INTERFACIAL INSTABILITIES DURING THE SOLIDIFICATION OF A PURE MATERIAL FROM ITS MELT

By

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To my Mom and my Dad
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Solidification of materials is important in the semiconductor and electronics industry. It is ordinarily required that crystals grown industrially have uniform mechanical and electrical properties to ensure better quality and reproducibility of the final devices that are produced from them. Thus there is a considerable economic incentive in producing uniform crystals. However, the occurrence of morphological defects at the growing solidification interface arising from growth instabilities leads to undesirable electro-mechanical properties of such crystals. It is the goal of this work to thoroughly understand the physics and causes of morphological instability in solidification.

Inasmuch as the problem of morphological instability of a solid-liquid interface has been considered in the past, many questions remain unanswered. Of central interest is the pattern that evolves when an instability occurs. To begin to answer this question one begins to address the earlier question of what the magnitude of the wavelength of the initial instability might be. My research focuses on this earlier issue. And a set of questions begin to present themselves. They are: What is the reason for the instability at a solid-liquid interface? When does the instability set in? How can one explain the dependence of roughness growth rate on its wave number? Why is a
maximum growth rate seen in problems like precipitation and solidification? What happens after the instability sets in? Does the front speed up or slow down compared to its predicted base value? Why are cellular patterns observed in solidification whereas precipitation is incapable of giving anything as interesting? Can one determine the nature of the branching to the non-planar steady state in the post-onset regime? Many important findings have been made in the course of answering these questions.

The primary discoveries of this work are: First, the shapes of the disturbance growth curves in solidification require the effect of transverse heat diffusion for their explanation. The neutral curves in solidification are found to give rise to the possibility of a cellular pattern at the onset of instability whereas for other solid-liquid front growth problems independent of thermal transport, such as precipitation from a supersaturated solution or electrodeposition of a metal from an ionic electrolyte, the onset of an instability from a planar state leads to a single crest and trough. Second and more important, a solid-liquid front that grows on account of temperature gradients is the only one amongst all solid-liquid front growth problems where a critical wavelength, independent of surface energy, can occur. This critical wavelength is of the order of the size of the container in which the growth takes place and as such is the only critical point with which fluid convection can interact. Third, a solidification front always demonstrates a “speed-up” upon becoming unstable, which is to say that it always moves ahead of its predicted base value. This is in contrast with other solid-liquid growth instability problems like precipitation. Finally the nature of the bifurcation in a solid-liquid growth problem where growth occurs on account of thermal gradients may be a forward pitchfork, leading to cellular growth, or a backward pitchfork, leading to dendritic growth. This stands in contrast to other growth problems where the post onset region is ordinarily characterized by dendritic growth.
CHAPTER 1
INTRODUCTION

This dissertation focuses on investigating the instability of the solid-liquid interfaces that occurs during precipitation from a supersaturated solution or during solidification from an undercooled melt. In both ways of growing a solid, an erstwhile planar interface can suddenly lose its stability and change its shape as a control parameter is advanced beyond its critical value. An instability occurring in such a fashion is often called a morphological instability [1]. Now the occurrence of morphological instability during solidification has implications in crystal growth as it leads to undesirable electro-mechanical properties of crystals that are often needed in the semiconductor industry [2]. To tackle this problem requires an understanding of the physics of the instability.

Now solidification is a typical ‘moving front’ problem where the liquid phase turns into solid phase by rejecting the latent heat from the interface [3]. The speed of the solidification front depends on how fast the latent heat released there can be conducted through one or both phases. The process of precipitation, on the other hand, occurs when a solid crystal is in contact with its supersaturated solution. In solidification as well as precipitation, the speed and the direction of the front determine its stability, and hence the state beyond which an erstwhile planar front loses its stability.

Hence, in both, the solid surface can acquire roughness and understanding the shape of the growth rate curve, where growth rate is plotted against the disturbance wave number, is an important step in understanding the source of the instabilities that arise during the growth. Finding how roughness growth rate, $\sigma$, varies with the wave number of the roughness, $k$, has been the object of many experimental studies [4,5]. One of the main goals of the present work is to explain the correspondence between these growth curves and the factors contributing to the
stability or instability of the surface, such as diffusion normal to the surface (longitudinal
diffusion), diffusion parallel to the surface (transverse or lateral diffusion), surface tension etc. In
fact, a greatest growth rate occurs at a finite wavelength in some, but not all moving front
problems, and the appearance of such a maximum growth rate in solidification is an example of
an observation that needs to be explained. As discussed by Coriell and coworkers [6], the
wavelength having the largest initial growth rate might be expected to be predominant during the
evolution of the instability, and it is therefore important from the point of view of pattern
selection. Therefore, while explaining the shapes of the growth curves in precipitation and
solidification, we emphasize the reason for the existence of a maximum growth rate. We will see
later that this has to do with transverse diffusion of heat in the liquid at the interface.

Now the $\sigma$ vs. $k^2$ curves at various values of a control variable tell us what the critical
wavelengths are, these being the wavelengths at zero growth rate. Thus they predict the shape of
the neutral curve, a curve where the control variable is given as a function of $k^2$. This curve is
useful in understanding what might be seen in a series of experiments as the control variable
slowly increases to, and just beyond its critical value. Of central interest is the pattern that
evolves during the early stages of instability. We will find that the neutral curve in precipitation
is monotonically increasing, hence only one crest and trough will be seen in precipitation. In
solidification, when heat is withdrawn only through the liquid, the neutral curves are as simple as
those in precipitation. Upon withdrawing heat through the solid as well, neutral curves like those
seen in the Rayleigh-Bénard convection problem [7] can be found. And by adjusting the depths
of the phases, we can go beyond this and get something new, viz., critical points that are due to
transverse diffusion in the solid phase, and not due to surface tension. Hence, the central result of
our linear theory is this: In the solidification of a pure material it is possible to obtain zero, one,
two, or three critical points, and a critical wavelength independent of surface energy can occur. This critical wavelength is of the order of the size of the container in which the growth takes place.

The reader is encouraged to refer to Cross and Hohenberg [8] who review pattern formation at great length, never finding neutral curves like the new ones discovered by us. In fact, it turns out that getting three critical points is a feature typical of pure solidification when the latent heat is rejected through both phases, when the control variable is made explicit, and when the depths of the two phases are taken to be finite. The Mullins and Sekerka [9] model for the solidification of a dilute binary alloy and the Wollkind and Notestine [10] model for pure solidification fail to give anything as interesting; they can give at most two critical points.

Now to understand why one might expect three critical points in solidification, let us see why a solidification front might be unstable and how factors such as surface curvature and transverse diffusion affect the stability. The usual explanation for the instability of a growing interface from an undercooled melt (cf., Langer [11]) is that a displacement of the surface into the melt in the form of a crest increases the temperature gradient at its tip, which reinforces the growth of the crest. Figure 1.1 depicts a growing front in an undercooled melt and one sees that longitudinal diffusion in the liquid phase is strengthened at a crest thereby destabilizing the surface. It is also clear from Figure 1.1 that longitudinal diffusion in the solid phase acts to stabilize the interface. The effect of longitudinal diffusion does not depend on the wavelength of the disturbance, i.e., it is a $k$-independent effect.

Now the melt temperature at a solid-liquid interface depends on its morphology. In other words, on account of the curvature of the non-planar interface itself, the melt temperature at a curved interface is different from the normal melt temperature at a planar interface. This is
explained by Delves [12]. Figure 1.2 shows this effect where surface curvature lowers the melt temperature at a crest while increasing it at a trough. Hence, surface tension weakens the instability caused by longitudinal diffusion in the liquid, while strengthening its stabilizing effect in the solid. The stabilizing effect of surface tension is $k$-dependent, the stabilization being stronger for shorter wavelengths.

Figure 1.1 – A picture argument for the effect of longitudinal diffusion in solidification

Figure 1.2 – A picture argument for the effect of surface curvature in solidification
Finally, let us look at the effect of transverse diffusion in the two phases. Setting surface tension aside, the effect of the displacement is as shown in Figure 1.3. On the melt side, the displacement of the surface strengthens the temperature gradient at a crest, weakening it at a trough; this induces transverse temperature gradients, carrying heat away from crests toward troughs. This tends to build crests up. Transverse diffusion is therefore destabilizing on the melt side of the surface. A similar argument made in the solid phase tells us that transverse diffusion is stabilizing in the solid phase. In both phases, the effect of transverse diffusion, whether stabilizing or destabilizing, is $k$-dependent.

Figure 1.3 – A picture argument for the effect of transverse diffusion in solidification

This is enough to speculate the occurrence of three critical points in solidification. Here is what is required: The longitudinal diffusion in the liquid should lead to positive values of $\sigma$ at $k^2 = 0$, then the transverse diffusion in the solid should drive $\sigma$ negative, providing the low-$k^2$ critical point. Thereafter the transverse diffusion in the liquid should drive the $\sigma$ positive for further increase in $k^2$, resulting in a second critical point. Finally, the stabilizing effect of surface tension should drive $\sigma$ down to zero for large enough $k^2$, providing a third critical point.
From a mathematical point of view, we first write the governing domain equations along with appropriate interface conditions and far-field conditions. These model equations are non-linear as the position of the interface depends upon the temperature gradient there, and the gradient, in turn, depends upon the position and morphology of the interface. This nonlinearity is the reason for the interface to depart from its flat base state, trying to become unstable. We write the model equations in terms of an observer moving at the speed of the front. Such an observer can find a steady planar solution to our nonlinear equations. To obtain the $\sigma$ vs. $k^2$ curves in solidification, we introduce a perturbation of a steady base solution, as did Mullins and Sekerka [9], whose work grew out of the earlier work of Rutter et al [13] and Tiller et al [14]. More detail can be found in the book by Davis [15] who presents the theory of front instabilities in the case of binary alloys.

Many of the models [9-11,16,17] proposed for pure solidification are based on local equilibrium at the interface and isotropic interfacial properties. Convection induced by density differences is neglected and steady thermal and diffusion fields are assumed [9,11] in the interior of the solid and liquid phases. These assumptions are made by us as well. To maintain our focus on the effects that longitudinal and transverse diffusion have on the growth rate of surface roughness, most other effects, however important they may be, are omitted. These effects have been dealt elsewhere. For example, the effect of convective flow on morphological instability was studied by Coriell and Sekerka [18]. The effect of solutal convection has been studied by Hurle et al [19], while Favier and Rouzaud [20] have given a detailed account of the effect of a deformable boundary layer. The effect of Soret diffusion has been explained by Hurle [21]. The effect of departure from local equilibrium has been considered by Coriell and Sekerka [22]. In a different paper, Coriell and Sekerka [23] have considered the effect of anisotropic surface
tension and interface kinetics. Wollkind and coworkers [10, 24] have considered surface tension as a function of temperature.

Now we may have neglected the effect of convection and the anisotropy of interfacial properties. But we do take into account the finite thickness of the solid and liquid phases. They are not taken to be of infinite extent as they are by Wollkind et al [10]. This gives us a way of altering the relative strengths of transverse diffusion in the two phases and hence of altering the shapes of the growth curves, and this, in turn, gives us a way to obtain three critical points in pure solidification.

Up till now our emphasis has been on the linear stability analysis in investigating the interfacial instability during precipitation and solidification. It turns out that we discover two more important results in the post onset regime after the instability sets in. These results emanate from a weakly nonlinear calculation which is done by going to second and third orders in the amount by which the control parameter is increased. The first of these results has to do with the correction to the front speed on account of morphological instability. We find that once the instability sets in, a solidification front always speeds up compared to what its base value would have been, i.e., it moves ahead of its predicted base value. This is in contrast with a precipitation front which demonstrates an unconditional “slow-down” upon becoming unstable.

The second important result of the nonlinear calculations has to do with the nature of the branching to the new non-planar solutions once the instability sets in. The book by Strogatz [25] gives an excellent description of bifurcations in several applied problems. Bifurcations are important scientifically as they provide essential information about the kind of transition from one steady state to another as some control parameter is varied. We discover that in solidification, the nature of the bifurcation depends on the dimensions of the container in which
the growth takes place. The branching may be a forward pitchfork, leading to cellular growth, or a backward pitchfork, leading to a dendritic growth. This is in contrast to the precipitation problem, where the onset of instability is ordinarily characterized by a dendritic growth on account of a backward pitchfork. However, precipitation is also capable of demonstrating a transcritical bifurcation. In fact, we discover that the nature of bifurcation in precipitation depends on the cross section of the growth container. We deduce a condition to decide whether a container of a given cross sectional shape will demonstrate a backward pitchfork or a transcritical bifurcation.

Finally, before moving on to explain the organization of this dissertation, we would like to emphasize that a thorough understanding of theoretical results mentioned above is extremely helpful in designing good experiments. As explained in the book by Montgomery [26], a successful design of experiments requires a good theoretical knowledge of all important factors. And it is our belief that the proposed theory should lead to a more rational design and interpretation of solidification experiments.

**Organization of the Research:** The remainder of this dissertation is dedicated to theoretical investigation of interfacial instability in precipitation and solidification via mathematical models and to explain the results using simple physical arguments. As mentioned, our primary goal is to understand the underlying causes and implications of such instabilities.

Chapter 2 delineates the physics of instability in precipitation. Being a one-phase problem, precipitation offers a simple way of understanding the concept of longitudinal diffusion, transverse diffusion, and surface tension etc. We also learn how the various factors compete with each other to result in an instability. The governing equations along with the relevant interface and boundary conditions are presented. This chapter also explains the theoretical concept of a
linear stability analysis which is used to predict whether or not a planar interface can remain planar in the face of small disturbances. This chapter forms the framework for understanding the physics of instability in the more complicated problem of solidification.

Chapter 3 focuses on the interfacial instability during solidification. The first half of this chapter is devoted to understanding the physics of the instability and in deriving the formula for the growth rate of a disturbance. This is followed by an analysis that predicts the wavelength of the cellular pattern observed at the onset of instability. We show how one can obtain interesting growth curves having up to three critical points.

Chapter 4 addresses the question whether the domain transport dynamics is important compared to the transport dynamics at a solid-liquid interface. A simple precipitation model is studied to investigate whether the time derivatives in the domain equations are important relative to the time derivative of the interface position introduced via interfacial mass balance.

Chapter 5 presents a weak nonlinear calculation in the problem of precipitation, where the goal is to examine what happens beyond the onset of the instability. We first work out the problem in a rectangular geometry and then in a circular geometry. In each case, we first find the critical value of the control parameter using the linear stability analysis. This is followed by a weak nonlinear calculation where we look for steady solutions just beyond this critical point by going to second and third orders in the amount by which the control parameter is increased. Our main goal is to find out the nature of the bifurcation to the new non-planar solution. Through our calculations, we also wish to discover whether the front speeds up or slow down compared to its base value once the instability sets in. Toward the end of the chapter, we deduce a condition that determines whether a cross section of an arbitrary shape will lead to a pitchfork or a transcritical bifurcation.
Chapter 6 deals with the weak nonlinear calculation in the problem of solidification. The goal is to understand the early stages of the growth of surface roughness in solidification. Again, as in Chapter 5, we try to answer two key questions: Does a solidification front speed up or slow down compared to its predicted base value once the instability sets in? Is the branching to the new non-planar solution a forward or a backward pitchfork?

Chapter 7 presents a general conclusion along with a scope for future studies.
CHAPTER 2
PRECIPITATION: LINEAR THEORY

Introduction

In this chapter, our goal is to investigate the causes of instability during precipitation from a supersaturated solution and to quantify the growth and neutral curves by using a linear perturbation theory. First, picture arguments are given to establish the role of longitudinal diffusion, transverse diffusion, and surface tension with regard to the observed instability. To quantify our arguments, we then give the nonlinear model equations which are written in a moving frame. These equations are then scaled and linearized around a base state. This base state solution is slightly perturbed to obtain the formula for $\sigma$, the growth constant. The playoff between the various terms in this formula is then explained in terms of the effect of diffusion (in two directions), surface tension, and surface speed. Based on this, the shapes of the growth curve and the neutral curve are then explained. The chapter is concluded by predicting the number of crests observed in a precipitation experiment when the supersaturation in the solution is slowly increased to its critical value. It is found that at most one crest and one trough will be seen at the onset of instability.

We now move on to discuss the physics of the instability observed when precipitation occurs from a supersaturated solution.

The Cause of the Instability

Consider the schematic shown in Figure 2.1 which shows a moving precipitation front. Let a solid of density $c_s$ lie to the left of a supersaturated solution. The two phases are divided by a plane interface that advances to the right as the reservoir at $z = L$ supplies the solute at a fixed concentration $c_L$, which is higher than $c_{Sat}$, the saturation concentration at a planar interface.
Let \( L_c \) be the control variable. Increasing it increases the speed of the front. At some value of \( L_c \) the plane front loses its stability and becomes non-planar. The explanation for the instability can be understood from Figure 2.2. Consider a perturbation of the planar front to the right, a crest where the local speed runs above the speed of the planar front. To sustain this increased speed, the crest must be supplied more solute from the reservoir, which is reinforced.
by the increased concentration gradient due to the perturbation. Similarly, a displacement in the form of a slower moving trough is reinforced by a decreased concentration gradient at its tip. Longitudinal diffusion in the liquid is therefore destabilizing; it acts more strongly the faster the front is moving and the steeper the solute gradient feeding the growth. But it does not depend on the wavelength of the disturbance, i.e., it is $k$-independent.

Operating against this is the effect of surface curvature which plays a stabilizing role. This is shown in Figure 2.3. At a crest, $c_{EQ}$, the equilibrium concentration, is higher than $c_{sat}$ [3]. By reducing the local concentration gradient at a crest, surface tension weakens the instability caused by longitudinal diffusion. For short wavelengths, the stabilization is strong; for large wavelengths, it is weak; hence surface tension is a $k$-dependent stabilizing effect.

Figure 2.3 – A picture argument for the effect of surface curvature in precipitation

These two effects would then predict instability at low values of $k$, and stability for high values of $k$. But by themselves they cannot explain an increase in instability as $k$ increases from zero. There is, however, another effect, and it has to do with transverse diffusion in the liquid. Setting surface tension aside, the displacement of the surface strengthens the solute gradient at a crest, weakening it at a trough (cf., Figure 2.4). This induces transverse solute gradients, carrying
solute away from troughs toward crests. This is destabilizing. It tends to build crests up and the effect is stronger the higher the $k$, i.e., the closer together the crests and troughs. Also, this effect is stronger the faster the front is moving. The effect of surface tension on transverse diffusion is again stabilizing. Its effect on the surface concentration works against transverse diffusion just as it works against longitudinal diffusion. By reducing the local concentration gradient at a crest while increasing it at a trough (cf., Figure 2.3), surface tension weakens the solute gradients in the transverse direction, hence weakening the instability caused by transverse diffusion.

![Figure 2.4 – A picture argument for the effect of transverse diffusion in precipitation](image.png)

Now in precipitation the solid phase plays no role. Consequently, the effects that will concern us are three in number: the destabilizing effect of longitudinal and transverse diffusion in the liquid and the stabilizing effect of surface tension which offsets each of these. To make these qualitative ideas quantitative, we turn to a model.

**The Nonlinear Equations**

The sketch given in Figure 2.1 fixes the basic ideas and presents some formulas. The solid phase is passive and the solute concentration in the solid is $c_s$ everywhere and for all time. Of interest are the equation of solute diffusion in the liquid phase, and the interface equations for the
local motion of the front. The liquid phase depth is maintained constant and the problem is taken
to be two-dimensional, $x$ and $z$ being parallel and perpendicular, respectively, to the base
surface. The equations will be written in a frame moving with a constant velocity $\vec{U} = U \vec{k}$, where $U$ is the base state speed of the precipitation front as seen by a laboratory observer.

Then, in the liquid phase, the equation for the solute concentration is given by

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

(2.1)

for $Z < z < L$ and $0 < x < W$, where $L$ is the depth of the liquid phase and $W$ is the width of the precipitation cell; $D$ denotes the diffusivity of the solute in the liquid phase. The solute concentration must meet two requirements along the solid-solution interface, viz., along $z = Z(x,t)$. First, phase equilibrium requires, after accounting for the correction due to surface curvature

$$c = c_{sat} - \mathcal{A} \gamma [2H]$$

(2.2)

where $\mathcal{A}$ denotes $\frac{1}{RT} \frac{c_{sat}}{c_s}$, and where $\gamma$ denotes the surface tension. Second, the solute surplus or deficit induced by the motion of the interface must be made good by solute diffusion into or out of the solution, i.e.,

$$[c_s - c]\left[ U \vec{k} \cdot \vec{n} + u \right] = D \vec{n} \cdot \nabla c$$

(2.3)

where $u$ denotes the local surface speed of the perturbed front. The far field condition is given by

$$c(z = L) = c_L$$

(2.4)

Finally we impose side wall conditions such that both $\partial c/\partial x$ and $\partial Z/\partial x$ vanish at $x = 0$ and at
\( x = W \). The formulas for the surface normal, \( \vec{n} \), the surface speed, \( u \), and the mean curvature \( 2H \), are given in Appendix A.

**Scaled Nonlinear Equations**

The nonlinear equations will now be presented in dimensionless form. All lengths are scaled by \( L \) and all speeds are scaled by \( D/L \). Time is scaled by \( L^2/D \). Concentration is measured from a reference point corresponding to \( c_{\text{SAT}} \), and is scaled by \( c_s - c_{\text{SAT}} \), i.e.,

\[
c_{\text{scaled}} = \frac{c - c_{\text{SAT}}}{c_s - c_{\text{SAT}}}.
\]

All variables used hereon are scaled variables.

Then, in the liquid phase, the equation for the scaled solute concentration is given by

\[
\frac{\partial c}{\partial t} = \nabla^2 c + U \frac{\partial c}{\partial z}
\]

for \( Z < z < 1 \) and \( 0 < x < W \). The equations along the interface, viz., along \( z = Z(x,t) \) now become

\[
c = -A [2H]
\]

and

\[
\vec{n} \cdot \nabla c = [1 - c] \left[ U \vec{k} \cdot \vec{n} + u \right]
\]

where \( A \), a dimensionless parameter introduced by our scaling, denotes \( \frac{\gamma}{LRT} \frac{1}{c_s} \frac{1}{c_s - c_{\text{SAT}}} \).

The far field condition is given by

\[
c(z = 1) = c_L
\]

Side wall conditions are Neumann, i.e.,

\[
\frac{\partial c}{\partial x} (x = 0,W) = \frac{\partial Z}{\partial x} (x = 0,W) = 0.
\]
Notice that these model equations are non-linear as the position of the interface depends upon the concentration gradient there, and this gradient, in turn, depends upon the position and morphology of the interface. This is clearly seen in Eq. (2.6) which couples the interface concentration \( c \) to the interface position \( Z(x,t) \) via the surface curvature \( 2H \). This coupling leads to non-linearity, which forms the heart of the problem. It is the reason for the interface to depart from its flat base state, trying to become unstable. Now to investigate the instability during precipitation, we will study the effect of small disturbances on a planar front which is moving with a constant speed \( U \). To do so, we now turn to the process of linearization of the equations.

