ES}) \right] \]

with \( y = \sqrt{D\tau_{\text{des}}} \) and \( \Delta \) as defined in Eq. 2.22. This leads to a very manageable expression for the surface adatom current:

\[ j(l) = \frac{(\Delta^2 - 1)(l_{ES} - a_\parallel) \left( \frac{a_\parallel K}{\tau_{\text{des}}} - \frac{D\Delta F}{a_\parallel} \right)}{(\Delta^2 + 1) \sqrt{\frac{D}{\tau_{\text{des}}} (l_{ES} + a_\parallel) + (\Delta^2 - 1) \left( \frac{a_\parallel l_{ES}}{\tau_{\text{des}}} + D \right)}} \]

which is Eq. 2.21.
Appendix C

Finite difference scheme for nonlinear derivatives

Figure C.1: (a) Application of the normal growth algorithm to a discrete representation of a 1D surface. The surface is translated outwards by an amount $ds = \lambda dt$, leading to a growth rate in the vertical direction of $dh$. (b) The 2D stencil $[ABCDP]$ used to calculate the $(\nabla h)^2$ term at point $P$.

Conventional finite difference schemes for the nonlinear term $(\nabla h)^2$ in the KPZ equation (Eq. 3.11) are usually based on a centered difference approximation, such as the second order accurate

$$ \nabla h = \frac{h_{i+1} - h_{i-1}}{2\Delta x} + O(\Delta x^2) \quad (C.1) $$

where $h_i$ is the height at the $i^{th}$ point on the 1D surface, $\Delta x$ is the spacing between the points and $O$ is the usual "big-O" notation that signifies "approximation error on the order of $\{\}$". As noted in Ref. [NB96], this

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1A version of this Chapter has been published. A. Ballestad, B. J. Ruck, J. H. Schmid, M. Adamczyk, E. Nodwell, C. Nicoll and T. Tiedje (2002) Surface morphology during GaAs
implementation fails to include the grid point \( h_i \), and can be highly unstable. This restricts the range of parameters which can be used in simulations, more specifically it sets an upper limit to the ratio of the KPZ parameters \( \lambda/\nu \) to a value that is too small for what we require in our morphology simulations. Therefore, we have used an alternate implementation based on the normal growth interpretation of the KPZ term (Eq. 3.13), where the surface is translated outwards from the local surface normal by a constant amount.

Consider the 1D discrete representation of a surface shown in Figure C.1a. The dashed lines show the positions of each surface element after translation outwards by a uniform amount. The thick solid line shows the new surface generated from the dashed lines, by choosing the maximum at any point where there is ambiguity in the choice of the new height. This procedure can be generalized to 2D. Figure C.1b shows the stencil used for the 2D calculation, where the relevant surface elements have been shaded. At most only one of the four shaded surface elements will actually decide the final height increment at point \( P \). To determine which this is, we find the largest of \( h_A, h_B, h_C, \) and \( h_D \), and call this \( h_1 \). Of the two remaining points of \( A, B, C, \) and \( D \) which are closest to this point, we find the one with the next largest \( h \), and call this \( h_2 \). Then, assuming \( \Delta x = \Delta y \),

\[
\Delta h_P = \begin{cases} 
\lambda dt, & \text{if } [h_1 \leq h_P \& \ h_2 \leq h_P] \\
\lambda dt \sqrt{1 + \left( \frac{h_P-h_1}{\Delta x} \right)^2}, & \text{if } [h_1 > h_P \& \ h_2 \leq h_P] \\
\lambda dt \sqrt{1 + \left( \frac{h_P-h_1}{\Delta x} \right)^2 + \left( \frac{h_P-h_2}{\Delta x} \right)^2}, & \text{if } [h_1 > h_P \& \ h_2 > h_P]
\end{cases}
\]  

(C.2)

The final step is to subtract \( \lambda dt \) from the matrix of height increments, thus leaving a matrix of values closely approximating \( \lambda (\nabla h)^2/2 \). This algorithm is stable for any ratio \( \lambda/\nu \), as long as the time step is not excessive. Furthermore, the simulation code can be fully vectorized, leading to a 16-fold decrease in calculation time over an implementation using nested for loops to access the matrix elements. The algorithm has been fully tested on artificial surfaces for which \( (\nabla h)^2 \) can be calculated exactly.

The conservative form of the KPZ equation (Eq. 3.15) is implemented via an extension to the nonconservative KPZ simulation. After calculating \( \Delta h \) on an \( N \times N \) matrix for a given time step using Eq. C.2, the total volume represented by \( \Delta h \) is determined: \( dV = \sum \Delta x^2 \Delta h \). This is done
prior to subtracting $\lambda dt$ from $\Delta h$. The new matrix $\Delta h_C$ is then calculated:

$$
\Delta h_C = \Delta h(dV/dV_0) - \lambda dt,
$$

where $dV_0 = \lambda(N\Delta x)^2$ is the volume that would be added to a flat surface during the same time step using the growth rule Eq. C.2. Note that this is not the same as ensuring a conservative growth term by simply subtracting the average surface height at each time step.

The second order linear derivative term is implemented using a five point stencil on the 2D lattice, i.e.

$$
\nabla^2 h \approx \nu_x \left[ \frac{h_{i+1,j} - 2h_{i,j} + h_{i-1,j}}{\Delta x^2} \right] + \nu_y \left[ \frac{h_{i,j+1} - 2h_{i,j} + h_{i,j-1}}{\Delta y^2} \right] \quad (C.3)
$$

where $\Delta x = \Delta y$ in our simulations. The fourth order linear term is implemented with a nine point stencil as

$$
\nabla^4 h \approx \kappa_x \left[ \frac{h_{i+2,j} - 4h_{i+1,j} + 6h_{i,j} - 4h_{i-1,j} + h_{i-2,j}}{\Delta x^4} \right] + \\
\kappa_y \left[ \frac{h_{i,j+2} - 4h_{i,j+1} + 6h_{i,j} - 4h_{i,j-1} + h_{i,j-2}}{\Delta y^4} \right] \quad (C.4)
$$

The different coefficients ($\nu_x, \nu_y, \kappa_x, \kappa_y$) allow for the inclusion of anisotropy in the simulations. Linear transformations of the terms in the numerical calculation allow the anisotropy axis to be rotated such that they match the elongation axis of the AFM images. It is obvious from Eq. 3.12 that this algorithm can also be used to simulate the fourth order nonlinear term, by simply applying the $\nabla^2$ scheme to the matrix of $(\nabla h)^2$ values generated in the manner described above.
Appendix D

Scaling of coupled growth equations

The importance of scaling equations should be obvious to epitaxial growth modelers: we are trying to unite the physics of the atomic scale with the observable evolution of the large scale surfaces on the meso- to macroscale. Much of the work in this thesis is dedicated to exactly this problem: we utilize SOS models in order to simulate the underlying physics at the microscopic or atomistic scale, while we use coarse grained partial differential equations in order to model what we observe with AFM images of surfaces grown (and etched) by MBE. In this Appendix, we outline the simple scaling behaviour of the coupled growth equations model that we developed in Chapter 5.

D.1 Lateral scaling: $x \rightarrow bx$

We start by reminding the reader of the full form of the CGE model\(^1\)

\[
\begin{align*}
\partial_t n + \nabla \cdot j &= F - a_{||}^{-1} \partial_t (a_{\perp}^{-1} h) \\
\partial_t (a_{\perp}^{-1} h) &= aDn^2 + (\beta Dn - a_{||} K)S \\
j &= -D(a_{\perp}^{-1} \zeta n \nabla h + \nabla n) \\
S &= \sqrt{S_0^2 + (a_{\perp}^{-1} \nabla h)^2}
\end{align*}
\]

While it is a well known fact that a large pitch grating will smooth at a slower rate than a small pitch grating, it is not equally clear whether Eqs. D.1 will reproduce the complex shape evolutions that we witnessed in Ch. 5 if the lateral pitch of a grating is changed. This is the question that we wish to address in this Section: will changing the pitch of the surface pattern simply result in a different decay rate during growth, or will