**Theoretical Approach and the Linearization of Model Equations**

A system in steady state is said to be stable if all disturbances imposed on it decay with time; it is called unstable if any disturbance grows. Such an instability arises when a steady state system is driven away from its steady state upon imposing small perturbations. Very often, an instability arises in growth problems when a control variable exceeds its critical value. For instance, in the problem of precipitation, the supersaturation in the liquid phase may be taken to be the control variable, which, when exceeded beyond a critical value, will lead to instability.

To study instability in precipitation, our plan is to evaluate the time dependence of the amplitude of a sinusoidal perturbation of infinitesimal initial amplitude introduced on the planar interface. For this purpose, it is sufficient to analyze a linearized model where the linearization is done over a base state. The idea behind linearizing the equations is this: Once all equations are linearized, the evolution of a sinusoidal perturbation is simply a superposition of the evolution of its Fourier components. The interface is unstable if any Fourier component of the sinusoidal wave grows; it is stable if all decay with time.
Now a base state can often be guessed for most problems; for precipitation, it is a planar front which is moving with a constant speed. Denoting the base state concentration by $c_0$, the domain concentration $c$ can be expanded as

$$c = c_0 + \varepsilon \left[ c_1 + z_1 \frac{\partial c_0}{\partial z} \right] + ..$$

(2.9)

where $\varepsilon$ denotes the amplitude of the perturbation; $z_1$ represents the first order mapping from the current domain to the reference domain. The first order mapping at the interface is denoted $Z_1$, and it needs to be determined as a part of the solution. Because the current domain is unknown (it is a part of the solution), it becomes imperative that we solve the problem on a known reference domain, i.e., one that has all planar boundaries. The meaning of the mappings $z_1$ and $Z_1$, and of the correction $c_1$ is explained in Appendix B.1. The first order variables can be further expanded using a normal mode expansion [9] as

$$c_1 = \hat{c}_1 \cos(kx)e^{\sigma t} \quad \text{and} \quad Z_1 = \hat{Z}_1 \cos(kx)e^{\sigma t}$$

(2.10)

where $k$ is the wave number of the disturbance and $\sigma$ denotes the growth (or decay) constant, also known as the inverse time constant. It is an output variable, and a positive value of $\sigma$ for a given $k$ means that the disturbance grows, leading to instability.

**The Solutions to the Base and the Perturbation Problems**

The base state is one in which the precipitation front is a plane at rest in the moving frame. The base state variables are denoted by the subscript 0 and they satisfy

$$\frac{d^2 c_0}{dz^2} + U \frac{dc_0}{dz} = 0$$

(2.11)

in the liquid phase, $0 < z < 1$. The equations at the planar interface, $z = 0$ are given by

$$c_0 = 0$$

(2.12)
The far field condition is
\[ c_0(z = 1) = c_L \]  

Then a solution to equations (2.11-2.14) is given by
\[ c_0(z) = 1 - e^{-LU} \]  

where \( U \) is given by
\[ U = -\ln[1-c_L] \]  

Besides the physical properties, the input variables in the base state are \( L \) and \( c_L \), and the output is the front speed, \( U \). To determine if this base solution is stable, we impose a small displacement on the surface at fixed values of \( c_L \) and \( U \), and determine its growth rate, \( \sigma \), as a function of its wave number \( k \), whence \( k \) is an input to the perturbation problem. We solve the perturbation problem on the base domain by expanding the surface shape and the solute concentration at the surface in the form
\[ Z = Z_0 + \varepsilon Z_1 = Z_0 + \varepsilon \hat{Z}_1 \cos(kx)e^{\sigma t} \]  

and
\[ c = c_0 + \varepsilon \left[ c_1 + Z_1 \frac{dc_0}{dz} \right] = c_0 + \varepsilon \left[ \hat{c}_1 + \hat{Z}_1 \frac{dc_0}{dz} \right] \cos(kx)e^{\sigma t} \]

where the side wall conditions determine the admissible values of \( k \). The subscript 1 denotes a perturbation variable. Then using the expansions given above, the perturbation equations for \( \hat{c}_1 \) and \( \hat{Z}_1 \) are given by
\[\sigma \hat{c}_i = \left[ \frac{d^2}{dz^2} - k^2 \right] \hat{c}_i + U \frac{d \hat{c}_i}{dz}\]  \hspace{1cm} (2.19)

in the solution, \(0 < z < 1\). The equations that need to be satisfied across the interface, \(z = 0\), are

\[\left[ \hat{c}_i + Z_1 \frac{dc_0}{dz} \right] = \left[ \mathcal{A} k^2 \right] \hat{Z}_1 \]  \hspace{1cm} (2.20)

and

\[\sigma \hat{Z}_1 = \left[ \frac{d \hat{c}_i}{dz} + U \hat{c}_i \right]\]  \hspace{1cm} (2.21)

The far-field equation is

\[\hat{c}_i(z = 1) = 0\]  \hspace{1cm} (2.22)

A solution to the domain equation satisfying Eqs. (2.20) and (2.22) is given by

\[\hat{c}_i = \left[ \mathcal{A} k^2 - \frac{dc_0}{dz}(z = 0) \right] \frac{1}{\left[ e^{m_+ - m_-} - e^{-m_+ - m_-} \right]} \left[ e^{m_+ z} - e^{m_+ - m_-} e^{m_- z} \right] \hat{Z}_1\]  \hspace{1cm} (2.23)

where \(2m_\pm = -U \pm \sqrt{U^2 + 4\left[ k^2 + \sigma \right]}\). Finally, using the mass balance across the interface, Eq. (2.21), there obtains

\[\sigma = \left[ \mathcal{A} k^2 - \frac{dc_0}{dz} \right] N + \mathcal{A} k^2 U + \frac{d^2 c_0}{dz^2}\]  \hspace{1cm} (2.24)

\[\text{I I I I V}\]

where \(N = \left[ \frac{m_+ - m_- e^{(m_+ - m_-)}}{1 - e^{(m_+ - m_-)}} \right]\).

Eq. (2.24) gives \(\sigma\) implicitly in terms of \(k^2\) and the derivatives of the base concentration at the reference surface, viz., at \(z = 0\). A graph of \(\sigma\) vs. \(k^2\) can be drawn from this equation,
but the equation is not explicit in $\sigma$. Now $\sigma$ appears in the problem in two ways. It appears in
the domain equation where it has to do with solute depletion in the liquid as the front advances.
It also appears in the surface solute balance where it has to do with the local speed of a crest or a
trough. We will drop $\sigma$ on the domain (cf., Chapter 4) on the grounds that the solute depleted by
the growth of a slowly moving front is easily supplied by diffusion. Then the dominant growth
rate is given by Eq. (2.24), where $N$ remains as defined, but $m_\pm$ are now given by

$$2m_\pm = -U \pm \sqrt{U^2 + 4k^2},$$

and where $m_+$ is always positive and $m_-$ is always negative.

Consequently $N$ is always negative, and terms I and IV in Eq. (2.24) are negative, hence
stabilizing, while terms II and III are positive, hence destabilizing.

Other than the wave number of the displacement, the growth rate depends only on the base
solute gradient, $\frac{dc_0}{dz}(z = 0) = U$, and its correction $\frac{d^2c_0}{dz^2}(z = 0) = -U^2$. The physical factors that
each term takes into account are these: Term II, the essential destabilizing term, combines the
two effects of the longitudinal solute gradient. The primary effect is that a displacement
strengthens the gradient at a crest, and the secondary effect is that a strengthened gradient at a
crest and a weakened gradient at a trough induce transverse solute diffusion from a trough to a
crest; both destabilizing. Term IV which is stabilizing, is in fact a correction to term II,
weakening its destabilizing effect. It corrects for the fact that the solute gradient is not uniform,
being stronger at the base surface than in the nearby solution (cf., Figure 2.5). Hence a crest
projected into the supersaturated solution is fed by a less steep gradient than $\frac{dc_0}{dz}(z = 0)$.

Term I, the essential stabilizing term, combines two of the three effects of surface tension,
cutting into the destabilizing effect of both longitudinal diffusion and transverse diffusion. Term
III, the remaining effect of surface tension is destabilizing. It accounts for the fact that at a crest,
the amount of solute that must be supplied to move the crest is lessened as the solute concentration rises at the surface (cf., Figure 2.6). Such a term will not be seen in solidification (cf., Chapter 3) unless the latent heat is perturbed.

Figure 2.5 – A cartoon illustrating the non-uniform concentration gradient in the supersaturated solution in precipitation

Figure 2.6 – A picture argument illustrating the destabilizing effect of surface tension in precipitation

A significant algebraic simplification can be obtained by observing that $c_s$, the density of the solid, is usually very high (cf., Table 2.1) compared to $[c_L - c_{STR}]$, the supersaturation. The scaled value of $c_L$ therefore is ordinarily small ($c_L \approx 0.1$), and consequently $U$ must also be
small \((U \approx 0.1)\). The base state concentration profile in the liquid phase must then be nearly linear and a low \(U\) result may be obtained by dropping \(U\) from the domain equation. The base speed and the \(\sigma\)-formula are then given by

\[ U = c_L \quad \text{and} \quad \sigma = -\left[\mathcal{A}k^2 - U\right] \left[\frac{k}{\tanh k}\right] + \mathcal{A}k^2U \]  

(2.25)

and at the small values of \(\mathcal{A}\) ordinarily encountered, viz., \(\mathcal{A} \approx 10^{-9}\), the following formulas are useful in sketching a graph of \(\sigma\) vs. \(k^2\):

\[ \sigma(k^2 = 0) = U \]  

(2.26)

\[ \frac{d\sigma}{dk^2}(k^2 = 0) = \frac{1}{3}U \]  

(2.27)

\[ \sigma(k^2 \text{ large but not too large}) = kU \]  

(2.28)

and

\[ \sigma(k^2 \text{ very large}) = -A_k^3 \]  

(2.29)

Table 2.1 – Thermo-physical properties of CuSO4.5H2O

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturation concentration, (c_{sat})</td>
<td>243 (kg/m³)</td>
</tr>
<tr>
<td>Density of solid, (c_s)</td>
<td>2284 (kg/m³)</td>
</tr>
<tr>
<td>Diffusivity, (D)</td>
<td>10⁻⁹ (m²/s)</td>
</tr>
<tr>
<td>Gas constant, (R)</td>
<td>8.314 (J/mol K)</td>
</tr>
<tr>
<td>Surface Tension, (\gamma)</td>
<td>8.94 x 10⁻³ (N/m)</td>
</tr>
</tbody>
</table>

**The \(\sigma\) vs. \(k^2\) Curves**

A typical growth curve is shown in Figure 2.7. It starts positive. Then \(\sigma\) increases as \(k^2\) increases and the curve passes through a maximum before decreasing and passing through zero.

The value of \(\sigma\) at \(k^2 = 0\) is positive, and this is due entirely to longitudinal diffusion (cf., Figure 2.2). In fact, one might have predicted intuitively that the value of \(\sigma\) at \(k^2 = 0\) could
never have been negative for the precipitation model presented here. Now at \( k^2 = 0 \), only
longitudinal diffusion is important. And since precipitation has only one active phase, and
longitudinal diffusion is destabilizing there, we do not have any reason to expect stability at
\( k^2 = 0 \). Notice that the analog will not hold in the solidification problem (cf., Chapter 3) where
the latent heat can be rejected through the solid as well as via the subcooled liquid.

The increase in \( \sigma \) as \( k^2 \) increases is due to the fact that the longitudinal solute gradient
induces transverse diffusion (cf., Figure 2.4) from a trough to the adjacent crest. This is \( k \)-
dependent, and \( \sigma \) increases linearly in \( k \). Eventually surface tension comes into play, driving \( \sigma \)
downward as \( k^3 \). The separation of the effects of transverse diffusion and surface tension allows
us to see first an increase in \( \sigma \) followed by a decrease. This is due to the small value of \( A \),
which delays the effect of surface tension. Hence a range of \( k^2 \) exists upward from zero where
\( \sigma \) increases due to transverse diffusion. And this explains the existence of a greatest growth rate,
\( \sigma_{\text{max}} \), at a value of \( k^2 \), denoted by \( k^2_{\text{max}} \).

\[
\text{Figure 2.7 - Typical growth curve in precipitation}
\]

Now the effect of surface tension cannot become important until \( k^2 \) becomes large.

Consequently, the value of the term \( \sqrt{U^2 + 4k^2} \), coming via \( m_e \), will be large at the point of
maximum growth rate, and $N$ may then be approximated as $m_-$. With this simplification it is easy to obtain

$$k^2_{\text{max}} = \frac{U}{3\mathcal{A}} \quad \text{and} \quad \sigma_{\text{max}} = \frac{2U^{3/2}}{3\sqrt{3}\sqrt{\mathcal{A}}}$$

whence for most cases of interest, $k^2_{\text{max}}$ is one-third the critical value of $k^2$, denoted $k^2_{\text{crit}}$, which is the value of $k^2$ at $\sigma = 0$.

Finally observe that in the model of precipitation presented here, we can have one and only one critical point. Again, this is because of the fact that the growth curve must start positive at zero wave number (due to longitudinal diffusion in the solution), rise initially as the wave number increases (due to transverse diffusion in the solution), and eventually fall down (due to surface tension), giving a critical point. Again notice that since the solidification problem (cf., Chapter 3) has two active phases through which the latent heat can be rejected, we have a possibility of seeing more than one critical point. But before going on to solidification, let us look at the neutral curves in precipitation.

**The Neutral Curves: $U$ vs. $k^2$ at $\sigma = 0$**

Turning our attention to the neutral curve, viz., the $U$ vs. $k^2$ curve at $\sigma = 0$, we have, from Eq. (2.24),

$$[\mathcal{A}k^2 - U][N + U] = 0$$

But $N$ is always less than $-U$ for all positive values of $k^2$, hence the root $N = -U$ can be ruled out. There obtains $U = \mathcal{A}k^2$ and the neutral curve is a straight line as shown in Figure 2.8. For a fixed $k^2$, the system is initially stable for small values of $U$, becoming unstable as $U$ increases.
The width of the precipitation cell plays an important role in determining the stability of a system. For a precipitation cell of scaled width $W$, the maximum admissible wavelength of a disturbance is $2W$, and the admissible values of the wave number are restricted to $k = n\pi/W$, $n = 1, 2, \ldots$; the case $n = 0$ is ruled out on the grounds that the volume of the supersaturated solution is held constant. One can then find the lowest possible value of $U$ for which $\sigma = 0$. It occurs for the lowest allowable value of $k^2$, viz., for $k^2 = \pi^2/W^2$. Therefore, in an experiment, we expect to see at most one crest when the front just becomes unstable. The critical $U$ is

$$U_{crit} = A \left[ \frac{\pi^2}{W^2} \right]$$

and the corresponding critical value of the control parameter $c_L$ is given by

$$c_{L,\text{cr}} = 1 - e^{-A \left[ \pi^2/W^2 \right]}$$

**Concluding Remarks**

What we have found in precipitation is this: the shape of the growth curve requires the effect of transverse diffusion for its explanation. The corresponding neutral curve is monotonically increasing, implying only one crest at critical. In other words, since the neutral curve in precipitation does not have a “dip”, it is not possible to observe a “cellular” pattern or
multiple cells in precipitation when the instability is approached by raising a control parameter and crossing its critical value.

Next let us try to get an idea as to when exactly does the instability set in when one creeps up on the control parameter. Using the thermo-physical properties given in Table 2.1, assuming the temperature to be $T = 300K$, and taking the depth of the liquid solution to be $L = 1cm$, the scales for concentration difference, velocity and time are: $c_s - c_{SAT} \approx 2041 \text{ kg/m}^3$, $D/L \approx 10^{-7}$ m/s and $L^2/D \approx 10^5$ s. The value of the surface tension group is $\mathcal{A} \approx 4.67 \times 10^{-9}$. Let us take the width of the precipitation cell to be $W = 1cm$. Then Eq. (2.32) predicts the scaled value of $U_{crit} = \mathcal{A}\left(\pi^2/W^2\right)$ to be around $4.6 \times 10^{-4}$. This corresponds to a scaled value of $c_{L, on} = 1 - e^{-\mathcal{A}(\pi^2/W^2)}$ to be $4.6 \times 10^{-4}$, i.e., $c_{scaled} = \frac{c - c_{SAT}}{c_s - c_{SAT}} = 4.6 \times 10^{-4}$. This means that unscaled $c_{L, on} = c_{SAT} + 4.6 \times 10^{-4} \times (2284-243) \text{ kg/m}^3 \approx c_{SAT}$. Because $c_{L, on}$ is very close to $c_{SAT}$, it is extremely hard to run reasonable experiments to study precipitation as the front will become unstable as soon as we tweak up $c_L$ even slightly above $c_{SAT}$. Notice that this is due to the small value of the surface tension group, $\mathcal{A}$. Because of reasons to be discussed later, the physical numbers for parameters like critical undercooling etc. in solidification turn out to be much more reasonable and interesting. Nevertheless precipitation was interesting in itself and presented us with the opportunity to understand concepts such as longitudinal diffusion, transverse diffusion and surface tension in a relatively easier one-phase set up.

Finally notice that because the precipitation model is “one-sided”, there are no domain length scales to adjust. One can only have a scaled capillary length. The reader’s attention is drawn to the fact that the results will change substantially for solidification (cf., Chapter 3) where the latent heat can be rejected through two phases. In solidification, we will have the ratio
of the liquid to solid phase depth as an important control, as also a capillary length, in addition to the control variables arising from the solid and liquid far-field temperatures. We will revisit precipitation when we discuss solidification and recall some of the results discussed here.
CHAPTER 3
SOLIDIFICATION: LINEAR THEORY

Introduction

The nature of instability during solidification of a pure substance is investigated in this chapter. The latent heat is assumed to be rejected through the subcooled liquid as well as through the solid phase. Consequently, unlike precipitation, solidification is a two-phase problem where the solid phase is not passive any more. We find that transverse diffusion, as well as longitudinal diffusion, have opposite effects in the two phases, and hence, compared to precipitation, we find a greater variety of growth curves in solidification.

As in Chapter 2, we start by giving picture arguments, where we explain the role of longitudinal diffusion, transverse diffusion, and surface tension with regard to the observed instability during solidification. An important difference from precipitation is that we now need to understand the effects of diffusion and surface tension in two phases. We give a simple model for pure solidification where we assume local equilibrium at the interface and isotropic interfacial properties; convection induced by density differences is neglected. Then we derive the $\sigma$-formula by using linear stability methods, and explain the various terms in the formula. Next we draw several $\sigma$ vs. $k^2$ curves, and our emphasis is on the importance of transverse diffusion in explaining the shapes of these curves.

The growth curves imply the shape of the neutral stability curve. This curve is useful in understanding what might be seen in a series of experiments as the control variable increases to, and just beyond its critical value. When heat is withdrawn only through the liquid, the neutral curves in solidification are as simple as those in precipitation. Upon withdrawing heat through the solid as well, neutral curves like those seen in the problem of heating a fluid from below [7] can be found as shown by Wollkind et al. [10]. And by adjusting the depths of the phases, we can
go beyond this and get something new, viz., critical points that are not due to surface tension. This means that interesting experiments can be run by controlling the transverse extent of the solid, thereby making the allowable values of the wavelength an input variable. We draw some conclusions along these lines toward the end of the chapter.

The central result is this: In the solidification of a pure material it is possible to obtain zero, one, two, or three critical points, at least one having nothing to do with the surface curvature. In the solidification of a dilute binary alloy [9] only zero or two can be found.

Before moving on to discuss the causes of instability in solidification, we would like to make a comment on the reason for considering the finite depths of the solid and the liquid phase. We have already mentioned that we do not account for convection. Now the wavelengths characteristic of convection are much longer than those of interest in solidification, in the absence of convection, dominated as they are by surface curvature, cf., [15]. Our plan is to show that in solidification of a pure material, there are critical wave numbers in the convection range and that these can be found in ordinary experiments if one knows where to look.

But if convection is ultimately to be of interest, bounded experiments are essential, hence we investigate solidification, by itself, in the case where the depths of the liquid and the solid phases are finite. There is an advantage in doing this. The theory of solidification is ordinarily presented for phases of infinite depth in terms of the gradients at the solid-melt interface, cf., [9]. These gradients can be controlled in two ways in experiments at finite depths, by depth of the phase and by the temperature at its edge. With this additional flexibility of control, critical points can be found at much longer wave lengths than those determined by surface curvature. It is these critical points that ought to couple strongly to convection.
Coriell et al. [27] study phases of finite depth in the solidification of a dilute binary alloy. Davis [15] explains how such experiments can be set up.

We now move on to discuss the various causes of instability during solidification from a subcooled melt. Whenever possible, we will try to point out similarities and differences from precipitation.

**The Cause of the Instability**

![Figure 3.1 – A moving solidification front](image)

Let a solid lie to the left of its subcooled melt. This is shown in Figure 3.1 where the two phases are divided by a planar interface that advances to the right as the liquid turns into solid, releasing its latent heat to both phases. Taking \( T_L \) to be the control variable, decreasing \( T_L \) increases the speed of the front, and for some value of \( T_L \), the planar front becomes unstable, acquiring a non-planar shape.
The effect of longitudinal diffusion is shown in Figure 3.2. A displacement of the surface in the form of a crest increases the liquid side temperature gradient at its tip, which reinforces the growth of the crest; hence longitudinal diffusion in the liquid acts to destabilize the surface, just as it did in precipitation. However, the solid side temperature gradient is weakened at the crest, and this tends to flatten out the crest; hence longitudinal diffusion is stabilizing in the solid phase. A similar effect was obviously not seen in precipitation as the solid phase was passive there. Again, the strength of longitudinal diffusion does not depend on the wavelength of the disturbance; hence it is a $k$-independent effect. Setting aside the effect due to non-uniform temperature gradients, longitudinal diffusion by itself acts more strongly the faster the front moves.

Next let us consider the effect of surface tension on the stability of the front. It is stabilizing. This can be understood from the fact (cf., Figure 3.3) that the melt temperature depends on the shape of the solid-liquid interface; the surface curvature lowers the melt temperature at a crest while increasing it at a trough. Hence, surface tension weakens the instability caused by longitudinal diffusion in the liquid, while strengthening its stabilizing effect.
in the solid. Again, the stabilizing effect of surface tension is $k$-dependent, the stabilization being stronger for shorter wavelengths.

Figure 3.3 – A picture argument for the effect of surface curvature in solidification

Finally, let us look at the effect of transverse diffusion in the two phases. Setting surface tension aside, the effect of the displacement is as shown in Figure 3.4. On the melt side, the displacement of the surface strengthens the temperature gradient at a crest, weakening it at a trough; this induces transverse temperature gradients, carrying heat away from crests toward troughs. This tends to build crests up. Transverse diffusion is therefore destabilizing on the melt side of the surface. A similar argument can be made in the solid phase, where the displacement of the surface weakens the temperature gradient at a crest, strengthening it at a trough. This tends to flatten out the displacement by carrying heat away from troughs toward crests. Hence transverse diffusion is stabilizing in the solid phase. In both phases, the effect of transverse diffusion, whether it is stabilizing or destabilizing, is stronger the higher the $k$, i.e., the closer together the crests and troughs. Having learned the effect of transverse diffusion in the two phases in the absence of surface tension, here is how surface tension modifies the argument. By reducing the melt temperature at a crest, surface tension weakens the instability caused by
transverse diffusion in the liquid while strengthening its stabilizing effect in the solid. Hence surface tension is seen to be stabilizing yet again.

Figure 3.4 – A picture argument for the effect of transverse diffusion in solidification

What we have learned so far is this: On the liquid side, we have both longitudinal and transverse diffusion, and they are destabilizing just as they were in precipitation. And surface tension weakens both effects. On the solid side, we also have both longitudinal and transverse diffusion. It turns out that these are stabilizing, and surface tension strengthens their stabilizing effect. Thus in solidification, diffusion (in both directions) has opposite effects in the two phases, and we might therefore expect growth curves that are significantly different from those found in precipitation. What is more interesting is that the introduction of the solid phase gives us an extra parameter in the form of the ratio of the depths of the two phases, and this can be seen as an additional degree of control. It would appear, then, by fixing $T_s$ to establish a stable framework, that we can arrange to find diffusive critical states, independent of capillary effects by controlling the strength of liquid and solid transverse diffusion, which, in turn, are controlled by the depths of the two phases. To quantify this, we turn to a model.
The Nonlinear Equations

The sketch given in Figure 3.1 fixes the principal ideas and gives some useful formulas. The liquid and solid phase depths are maintained constant and all equations are written in a frame moving with a constant velocity \( \mathbf{U} = U \mathbf{k} \), where \( U \) is the base state speed of the solidification front. All variables introduced are moving-frame variables; the superscript * denotes a liquid phase variable.

Then, the temperature in the solid phase must satisfy

\[
\frac{\partial T}{\partial t} = \alpha \nabla^2 T + U \frac{\partial T}{\partial z}
\]

for \(-S < z < Z\) and \(0 < x < W\), where \( S \) is the depth of the solid phase and \( W \) is the width of the solidification cell and \( \alpha \) is the thermal diffusivity of the solid phase. In the liquid phase

\[
\frac{\partial T^*}{\partial t} = \alpha^* \nabla^2 T^* + U \frac{\partial T^*}{\partial z}
\]

must hold for \(Z < z < L\) and \(0 < x < W\) where \( \alpha^* \) is the thermal diffusivity of the liquid phase.

Two demands must be met along the solid-liquid interface, viz., along \( z = Z(x, t) \). First, phase equilibrium, taking into account the curvature due to the interface, requires

\[
T = T_M^* + \frac{\gamma T_M}{L_H} 2H = T^*
\]

where \( L_H \) is latent heat of solidification per unit volume of the solid, and where \( \gamma \) denotes the surface tension; \( T_M^* \) is the melt temperature at a flat surface. Second, the rate at which the latent heat is being released due to the motion of the solidification front must be the same as the rate at which heat is being conducted away from the interface, viz.,

\[
\lambda \mathbf{n} \cdot \nabla T - \lambda^* \mathbf{n} \cdot \nabla T^* = L_H \left[ U \mathbf{k} \cdot \mathbf{n} + u \right]
\]

(3.4)
where $\lambda$ and $\lambda^*$ denote the thermal conductivity of the solid and liquid phase respectively and $u$ denotes the local surface speed of the perturbed front. Far-field conditions are given by

$$T(z = -S) = T_s$$

(3.5)

and

$$T^*(z = L) = T_L$$

(3.6)

Finally we impose side wall conditions such that $\partial T/\partial x$, $\partial T^*/\partial x$ and $\partial Z/\partial x$ all vanish at $x = 0$ and at $x = W$.

Eq. (3.4) in solidification corresponds to Eq. (2.3) in precipitation (cf., Chapter 2); however, in Eq. (2.3), the term $[c_s - c]$ was perturbed and this introduced a term in the perturbation equations that will not be seen in solidification unless the latent heat is perturbed (cf., [3]).

**Scaled Nonlinear Equations**

To scale the modeling equations we introduce the length scale via $S$, the depth of the solid phase. All speeds are scaled by $\alpha / S$ while time is scaled by $S^2 / \alpha$. Temperature is measured below a reference point corresponding to $T_m$, and it is scaled by $\alpha L_H / \lambda$, i.e., $T_{scaled} = \frac{T_m - T}{\alpha L_H / \lambda}$.

Then, assuming both the thermal conductivity and the thermal diffusivity to be the same in the two phases, an approximation, that is sometimes reasonable, sometimes not, the scaled temperature in the solid phase must satisfy

$$\frac{\partial T}{\partial t} = \nabla^2 T + U \frac{\partial T}{\partial z}$$

(3.7)

for $-1 < z < Z$ and $0 < x < W$, while in the liquid phase

$$\frac{\partial T^*}{\partial t} = \nabla^2 T^* + U \frac{\partial T^*}{\partial z}$$

(3.8)
must hold for $Z < z < L$ and $0 < x < W$. The equations along the interface, viz., along $z = Z(x, t)$ now become

$$T = -\mathcal{A}[2H] = T^* \quad \text{(3.9)}$$

and

$$n \nabla T - n \nabla T^* = \left[ U \mathbf{k} \cdot n + u \right] \quad \text{(3.10)}$$

where $\mathcal{A}$, a dimensionless parameter introduced by our scaling, denotes $\left[ -\frac{\gamma_0}{\alpha L_H S} \right] T_M$. Far-field conditions are given by

$$T(z = -1) = T_s \quad \text{(3.11)}$$

and

$$T^*(z = L) = T_L \quad \text{(3.12)}$$

Again, the equations of the model are non-linear as the interface temperature gradients and the position of the interface are coupled to each other, which is clear from Eq. (3.9). Hence the problem is capable of admitting a non-trivial solution besides the trivial base solution. This is to say that the problem is capable of departing from its steady base state solution (a planar front at rest in the moving frame), leading to an unstable non-planar front. We take the scaled solid far-field temperature, the scaled liquid depth and $\mathcal{A}$ to be input variables while $U$ and the temperature fields as well as amplitudes of the temperature and interface deflection to be outputs that depend on these inputs.

To investigate this instability during solidification, we now turn to study the effect of small disturbances on the base state.
The Solutions to the Base and the Perturbation Problems

The base state variables satisfy

$$\frac{d^2T_0}{dz^2} + U \frac{dT_0}{dz} = 0$$  \hspace{1cm} (3.13)

in the solid phase, $-1 < z < 0$ and $0 < x < W$, while in the liquid phase

$$\frac{d^2T_0^*}{dz^2} + U \frac{dT_0^*}{dz} = 0$$  \hspace{1cm} (3.14)

must hold for $0 < z < L$ and $0 < x < W$. The equations at the planar interface, $z = 0$ are given by

$$T_0 = 0 = T_0^*$$  \hspace{1cm} (3.15)

and

$$\frac{dT_0}{dz} - \frac{dT_0^*}{dz} = -U$$  \hspace{1cm} (3.16)

The far-field conditions are given by

$$T_0(z = -1) = T_S$$  \hspace{1cm} (3.17)

and

$$T_0^*(z = L) = T_L$$  \hspace{1cm} (3.18)

A solution to equations (3.13-3.18) is given by

$$T_0(z) = \left[ \frac{T_S}{1 - e^U} \right] \left[ 1 - e^{-Uz} \right]$$  \hspace{1cm} (3.19)

and

$$T_0^*(z) = \left[ \frac{T_L}{1 - e^{-UL}} \right] \left[ 1 - e^{-ULz} \right]$$  \hspace{1cm} (3.20)

where $U$ is obtained from
\[
\frac{T_s}{e^U - 1} + \frac{T_l}{1 - e^{-UL}} = 1
\]  
(3.21)

This corresponds to a planar solidification front at rest in the moving frame.

To determine the growth rate of a small disturbance of wave number \( k \) imposed on the steady base solution, we expand the surface variables \( Z, T \) and \( T^* \) as

\[
Z = Z_0 + \varepsilon Z_1 = Z_0 + \varepsilon \hat{Z}_1 \cos(kx)e^{\sigma t}
\]  
(3.22)

\[
T = T_0 + \varepsilon \left[ T_1 + Z_1 \frac{dT_0}{dz} \right] = T_0 + \varepsilon \left[ \hat{T}_1 + \hat{Z}_1 \frac{dT_0}{dz} \right] \cos(kx)e^{\sigma t}
\]  
(3.23)

and

\[
T^* = T_0^* + \varepsilon \left[ T_1^* + Z_1 \frac{dT_0^*}{dz} \right] = T_0^* + \varepsilon \left[ \hat{T}_1^* + \hat{Z}_1 \frac{dT_0^*}{dz} \right] \cos(kx)e^{\sigma t}
\]  
(3.24)

where the side wall conditions determine the admissible values of \( k \). Then the perturbation equations for \( \hat{T}_1, \hat{T}_1^* \) and \( \hat{Z}_1 \) are given by

\[
\sigma \hat{T}_1 = \left[ \frac{d^2}{dz^2} - k^2 \right] \hat{T}_1 + U \frac{d\hat{T}_1}{dz}
\]  
(3.25)

in the solid phase, \(-1 < z < 0\) and \(0 < x < W\), while in the liquid phase

\[
\sigma \hat{T}_1^* = \left[ \frac{d^2}{dz^2} - k^2 \right] \hat{T}_1^* + U \frac{d\hat{T}_1^*}{dz}
\]  
(3.26)

must hold for \(0 < z < L\) and \(0 < x < W\). The equations at the planar interface, \( z = 0 \) are given by

\[
\left[ \hat{T}_1 + \hat{Z}_1 \frac{dT_0}{dz} \right] + \left[ -\mathcal{A}k^2 \right] \hat{Z}_1 = 0
\]  
(3.27)

\[
\left[ \hat{T}_1^* + \hat{Z}_1 \frac{dT_0^*}{dz} \right] + \left[ -\mathcal{A}k^2 \right] \hat{Z}_1 = 0
\]  
(3.28)

and
\[
\begin{align*}
\frac{dT_{1}^{\hat{}}}{dz} - \frac{dT_{1}^{*}}{dz} + \hat{Z}_{1}\left[\frac{d^{2}T_{0}}{dz^{2}} - \frac{d^{2}T_{0}^{*}}{dz^{2}}\right] &= -\sigma \hat{Z}_{1} \\
\text{(3.29)}
\end{align*}
\]

The far-field equations are

\[
\hat{T}_{1}(z = -1) = 0 \quad \text{(3.30)}
\]

and

\[
\hat{T}_{1}^{*}(z = L) = 0 \quad \text{(3.31)}
\]

A solution to the domain equations satisfying Eqs. (3.27, 3.28) and (3.30, 3.31) is given by

\[
\hat{T}_{1}(z) = \left[\frac{Ak^{2} - \frac{dT_{0}}{dz}(z = 0)}{1 - e^{m_{z}}e^{-m_{z}}\sigma}}\right]^{\hat{Z}_{1}}e^{m_{z}} - e^{m_{z}}\sigma}\]

\[
\text{(3.32)}
\]

and

\[
\hat{T}_{1}^{*}(z) = \left[\frac{Ak^{2} - \frac{dT_{0}^{*}}{dz}(z = 0)}{1 - e^{m_{z}}e^{-m_{z}}\sigma}}\right]^{\hat{Z}_{1}}e^{m_{z}} - e^{m_{z}}\sigma}\]

\[
\text{(3.33)}
\]

where

\[
2m_{z} = -U \pm \sqrt{U^{2} + 4\left(k^{2} + \sigma\right)}.
\]

Finally, using the energy balance across the interface, Eq. (3.29), there obtains

\[
\sigma = \left(-Ak^{2} + \frac{dT_{0}}{dz}\right)M - \left(-Ak^{2} + \frac{dT_{0}^{*}}{dz}\right)N - \left[\frac{d^{2}T_{0}}{dz^{2}} - \frac{d^{2}T_{0}^{*}}{dz^{2}}\right]
\]

\[
\text{(3.34)}
\]

\[
\begin{align*}
\text{I} & \quad \text{II} & \quad \text{III} & \quad \text{IV} & \quad \text{V} \\
\text{where } M &= \left[\frac{m_{z} - m_{e}[m_{z}]}{1 - e^{m_{z}}}\right] \text{ and } N = \left[\frac{m_{z} - m_{e}[m_{z}]}{1 - e^{m_{z}}}\right].
\end{align*}
\]
Eq. (3.34) gives $\sigma$ in terms of $k^2$ and the derivatives of the base temperatures at the reference surface, viz., at $z = 0$. Again $\sigma$’s on the domain are not important (cf., Chapter 4), and dropping them, we find that the dominant growth rate is given explicitly by Eq. (3.34), but $m_{\pm}$ are now given by $2m_{\pm} = -U \pm \sqrt{U^2 + 4k^2}$. Then $m_+$ is always positive and $m_-$ is always negative. Consequently, $M$ is always positive and $N$ is always negative, and the signs of the terms I, II, III and V are negative while term IV is positive.

Term IV in Eq. (3.34) accounts for the effect of longitudinal and transverse diffusion in the liquid, both destabilizing. Term II accounts for the stabilizing effect of longitudinal and transverse diffusion in the solid; a term like this did not appear in precipitation. Term V is stabilizing and it is like term IV in precipitation. It takes account of the fact that the base temperature gradient gets weakened in the liquid on moving away from the interface, while it gets strengthened on the solid side. The stabilizing effect of surface tension appears in terms I and III. Term III accounts for the fact that surface tension cuts into the destabilizing effect of longitudinal and transverse diffusion in the liquid. Term I accounts for the fact that surface tension enhances the stabilizing effect of longitudinal and transverse diffusion in the solid. Next, we move on to draw and explain the $\sigma$ vs. $k^2$ curves obtained from Eq. (3.34).

The $\sigma$ vs. $k^2$ Curves

Our aim is to explain how the various terms in Eq. (3.34) get together to produce a curve of $\sigma$ vs. $k^2$. The values of $T_s$, $T_L$, $\mathcal{A}$ and $L$ define a given curve. First we set the value of $T_s$, which for $T_s > 0$, imposes a basic stabilization on the curves. Then we set the value of $T_L > 0$, and hence of $U > 0$. The higher the value of $T_L$, the stronger the destabilization. The remaining two inputs are $\mathcal{A}$ and $L$. The first determines the value of $k^2$ where surface tension begins to
exert its effect; the second, the ratio of the depths of the phases, establishes the relative
importance of diffusion in the two phases.

Now most of the difficulty in seeing what Eq. (3.34) is trying to tell us stems from the
effect of $U$ on the domain in both the base and the perturbation problems. As a first step
therefore, we look at Eq. (3.34) in the low $U$ limit. A low $U$ result obtains by dropping the term
in $U$ from Eqs. (3.1) and (3.2), whence the base speed and the growth rate are given by

$$U = T_s + \frac{T_L}{L}$$  \hspace{1cm} (3.35)

and

$$\sigma = -T_s \left[ \frac{k}{\tanh k} \right] + T_s \left[ \frac{kL}{\tanh kL} \right] - \mathcal{A} k^3 \left[ \frac{1}{\tanh k} + \frac{1}{\tanh kL} \right]$$  \hspace{1cm} (3.36)

Notice that if $k^2$ is large enough that $\tanh k$ and $\tanh kL$ are nearly 1, we obtain

$$\sigma = k \left[ -T_s + \frac{T_L}{L^2} \right] - 2 \mathcal{A} k^3$$, and we see that surface tension becomes important only at values of

$k^2$ above $\frac{1}{2 \mathcal{A}} \left[ -T_s + \frac{T_L}{L} \right]$. Now the value of $\mathcal{A}$ is typically about $10^{-6}$. Hence, unless $-T_s + \frac{T_L}{L}$
is close to zero, there is a range of $k^2$ up to around 10000 on which the third term is not
important, and we can deduce the shape of the $\sigma$ vs. $k^2$ curve from the first two terms in Eq.
(3.36), which have to do only with diffusion in the two phases.

To illustrate the predictions of Eqs. (3.34) and (3.36) we base our calculations on the
physical properties of succinonitrile (SCN) [28] which are listed in Table 3.1. Taking the depth
of the solid to be $S = 1 \text{cm}$, the scales for temperature difference, velocity and time are

$$\alpha L / \lambda \approx 24 \text{K}, \quad \alpha / S \approx 10^{-5} \text{m/s} \quad \text{and} \quad S^2 / \alpha \approx 900 \text{ s}. \quad \text{The value of the surface tension group is}$$

$$\mathcal{A} \approx 0.26 \times 10^{-6}.$$
The $\sigma$ vs. $k^2$ curves are presented in Figures 3.5, 3.6, 3.7 and 3.8 as qualitatively correct sketches. Figures 3.5 and 3.6 illustrate the low $U$ formula, whether or not $U$ is low; Figures 3.7 and 3.8 include the effect of $U$ on the domain. The values of $T_s$, $T_L$, $L$ and $k^2$ given on the sketches were used in Eqs. (3.34) and (3.36) to determine the trends, and these input values are experimentally realizable. To indicate the importance of the depths of the two phases, curves are drawn for two values of $L$. In each figure, a value of $T_s$ is set, which gives stabilization at $T_L = 0$. Then a value of $L$ is set to strengthen or weaken the diffusion effects in the two phases. Curves are then drawn for increasing values of $T_L$, increasing the speed of the front.

To understand the curves in Figures 3.5 and 3.6, it is helpful to note the following formulas which hold for low $U$, and which can be obtained from Eq. (3.36):

$$\sigma(k^2 \text{ low}) = \left[-T_s + \frac{T_L}{L} \frac{1}{1 + \frac{k^3}{3}} \left(-T_s + \frac{T_L}{L} L\right)\right]$$

(3.37)

$$\sigma(k^2 \text{ intermediate}) = k \left[-T_s + \frac{T_L}{L}\right]$$

(3.38)

and

$$\sigma(k^2 \text{ high}) = -2AK^3$$

(3.39)

Table 3.1 – Thermo-physical properties of succinonitrile used in calculations

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point, $T_M$</td>
<td>331 (K)</td>
</tr>
<tr>
<td>Density of solid, $\rho$</td>
<td>1016 (kg/m$^3$)</td>
</tr>
<tr>
<td>Density of solid, $\rho^*$</td>
<td>988 (kg/m$^3$)</td>
</tr>
<tr>
<td>Thermal Conductivity of solid, $\lambda$</td>
<td>0.225 (W/m K)</td>
</tr>
<tr>
<td>Thermal Conductivity of liquid, $\lambda^*$</td>
<td>0.223 (W/m K)</td>
</tr>
<tr>
<td>Thermal Diffusivity of solid, $\alpha$</td>
<td>$1.16 \times 10^{-7}$ (m$^2$/s)</td>
</tr>
<tr>
<td>Thermal Diffusivity of liquid, $\alpha^*$</td>
<td>$1.12 \times 10^{-7}$ (m$^2$/s)</td>
</tr>
<tr>
<td>Surface Tension (solid-liquid), $\gamma$</td>
<td>$8.94 \times 10^{-3}$ (N/m)</td>
</tr>
<tr>
<td>Latent Heat of Fusion, $L_H$</td>
<td>$0.48 \times 10^8$ (J/m$^3$)</td>
</tr>
</tbody>
</table>
Figure 3.5 – $\sigma$ vs. $k^2$ for the low $U$ model with $S = 1 \text{cm}$, $L = \frac{1}{2} \text{cm}$, $T_s = 0.2$.
Figure 3.6 – $\sigma$ vs. $k^2$ for the low $U$ model with $S = 1\text{cm}$, $L = 2\text{cm}$, $T_s = 0.2$.
Figure 3.7 – $\sigma$ vs. $k^2$ for the complete model with $S = 1\, cm$, $L = \frac{1}{2}\, cm$, $T_s = 0.2$
Figure 3.8 – $\sigma$ vs. $k^2$ for the complete model with $S = 1 cm$, $L = 2 cm$, $T_s = 0.2$
These formulas show that for sufficiently low values of $T_L$, $\sigma$ is negative at $k^2 = 0$, $\frac{d\sigma}{dk^2}$ is negative at $k^2 = 0$, and $\sigma$ remains negative in the intermediate range of $k^2$. The effect of surface tension is always to make $\sigma$ more and more negative at larger and larger values of $k^2$. As $T_L$ increases, and before surface tension comes in, $\sigma$ at $k^2 = 0$, $\frac{d\sigma}{dk^2}$ at $k^2 = 0$, and $\sigma$ at intermediate values of $k^2$, all pass through zero and become positive, and they do this for physically interesting values of $T_L$. The order in which these variables turn positive depends on the value of $L$. Notice that in the low-$U$ formulas for low and intermediate ranges of $k^2$, we see $-T_s$, the solid side base temperature gradient, combined with $\frac{T_L}{L}$, the liquid side base temperature gradient in three ways. The liquid side temperature gradient is multiplied by $\frac{1}{L}$, $L$, and 1 in the three terms, whence the ratio of the depths of the two phases plays a very important role as far as the growth curves are concerned. For $L < 1$, cf., Figure 3.5, $\sigma$ at $k^2 = 0$ turns positive first, then $\sigma$ for intermediate values of $k^2$, and finally $\frac{d\sigma}{dk^2}$ at $k^2 = 0$. For $L > 1$, cf., Figure 3.6, the order gets reversed. These facts alone permit the $\sigma$ vs. $k^2$ curve to be sketched correctly.