\(^1\)The complete units are listed here: $[n]=1/L$, $[j]=1/T$, $[F]=1/LT$, $[a_{||}]=L$, $[h]=L$, $[a]=\beta=[\zeta]=1$, $[D]=L^2/T$, $[K]=1/T$, $[S]=S_0=1/L$, where $L$ is length and $T$ is time.
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the shape evolution also change? We address this question by defining the
desired variable transformation

$$x \rightarrow \tilde{x} = bx$$  \hspace{1cm} (D.2)

where $b$ is the scaling factor with which we wish to scale the initial surface,
and $\tilde{x}$ is the spatial variable in the new coordinate system. The remaining
variables $h$, $n$ and $t$ all stay the same under this transformation.

The variable transformation in Eq. D.2 requires the derivatives in the
CGE to be changed according to:

$$\nabla \rightarrow \tilde{\nabla} = b^{-1}\nabla, \quad \nabla^2 \rightarrow \tilde{\nabla}^2 = b^{-2}\nabla^2$$  \hspace{1cm} (D.3)

The candidates for a transformation are $\nabla \rightarrow \tilde{\nabla}$, $F \rightarrow \tilde{F}$, $\alpha \rightarrow \tilde{\alpha}$,
$D \rightarrow \tilde{D}$, $\beta \rightarrow \tilde{\beta}$, $K \rightarrow \tilde{K}$, $\zeta \rightarrow \tilde{\zeta}$ and $S_0 \rightarrow \tilde{S}_0$. We rewrite Eq. D.1a
in the transformed variable set (denoted with the tilde):

$$\partial_t n = \tilde{F} - \tilde{\nabla} \cdot j - a_{||}^{-1} \partial_t (a_{\perp}^{-1} h)$$
$$= \tilde{F} - \tilde{\nabla} \cdot (-a_{\perp} \tilde{D} \nabla h - \tilde{D} \nabla n) - a_{||}^{-1} \partial_t (a_{\perp}^{-1} h)$$
$$= \tilde{F} + a_{\perp} \tilde{D} \tilde{\nabla} \cdot (n \nabla h) + \tilde{D} \nabla^2 n - a_{||}^{-1} \partial_t (a_{\perp}^{-1} h)$$
$$\downarrow$$

$$\partial_t n = \tilde{F} + a_{\perp} \tilde{D} \tilde{\nabla} b^{-2} \cdot (n \nabla h) + \tilde{D} b^{-2} \nabla^2 n - a_{||}^{-1} \partial_t (a_{\perp}^{-1} h)$$  \hspace{1cm} (D.4)

The following transformation for our free parameters will do:

$$\tilde{F} = F, \quad \tilde{D} = b^2 D, \quad \tilde{\zeta} = \zeta$$  \hspace{1cm} (D.5)

The surface height itself (Eq. D.1b) undergoes the following transformation

$$\partial_t (a_{\perp}^{-1} h) = \tilde{\alpha} \tilde{D} n^2 + \tilde{\beta} \tilde{D} n \tilde{S} - a_{||} \tilde{K} \tilde{S}$$
$$\downarrow$$

$$\partial_t (a_{\perp}^{-1} h) = \tilde{\alpha} (b^2 D) n^2 + \tilde{\beta} (b^2 D) n \tilde{S} - a_{||} \tilde{K} \tilde{S}$$  \hspace{1cm} (D.6)

We can immediately pick out the transformation

$$\tilde{\alpha} = b^{-2} \alpha$$  \hspace{1cm} (D.7)

however, for the determination of $\tilde{\beta}$ and $\tilde{S}_0$, we need to analyze the step
density

$$\tilde{S}^2 = \tilde{S}_0^2 + (a_{\perp}^{-1} \nabla h)^2$$
$$= \tilde{S}_0^2 + b^{-2}(a_{\perp}^{-1} \nabla h)^2$$  \hspace{1cm} (D.8)
so the following transformation will do
\[ \tilde{S}_0 = b^{-1}S_0, \quad \tilde{S} = b^{-1}S \] (D.9)
which gives us
\[ \tilde{\beta} = b^{-1}\beta, \quad K = bK \] (D.10)
All our findings will be tabulated at the end of this chapter.