The intermediate formula for $\sigma$, cf., Eq (3.38), holds once the value of $k^2$ is large enough that the wavelength of a displacement is smaller than the depths of the two phases, but not so small that surface curvature begins to exert its influence by affecting the melt temperature. In this range, the value of $\sigma$ is determined entirely by diffusion parallel to the surface, viz., by transverse diffusion in the two phases. The strength of the base gradients combines directly with the surface displacement to determine the strength of the trough-to-crest diffusion in the solid
phase, and the crest-to-trough diffusion in the liquid phase. This is illustrated in Figure 3.4. We also note that the value of $\sigma$ for intermediate values of $k^2$, is a multiple of $k$ or \[
\frac{1}{\text{wavelength of displacement}}.\] Hence $\sigma$ is positive and rising or negative and falling for these intermediate values of $k^2$, according as $-T_s + \frac{T_L}{L}$ is positive or negative. As $k$ continues to increase and the melt temperature begins to respond to the curvature, the rising curves turn downward causing a greatest growth rate to appear in the intermediate range of $k^2$. The falling curves simply fall faster once the effect of surface curvature takes over at larger values of $k^2$.

The low $k^2$ variation of $\sigma$ is also due to transverse diffusion, but the wavelength of the surface displacement is now greater than the depths of the phases. The near-surface region is therefore influenced by the sinks, and an explanation based on base gradients is no longer easy to present in picture form. Nonetheless, at low $U$, the second term in Eq. (3.37), and Eq. (3.38) indicate that stabilizing diffusion in the solid can dominate destabilizing diffusion in the liquid at low values of $k^2$, before their contributions are reversed at intermediate values of $k^2$, and this depends on $L$, i.e., on whether the depth of the liquid is greater or lesser than the depth of the solid. The curves show a least $\sigma$ at low $k^2$ if $L < 1$ (Figure 3.5) and a greatest $\sigma$ at low $k^2$ if $L > 1$ (Figure 3.6). To see the effect of the ratio of the phase depths, Figures 3.5 and 3.6 are drawn at values of $T_L$ chosen so that $\frac{T_L}{L}$, and therefore $-T_s + \frac{T_L}{L}$, is the same in both figures. Hence the intermediate and large $k^2$ regions of the curves in the two figures at the same values of $-T_s + \frac{T_L}{L}$ are the same. They differ only at small values of $k^2$, say up to $k^2 = 100$. The curves that fall for low values of $k^2$ in Figure 3.5 do not fall as strongly and may even rise in Figure
3.6. Again, this may not be easily explained from a picture argument, but the second term in Eq. (3.37) shows that at small values of \( k^2 \), larger \( L \)’s weigh diffusion in the liquid more strongly than diffusion in the solid.

Next we take \( U \) into account on the domain, and the corresponding curves are shown in Figures 3.7 and 3.8. Again, we draw two sets of curves: Figure 3.7 is drawn for \( L = \frac{1}{2} \), whereas Figure 3.8 shows the results for \( L = 2 \). All the values of \(-T_s + \frac{T_L}{L}\) in Figures 3.5 and 3.6 are in Figures 3.7 and 3.8, but a few more are included. Given \( T_s, L \) and \( T_L \), the effect of including \( U \) on the domain, if it is large enough, is to weaken the base gradient at the planar surface in the solid phase and to strengthen it in the liquid. This in turn weakens the effect of transverse diffusion in the solid, strengthening it in the liquid. This is enough to explain the majority of changes in going from Figures 3.5 and 3.6 to Figures 3.7 and 3.8. Hence, wherever \( \sigma \) is falling in Figures 3.5 and 3.6, in Figures 3.7 and 3.8 it is not falling as fast and may even rise, and wherever \( \sigma \) is rising in Figures 3.5 and 3.6, it is now rising more strongly in Figures 3.7 and 3.8. As a result, the intermediate region grows into both the small \( k^2 \) and high \( k^2 \) regions and this delays the effect of surface tension, pushing the values of \( k^2 \) at the greatest growth rate to the right. In the intermediate region, \( \sigma \) is given by \[ \frac{1}{2} U \sqrt{U^2 + 4k^2} \left[ 1 - \frac{2T_s}{e^{U^2/2} - 1} \right] - \frac{1}{2} U^2, \] whence \( \sigma \) rises or falls depending on whether \( T_L \) is greater or lower than \[ \frac{1}{2} \left[ 1 - \left[ 1 + 2T_s \right]^{+} \right], \] or what is the same, whether \( U \) is greater or lower than \( \ln \left( 1 + 2T_s \right) \).

For small values of \( L \), cf., Figure 3.7, we see that for small values of \( T_L \), \( \sigma \) is negative for all values of \( k^2 \). Upon increasing \( T_L \), say for \( 0.05 < T_L < 0.078 \), \( \sigma \) turns positive for small
values of $k^2$ and a critical point appears in the range $0 < k^2 < 25$. It is due to transverse diffusion in the solid phase and it is independent of surface tension. It is seen in Figure 3.5 as well, whence it is not due to $U$ on the domain. However, if $U$ on the domain is not accounted for (cf., Figure 3.5), no further critical points can be seen, the only one found, at first due to solid transverse diffusion, eventually is due to melting point lowering, the transition being due to the growing destabilizing effect of transverse diffusion in the liquid phase as $T_L$ increases. The effect of $U$ on the domain is to turn base states stabilized by solid phase transverse diffusion at low $k^2$ into unstable states at higher value of $k^2$, an effect that cannot be seen if $U$ on the domain is not taken into account. Hence, with $U$ on the domain, we find that further increasing $T_L$ leads to three critical points as liquid transverse diffusion is strengthened. In Figure 3.7, these occur for $0.078 < T_L < 0.085$, and the three critical points are due to solid transverse diffusion, liquid transverse diffusion and surface tension. This is not seen in Figure 3.5 due to the fact that the liquid transverse diffusion comes in too late, i.e., after $\sigma$ at $k^2 = 0$ has already become strongly positive. For yet higher values of $T_L$, the two critical points due to solid and liquid transverse diffusion disappear, giving only one critical point due to surface tension. What we have found is this: Upon increasing $T_L$ at small $L$, viz., $L = \frac{1}{2}$, the number of critical points is first zero, then one, then three, and finally, again one.

It turns out that getting three critical points is a feature typical of pure solidification when the depths of the two phases are taken to be finite, and when the control variable is defined explicitly. The Mullins and Sekerka [9] model for the solidification of a dilute binary alloy fails to give anything as interesting as has been found above; this is mainly because the depths of the two phases are taken to be of infinite extent in their analysis. Also there is no thermal
undercooling in the Mullins and Sekerka model. Similarly, the Wollkind and Notestine [10] model for pure solidification gives at most two critical points. The fact that we get three critical points has important implications from the point of view of an experiment where the liquid side undercooling is slowly increased up to its critical value, and this will be explained in detail toward the end of the chapter where we discuss the neutral curves.

Turning our attention to Figure 3.8 to see the effect of increasing $L$, many changes from Figure 3.7 are like those seen in going from Figure 3.5 to Figure 3.6. Most interesting, however, are the changes at low values of $k^2$. Increasing $L$ weakens transverse diffusion in the liquid which might be expected to enlarge the region of solid transverse induced critical points seen in Figure 3.7. But increasing $L$ also weakens longitudinal diffusion in the liquid causing the values of $\sigma$ at low values of $k^2$ to be negative, thereby eliminating the possibility of solid transverse diffusion induced critical points. Hence at large $L$, we find no critical points for small values of $T_L$, then upon increasing $T_L$ we find two critical points, the first of these due to liquid transverse diffusion, followed by a second critical point due to melting point lowering. So at $L = 2$ there are no critical points at low values of $T_L$, two at higher values of $T_L$. An important effect of increasing $L$ is this: at low $L$, there are critical points at small values of $T_L$, while on increasing $L$, the value of $T_L$ at which critical points are first seen increases. If $T_s$ were lower, the curves at $L = 2$ might be more like those at $L = \frac{1}{2}$, but then increasing $L$ above $2$ ought to restore the curves at $L = 2$ at the higher values of $T_s$.

Next, we move on to understand the neutral curves in solidification, which are derived from growth curves, though they are much more convenient while trying to understand what
goes on in an experiment where the undercooling in the melt is slowly crept up to its critical value.

The Neutral Curves: $U$ vs. $k^2$ at $\sigma = 0$

In neutral curves, the speed of the front $U$ is plotted against $k^2$ at $\sigma = 0$. Each set of $\sigma$ vs. $k^2$ curves at a given $T_s$ and $L$ leads to a $U$ vs. $k^2$ curve. For example, Figure 3.7 leads to Figure 3.9, and Figure 3.8 leads to Figure 3.10. Again, no scale is given on the ordinate and the reader’s attention is drawn only to the shapes of the curves. As long as $T_s$ is not zero, all possible neutral curves look like Figure 3.9 or 3.10. The first thing to notice is this: no matter the value of $T_s > 0$ and $L$, once $k^2$ is large enough, $U$ is a decreasing then increasing function of $k^2$, i.e., the curves all have a dip. This is neither true in precipitation nor in solidification at $T_s = 0$, where the neutral curve is a straight line as shown in Figure 2.8 of Chapter 2.

The curve in Figure 3.10, at a high value of $L$, shows only the dip, and its shape is like the neutral curve obtained in the problem of heating a fluid from below [7]. But here, the rising side has a very gradual slope due to the small value of $A$, and this leads to a very flat minimum.

The dip is not new; it was seen by Wollkind et al. [10] but it was not explained. Two things are required for a dip: First, $\sigma$ should be negative at small values of $k^2$. In Figure 3.8, $\sigma$ is negative at $k^2 = 0$, because large values of $L$ weaken longitudinal diffusion in the liquid; in Figure 3.7, solid transverse diffusion can cause positive $\sigma$’s at $k^2 = 0$ to become negative for small values of $k^2$. Second, transverse diffusion in the liquid should cause $\sigma$ to increase and become positive, before surface tension drives it back to zero. Hence, the falling branch of the dip is due to liquid transverse diffusion while the rising branch is due to surface tension.
Figure 3.9 – An unusual neutral curve in solidification

Figure 3.10 – Typical neutral curve in solidification

Figure 3.9, at small $L$, shows something new; it appears at small values of $k^2$ and it is due to transverse diffusion in the solid. The curve shows a sharply rising branch feeding into the falling branch of the dip. At small $L$, longitudinal diffusion in the liquid leads to positive values of $\sigma$ at $k^2 = 0$. Solid transverse diffusion then drives $\sigma$ negative, providing a basis for the dip.
In the course of doing this, another critical point is produced. This is seen in Figure 3.9 as the initially rising branch. The reader’s attention is drawn to the fact that a neutral curve like the one shown in Figure 3.9 cannot be obtained if \( U \) on the domain is not accounted for. In fact, one can prove that if \( U \) is dropped from the domain equations, then one can get zero, one or at most two critical points, but never three. Figure 6.5 in Chapter 6 shows this.

Notice that a neutral curve like the one seen in Figure 3.9 is special to solidification.

Nothing like it is observed in the closely related diffusion-controlled problems:

- precipitation, a one phase-one surface problem
- electrodeposition, a one phase-two surface problem
- viscous fingering, a two phase-one surface problem

The setup in viscous fingering is most like that in solidification, but solidification presents us with an extra degree of freedom. In solidification, unlike these other problems, we have three \( k \)-dependent effects determining the \( \sigma \) vs. \( k^2 \) curves. Also, solidification takes place at a thermodynamically specified temperature, giving us the option of setting the control temperature above or below the phase change value.

The reader is referred to Cross and Hohenberg [8] who review pattern formation at a great length in a variety of problems, never finding neutral curves like the new one given in Figure 3.9.

It is clear by now that the value of \( L \) is important. The transition between the two types of curves shown in Figures 3.9 and 3.10 might seem to be at \( L = 1 \). And that would be true if \( U \) on the domain is not accounted for. But with \( U \) on the domain, it is only roughly true. It depends on \( T_s \) and \( A \), and for \( T_s = 0.2 \), it is around \( L = 0.85 \) for succinonitrile.

The neutral curves can be used to answer the question: What does one expect to see in an experiment? For example, how many crests are seen when a plane front loses its stability? In a sequence of experiments, let the values of \( A \), \( S \), \( L \) and \( T_s \) be set. Then \( W \) must be set and its
role is to determine the admissible values of the wave number as \( k = n\pi/W \), \( n = 1, 2, \ldots \). Hence not all points on the neutral curve are of interest. The value of \( T_n \), and therefore the value of \( U \), is then increased from one experiment to another until a critical point is reached, i.e., a point where a line of constant \( U \) first crosses the neutral curve at an admissible value of \( k \). Our aim is to predict the effect of \( W \) on the number of crests appearing at a critical point.

Now Figures 3.9 and 3.10 both show a dip and this dip implies that the critical value of \( U \) need not correspond to the least allowable value of \( k^2 \). In fact, \( n \) might be any of the numbers: 1, 2, 3, \ldots, and hence multiple crests might be seen. This is not true of precipitation, where we found that one can get at most one crest at critical.

A neutral curve like the one shown in Figure 3.10 can be obtained for \( S = 1 \text{cm} \), \( L = 2 \text{cm} \), \( T_s = 326.2 \text{K} \) (4.8 K solid cooling). The value of \( k^2 \) at the dip would then be around \( 1.5 \times 10^7 \text{m}^{-2} \). The critical wave number will depend on the value of \( W \). For \( W = 0.08 \text{cm} \), the critical value of \( k^2 \) occurs near \( k_{dip}^2 \), viz., \( k_{crit}^2 = 1.54 \times 10^7 \text{m}^{-2} \). It corresponds to \( n = 1 \), whence only one crest will be seen at critical, and this is true for all smaller values of \( W \). The corresponding critical interface speed is \( 3.8 \mu \text{m/s} \), and the critical undercooling is 5.9 K. For a larger width, more crests will be seen at critical. For example, for \( W = 0.5 \text{cm} \), the critical value of \( k^2 \) corresponds to \( n = 6 \). As \( W \) increases further, we would expect to see even more crests.

A neutral curve like the one in Figure 3.9 can be obtained for input values: \( S = 1 \text{cm} \), \( L = 0.5 \text{cm} \), \( T_s = 326.2 \text{K} \) (4.8 K solid cooling). Let us again start with a small value of \( W \) and see what happens as \( W \) is increased. For \( W = 0.08 \text{cm} \), the critical value of \( k^2 \) corresponds to \( n = 1 \) giving one crest at critical. For a higher value of \( W \), viz., for \( W = 0.5 \text{cm} \), the critical \( k^2 \) corresponds to multiple crests, viz., \( n = 6 \). Here too, increasing the width further will give more
crests until $W$ is chosen large enough that the first allowable value of $k^2$, viz., $\frac{\pi^2}{W^2}$ corresponds to a point on the sharply increasing part of the neutral curve which is below the dip. For example, for $W = 2 \text{ cm}$, the first allowable value of $k^2$ is given by $2.5 \times 10^4 \text{ m}^{-2}$, and it corresponds to an onset of instability giving only one crest. And the critical value of $k^2$ is now independent of the value of $A$, and hence is not like those seen above. The critical interface speed is now $3.5 \mu \text{m/s}$, and the critical undercooling is $1.6 \text{ K}$.

Hence for small enough values of $W$ the expectation is one crest at critical, as in precipitation. For larger values of $W$, the expectation is multiple crests at critical, until, at small values of $L$, for high enough values of $W$, the expectation returns to one crest at critical at a value of $k^2$ now independent of surface tension.

**Concluding Remarks**

Our view is that problems of phase change often lead to problems in pattern formation. Hence one role of theoretical work is to decide what experiments might be interesting. We suggest that experiments ought to be run by increasing the control variable, here $T_m - T_L$ or $U$, to its critical value and then just beyond. Looked at in this way there is only one critical point in any given experiment, notwithstanding the fact that our $\sigma$ versus $k^2$ curves show three critical points at small values of $\frac{L}{S}$, two at low values of $k^2$, and two critical points at large values of $\frac{L}{S}$, one at a low value of $k^2$. In both cases, the low-$k^2$ critical points are determined by heat conduction in its various manifestations, independent of surface tension.

It is the neutral curve, not the $\sigma$ curves, that bears on the design and interpretation of experiments. As $U$ is increased, at the wave numbers consistent with the width of the cell, the
lowest intersections of lines of constant $U$ and the neutral curve predict the critical point that ought to be observed. Hence at small values of $\frac{L}{S}$, there may be a critical point at low values of $k^2$, independent of surface tension, at large values of $\frac{L}{S}$ there cannot be such a low-$k^2$ critical point.

We present a simple model that includes only the most important factors: heat conduction on the domain and surface tension at the moving front - not unlike the models used by Wollkind and Notestine [10] and Mullins and Sekerka [9]. But instead of introducing control via the gradients at the front, we propose far-field conditions more akin to how an experiment might be run. This adds the depths of the two phases as interesting input variables and these variables influence the strength of the effect of crest-to-trough heat conduction in both phases, an effect that is stabilizing in the solid, destabilizing in the melt. It is by doing this that we discover the existence of a critical point at small wave numbers independent of the effect of surface tension.

The width of the solidification cell strongly affects the patterns that can be obtained in an experiment and we explain what ought to be seen as a function of the three lengths that can be controlled: the two depths and the width.
CHAPTER 4
ON THE IMPORTANCE OF BULK TRANSPORT ON INTERFACIAL INSTABILITY

Introduction

Our goal is to understand whether or not domain transport dynamics is important compared to the dynamics at the interface. In other words we wish to investigate if it is reasonable to drop \( \sigma \) s from the domain equations. To study this we will consider two problems using precipitation physics as a guide. Both problems are done in rectangular geometry. First we consider an equilibrium problem where the planar front is at rest. Second, we consider a non-equilibrium problem where the front is moving with a non-zero base speed. In each case we derive a condition that dictates whether or not \( \sigma \) s can be dropped from the domain equations. In both cases we illustrate that the transport dynamics at the interface is ordinarily much more important compared to the domain transport dynamics, whence dropping \( \sigma \) s from the domain equations is a good approximation. In precipitation, this result is due to the extremely small value of capillary length.

The endnote discusses two problems. First we consider a solid cylinder in equilibrium with its solution at a uniform concentration. Second we consider a solid cylinder in equilibrium with its subcooled melt at a uniform temperature. In each case we derive a formula for the growth rate \( \sigma \) and hence a condition that must be met if \( \sigma \) s are to be dropped from the domain equations.

Case 1: Equilibrium Precipitation Problem in Rectangular Geometry

Consider the schematic shown in Figure 4.1 which shows a solid of density \( c_s \) in equilibrium with its solution which is held at a uniform concentration \( c_{\text{SAT}} \).

Then, in the liquid phase, the equation for the solute concentration is given by

\[
\frac{\partial c}{\partial t} = D \nabla^2 c
\]  

(4.1)
for $Z < z < L$ and $0 < x < W$, where $L$ is the depth of the liquid phase and $W$ is the width of the precipitation cell; $D$ denotes the diffusivity of the solute in the liquid phase. The equations along the interface, viz., along $z = Z(x,t)$ are given by

$$c = c_{\text{SAT}} - \left[ \frac{\gamma}{RT} \frac{c_{\text{SAT}}}{c_s} \right] 2H$$

(4.2)

and

$$[c_s - c]u = D n \cdot \nabla c$$

(4.3)

where $\gamma$ denotes the surface tension, and where $u$ denotes the local surface speed of the perturbed front. The far field condition is given by

$$c(z = L) = c_{\text{SAT}}$$

(4.4)

Finally we impose side wall conditions so that $\partial c / \partial x$ and $\partial Z / \partial x$ vanish at $x = 0$ and at $x = W$.

Figure 4.1 – A precipitation front at rest

The Base State and the Perturbation Eigenvalue Problem

Since $U = 0$, the concentration gradient in the base state is zero. The concentration in the liquid is constant everywhere, viz., $c_0(z) = c_{\text{SAT}}$. 

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To determine if this base solution is stable, we impose a small displacement on the surface at fixed values of $c_L$ and $U$, and determine its growth rate, $\sigma$, as a function of its wave number $k$. We expand

$$Z = Z_0 + \varepsilon Z_1 = Z_0 + \varepsilon \hat{Z}_1 \cos(kx)e^{\sigma t} \quad (4.5)$$

and

$$c = c_0 + \varepsilon \left[ c_1 + Z_1 \frac{dc_0}{dz} \right] = c_0 + \varepsilon \left[ \hat{c}_1 + \hat{Z}_1 \frac{dc_0}{dz} \right] \cos(kx)e^{\sigma t} \quad (4.6)$$

whence the perturbation equations for $\hat{c}_1$ and $\hat{Z}_1$ are given by

$$\left[ \frac{d^2}{dz^2} - \left( k^2 + \frac{\sigma}{D} \right) \right] \hat{c}_1 = 0 \quad (4.7)$$

in the solution, $0 < z < 1$, $0 < x < W$. The equations that need to be satisfied across the interface, $z = 0$, are

$$[c_s - c_{sat}] \sigma \hat{Z}_1 = D \frac{d \hat{c}_1}{dz} \quad (4.8)$$

and

$$\hat{c}_1(z = 1) = 0 \quad (4.9)$$

The far-field equation is

$$\hat{c}_1(z = 1) = 0 \quad (4.10)$$

These equations can be solved in the usual manner to obtain a formula for the growth rate:

$$\sigma = D \left[ \frac{\gamma}{RT} \frac{c_{sat}}{c_s} \frac{1}{c_s - c_{sat}} \right] k^2 N \quad (4.11)$$
where $N = \left( \frac{m_- - m_e e^{[m_- - m_e]L}}{1 - e^{[m_- - m_e]L}} \right)$ and $m_\pm = \pm \sqrt{k^2 + \frac{\sigma}{D}}$. The formula for the growth rate becomes much simpler if we let $L \to \infty$, whereupon the factor $N$ reduces to $m_-$, whence

$$\frac{\sigma}{m_\pm D} = L_{cap} k^2 \tag{4.12}$$

where $L_{cap}$ represents the capillary length, defined as $L_{cap} = \left[ \frac{\gamma c_{SAT}}{RT} \frac{1}{c_s - c_{SAT}} \right]$. Next let us define $\sigma_s$ as the value of $\sigma$ due to the surface only. Hence $\sigma_s$ represents the value of the growth rate if $\sigma$ is dropped from the domain equation. Hence we have

$$\frac{\sigma_s}{k D} = L_{cap} k^2 \tag{4.13}$$

Dividing Eq. (4.12) by Eq. (4.13), there obtains

$$\frac{\sigma}{\sigma_s} = m_- \frac{1}{k^2} \sqrt{1 + \frac{\sigma}{\sigma_s \frac{D K}{k^2}}} \tag{4.14}$$

Hence the sufficient condition for $\sigma \approx \sigma_s$ is given by $\left| \frac{\sigma_s}{D K} \right| < 1$ or $\left| \frac{-k L_{cap} K}{D K^2} \right| < 1$. Hence the quantity $k L_{cap}$ should be much less than unity if one is to justify dropping $\sigma$ from the domain equation. Therefore $k < \frac{1}{L_{cap}}$ is a sufficient condition for $\sigma \approx \sigma_s$ or equivalently for dropping $\sigma$ from the domain equation.

<table>
<thead>
<tr>
<th>Table 4.1 – Thermo-physical properties of CuSO$_4$.5H$_2$O</th>
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</thead>
<tbody>
<tr>
<td>Saturation concentration, $c_{SAT}$</td>
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<tr>
<td>Density of solid, $c_s$</td>
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<tr>
<td>Diffusivity, $D$</td>
</tr>
<tr>
<td>Gas constant, $R$</td>
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<tr>
<td>Surface Tension, $\gamma$</td>
</tr>
</tbody>
</table>
As an example, let us consider the precipitation of \(\text{CuSO}_4\cdot5\text{H}_2\text{O}\). Using the thermo-physical properties given in Table 4.1, and assuming \(T = 300K\), the capillary length is found to be

\[ L_{\text{cap}} = 4.67 \times 10^{-11} \text{ meters} \]

which is extremely small. Hence the \(\sigma\) vs. \(k^2\) curve should be the same as the \(\sigma_s\) vs. \(k^2\) curve so long as \(k^2 << 10^{20}\). Consequently, for most practical purposes we can easily drop \(\sigma\) from the domain equations and this is due to the ordinarily small values of \(L_{\text{cap}}\).

In fact it is easy to get an explicit formula for \(\sigma\) vs. \(k^2\). From Eq. (4.12), we get

\[
\sigma = -DL_{\text{cap}}k^2 \sqrt{\frac{\sigma}{D} + k^2}
\]

which is a quadratic in \(\frac{\sigma}{D}\). Keeping in mind that the growth rate must be negative, we get

\[
\frac{\sigma}{D} = \frac{1}{2} k^4 L_{\text{cap}}^2 \left[ 1 - \sqrt{1 + \frac{4}{k^2 L_{\text{cap}}^2}} \right] \tag{4.17}
\]

For small values of \(kL_{\text{cap}}\) we can rearrange Eq. (4.17) to get

\[
\frac{\sigma}{D} = \frac{1}{2} k^4 L_{\text{cap}}^2 \left[ 1 - \frac{2}{kL_{\text{cap}}} \sqrt{1 + \frac{k^2 L_{\text{cap}}^2}{4}} \right] \approx \frac{1}{2} k^4 L_{\text{cap}}^2 \left[ 1 - \frac{2}{kL_{\text{cap}}} \left[ 1 + \frac{k^2 L_{\text{cap}}^2}{4} \right] \right] \tag{4.18}
\]

Hence
\[
\frac{\sigma}{D} \approx \frac{1}{2} k^4 l^2_{\text{cap}} \left[-2 \left( kL_{\text{cap}} \right)^{-1} + \left( kL_{\text{cap}} \right)^0 - \frac{1}{4} \left( kL_{\text{cap}} \right)^1 \right] \approx \frac{1}{2} k^4 l^2_{\text{cap}} \left[ 1 - \frac{2}{kL_{\text{cap}}} \right] \quad (4.19)
\]

or

\[
\frac{\sigma}{D} \approx -k^3 L_{\text{cap}} \left[ 1 - \frac{1}{2} kL_{\text{cap}} \right] \approx \frac{\sigma_s}{D} \left[ 1 - \frac{1}{2} kL_{\text{cap}} \right] \quad (4.20)
\]

This means that \( \sigma \) is less negative compared to \( \sigma_s \). In other words, neglecting \( \sigma \) on the domain over-predicts the stability. However it is clear from Eq. (4.20) that the correction is negligible.

For large values of \( kL_{\text{cap}} \) we can rearrange Eq. (4.17) to get

\[
\frac{\sigma}{D} = \frac{1}{2} k^4 l^2_{\text{cap}} \left[ 1 - \sqrt{1 + \frac{4}{k^2 l^2_{\text{cap}}}} \right] \approx \frac{1}{2} k^4 l^2_{\text{cap}} \left[ 1 - \left[ 1 + \frac{1}{2} k^2 l^2_{\text{cap}} \right] \right] \approx -k^2 \quad (4.21)
\]

or

\[
\frac{\sigma}{D} \approx -k^2 = \frac{\sigma_s}{L_{\text{cap}}k} = \frac{\sigma_s}{D} \frac{1}{L_{\text{cap}}k} \quad (4.22)
\]

Again \( \sigma \) is less negative compared to \( \sigma_s \) and neglecting \( \sigma \) on the domain over-predicts the stability. And it is clear from Eq. (4.22) that the correction can be significant if the quantity \( kL_{\text{cap}} \) is large enough. And we again conclude that dropping \( \sigma \) from the domain is a bad approximation if \( k > \frac{1}{L_{\text{cap}}} \) or equivalently if the wavelength of the disturbance is much less than the capillary length.

The graph given in Figure 4.2 is drawn for \( L_{\text{cap}} = 4.67 \times 10^{-11} \) meters and it illustrates the \( \sigma \) vs. \( k^2 \) curve superposed over the \( \sigma_s \) vs. \( k^2 \) curve. \( \sigma \) is drawn from Eq. (4.17) and \( \sigma_s \) is drawn from Eq. (4.13). Clearly we cannot see any difference as \( \sigma \) and \( \sigma_s \) are in excellent agreement.
agreement. Figure 4.3 is drawn for a much larger value of \( L_{cap} \), viz., \( L_{cap} = 10^3 \) meters, to emphasize that the magnitude of capillary length plays a key role in deciding the importance of bulk transport compared to the interface transport. We see that the difference between \( \sigma \) and \( \sigma_s \) is very subtle for a high value of \( L_{cap} \).

Next we move on to the usual precipitation case where a planar front is moving at a constant speed in the base state.

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Figure 4.2 – \( \sigma \) vs. \( k^2 \) for the equilibrium precipitation problem with \( L_{cap} = 4.67 \times 10^{11} \) meters
Case 2: Non-equilibrium Precipitation Problem in a Rectangular Geometry

This is identical to the previous case except that the precipitation front is now moving with a speed \( U \). Then, in the liquid phase, the equation for the solute concentration is given by

\[
\frac{\partial c}{\partial t} = D \nabla^2 c + U \frac{\partial c}{\partial z}
\]  

(4.23)

for \( Z < z < L \) and \( 0 < x < W \), where \( L \) is the depth of the liquid phase and \( W \) is the width of the precipitation cell. The equations along the interface, viz., along \( z = Z(x,t) \) are given by
\[ c = c_{SAT} - \left[ \frac{\gamma}{RT} \frac{c_{SAT}}{c_S} \right] 2H \]  

(4.24)

and

\[ [c_S - c] \left[ U \nabla n + u \right] = D \nabla^2 c \]  

(4.25)

The far field condition is given by

\[ c(z = L) = c_L \]  

(4.26)

The side wall conditions are Neumann, whence \( \partial c / \partial x \) and \( \partial Z / \partial x \) vanish at \( x = 0 \) and at \( x = W \).

**The Base State and the Perturbation Eigenvalue Problem**

A base state solution is given by

\[ c_0(z) = c_s + [c_{SAT} - c_s] e^{[U_0/D]z} \]  

(4.27)

where \( U_0 \) is given by

\[ U_0 = -\frac{D}{L} \ln \left( 1 - \frac{c_L - c_{SAT}}{c_S - c_{SAT}} \right) \]  

(4.28)

Expanding \( Z \) and \( c \) as in Eqs. (4.5, 4.6), and solving the perturbation eigenvalue problem, there obtains the following formula for the growth, \( \sigma \):

\[ \sigma = D \left[ L_{cap} k^2 - \frac{U_0}{D} \right] \left[ N + \frac{U_0}{D} \right] \]  

(4.29)

where \( L_{cap} = \left[ \frac{\gamma}{RT} \frac{c_{SAT}}{c_S} \frac{1}{c_S - c_{SAT}} \right] \), \( N = \left[ \frac{m_- - m_+ e^{m_- m_+ L}}{1 - e^{m_- m_+ L}} \right] \) and \( m_+ = -\frac{U_0}{D} \pm \sqrt{\frac{U_0^2}{D^2} + \frac{4\sigma}{D} + 4k^2} \).

The formula for the growth rate becomes much simpler if we let \( \frac{U_0 L}{D} \rightarrow \infty \), whereupon the factor \( N \) reduces to \( m_- \), whence
\[ \sigma = D \left[ L_{cap}k^2 - \frac{U_0}{D} \right] \left[ m + \frac{U_0}{D} \right] \] (4.30)

or

\[ \sigma = \frac{1}{2} U_0 \left[ L_{cap}k^2 - \frac{U_0}{D} \right] \left[ 1 - \sqrt{1 + 4 \frac{k^2 D^2}{U_0^2}} \right] \left[ 1 + \frac{4 \sigma}{D} \right] \] (4.31)

Next define \( \sigma_s \) as the value of \( \sigma \) due to the surface only. Then

\[ \sigma_s = \frac{1}{2} U_0 \left[ L_{cap}k^2 - \frac{U_0}{D} \right] \left[ 1 - \sqrt{1 + 4 \frac{k^2 D^2}{U_0^2}} \right] \] (4.32)

Dividing Eq. (4.31) by Eq. (4.32), there obtains

\[ \frac{\sigma}{\sigma_s} = \frac{1 - \sqrt{1 + 4 \frac{k^2 D^2}{U_0^2}}}{1 - \sqrt{1 + 4 \frac{k^2 D^2}{U_0^2}}} \] (4.33)

Hence the sufficient condition for \( \sigma \approx \sigma_s \) is given by \( \frac{4 \sigma}{D} \frac{\sigma_s}{U_0^2 + 4k^2} \ll 1 \) and one can justify dropping \( \sigma \) from the domain equation if this condition is satisfied.

Again considering the precipitation of \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \) at \( T = 300K \), we have

\[ L_{cap} = 4.67 \times 10^{-11} \text{ meters} \] which is extremely small. Taking \( c_L = 2c_{sAT} = 486 \text{kg/m}^3 \), \( L = 1 \text{cm} \), we obtain from Eq. (4.28), \( U_0 = 2.12 \times 10^{-7} \text{m/sec} \). A graph of \( \sigma_s \) vs. \( k^2 \) can then be plotted using Eq. (4.32) and this is shown in Figure 4.4. Typically \( \sigma_s \) is of the order of \( \sigma_s \approx 0.1/\text{sec} \). Hence
4\frac{\sigma_s}{D} is of the order of $10^9 m^2$. But the interesting $k^2$ s are of the order of $10^{12} m^{-2}$. Hence

\begin{equation*}
\left| \frac{4\frac{\sigma_s}{D}}{\frac{U_0^2}{D^2} + 4k^2} \right|
\end{equation*}

is ordinarily much less than unity.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{sigma_vs_k2.png}
\caption{\(\sigma\) vs. \(k^2\) for the non-equilibrium precipitation problem with \(L_{cap} = 4.67 \times 10^{11}\) meters}
\end{figure}

Therefore dropping \(\sigma\) from the domain equation is again found to be a good approximation for precipitation under non-equilibrium conditions. In fact, for a given set of input parameters, after evaluating \(\sigma_s\) using Eq. (4.32), one can use Eq. (4.33) to solve for the ratio

\[\frac{\sigma}{\sigma_s}\]

and hence to find \(\sigma\). It is found that for unstable wave numbers, \(\frac{\sigma}{\sigma_s}\) is slightly greater than unity, hence putting \(\sigma_s\) on the domain predicts more positive growth rates compared to their

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value had $\sigma$ been dropped from the domain equation. For stable wave numbers, $\frac{\sigma}{\sigma_s}$ is slightly less than unity, whence in the stable regime, $\sigma$ is less negative compared to $\sigma_s$.

**Concluding Remarks**

We have demonstrated that the transport dynamics in the bulk of the domain is ordinarily insignificant compared to the interfacial transport dynamics, whence dropping $\sigma_s$ from the domain equations is a good approximation for most cases of interest.

**Endnote 1: Equilibrium Precipitation Problem in Cylindrical Geometry**

Consider a vertical solid cylinder of radius $R_0$ and of density $c_s$ in equilibrium with its solution which is held at a uniform concentration.

Then, in the liquid phase, the equation for the solute concentration is given by

$$\frac{\partial c}{\partial t} = D \nabla^2 c$$

for $R_0 < r < \infty$ and $0 < z < W$, where $W$ is the height of the cylinder. The equations along the interface, viz., along $r = R(z,t)$ are given by

$$c = c_{\text{SAT}} - \left[ \frac{\gamma}{RT} \frac{c_{\text{SAT}}}{c_s} \right] 2H$$

and

$$[c_s - c]u = D \n \nabla c$$

where $\gamma$ denotes the surface tension, and where $u$ denotes the local surface speed of the perturbed front. $2H$ denotes the curvature of the surface. The far field condition is given by

$$c(r \to \infty) = \text{finite}$$
Assuming axisymmetry, the surface normal and surface speed are respectively given by
\[ \mathbf{n} = \frac{i - R \mathbf{R}_z}{\sqrt{1 + R_z^2}} \quad \text{and} \quad u = \frac{R_v}{\sqrt{1 + R_z^2}}. \]
The side wall conditions require that both \( \frac{\partial c}{\partial z} \) and \( \frac{\partial R}{\partial z} \) vanish at \( z = 0 \) and at \( z = W \).

The Base State and the Perturbation Eigenvalue Problem

Since \( U = 0 \), the concentration gradient in the base state is zero. The concentration in the liquid is constant everywhere, viz., \( c_0(r) = c_{\text{SAT}} + \frac{1}{R_0} \left[ \frac{\gamma}{RT} c_{\text{SAT}} \right] \). Notice that the base state concentration is not \( c_{\text{SAT}} \) as it used to be for the planar case, cf., case 1. The appropriate correction is present due to the fact that the base surface is itself curved.

To determine whether or not this base state is stable, let a small disturbance of amplitude \( \varepsilon \) be imposed on the steady base solution. Then expanding \( R \) and \( c \) at \( r = R(z) \) as
\[ R = R_0 + \varepsilon R_1 \]
\[ c = c_0 + \varepsilon \left[ c_1 + R_1 \frac{dc_0}{dr} \right] \]
where the term involving the surface displacement, \( R_1 \), has been introduced so that the perturbation problem can be solved on the reference domain. To find the critical base state, we must solve the perturbation eigenvalue problem. It is given by
\[ \frac{\partial c_1}{\partial t} = D \nabla^2 c_1 \]
\[ \left[ c_s - c_{\text{SAT}} \right] \frac{\partial R_1}{\partial t} = D \frac{\partial c_1}{\partial r} \]
and
\[ c_1 = \left[ \frac{\gamma}{RT} \frac{c_{st}}{c_s} \right] \left[ \frac{\partial^2 R_i}{\partial z^2} + \frac{R_i}{\partial R_i^2} \right] \]  

(4.42)

The far-field equation is
\[ c_1(r \to \infty) = 0 \]  

(4.43)

Expanding
\[ R_i = R_i \cos(kz)e^{\sigma t}, \quad c_1 = c_1(r) \cos(kz)e^{\sigma t} \]  

(4.44)

the perturbation equations for \( \hat{c}_i \) and \( \hat{Z}_i \) are given by
\[ \left[ \frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} - \left[ k^2 + \frac{\sigma}{D} \right] \right] \hat{c}_i = 0 \]  

(4.45)

in the solution, \( R_0 < r < \infty \). The equations that need to be satisfied across the interface, \( r = R_0 \),

are
\[ [c_s - c_0] \sigma \hat{R}_i = D \frac{d}{dr} \hat{c}_i \]  

(4.46)

and
\[ \hat{c}_1 = \left[ \frac{\gamma}{RT} \frac{c_{st}}{c_s} \right] \left[ 1 - \frac{k^2}{R_0^2} \right] \hat{R}_i \]  

(4.47)

The far-field equation is
\[ \hat{c}_1(r \to \infty) = 0 \]  

(4.48)

Defining \( \lambda^2 = k^2 + \frac{\sigma}{D} \), a solution to the domain equation, Eq. (4.45) is given as
\[ \hat{c}_1(r) = AI_0(\lambda r) + BK_0(\lambda r) \]  

(4.49)
where $I_0$ and $K_0$ are modified Bessel’s functions of zeroth order. Since we require the solution to be bounded at $r \to \infty$, we have $A = 0$, whence

$$\hat{c}_1(r) = BK_0(\lambda r) \quad \text{(4.50)}$$

and using Eqs. (4.46) and (4.47), there obtains

$$[c_S - c_0]\sigma \hat{R} = DB\lambda K_0(\lambda R_0) \quad \text{(4.51)}$$

and

$$BK_0(\lambda R_0) = -\left[\frac{\gamma}{RT} \frac{c_{SAT}}{c_S} \left[1 - \frac{1}{R_0^2} k^2\right]\hat{R}\right] \quad \text{(4.52)}$$

respectively, where $K_0'(x) = \frac{d}{dx}\left[K_0(x)\right]$. Dividing Eq. (4.51) by (4.52), we get

$$\sigma = -D\lambda \frac{L_{cap}}{R_0^2} \left[1 - k^2 R_0^2\right] \left[\frac{K_0(\lambda R_0)}{K_0(\lambda R_0)}\right] \quad \text{(4.53)}$$

where $L_{cap}$ represents the capillary length, defined as:

$$L_{cap} = \left[\frac{\gamma}{RT} \frac{c_{SAT}}{c_S} \frac{1}{c_S - c_0}\right] = \left[\frac{\gamma}{RT} \frac{c_{SAT}}{c_S} \frac{1}{c_S - c_{SAT}} - \frac{\gamma}{RT} \frac{c_{SAT}}{c_S} \frac{1}{R_0}\right].$$

Next let us define $\sigma_S$ as the value of $\sigma$ due to the surface only. Hence $\sigma_S$ represents the value of the growth rate if $\sigma$ is dropped from the domain equation. Hence we have

$$\sigma_S = -DK \frac{L_{cap}}{R_0^2} \left[1 - k^2 R_0^2\right] \left[\frac{K_0'(kR_0)}{K_0(kR_0)}\right] \quad \text{(4.54)}$$

Dividing Eq. (4.53) by Eq. (4.54), there obtains

$$\frac{\sigma}{\sigma_S} = \frac{\lambda}{k} \left[\frac{K_0(\lambda R_0)}{K_0(\lambda R_0)}\right] \left[\frac{K_0(\lambda R_0)}{K_0(\lambda R_0)}\right] \quad \text{(4.55)}$$
Substituting \( \frac{\lambda}{k} = \sqrt{1 + \frac{\sigma}{Dk^2}} \), there obtains

\[
\frac{\sigma}{\sigma_s} = \sqrt{1 + \frac{\sigma}{\sigma_s} \frac{\sigma_s}{Dk^2} - kR_0} \left[ \frac{K_0' \left( \sqrt{1 + \frac{\sigma}{\sigma_s} \frac{\sigma_s}{Dk^2} - kR_0} \right)}{K_0 \left( kR_0 \right)} \right]
\]

(4.56)

Hence the sufficient condition for \( \sigma \approx \sigma_s \) is given by \( \left| \frac{\sigma_s}{Dk^2} \right| < 1 \). Therefore

\[
\left| - \frac{1}{k} \frac{L_{\text{cap}}}{R_0^2} \left[ 1 - kR_0^2 \right] \left[ \frac{K_0' \left( kR_0 \right)}{K_0 \left( kR_0 \right)} \right] \right| < 1
\]

is a sufficient condition to justify dropping \( \sigma \) from the domain equation.

**Endnote 2: Equilibrium Solidification Problem in Cylindrical Geometry**

Consider a solid cylinder of radius \( R_0 \) and at a uniform temperature in equilibrium with its subcooled melt which is held at a uniform temperature. The cylindrical front is at rest in the base state. We will scale the temperature so that it is measured from a reference point corresponding to \( T_M \), and it is scaled by \( \alpha L_{\text{tt}} / \lambda \), where \( \alpha \) is the thermal diffusivity of the solid phase, \( \lambda \) is the thermal conductivity of the solid phase, and \( L_{\text{tt}} \) denotes the latent heat of solidification per unit volume of the solid, viz., \( T_{\text{scaled}} = \frac{T_M - T}{\alpha L_{\text{tt}} / \lambda} \). We assume the thermal conductivities and the thermal diffusivities of the two phases to be the same.

Then, in the solid phase, the equation for the scaled temperature is given by

\[
\frac{\partial T}{\partial t} = \alpha \nabla^2 T
\]

(4.57)

for \( 0 < r < R_0 \) and \( 0 < z < W \), where \( W \) is the height of the cylinder. The equation for the scaled temperature in the liquid phase is given by
\[
\frac{\partial T^*}{\partial t} = \alpha \nabla^2 T^* \tag{4.58}
\]

The equations along the interface, viz., along \( r = R(z,t) \) are given by

\[
T = T^* = -L_{\text{cap}} \left[ 2H \right] \tag{4.59}
\]

and

\[
\vec{n} \cdot \nabla T - \vec{n} \cdot \nabla T^* = -\left[ \frac{1}{\alpha^*} \right] u \tag{4.60}
\]

where \( L_{\text{cap}} \) represents the capillary length, defined as \( L_{\text{cap}} = \left[ \frac{\gamma \lambda}{\alpha L_{\text{il}}^2} \right] T_M \). \( \gamma \) denotes the surface tension and \( u \) denotes the local surface speed of the perturbed front. The far-field condition is given by

\[
T(r = 0) = \text{finite} \tag{4.61}
\]

and

\[
T^*(r \to \infty) = L_{\text{cap}} \left[ \frac{1}{R_0} \right] \tag{4.62}
\]

The side wall conditions require that \( \partial T / \partial z, \partial T^* / \partial z \) and \( \partial R / \partial z \) vanish at \( z = 0 \) and at \( z = W \).