D.2 Vertical scaling: \( h \to ch \)

Our second transformation deals with the increase in surface height of the surface structures:
\[ h \to \tilde{h} = ch \] (D.11)
where \( c \) is the vertical scaling factor. It is important to point out now that the lateral variable \( x \) remains the same, as does time \( t \). However, from Eq. D.1a we see that whatever transformation is done to \( h \) must also be done to \( n \), so vertical scaling implies that
\[ n \to \tilde{n} = cn \] (D.12)
All the temporal and spatial derivates remain the same under this transformation. Again, we rewrite the first part of the CGE in the transformed variable set:
\[
\begin{align*}
\partial_t \tilde{n} &= \tilde{F} + \tilde{D} \nabla^2 \tilde{n} + a_{\perp}^{-1} \tilde{D} \tilde{\zeta} \nabla \cdot (\tilde{n} \nabla \tilde{h}) - a_{\parallel}^{-1} \partial_t (a_{\perp}^{-1} \tilde{h}) \\
&\downarrow \\
c \partial_t n &= \tilde{F} + c \tilde{D} \nabla^2 n + c^2 a_{\perp}^{-1} \tilde{D} \tilde{\zeta} \nabla \cdot (n \nabla h) - ca_{\parallel}^{-1} \partial_t (a_{\perp}^{-1} h) \quad (D.13)
\end{align*}
\]
This time, the following transformations are necessary:
\[ \tilde{F} = cF, \quad \tilde{D} = D, \quad \tilde{\zeta} = c^{-1} \zeta \] (D.14)
The step density itself sees the following change:
\[
\begin{align*}
\tilde{S}^2 &= \tilde{S}_0^2 + (a_{\perp}^{-1} \nabla \tilde{h})^2 \\
&= \tilde{S}_0^2 + c^2 (a_{\perp}^{-1} \nabla h)^2 \\
&\downarrow \\
\tilde{S}_0 &= cS_0, \quad \tilde{S} = cS \quad (D.15)
\end{align*}
\]
Appendix D. Scaling of coupled growth equations

We then get

\[
\partial_t (a_{\perp} h) = \tilde{\alpha} \tilde{D} \tilde{n}^2 + \tilde{\beta} \tilde{D} \tilde{n} \tilde{S} - a_{\parallel} \tilde{K} \tilde{S} \\
\downarrow \\
c\partial_t (a_{\perp} h) = \tilde{\alpha} D (cn)^2 + \tilde{\beta} D (cn) (cS) - a_{\parallel} \tilde{K} (cS)
\] (D.16)

so that the complete transformation is:

\[
\tilde{\alpha} = e^{-1} \alpha, \quad \tilde{\beta} = e^{-1} \beta, \quad \tilde{K} = K
\] (D.17)

### D.3 Time scaling: \( t \to dt \)

Our final transformation deals with stretching of time:

\[
t \to \tilde{t} = dt
\] (D.18)

where \( d \) is the scaling factor. In this transformation, the surface itself, and hence also the adatom concentration \( n \), undergo no transformation. The spatial derivatives remain unchanged, but the time derivative change according to

\[
\partial_t \to \partial_{\tilde{t}} = d^{-1} \partial_t
\] (D.19)

We proceed as usual:

\[
\partial_{\tilde{t}} n = \tilde{F} + \tilde{D} \nabla^2 n + a_{\perp}^{-1} \tilde{D} \tilde{\zeta} \nabla \cdot (n \nabla h) - a_{\parallel}^{-1} \partial_{\tilde{t}} (a_{\perp}^{-1} h)
\]

\[
\downarrow \\
\tilde{d}^{-1} \partial_{\tilde{t}} n = \tilde{F} + \tilde{D} \nabla^2 n + a_{\perp}^{-1} \tilde{D} \tilde{\zeta} \nabla \cdot (n \nabla h) - \tilde{d}^{-1} a_{\perp}^{-1} \partial_{\tilde{t}} (a_{\perp}^{-1} h)
\] (D.20)

from which we find that

\[
\tilde{F} = d^{-1} F, \quad \tilde{D} = d^{-1} D, \quad \tilde{\zeta} = \zeta
\] (D.21)