**The Base State and the Perturbation Eigenvalue Problem**

Since \( U = 0 \), the temperature gradient in the base state is zero in both phases. The temperature is constant everywhere in the solid and the liquid phase. It is given by

\[
T_0(r) = T^*_0(r) = L_{\text{cap}} \left[ \frac{1}{R_0} \right]. \text{Notice that an appropriate correction is present in the base itself because the base surface is curved.}
\]

To determine whether or not this base state is stable, let a small disturbance of amplitude \( \varepsilon \) be imposed on the steady base solution. Then expanding \( R, T \) and \( T^* \) at \( r = R(z) \) as
\[ R = R_0 + \varepsilon R \]  

\[ T = T_0 + \varepsilon \left[ T_i + R_i \frac{dT_0}{dr} \right] \]  

and

\[ T^* = T_0^* + \varepsilon \left[ T_i^* + R_i \frac{dT_0^*}{dr} \right] \]  

where the term involving the surface displacement, \( R_i \), has been introduced so that the perturbation problem can be solved on the reference domain. To find the critical base state, we must solve the perturbation eigenvalue problem. It is given by

\[ \frac{\partial T_i}{\partial t} = \alpha \nabla^2 T_i \]  

\[ \frac{\partial T_i^*}{\partial t} = \alpha \nabla^2 T_i^* \]  

\[ T_i = T_i^* = -L_{cap} \left[ \frac{\partial^2 R_i}{\partial z^2} + \frac{R_i}{R_0^2} \right] \]  

and

\[ \left[ \frac{\partial T_i}{\partial r} - \frac{\partial T_i^*}{\partial r} \right] = -\frac{1}{\alpha} \frac{\partial R_i}{\partial t} \]  

The far-field equations are

\[ T_i(r = 0) = 0 \]  

and

\[ T_i^*(r \to \infty) = 0 \]  

Expanding

\[ R_i = \hat{R}_i \cos(kz)e^{\sigma t}, \quad T_i = \hat{T}_i(r) \cos(kz)e^{\sigma t}, \quad T_i^* = \hat{T}_i^*(r) \cos(kz)e^{\sigma t} \]
the perturbation equations for $\hat{T}_1^T$, $\hat{T}_1^*$ and $\hat{Z}_1$ are given by

$$\left[ \frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} \left[ k^2 - \sigma \alpha \right] \right] \hat{T}_1 = 0$$ \hspace{1cm} (4.73)

in the solid phase, $0 < r < R_0$, and

$$\left[ \frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} \left[ k^2 + \sigma \alpha \right] \right] \hat{T}_1^* = 0$$ \hspace{1cm} (4.74)

in the solution, $R_0 < r < \infty$. The equations across the interface, $r = R_0$, are

$$\hat{T}_1 = \hat{T}_1^* = -L_{cap} \left[ \frac{1}{R_0^2} - k^2 \right] R_1$$ \hspace{1cm} (4.75)

and

$$\frac{d \hat{T}_1}{dz} - \frac{d \hat{T}_1^*}{dz} = -\frac{\sigma R_1}{k_1}$$ \hspace{1cm} (4.76)

The far-field equations are

$$\hat{T}_1(r = 0) = 0$$ \hspace{1cm} (4.77)

and

$$\hat{T}_1^*(r \to \infty) = 0$$ \hspace{1cm} (4.78)

Defining $\lambda^2 = k^2 + \frac{\sigma}{\alpha}$, a solution to the domain equations, Eqs. (4.73) and (4.74) is given as

$$\hat{T}_1(r) = A I_0(\lambda r) + B K_0(\lambda r)$$ \hspace{1cm} (4.79)

$$\hat{T}_1^*(r) = B^* I_0(\lambda r) + A^* K_0(\lambda r)$$ \hspace{1cm} (4.80)
where \( I_0 \) and \( K_0 \) are modified Bessel’s functions of zeroth order. Since we require \( \hat{T}_1 \) to be bounded at \( r \to 0 \), we have \( B = 0 \). Similarly since \( \hat{T}_1^* \) must be bounded at \( r \to \infty \), we have \( B^* = 0 \) whence

\[
\hat{T}_1(r) = A I_0(\lambda r)
\]  

(4.81)

and

\[
\hat{T}_1^*(r) = A^* K_0(\lambda r)
\]  

(4.82)

where \( A \) and \( A^* \) are given by Eq. (4.75) as

\[
A = -\frac{L_{\text{cap}} \left( \frac{1}{R_0^3} R_0^2 \lambda^2 \right)}{I_0(\lambda R_0)} \hat{R}_1
\]

and

\[
A^* = -\frac{L_{\text{cap}} \left( \frac{1}{R_0^3} R_0^2 \lambda^2 \right)}{K_0(\lambda R_0)} \hat{R}_1
\]

respectively. Substituting in Eq. (4.76) there obtains

\[
\sigma = \alpha \left[ \frac{L_{\text{cap}}}{R_0^3} \right] \lambda R_0 \left[ 1 - k^2 R_0^2 \right] \left[ \frac{I'_0(\lambda R_0)}{I_0(\lambda R_0)} - \frac{K'_0(\lambda R_0)}{K_0(\lambda R_0)} \right]
\]  

(4.83)

where \( I'_0(x) = \frac{d}{dx} [I_0(x)] \) and \( K'_0(x) = \frac{d}{dx} [K_0(x)] \). Denoting \( \sigma_s \) as the value of the growth rate if \( \sigma \) is dropped from the domain equation there obtains

\[
\sigma_s = \alpha \left[ \frac{L_{\text{cap}}}{R_0^3} \right] k R_0 \left[ 1 - k^2 R_0^2 \right] \left[ \frac{I'_0(k R_0)}{I_0(k R_0)} - \frac{K'_0(k R_0)}{K_0(k R_0)} \right]
\]  

(4.84)

Dividing Eq. (4.83) by Eq. (4.84), there obtains

\[
\frac{\sigma}{\sigma_s} = \frac{\lambda}{k} \left[ \frac{I'_0(\lambda R_0)}{I_0(\lambda R_0)} - \frac{K'_0(\lambda R_0)}{K_0(\lambda R_0)} \right] \left[ \frac{I'_0(k R_0)}{I_0(k R_0)} - \frac{K'_0(k R_0)}{K_0(k R_0)} \right]
\]  

(4.85)

Substituting \( \frac{\lambda}{k} = \sqrt{1 + \frac{\sigma}{\alpha k^2}} \), there obtains
\[
\frac{\sigma}{\sigma_s} = \sqrt{\frac{1 + \frac{\sigma}{\sigma_s} \frac{\sigma_s}{\sigma_s D k^2}}{1 + \frac{\sigma}{\sigma_s} \frac{\sigma_s}{\sigma_s D k^2}}} = \frac{I_0(kR_0) \sqrt{\frac{1 + \frac{\sigma}{\sigma_s} \frac{\sigma_s}{\sigma_s D k^2}}{1 + \frac{\sigma}{\sigma_s} \frac{\sigma_s}{\sigma_s D k^2}}}}{K_0(kR_0) \sqrt{\frac{1 + \frac{\sigma}{\sigma_s} \frac{\sigma_s}{\sigma_s D k^2}}{1 + \frac{\sigma}{\sigma_s} \frac{\sigma_s}{\sigma_s D k^2}}}} - \frac{I_0'(kR_0)}{I_0(kR_0)} = \frac{K_0'(kR_0)}{K_0(kR_0)}
\]

(4.86)

Hence the sufficient condition for \( \sigma \approx \sigma_s \) is given by \( \left| \frac{\sigma_s}{\alpha k^2} \right| << 1 \) or equivalently by

\[
\left| \frac{L_{cap}}{R_0} \frac{1}{kR_0} \frac{1}{1 - k^2 R_0^2} \right| \left| \frac{I_0'(kR_0)}{I_0(kR_0)} - \frac{K_0'(kR_0)}{K_0(kR_0)} \right| << 1.
\]
CHAPTER 5
WEAK NONLINEAR ANALYSIS IN PRECIPITATION: GEOMETRIC EFFECTS ON ROUGHNESS

Introduction

In Chapter 2, linear stability methods were used to analyze the precipitation of a solid from a supersaturated solution. The physics of the instability in precipitation was explained in terms of diffusion and surface tension. We concluded that a steady planar interface becomes unstable and transforms into a non-planar shape as the solute concentration in the supersaturated solution is increased beyond its critical value.

In this chapter, we will be interested in examining what happens beyond the onset of instability. In doing so, our goal is to understand the early stages of the growth of surface roughness in precipitation. The notation used in this chapter is the same as that used in Chapter 2, and the schematic is again shown in Figure 5.1.

Figure 5.1 – A precipitation front growing into a supersaturated solution

Again, $c_L$, the solute concentration, is taken to be the control variable. Now to observe surface roughness, one might imagine running a series of experiments in which $c_L$ is increased
to, and just beyond its critical value. In studying precipitation, we would like to know: Can the critical point be detected in an experiment? What is the nature of the branching to the new non-planar solution? Is it a pitchfork? Is it forward or backward? Or is it a transcritical bifurcation? What is the effect on the mean front speed as $c_L$ just crosses its critical value? Is it higher or lower than the values predicted by the base formulas?

Our plan is to begin by presenting again the nonlinear equations in scaled form, and working out the base solution and the solution to the perturbation eigenvalue problem to find the critical value of $c_L$. To do this we follow the same steps as in Chapter 2, but nonetheless, we will rewrite the perturbation equations, now for $\sigma = 0$, so as to formulate an eigenvalue problem. Having found the critical value of $c_L$, we look for steady solutions just beyond this critical point by going to second and third orders in the amount by which $c_L$ is increased. We discover that the cross-sectional shape of the precipitation cell is important in deciding the nature of the bifurcation. Ordinarily, a rectangular cross section leads to a backward pitchfork; a circular cross section with symmetric disturbances gives a transcritical bifurcation. Toward the end of the chapter, we deduce a symmetry condition that determines whether a cross section of an arbitrary shape will lead to a pitchfork or a transcritical bifurcation. Then some other specific cross sectional shapes are studied and it is found that a transcritical bifurcation is more likely to occur. Finally, regardless of the nature of the branching, it is concluded that the surface speed always decreases compared to what its base value would have been.
Rectangular Cross Section

The Steady State Nonlinear Equations

The dimensionless nonlinear model equations are the same as given in Chapter 2.

However, we set all \( \frac{\partial}{\partial t} \) terms to zero as our goal is to investigate the nature of the steady state solutions to the problem upon crossing the threshold. Again, all variables used here are scaled.

In the liquid phase, the equation for the scaled solute concentration is given by

\[
\nabla^2 c + U \frac{\partial c}{\partial z} = 0
\]

(5.1)

for \( Z < z < 1 \) and \( 0 < x < W \). The equations along the interface, viz., along \( z = Z(x) \) are

\[
c = -\mathcal{A}[2H]
\]

(5.2)

and

\[
\vec{n} \cdot \nabla c = [1 - c] U \kappa \cdot \vec{n}
\]

(5.3)

where \( \mathcal{A} \) denotes \( \frac{\gamma}{L} \frac{1}{RT} \frac{c_{sat}}{c_s} \frac{1}{c_s - c_{sat}} \). The solute concentration at the reservoir is given by

\[
c(z = 1) = c_L
\]

(5.4)

Side wall conditions are Neumann, i.e., \( \frac{\partial c}{\partial x}(x = 0, W) = \frac{\partial Z}{\partial x}(x = 0, W) = 0 \). Finally, the volume of the supersaturated solution must be maintained fixed, whence

\[
\int_0^W Z(x) dx = 0
\]

(5.5)

Once a material is chosen, the physical properties are fixed. Once a cell is built, other variables such as \( L \) and \( W \) remain fixed. In running a sequence of experiments, \( c_L \) is increased from one
steady experiment to another. In each experiment, the mean interface speed, $U$, and the interface shape, $Z(x)$, are the outputs.

**The Base Solution**

The base state variables are denoted by the subscript 0. A base state solution is given by

$$c_0(z) = 1 - e^{-U_0 z}$$  \hspace{1cm} (5.6)

where $U_0$ is given by

$$U_0 = -\ln(1 - c_L)$$  \hspace{1cm} (5.7)

Besides the physical properties, the input variables in the base state are $L$ and $c_L$, and the output is $U_0$.

**The Eigenvalue Problem at Neutral Conditions**

On increasing $c_L$, we expect the planar interface to lose its stability. To determine the critical value of $c_L$, let a small disturbance be imposed on the steady base solution at fixed values of $c_L$ and $U_0$, where $c_L$ and $U_0$ satisfy Eq. (5.7). Then expanding $z = Z(x)$ as

$$Z = Z_0 + \varepsilon Z_1, \quad Z_0 = 0$$  \hspace{1cm} (5.8)

the solute concentration at the surface is given by

$$c = c_0 + \varepsilon \left[ c_1 + Z_1 \frac{dc_0}{dz} \right]$$  \hspace{1cm} (5.9)

where the term involving the surface displacement, $Z_1$, has been introduced so that the perturbation problem can be solved on the base domain (cf., Appendix B.1). To find the critical base state, the perturbation eigenvalue problem must be solved at zero growth rate, whence

$$\nabla^2 c_1 + U_0 \frac{\partial c_1}{\partial z} = 0$$  \hspace{1cm} (5.10)
on the domain, $0 < z < 1$, $0 < x < W$, where, at $z = 0$,

$$c_i = -\mathcal{A} \frac{d^2 Z_i}{dx^2} - Z_i \frac{dc_0}{dz}$$  \hspace{1cm} (5.11)$$

and

$$\frac{\partial c_i}{\partial z} + U_0 c_i = 0$$  \hspace{1cm} (5.12)$$

must hold, and where, at the reservoir, $z = 1$,

$$c_i = 0$$  \hspace{1cm} (5.13)$$

must hold. The sidewall conditions require $\partial c_i / \partial x = 0$ and $dZ_i / dx = 0$ at $x = 0$ and at $x = W$.

Thus the problem is homogeneous in $c_i$ and $Z_i$, and it has solutions of the form

$$c_i = c_1(z) \cos(kx) \text{ and } Z_i = A \cos(kx)$$  \hspace{1cm} (5.14)$$

which satisfy the side wall conditions so long as $k = n\pi / W$, $n = 1, 2, \ldots$, where $k$ is the wave number of the disturbance and $n = 0$ is ruled out by the condition

$$\int_{0}^{W} Z_i dx = 0$$  \hspace{1cm} (5.15)$$

which holds the volume of the solution fixed. Equations (5.10), (5.12) and (5.13) imply that $c_i$

must be zero, and therefore, at $z = 0$, $Z_i$ must satisfy

$$Z_i \frac{dc_0}{dz} = -\mathcal{A} \frac{d^2 Z_i}{dx^2}$$  \hspace{1cm} (5.16)$$

where $\frac{dc_0}{dz}(z = 0) = U_0$. Then Eq. (5.16) is satisfied for all values of $A$ so long as

$$U_0 = \mathcal{A} k^2$$  \hspace{1cm} (5.17)$$
The corresponding neutral curve is a straight line as shown in Figure 2.7 (b) (cf., Chapter 2), where the ordinate must be replaced by \( U \) now. Given \( W \), and hence a value of \( k^2 \), Eq. (5.17) determines the critical value of the interface speed, \( U \). The most dangerous value of \( k^2 \) corresponds to \( n = 1 \) or to \( k = \pi/W \), hence only one crest is seen at critical. As the control variable \( c_L \) increases upward from zero, the output variable \( U \) increases from zero, until there comes a point when Eq. (5.17) is satisfied. The corresponding value of \( U \) will be referred as its critical value. Henceforth the subscript zero will refer to this critical state. At values of \( U \) higher than \( U \), the base solution loses its stability. The critical value of \( c_L \), denoted \( c_{L0} \), corresponds to the critical value of \( U \) via Eq. (5.7).

Ordinarily then, one might increase the control parameter \( c_L \) to its critical value, and then slightly beyond, in order to discover the new steady states that ensue. Assuming with some evidence that the bifurcation would be pitchfork in nature, one can only hope to get a locally forward pitchfork by advancing the control variable beyond its critical value. However it turns out that our hope of finding a forward pitchfork is not realized upon proceeding in this way. The branching to non-planar steady solution is, in fact, a backward pitchfork. Hence we introduce \( \frac{1}{2} \varepsilon^2 \) as an input giving the amount by which \( c_L \) is decreased from its critical value (note that \( \varepsilon \) will no longer be used as a measure of the amplitude of a disturbance as it was in the eigenvalue problem). Now the new subcritical solution will not have the speed of the corresponding base solution, hence we first find the change in the base speed corresponding to a given change in \( c_L \). Eq. (5.7) indicates that for a small decrease in \( c_L \) from \( c_{L0} \), the corresponding change in \( U \) from \( U_0 \), per unit change in \( c_L \) is given by \( -\varepsilon^{U_0} \).
The First and Higher Order Problems

To find the steady backward branches, we write

\[ c_L = c_{t_0} - \frac{1}{2} \epsilon^2 \] \hspace{1cm} (5.18)

where \( \frac{1}{2} \epsilon^2 \) is an input. We then expand \( U \) and \( Z \) as

\[ U = U_0 + \epsilon U_1 + \frac{1}{2} \epsilon^2 U_2 + \frac{1}{6} \epsilon^3 U_3 + \ldots \] \hspace{1cm} (5.19)

and

\[ Z = Z_0 + \epsilon Z_1 + \frac{1}{2} \epsilon^2 Z_2 + \frac{1}{6} \epsilon^3 Z_3 + \ldots \] \hspace{1cm} (5.20)

Using the formula for the surface normal vector given in Figure 5.1, and observing that the factor \( \sqrt{Z_x^2 + 1} \) in the denominator cancels from both sides of Eq. (5.3), only the numerator of \( \vec{n} \cdot \vec{U} \) is needed, where \( \vec{U} = U \vec{k} \). Hence the expansion of \( \vec{n} \cdot \vec{U} \) is given by Eq. (5.19). This and the other expansions (cf., Appendix B.2) lead to the respective problems at first and higher orders in \( \epsilon \).

The First Order Problem

The first order problem differs from the eigenvalue problem in that the system now must respond to a change in \( c_L \), and this may lead to a change in \( U \), whence, at first order, we must determine \( c_1, Z_1 \) and also \( U_1 \). The first order problem is given by

\[ \nabla^2 c_1 + U_0 \frac{\partial c_1}{\partial z} = -U_1 \frac{dc_0}{dz} \] \hspace{1cm} (5.21)

on the domain, \( 0 < z < 1, \ 0 < x < W \),

\[ c_1 = -\mathcal{A} \frac{d^2 Z_1}{dx^2} - Z_1 \frac{dc_0}{dz} \] \hspace{1cm} (5.22)
and

\[ \frac{\partial c_i}{\partial z} + U_0 c_i = U_1 \]  \hspace{1cm} (5.23)

at \( z = 0 \),

\[ c_i = 0 \]  \hspace{1cm} (5.24)

at \( z = 1 \), and

\[ \int_0^W Z_i dx = 0 \]  \hspace{1cm} (5.25)

The sidewall conditions require \( \frac{\partial c_i}{\partial x} \) and \( dZ_i/dx \) to vanish at \( x = 0 \) and at \( x = W \). Now Eqs. (5.21), (5.23) and (5.24) have a particular solution depending only on \( z \), while the corresponding homogeneous problem is just the eigenvalue problem whose solution is \( c_i = 0 \).

Hence we have

\[ c_i = U_1 [z - 1] e^{-U_0 z} \]  \hspace{1cm} (5.26)

and we can turn to Eq. (5.22), which is a differential equation for \( Z_i \). Using \( c_i (z = 0) = -U_1 \), along with Eq. (5.25) and \( dZ_i/dx = 0 \) at \( x = 0, W \), and integrating Eq. (5.22) over \( 0 < x < W \), we find that \( U_1 \) must be zero. Hence \( c_i \) must also be zero, whereupon Eq. (5.22) must have the solution

\[ Z_i = A \cos(kx) \]  \hspace{1cm} (5.27)

What we have so far is this: \( c_i = 0 \), \( U_1 = 0 \), \( Z_i = A \cos(kx) \). And we go on to the second order problem to find the value of \( A \). The speed of the surface does not change at order \( \varepsilon \) upon decreasing \( c_L \) from \( c_{L_0} \) by \( \frac{1}{2} \varepsilon^2 \).
The Second Order Problem

At second order, the new unknowns to be determined are \( c_2, Z_2 \) and \( U_2 \), and the unknown \( A \) which carries over from first order. The second order problem is

\[
\nabla^2 c_2 + U_0 \frac{\partial c_2}{\partial z} = -U_2 \frac{dc_0}{dz}
\]

(5.28)

in the liquid solution, \( 0 < z < 1, \ 0 < x < W \),

\[
c_2 + Z_1^2 \frac{d^2 c_0}{dz^2} = -A \frac{d^2 Z_2}{dx^2} - Z_2 \frac{dc_0}{dz}
\]

(5.29)

and

\[
\frac{\partial c_2}{\partial z} + U_0 c_2 = U_2
\]

(5.30)

at \( z = 0 \),

\[
c_2 = -1
\]

(5.31)

at \( z = 1 \), and

\[
\int_0^W Z_2 dx = 0
\]

(5.32)

The sidewall conditions require \( \frac{\partial c_2}{\partial x} = \frac{dZ_2}{dx} = 0 \) at \( x = 0 \) and at \( x = W \). Solving Eqs. (5.28), (5.30) and (5.31), we get

\[
c_2 = \left[ U_2 [z - 1] - e^{U_0} \right] e^{-U_0 z}
\]

(5.33)

And it remains to solve Eqs. (5.29) and (5.32) for \( Z_2 \). To find \( Z_2 \), a solvability condition must be satisfied. It is

\[
\int_0^W \left[ c_2 (z = 0) + Z_1^2 \frac{d^2 c_0}{dz^2} (z = 0) \right] \cos(kx) dx = 0
\]

(5.34)
and it is satisfied, no matter the value of \( A \), due to

\[
\int_{0}^{W} \cos(kx) \, dx = \int_{0}^{W} \cos^3(kx) \, dx = 0
\]  

(5.35)

Hence \( A \) cannot be found at second order, but we can find \( U_2 \) and \( Z_2 \). To get \( U_2 \), integrate Eq. (5.29) over \( 0 < x < W \), and use Eq. (5.32), along with \( dZ_2 / dx = 0 \) at \( x = 0, W \). The result is

\[
U_2 = -e^{U_0} - \frac{1}{2} U_0^2 A^2
\]  

(5.36)

where the first term is what \( U_2 \) would be if the base solution obtains at the new value of \( c_L \). This term was derived earlier. The second term is the correction corresponding to a curved front. It is negative. If a curved front could exist, its speed would be slower than that of the corresponding planar front. In other words, the mean speed of the interface runs behind its base value.

Before moving on to solve the third order problem, we would like to emphasize that an analogous weak nonlinear calculation will be performed in solidification (cf., Chapter 6) where we will demonstrate that once the instability sets in, the mean speed of the solidification front always runs ahead of its base value. In an attempt to delineate the key disparity between the two problems, differences will be traced to difference in the interfacial mass balance in one versus the energy balance in the other.

Now to go to third order, we need to solve Eq. (5.29) for \( Z_2 \). Substituting for \( c_2(z = 0) \) and \( U_2 \), the constant term disappears, and we see that \( Z_2 \) can be written as

\[
Z_2 = \hat{Z}_2 \cos(kx) + \hat{Z}_2 \cos(2kx)
\]  

(5.37)

where, while \( \hat{Z}_2 \) cannot be determined at this order, \( \hat{Z}_2 \) is given by
\[
\hat{Z}_2 = \left[ \frac{1}{2} \frac{U_0^2}{U_0 - 4 \mathcal{A} k^2} \right] A^2 \tag{5.38}
\]

Hence, \(\hat{Z}_2\) and \(A\) carry on to third order.

**The Third Order Problem**

The equations at the third order are given by

\[
\nabla^2 c_3 + U_0 \frac{\partial c_3}{\partial z} = -U_3 \frac{dc_0}{dz} \tag{5.39}
\]

on the domain, \(0 < z < 1, \ 0 < x < W\),

\[
\left[ c_3 + 3Z_1 \frac{dc_2}{dz} + 3Z_2 \frac{d^2 c_0}{dz^2} + Z_3 \frac{d^3 c_0}{dz^3} - 9\mathcal{A}\left( \frac{dZ_1}{dx} \right)^2 \frac{d^2 Z_1}{dx^2} \right] = -\mathcal{A} \frac{d^2 Z_3}{dx^2} - Z_3 \frac{dc_0}{dz} \tag{5.40}
\]

and

\[
\frac{\partial c_3}{\partial z} + U_0 c_3 = U_3 \tag{5.41}
\]

at \(z = 0\),

\[
c_3 = 0 \tag{5.42}
\]

at \(z = 1\), and

\[
\int_{0}^{W} Z_3 \, dx = 0 \tag{5.43}
\]

The sidewall conditions require \(\frac{\partial c_3}{\partial x} = dZ_3/dx = 0\) at \(x = 0\) and at \(x = W\). Again, \(c_3\),

like \(c_1\) and \(c_2\) is only a function of \(z\), and it is given by

\[
c_3 = U_3 [z - 1] e^{-U_0 z} \tag{5.44}
\]

which satisfies Eqs. (5.39), (5.41) and (5.42). This leaves Eqs. (5.40) and (5.43) to determine \(U_3\).
and $Z_3$. Now Eq. (5.40) is a differential equation for $Z_3$. And again, a solvability condition must be satisfied if $Z_3$ is to be solved for. This condition is

$$\int_0^W c_3(z=0) + 3Z_1 \frac{dc_2}{dz}(z=0) + 3Z_1Z_2 \frac{d^2c_0}{dz^2}(z=0) + Z_1^3 \frac{d^3c_0}{dz^3}(z=0) - 9\mathcal{A} \left( \frac{dZ_1}{dx} \right)^2 \frac{d^2Z_1}{dx^2} \cos(kx) \, dx = 0$$

(5.45)

and it is an equation for $A^2$. Substituting our results at orders zero, one and two, we find $A^2$ to be given by

$$A^2 = \frac{6e^{U_0}}{U_0^2 \left[ 3 \left( \frac{3}{2\mathcal{A}} - 1 \right) - U_0 \right]}$$

(5.46)

Ordinarily, $\mathcal{A}$ is of the order of $10^{-9}$, and $U_0$ is of the order of 0.1. Hence $A^2$ is positive and a backward pitchfork is confirmed. The value of $U_3$ can be found in terms of $A^2$ by integrating Eq. (5.40) over $0 < x < W$, and using Eq. (5.43), along with the side wall condition, $dZ_3/dx = 0$ at $x = 0, W$.

We started the nonlinear calculation by guessing the expansion to be $c_L = c_{L0} - \frac{1}{2} e^2$. And the reason we find a pitchfork branching in the case of a one-dimensional rectangle is because at second order, solvability does not determine $A$. This, in turn, is due to the fact that the eigenfunction $\cos(kx)$ satisfies $\int_0^W \cos^3(kx) \, dx = 0$. Had the solvability condition determined $A$ at second order, it would have determined $A = 0$, and the hypothesis of a pitchfork bifurcation would have failed.

If the cross section were a two-dimensional rectangle, a pitchfork would also have been found due to $\int_0^W \int_0^W \cos^3(kx) \cos^3(ky) \, dx \, dy = 0$. Indeed a two-dimensional rectangle, which is thin
enough such that there is no \( y \)-variation, reduces to the one-dimensional case presented above. But there is no reason to believe that an eigenfunction \( f \) of the Laplacian operator, \( \nabla^2 \), on an arbitrary cross section, satisfying Neumann conditions at the edges, should satisfy the condition
\[
\iint_{\text{Area}} f^3 dA = 0.
\]
Hence there is reason to imagine that for some cross section, we can determine the value of \( A \) to be zero at second order, whence we will have to choose a different expansion, and the branching will not be a pitchfork. To see this, we work out the case of a circular cross section with axisymmetric disturbances.

**Circular Cross Section with Axisymmetric Disturbances**

Now let the precipitation cell have a circular cross section of radius \( R \). To demonstrate the existence of a transcritical bifurcation, we will focus our attention on axisymmetric displacements, which may not be the most dangerous; a more general case allowing for the non-axisymmetric disturbances is also very interesting and it is discussed in the endnote to this chapter.

Since the base state variables depend only on \( z \), the base state remains the same as it was in the case of a rectangular cross section. The perturbation eigenvalue problem is nearly as it was before, only the curvature is a little different, hence the equilibrium condition at \( z = 0 \) is now
\[
c_1 = -\mathcal{A} \frac{1}{r} \frac{d}{dr} \left( r \frac{dZ_1}{dr} \right) - Z_1 \frac{dc_0}{dz}
\]  
where the \( \theta \)-dependence of the variable \( Z_1 \) has been ignored. The fixed volume condition is now given by
\[
\int_0^R Z_1 r dr = 0
\]  
and the sidewall conditions require that \( \partial c/\partial r \) and \( dZ/dr \) vanish at \( r = R \), whence
\[
\frac{\partial c_i}{\partial r} = 0 \text{ and } \frac{dZ_i}{dr} = 0 \text{ at } r = R
\]  
(5.49)

The remaining equations lead, as before, to \( c_i = 0 \), whence Eq. (5.47) has the solution

\[
Z_i = A J_0(kr)
\]  
(5.50)

where \( k \) can be any positive root of \( J_i(kR) = 0 \), and where the neutral curve is again given by \( U_0 = \mathcal{A} k^2 \). Hence, given \( R \), the critical value of \( U_0 \) is determined by the smallest positive root of \( J_i(kR) = 0 \), \( k = 0 \) being ruled out by Eq. (5.48).

Again, we start with the guess that the steady branches leave the critical point as

\[
c_L = c_{L_0} + \frac{1}{2} \varepsilon^2.
\]

Then using the expansions given in Eqs. (5.19) and (5.20) we find at first order that \( c_i = 0 \), \( U_i = 0 \), and \( Z_i = A J_0(kr) \). At second order, the solvability condition is not satisfied unless \( A^3 \) is zero, and therefore \( Z_i \) is zero. And going to higher orders, \( Z_2 \), \( Z_3 \) all turn out to be zero, indicating that our original guess for expansion of \( c_L \) was incorrect, and also indicating that the expansion

\[
c_L = c_{L_0} + \varepsilon
\]  
(5.51)

will work out.

Introducing \( \varepsilon \) as \( c_L - c_{L_0} \), and retaining Eqs. (5.19) and (5.20), the eigenvalue problem remains as before. It is written holding \( U = U_0 \), and it gives us the critical value of \( U_0 \) in terms of \( k^2 \), again \( U_0 = \mathcal{A} k^2 \) where the subscript zero henceforth denotes critical values. The surface normal vector is now given by

\[
\mathbf{n} = \frac{-Z_r \hat{i} + \hat{j}}{\sqrt{Z_r^2 + 1}}
\]

Then observing that the denominator \( \sqrt{Z_r^2 + 1} \) cancels from both sides of Eq. (5.3), only the numerator of \( \mathbf{n} \cdot \mathbf{U} \) is needed, and its expansion is
given by Eqs. (5.19). This leads to the problems at first and higher orders in \( \varepsilon \), and we solve them as \( c_\varepsilon \) increases by \( \varepsilon \) beyond its critical value.

**The First Order Problem**

The first order problem is

\[
\nabla^2 c_1 + U_0 \frac{\partial c_1}{\partial z} = -U_1 \frac{dc_0}{dz} \tag{5.52}
\]

on the domain, \( 0 < z < 1 \),

\[
c_1 = -A \frac{1}{r} \frac{d}{dr} \left( r \frac{dZ_1}{dr} \right) - Z_1 \frac{dc_0}{dz} \tag{5.53}
\]

and

\[
\frac{\partial c_1}{\partial z} + U_0 c_1 = U_1 \tag{5.54}
\]

at \( z = 0 \),

\[
c_1 = 1 \tag{5.55}
\]

at \( z = 1 \), and

\[
\int_0^R Z_1 r dr = 0 \tag{5.56}
\]

The sidewall conditions require that \( \frac{\partial c_1}{\partial r} \) and \( dZ_1/dr \) vanish at \( r = R \). Again, \( c_1 \) can depend at most on \( z \) and it is given by

\[
c_1 = \left[ U_1 \left[ z - 1 \right] + e^{U_0} \right] e^{-U_0 z} \tag{5.57}
\]

which satisfies Eqs. (5.52), (5.54) and (5.55). Eqs. (5.53) and (5.56) then determine both \( U_1 \) and \( Z_1 \). Multiplying Eq. (5.53) by \( r \), integrating the result over \( 0 \leq r \leq R \), and using Eq. (5.56) along with the side wall condition, \( dZ_1/dr = 0 \) at \( r = R \), there obtains
\[ \int_0^r c_1(z=0) r \, dr = 0 \quad (5.58) \]

whence
\[ U_1 = e^{U_0} \quad (5.59) \]

whereupon \( U_1 \) is no longer zero and the expression for \( c_1 \) can be simplified to
\[ c_1 = z e^{U_0} e^{-U_0 z} \quad (5.60) \]

The fact that \( c_1 \) and \( U_1 \) are not zero is another sign that a circular cross section differs from a rectangular cross section. However, \( c_1 \) is zero at \( z=0 \), and the solution to Eq. (5.53) is
\[ Z_1 = A J_0(kr) \quad (5.61) \]

but \( A \) cannot be determined at first order, and we turn to the second order problem.

**The Second Order Problem**

At second order, we must solve

\[ \nabla^2 c_2 + U_0 \frac{\partial c_2}{\partial z} = -U_2 \frac{dc_0}{dz} - 2U_1 \frac{\partial c_1}{\partial z} \quad (5.62) \]

on the domain, \( 0 < z < 1 \),

\[ \left[ c_2 + 2Z_1 \frac{dc_0}{dz} + Z_1^2 \frac{d^2 c_0}{dz^2} \right] = -A \frac{1}{r} \frac{d}{dr} \left( r \frac{dZ_2}{dr} \right) - Z_2 \frac{dc_0}{dz} \quad (5.63) \]

and

\[ \frac{\partial c_2}{\partial z} + U_0 c_2 = U_2 \quad (5.64) \]

at \( z = 0 \),

\[ c_2 = 0 \quad (5.65) \]

at \( z = 1 \), and
\[
\int_0^R Z_2 r \, dr = 0 \tag{5.66}
\]

The sidewall conditions require \( \partial c_2 / \partial r = dZ_2 / dr = 0 \) at \( r = R \). Solving Eqs. (5.62), (5.64) and (5.65), we get

\[
c_2 = \left[ z \left( -ze^{2U_0} + U_2 \right) + e^{2U_0} - U_2 \right] e^{-U_0 z} \tag{5.67}
\]

and it remains to solve Eq. (5.63) for \( Z_2 \), while satisfying Eq. (5.66). It is our hope that this will give us the value of \( \mathbf{A} \), as well as the value of \( U_2 \). Now Eq. (5.63) can be solved for \( Z_2 \) if and only if a solvability condition is satisfied. It is

\[
\int_0^R c_2 (z = 0) + 2Z_1 \frac{dc_1}{dz} (z = 0) + Z_1^2 \frac{d^2 c_0}{dz^2} (z = 0) \right] r J_0 (kr) \, dr = 0 \tag{5.68}
\]

and this is an equation for \( \mathbf{A} \). Substituting our results at zeroth and first orders, we get

\[
\mathbf{A} = \left[ \frac{2U_1}{U_0^2} \right] \frac{\int_0^R r J_0^2 (kr) \, dr}{\int_0^R r J_0 (kr) \, dr} \tag{5.69}
\]

whereupon using the formulas given in Table 5.1, we get

\[
\mathbf{A} = \left[ \frac{e^{U_0}}{U_0^2} \right] \frac{J_0^2 (kR)}{0.02} \tag{5.70}
\]

Table 5.1 – Some integrals concerning Bessel’s functions

| \[ \int_0^R r J_0^2 (kr) \, dr = \frac{1}{2} R^2 J_0^2 (kR) \text{ where } J_1 (kR) = 0 \] |
| \[ \int_0^R r J_0^3 (kr) \, dr = R^3 (0.02) \text{ where } J_1 (kR) = 0 \] |

Hence the branching to the new steady state is not a pitchfork; it is transcritical.
Multiplying Eq. (5.63) by \( r \), integrating the result over \( 0 \leq r \leq R \), and using the constant volume conditions, Eqs. (5.48) and (5.66), and side wall condition, \( dZ_2/dr = 0 \) at \( r = R \), we get

\[
c_2(z = 0) \frac{R^2}{2} = U_0^2 \int_0^R rZ_1^2 dr
\]

whence

\[
U_2 = e^{2U_0} - U_0^2 J_0^2 (kR) A^2
\]  

(5.72)

The first term on the right hand side, \( e^{2U_0} \), is what \( U_2 \) would be if the base solution obtains at the new value of \( c_L \). The second term is the correction corresponding to a curved front. It is again negative, as it was for a rectangular cross section, and we conclude again that the mean speed of the interface runs behind its base value.

What we have found so far is this: the nature of the branching to non-planar steady states is ordinarily a pitchfork for a rectangular cross section, while it is transcritical in the case of a circular cell with axisymmetric disturbances. The cross section dependence raises the question: How can we predict the nature of the branching for an arbitrary cross section? It is to this question that we now turn.

**A Cross Section with an Arbitrary Shape**

Let the cell have an arbitrary cross section, but we will work in Cartesian coordinates. The nonlinear equations, Eqs. (1-4) remain the same, but the fixed volume condition is now given by

\[
\iint_S Z(x, y) dx dy = 0
\]

(5.73)

where \( z = Z(x, y) \) defines the shape of the solid-liquid interface, and where the integral is carried out over the cross section \( S \). The mean curvature of the surface \( z = Z(x, y) \) is given by
\[ 2H = \left[1 + Z_y^2\right]Z_{xx} - 2Z_xZ_yZ_{xy} + \left[1 + Z_x^2\right]Z_{yy} \left[1 + Z_x^2 + Z_y^2\right]^{3/2} \]  
(5.74)

The sidewall conditions are now

\[ \vec{p}.\nabla c = 0 \quad \text{and} \quad \vec{p}.\nabla Z = 0 \quad \text{on} \ \partial S \]  
(5.75)

where \( \partial S \) denotes the boundary of \( S \), and \( \vec{p} \) denotes the outward normal to \( \partial S \).

The solution to base state equations, which depends only on \( z \), is given by Eqs. (5.6) and (5.7).

**The Eigenvalue Problem at Neutral Conditions**

The eigenvalue problem at neutral condition does not change much. It is given by

\[ \nabla^2 c_i + U_0 \frac{\partial c_i}{\partial z} = 0 \]  
(5.76)

on the domain, \( 0 < z < 1 \), where, at \( z = 0 \),

\[ c_i + Z_1 \frac{dc_i}{dz} = -A\nabla^2_i Z_i = -A \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right] Z_i \]  
(5.77)

and

\[ \frac{\partial c_i}{\partial z} + U_0 c_i = 0 \]  
(5.78)

must hold, and where, at the reservoir, \( z = 1 \),

\[ c_i = 0 \]  
(5.79)

must hold. This problem has solutions of the form

\[ c_i = \hat{c}_i(z) f(x,y) \quad \text{and} \quad Z_i = A f(x,y) \]  
(5.80)

where \( f(x,y) \) is an eigenfunction of \( \nabla^2_H \) on \( S \) subject to Neumann sidewall conditions. It satisfies
\[ \nabla^2 f(x,y) = -k^2 f(x,y) \text{ on } S; \quad \bar{p} \nabla f = 0 \text{ on } \partial S \quad (5.81) \]

Hence, denoting the eigenvalue by \(-k^2\), the solution \( f = \text{const.}, k^2 = 0 \) is ruled out by the condition

\[ \int_S Z_1(x,y) \, dx \, dy = 0 \quad (5.82) \]

Eqs. (5.76), (5.78) and (5.79) imply that \( c_1 \) must be zero, and therefore \( Z_1 \) must satisfy

\[ 0 = \mathcal{A} \nabla^2 Z_1 + \frac{dc_0}{dz}(z = 0) Z_1 \quad (5.83) \]

where \( \frac{dc_0}{dz}(z = 0) = U_0 \). And we find that the neutral curve is again given by \( U_0 = \mathcal{A} k^2 \). It holds regardless of the shape of the cross section. But the allowable values of \( k^2 \) do depend on the geometry. Again, the lowest positive value of \( k^2 \) determines the critical speed of the front.

Let us begin by assuming the branching to be a pitchfork, and expanding \( c_L \) as \( c_L = -\frac{1}{2} \varepsilon^2 \).

The expansions for \( U \) and \( Z \) are given by Eqs. (5.19) and (5.20) and we move on to solve the problem at the first and higher orders to find the steady subcritical solution.

**The First Order Problem**

The first order problem is given by

\[ \nabla^2 c_1 + U_0 \frac{\partial c_1}{\partial z} = -U_1 \frac{dc_0}{dz} \quad (5.84) \]

on the domain, \( 0 < z < 1 \),

\[ c_1 = -\mathcal{A} \nabla^2 Z_1 - \frac{dc_0}{dz} Z_1 \quad (5.85) \]

\[ \frac{\partial c_1}{\partial z} + U_0 c_1 = U_1 \quad (5.86) \]

and
\[
\iint_{\delta} Z_1(x, y) \, dx \, dy = 0 \tag{5.87}
\]

at \( z = 0 \), and

\[ c_i = 0 \tag{5.88} \]

at \( z = 1 \).

Eqs. (5.84), (5.86) and (5.88) have the solution

\[ c_i = U_1[z - 1] e^{-U_0 z} \tag{5.89} \]

Using this in Eq. (5.85), we find from Eq. (5.87) that \( U_1 \) must be zero, and hence \( c_i \) must be zero, whereupon \( Z_1 \) is given by

\[ Z_1 = A f(x, y) \tag{5.90} \]

where \( f(x, y) \) is an eigenfunction of \( \nabla_H^2 \) on \( S \), satisfying Neumann conditions on \( \partial S \) and it corresponds to the critical, or lowest, value of \( k^2 \), with \( k^2 = 0 \) ruled out. We go to second order to find the value of \( A \) but we already see that the speed of the interface does not change at order \( \varepsilon \) upon decreasing \( c_z \) from \( c_{i_0} \) by \( \frac{1}{2} \varepsilon^{-2} \).

**The Second Order Problem**

At second order, we must determine \( c_2, Z_2 \) and \( U_2 \), and the unknown \( A \) which carries over from first order. The second order problem is

\[ \nabla^2 c_2 + U_0 \frac{\partial c_2}{\partial z} = -U_2 \frac{dc_0}{dz} \tag{5.91} \]

on the domain, \( 0 < z < 1 \),

\[ c_2 + Z_1^2 \frac{d^2 c_0}{dz^2} = -\mathcal{A} \nabla_H^2 Z_2 - \frac{dc_0}{dz} Z_2 \tag{5.92} \]
\[
\frac{\partial c_2}{\partial z} + U_0 c_2 = U_2
\]  
(5.93)

and

\[
\iint_S Z_2(x, y) \, dx \, dy = 0
\]  
(5.94)

at \( z = 0 \), and

\[ c_2 = -1 \]  
(5.95)

at \( z = 1 \). Solving Eqs. (5.91), (5.93) and (5.95), we get

\[ c_2 = \left[ U_2 \left[ z - 1 \right] - e^{U_0} \right] e^{-U_0z} \]  
(5.96)

and it remains to solve Eqs. (5.92) and (5.94) for \( Z_2 \). To find \( Z_2 \), a solvability condition must be satisfied. It is

\[
\iint_S \left[ c_2(z = 0) + Z_1^2 \frac{d^2 c_0}{dz^2}(z = 0) \right] f(x, y) \, dx \, dy = 0
\]  
(5.97)

whence we have

\[ A^2 \iint_S f^3(x, y) \, dx \, dy = 0 \]  
(5.98)

At this point, there are two possibilities. One possibility is that the integral vanishes, whereupon solvability is satisfied no matter the value of \( A \). And as in the case of a rectangular cross section, we go on to third order to find \( A \). This is the pitchfork case. The second possibility is that the integral does not vanish and we must conclude that \( A \) is zero, whence the branching is not a pitchfork and we must propose a new expansion in \( \varepsilon \), cf., [29].
Cross Sections on which the Integral Does Not Vanish

If the integral \( \iint_S f^3(x, y) \, dx \, dy \) is not zero, as in the case of a circular cross section, we assume the branching is transcritical and propose to move beyond critical via the expansion

\[
c_L = c_L_0 + \varepsilon \quad (5.99)
\]

The base problem and the eigenvalue problem remain unchanged. But the first order problem is now

\[
\nabla^2 c_1 + U_0 \frac{\partial c_1}{\partial z} = -U_1 \frac{dc_0}{dz} \quad (5.100)
\]
on the domain, \( 0 < z < 1 \),

\[
c_1 = -\mathcal{A} \nabla^2 Z_1 - \frac{dc_0}{dz} Z_1 \quad (5.101)
\]

\[
\frac{\partial c_1}{\partial z} + U_0 c_1 = U_1 \quad (5.102)
\]

and

\[
\iint_S Z_1(x, y) \, dx \, dy = 0 \quad (5.103)
\]
at \( z = 0 \), and

\[
c_1 = 1 \quad (5.104)
\]
at \( z = 1 \). Eqs. (5.100), (5.102) and (5.104) have the solution

\[
c_1 = \left[ U_1 \left[ z - 1 \right] + e^{U_0 z} \right] e^{-U_0 z} \quad (5.105)
\]
whereupon integrating Eq. (5.101) over \( S \) and using Eq. (5.103), we have

\[
U_0 = \mathcal{A} k^2 \quad (5.106)
\]
and \( c_1 \) simplifies to
\[ c_i = ce^{i\phi}e^{-U_0}\zeta \quad (5.107) \]

whence \( c_1 \) must be zero at \( z = 0 \), and \( Z_1 \) is then

\[ Z_1 = A f(x, y) \quad (5.108) \]

To find \( A \) we go to second order, where we must solve

\[ \nabla^2 c_2 + U_0 \frac{\partial c_2}{\partial z} = -U_2 \frac{dc_0}{dz} - 2U_1 \frac{\partial c_1}{\partial z} \quad (5.109) \]

on the domain, \( 0 < z < 1 \),

\[ c_2 + 2Z_1 \frac{dc_1}{dz} + Z_1^2 \frac{d^2 c_0}{dz^2} = -A \nabla^2 Z_2 - \frac{dc_0}{dz} Z_2 \quad (5.110) \]

\[ \frac{\partial c_2}{\partial z} + U_0 c_2 = U_2 \quad (5.111) \]

and

\[ \iint_{S} Z_2(x, y) dx dy = 0 \quad (5.112) \]

at \( z = 0 \), and

\[ c_2 = 0 \quad (5.113) \]

at \( z = 1 \). Eqs. (5.109), (5.111) and (5.113) are satisfied by

\[ c_2 = \left[ z - ze^{2U_0} + U_2 \right] \left[ e^{2U_0} - U_2 \right] e^{-U_0\zeta} \quad (5.114) \]

and it remains to solve Eq. (5.110) for \( Z_2 \), while satisfying Eq. (5.112). The solvability condition for Eq. (5.110) is

\[ \iint_{S} \left[ c_2(z = 0) + 2Z_1 \frac{dc_1}{dz}(z = 0) + Z_1^2 \frac{d^2 c_0}{dz^2}(z = 0) \right] f(x, y) dx dy = 0 \quad (5.115) \]

This is an equation for \( A \) in which \( U_2 \) does not appear and we find
\[ A = \left[ \frac{2e^{\psi_0}}{U_0^2} \right] \left( \iint_S f^2(x, y) \, dx \, dy \right) \] (5.116)

whence a transcritical bifurcation is verified.