Since all the spatial derivatives are unchanged, the step-density remains unchanged, and this makes the second part of our analysis simple:

\[
\partial_{\tilde{t}} (a_{\perp}^{-1} h) = \tilde{\alpha} \tilde{D} \tilde{n}^2 + \tilde{\beta} \tilde{D} \tilde{n} \tilde{S} - a_{\parallel} \tilde{K} \tilde{S}
\]

\[
\downarrow \\
\tilde{d}^{-1} \partial_{\tilde{t}} (a_{\perp}^{-1} h) = \tilde{\alpha} (d^{-1} D) n^2 + \tilde{\beta} (d^{-1} D) n S - a_{\parallel} \tilde{K} S
\] (D.22)

so we do not need to change \( \tilde{\alpha} \) or \( \tilde{\beta} \), and the only remaining change required is:

\[
\tilde{K} = d^{-1} K
\] (D.23)
Appendix D. Scaling of coupled growth equations

D.4 Composite scaling: \((x, h, t) \rightarrow (bx, ch, dt)\)

The various transformations can be applied successively, so that in the same calculation, we can let all of \(x\), \(h\) and \(t\) scale simultaneously. In that case, the total transformation on our system parameters are as follows:

\[
\begin{align*}
\begin{array}{c}
x \\ h \\ (n) \\ t
\end{array} & \rightarrow \begin{array}{c}
bx \\ ch \\ cn \\ dt
\end{array} \\
\begin{array}{c}
D \\ K \\ F \\ \zeta \\ \alpha \\ \beta \\ S_0
\end{array} & \rightarrow \begin{array}{c}
b^{2d-1}D \\ bd^{-1}K \\ cd^{-1}F \\ c^{-1}\zeta \\ b^{-2c^{-1}}\alpha \\ b^{-1c^{-1}}\beta \\ b^{-1}cS_0
\end{array}
\end{align*}
\]

This summary can be rewritten in the conventional scaling form (See for example Barabasi [BS95]), where \(x \rightarrow x' = bx\), \(h \rightarrow h' = b^\alpha h\) (where \(\alpha\) is the roughness exponent that we discussed in Chapter 3) and \(t \rightarrow t' = b^\beta t\), simply by replacing \(c\) by \(b^\alpha\) and \(d\) by \(b^\beta\). This way, \(D\) scales as \(D \rightarrow D' = b^{2d-1}D\), \(F \rightarrow F' = b^{a-z}F\), and so forth.

D.5 Spatial frequency dependence

In the low amplitude limit, the morphology of a growing surface should be described well by the (deterministic) EW equation. By letting the surface undergo the composite scaling of section D.4, we obtain the following:

\[
\frac{\partial \tilde{h}}{\partial \tilde{t}} = \nu \nabla^2 \tilde{h} \\
\text{(D.24)}
\]

\[
\frac{c \partial h}{d \partial t} = \frac{\nu}{b^3} \nabla^2 h \\
\text{(D.25)}
\]

so the required scaling of \(\nu\) is

\[
\tilde{\nu} = \frac{b^2}{d} \nu \\
\text{(D.26)}
\]
We compare with our expression for $\nu$, derived in Ch. 5:

$$
\nu = a_0^2 \frac{\xi}{\beta} \left( \frac{F}{S_0} + K \right) \tag{D.27}
$$

\downarrow

$$
\tilde{\nu} = a_0^2 \frac{\frac{1}{\xi}}{\frac{1}{\beta}} \left( \frac{\frac{d}{ \beta} F}{\frac{d}{ \beta} S_0} + \frac{b}{d} K \right) \tag{D.28}
$$

\quad = \frac{b^2}{d} \nu \tag{D.29}

which is the same result that we got for EW above. In this linear approximation, the spatial frequency dependence goes as $q^2$, as we have come to expect from the EW equation.
Bibliography


[JT97] S. R. Johnson and T. Tiedje. Effect of substrate thickness, back surface texture, reflectivity, and thin film inter-
Bibliography


Bibliography.