The value of \( U_2 \) obtains upon integrating Eq. (5.110) over \( S \) to get

\[ U_2 = e^{2\psi_0} - U_0^2 A^2 \frac{1}{S} \iint_S f^2(x, y) \, dx \, dy \] (5.117)

where the first term on the right hand side gives the value \( U_2 \) if the base solution persists at the new value of \( c_L \). The second term is a correction due to the displacement of the front. It is always negative, predicting a slow down.

Thus if the integral \( \iint_S f^3(x, y) \, dx \, dy \) is not zero, the branching is transcritical and the front slows down.

**Cross Sections on which the Integral Vanishes**

If we have a cross section where the integral \( \iint_S f^3(x, y) \, dx \, dy \) is zero, then \( A \) cannot be determined at second order, but the solvability condition for Eq. (5.92) is satisfied no matter the value of \( A \).

Our job then is to solve Eq. (5.92) for \( Z_2 \) and then go to third order hoping to determine \( A \). To do this we first obtain \( U_2 \) by integrating Eq. (5.92) over \( S \), using \( Z_1 = A f(x, y) \),

\[ c_2(z = 0) = -U_2 - e^{\psi_0}, \text{Neumann side wall conditions and Eq. (5.94). The result is} \]

\[ U_2 = -e^{\psi_0} - U_0^2 A^2 \frac{1}{S} \iint_S f^2(x, y) \, dx \, dy \] (5.118)

whence we have
\[ c_2 (z = 0) = U_0^2 A^2 \int_\mathcal{S} \frac{1}{S} f^2 (x, y) \, dx \, dy \]  
\hspace{1cm} \text{(5.119)}

and Eq. (5.92) is then

\[ -\frac{U_0^2 A^2}{\mathcal{A}} \left[ \int_\mathcal{S} \frac{1}{S} f^2 (x, y) \, dx \, dy - f^2 (x, y) \right] = \left[ \nabla_n^2 + k^2 \right] Z_2 \]  
\hspace{1cm} \text{(5.120)}

whereupon \( Z_2 \) can be obtained as a series in the eigenfunctions of \( \nabla_n^2 \) on \( S \) subject to Neumann boundary conditions, viz.,

\[ Z_2 = B f + \sum_{n=2}^\infty B_n f_n \]  
\hspace{1cm} \text{(5.121)}

where the coefficients \( B_n \) depend on the expansion of the left hand side of Eq. (5.121) and where the eigenfunction 1 does not appear.

The equations to be solved at third order are

\[ \nabla^2 c_3 + U_0 \frac{\partial c_3}{\partial z} = -U_3 \frac{dc_0}{dz} \]  
\hspace{1cm} \text{(5.122)}

on the domain, \( 0 < z < 1 \),

\[ c_3 + 3Z_1 \frac{dc_2}{dz} + 3Z_2 Z_2 \frac{d^2 c_0}{dz^2} + Z_1^3 \frac{d^3 c_0}{dz^3} + \mathcal{A}N (Z_1) = -\mathcal{A} \nabla_n^2 Z_3 = \frac{dc_0}{dz} Z_3 \]  
\hspace{1cm} \text{(5.123)}

\[ \frac{\partial c_2}{\partial z} + U_0 c_3 = U_3 \]  
\hspace{1cm} \text{(5.124)}

and

\[ \int_\mathcal{S} Z_3 (x, y) \, dx \, dy = 0 \]  
\hspace{1cm} \text{(5.125)}

at \( z = 0 \), and

\[ c_3 = 0 \]  
\hspace{1cm} \text{(5.126)}
at $z = 1$ where $c_1 = 0 = U_1$ has been used and where $N(Z_1)$ denotes the nonlinear part of $2H_3$. It depends on $Z_1$ and introduces the factor $A^3$.

Eqs. (5.122), (5.124) and (5.126) can be solved for $c_3$, viz.,

$$c_3 = U_3 \left[ z - 1 \right] e^{-U_0 z} \quad \text{(5.127)}$$

leaving Eqs. (5.123) and (5.125) to be solved for $U_3$ and $Z_3$ where $Z_3$ can be obtained if and only of a solvability condition is satisfied. It is

$$\int c_3 (z = 0) + 3Z_1 \frac{d^2 c}{dz^2} (z = 0) + 3Z_1 Z_2 \frac{d^3 c_0}{dz^3} (z = 0) + Z_3 \frac{d^3 c_0}{dz^3} (z = 0) + AN (Z_1) \int f(x, y) dxdy = 0 \quad \text{(5.128)}$$

and it is an equation for $A^2$. If $A^2$ is not zero, the branching is a pitchfork, as assumed, and if $A^2$ is positive the pitchfork is backward, as assumed.

The equation for $A^2$ can be simplified somewhat without making $S$ definite. Using

$$Z_1 = A f(x, y) \quad \text{and, at } z = 0, \quad \frac{d^2 c_0}{dz^2} = -U_0^2, \quad \frac{d^3 c_0}{dz^3} = U_0^3 \quad \text{and} \quad \frac{dc_0}{dz} = [1 + U_0]U_2 + U_0 e^{U_0}, \quad \text{we have}$$

$$3A \left[ [1 + U_0]U_2 + U_0 e^{U_0} \right] \iint_S f^2 dxdy - 3U_0^2 A \iint_S f^2 Z_{2, \text{particular}} dxdy + A^3 U_0^3 \iint_S f^4 dxdy$$

$$+ AN \iint_S N (Z_1) f dxdy = 0 \quad \text{(5.129)}$$

where $Z_{2, \text{particular}}$ is a multiple of $A^2$, where $N(Z_1)$ is a multiple of $A^3$ and where

$$[1 + U_0]U_2 + U_0 e^{U_0} \quad \text{is given by} \quad -e^{U_0} - [1 + U_0]U_0^2 \frac{1}{S} \iint_S f^2 (x, y) dxdy. \quad \text{Hence the term in } A$$

does not vanish and a pitchfork is confirmed.

Thus if the integral $\iint_S f^3 (x, y) dxdy$ is zero, the branching is pitchfork and the front slows down.
An Equilateral Triangular and a Regular Hexagonal Cross Section

We explore two other cross sections: an equilateral triangle and a regular hexagon. Appendices C.1 and C.2 give the solution to the eigenvalue problem, Eq. (5.81), for these geometries. In the case of a regular hexagon, we find \( \iint_S f^3(x,y) \, dx \, dy = \frac{9\sqrt{3}}{4} L^2 \neq 0 \), whence the branching is transcritical. The branching is found to be transcritical on an equilateral triangle as well.

Concluding Remarks

We have given a condition that determines the nature of branching of a steady planar crystal-solution interface to a non-planar shape for an arbitrary cross section of a precipitation cell. Given any cross section of the cell, if one can find the solution \( f(x,y) \) to the eigenvalue problem, Eq. (5.81), then the nature of the branching to the steady non-planar solution can be predicted by finding whether or not the integral \( \iint_S f^3(x,y) \, dx \, dy \) is zero. The branching is usually a pitchfork if this integral is zero; if not, we expect a transcritical bifurcation. We find that for a rectangular cross section, the branching is ordinarily a backward pitchfork; it is transcritical for all other shapes that we have studied: circular (symmetric disturbances), triangular (equilateral), and hexagonal (regular). And it is our belief that transcritical bifurcation is what will be found in the case of a more general cross section. We also find that the surface speed always decreases compared to what its base value would have been.

Endnote 1: A Circular Cross Section with the Possibility of Non-symmetric Disturbances

Let us consider the possibility of non-symmetric displacements. If non-symmetric disturbances are admitted, the critical value of \( k^2 \) is given by the smallest positive root of \( J_1(kR) = 0 \) (5.130).
and this eigenvalue corresponds to the eigenfunction

\[ f = J_1(kr) \cos \theta \]  \hspace{1cm} (5.131)

where

\[ \int_0^\infty 2\pi \int_0^\pi r J_1^2(kr) \cos \theta drd\theta = 0 \]  \hspace{1cm} (5.132)

Hence the branching must be a pitchfork. Because non-symmetric disturbances are more dangerous, the branching in the case of a circular cross section must be a pitchfork.
CHAPTER 6
SOLIDIFICATION: WEAK NONLINEAR ANALYSIS

Introduction

We concluded in Chapter 3 that a steady planar interface becomes unstable and changes to a non-planar shape as the undercooling in the subcooled liquid is increased beyond a critical value. Linear stability methods were used to analyze the shapes of the various disturbance growth curves. In addition, the shape of the neutral curves showed that as many as three neutral points could be obtained, each depending upon the longitudinal and transverse and sizes of the solid and liquid phases. The occurrence of three possible neutral points was explained in terms of longitudinal diffusion, transverse diffusion and surface tension.

In this chapter, we are interested in examining the post-onset regime in solidification of a pure material. We shall use the techniques learned from our analysis of the precipitation problem in the vicinity of the instability. Again, our goal is to understand the early stages of the growth of surface roughness. The notation used in this chapter is the same as that used in Chapter 3. The liquid phase sink temperature, $T_L$, is taken to be the control variable. The idea is to imagine running a series of experiments in which $T_L$ is decreased to, and just below its critical value. We try to answer questions like: What is the effect on the mean front speed as $T_L$ just crosses its critical value? In other words, does the front speed up or slow down compared to its base value? Is the branching to the new non-planar solution a forward or a backward pitchfork?

We will consider three major cases. First, we consider a case where the latent heat is rejected only though the subcooled liquid while the solid phase is held at the melt temperature; both phases are taken to be of finite extent. Second, we consider a simplification of the first case where the solid phase is taken to be of infinite extent. This may be useful when the solid sink is far away from the interface. Third, we consider the most general case where the latent heat is
rejected though the frozen solid as well as the subcooled liquid and both phases are taken to be of finite extent. In all of these cases, we begin by presenting the nonlinear equations in scaled form. We work with a rectangular cross section and all derivations are done in Cartesian coordinates. We first work out the base solution and the solution to the perturbation eigenvalue problem to find the critical value of $T_L$. Having found the critical value of $T_L$, we look for steady solutions near this critical point by going to second and third orders in the amount by which $T_L$ is decreased from its critical value. All derivations are done in a manner similar to Chapter 5. Therefore the details of the derivations will not be presented in their entirety as they are straightforward enough that a reader can easily reproduce them. Our emphasis will be to point out important differences from the precipitation problem.

In all of these cases we will find that the mean speed of the surface is higher than its base speed. This is to say that once the instability sets in, the surface speeds up compared to its base value. This result is striking in its contrast to what was obtained in Chapter 5 for precipitation, where we found that the surface unconditionally slows down. The obvious question is: Can we explain this basic difference of a “speed-up” in solidification versus a “slow-down” in precipitation? In our quest to answer this question, we will go to a yet simpler model in a fourth case where the solid phase is completely ignored. It is as if the solid phase is there only for the sake of having an interface, but it is ignored for all other purposes such as transport etc. One might also look at it as if the solid is being chopped off as soon as it forms. We do not learn anything new, and again the front speeds up compared to its base value. But the model (although an artificial one) is now as close as one can get to the precipitation model, and the key disparity between the two problems becomes clear. We learn that the difference is posed by the heat balance (in solidification) versus mass balance (in precipitation) at the interface. And this is what
leads to the essential dissimilarity between the two problems regarding the correction to the front speed.

Now in order to learn the nature of the branching to the new non-planar solution, one must go to third order in the amount by which the undercooling in the subcooled liquid is increased. In general, we will find that one can obtain a forward as well as a backward pitchfork depending on the input parameters. We will identify regions in the input parameter space where the branching is forward and regions where it is backward.

To do all of this, let us start by performing a weak nonlinear analysis for a case where the frozen solid is maintained at its melt temperature and the latent heat is rejected only to the subcooled liquid, both phases being of finite extent.

**Case 1: Latent Heat Rejected Only to the Subcooled Liquid, Both Phases of Finite Extent**

![Diagram](image)

**Figure 6.1 – A moving solidification front**

The sketch given in Figure 6.1 fixes the principal ideas. The liquid and solid phase depths are maintained constant and all equations are written in a frame moving with a constant velocity,
\[ \vec{U} = U \vec{k} \] where \( U \) is the base state speed of the solidification front. All variables introduced are moving-frame variables; the superscript * denotes a liquid phase variable. All lengths are scaled by \( S \), the depth of the solid phase. All speeds are scaled by \( \alpha / S \), where \( \alpha \) is the thermal diffusivity of the solid phase. Temperature is measured from a reference point corresponding to \( T_M \), and it is scaled by \( \alpha L_H / \lambda \), where \( \lambda \) is the thermal conductivity of the solid phase, and \( L_H \) denotes the latent heat of solidification per unit volume of the solid, viz., \( T_{scaled} = \frac{T_M - T}{\alpha L_H / \lambda} \). Then, the scaled temperature in the solid phase must satisfy

\[ \nabla^2 T + U \frac{\partial T}{\partial z} = 0 \] (6.1)

for \(-1 < z < Z\), while in the liquid phase

\[ \nabla^2 T^* + U \frac{\partial T^*}{\partial z} = 0 \] (6.2)

must hold for \( Z < z < L \). Two demands must be met along the solid-liquid interface, viz., along \( z = Z(x) \). First, phase equilibrium, taking into account the curvature due to the interface, requires

\[ T = -A \cdot 2H = T^* \] (6.3)

where \( A \) denotes \( \left[ \frac{\gamma \lambda}{\alpha L_H^2 S} \right] T_M \), a dimensionless parameter introduced by our scaling, and where \( \gamma \) denotes the surface tension. Second, the rate at which the latent heat is being released due to the motion of the solidification front must be the same as the rate at which heat is being conducted away from the interface, viz.,

\[ \vec{n} \cdot \nabla T - \vec{n} \cdot \nabla T^* = -\vec{n} \cdot \vec{U} \vec{k} \] (6.4)
Far-field conditions are given by

\[ T(z = -1) = 0 \]  \hspace{1cm} (6.5) \]

and

\[ T(z = L) = T_L \]  \hspace{1cm} (6.6) \]

Side wall conditions are Neumann, i.e.,

\[ \frac{\partial T}{\partial x}(x = 0, W) = \frac{\partial T^*}{\partial x}(x = 0, W) = \frac{\partial Z}{\partial x}(x = 0, W) = 0. \]

Finally, the volume of the subcooled liquid must be maintained fixed, whence

\[ \int_{0}^{W} Z(x) \, dx = 0 \]  \hspace{1cm} (6.7) \]

Notice that these model equations are non-linear as the position of the interface depends upon the temperature gradients there, and these gradients, in turn, depend upon the position and morphology of the interface. This non-linearity forms the heart of the problem without which instability would not be possible.

**The Base Solution**

The base state is one in which the solidification front remains planar and at rest in the moving frame. The base state variables are denoted by the subscript 0, and they satisfy

\[ \frac{d^2 T_0}{dz^2} + U_0 \frac{dT_0}{dz} = 0 \]  \hspace{1cm} (6.8) \]

in the solid phase, \(-1 < z < 0\), \(0 < x < W\), and

\[ \frac{d^2 T^*_0}{dz^2} + U_0 \frac{dT^*_0}{dz} = 0 \]  \hspace{1cm} (6.9) \]

in the liquid phase, \(0 < z < L\), \(0 < x < W\). The equations at the planar interface, \(z = 0\) are given by

\[ T_0 = T^*_0 = 0 \]  \hspace{1cm} (6.10) \]
and

\[
\frac{dT_0}{dz} - \frac{dT^*_0}{dz} = -U_0
\]  

(6.11)

The far-field conditions are given by

\[
T_0(z = -1) = 0
\]  

(6.12)

and

\[
T^*_0(z = L) = T_L
\]  

(6.13)

Then, a solution to Eqs. (6.8-6.13) is given by

\[
T_0(z) = 0
\]  

(6.14)

\[
T^*_0(z) = 1 - e^{-U_0 z}
\]  

(6.15)

where \(U_0\) is given by

\[
U_0 = -\ln(1 - T_L)
\]  

(6.16)

whence \(\frac{dT^*_0}{dz}(z = 0) = U_0\), \(\frac{d^2T^*_0}{dz^2}(z = 0) = -U_0^2\), \(\frac{d^3T^*_0}{dz^3}(z = 0) = U_0^3\), \(\frac{d^4T^*_0}{dz^4}(z = 0) = -U_0^4\). Besides

the physical properties, the input variables in the base state are \(S, L,\) and \(T_L\), and the output is \(U_0\).

**The Perturbation Eigenvalue Problem**

On increasing \(T_L\), we expect the planar interface to lose its stability. To determine the

critical value of \(T_L\), let a small disturbance of amplitude \(\varepsilon\) be imposed on the steady base

solution at fixed values of \(T_L\) and \(U_0\), which satisfy Eq. (6.16). Then expanding \(Z, T,\) and \(T^*\),

at \(z = Z(x)\) as

\[
Z = Z_0 + \varepsilon Z_1, \quad Z_0 = 0
\]  

(6.17)
\[ T = T_0 + \varepsilon \left[ T_1 + Z_1 \frac{dT_\theta}{dz} \right] \] (6.18)

and

\[ T^* = T_0^* + \varepsilon \left[ T_1^* + Z_1 \frac{dT_\theta^*}{dz} \right] \] (6.19)

where the term involving the surface displacement, \( Z_1 \), has been introduced so that the perturbation problem can be solved on the reference domain (cf., Appendix B.1). To find the critical base state, we must solve the perturbation eigenvalue problem. It is given by

\[ \nabla^2 T_1 + U_0 \frac{\partial T_1}{\partial z} = 0 \] (6.20)

on the domain, \(-1 < z < 0\), \(0 < x < W\), and

\[ \nabla^2 T_1^* + U_0 \frac{\partial T_1^*}{\partial z} = 0 \] (6.21)

on the domain, \(0 < z < L\), \(0 < x < W\), where, at the base surface \( z = 0 \),

\[ T_1 = -A \frac{d^2 Z_1}{dx^2} - Z_1 \frac{dT_\theta/}{dz} \] (6.22)

\[ \left[ T_1 - T_1^* \right] + Z_1 \left[ \frac{dT_\theta/}{dz} - \frac{dT_\theta^*}{dz} \right] = 0 \] (6.23)

and

\[ \left[ \frac{\partial T_1}{\partial z} - \frac{\partial T_1^*}{\partial z} \right] + Z_1 \left[ \frac{d^2 T_\theta/}{dz^2} - \frac{d^2 T_\theta^*}{dz^2} \right] = 0 \] (6.24)

must hold, and where,

\[ T_1(z = -1) = 0 \] (6.25)

and
The stricken terms are shown to emphasize that for this case the solid temperature is taken to be uniform in the base state. The sidewall conditions require \( \partial T_0 / \partial x = 0 \), \( \partial T^*_0 / \partial x = 0 \) and

\[ dZ_0 / dx = 0 \] at \( x = 0 \) and at \( x = W \). Thus the problem is homogeneous in \( T_0, T^*_0 \) and \( Z_1 \), and it has solutions of the form

\[
T_0 = \hat{T}_i(z) \cos(kx), \quad T^*_0 = \hat{T}_i(z) \cos(kx) \quad \text{and} \quad Z_1 = A \cos(kx)
\]

which satisfy the side wall conditions so long as \( k = n\pi/W \), \( n = 1, 2, \ldots \), where \( k \) is the wave number of the disturbance. \( n = 0 \) is ruled out by the condition

\[
\int_0^W Z_1 dx = 0
\]

The expansions presented above give the equations for \( \hat{T}_i, \hat{T}^*_i, \hat{Z}_1 \). They are

\[
\left[ \frac{d^2}{dz^2} - k^2 \right] \hat{T}_i + U_0 \frac{d\hat{T}_i}{dz} = 0
\]

in the solid phase, \(-1 < z < 0\), \( 0 < x < W \), and

\[
\left[ \frac{d^2}{dz^2} - k^2 \right] \hat{T}^*_0 + U_0 \frac{d\hat{T}^*_0}{dz} = 0
\]

in the liquid phase, \( 0 < z < L \), \( 0 < x < W \),

\[
\hat{T}_i = \left[ Ak^2 - \frac{dT_0}{dz} \right] \hat{Z}_1
\]

\[
\left[ \hat{T}_i - \hat{T}^*_i \right] + \hat{Z}_1 \left[ \frac{dT_0}{dz} - \frac{dT^*_0}{dz} \right] = 0
\]

and
\[
\frac{d\hat{T}_i}{dz} - d\hat{T}_i^* = 0
\]
\[
\frac{d^2\hat{T}_0}{dz^2} - d^2\hat{T}_0^* = 0
\]  \(6.34\)

at \( z = 0 \),
\[
\hat{T}_i(z = -1) = 0
\]  \(6.35\)

and
\[
\hat{T}_i^*(z = L) = 0
\]  \(6.36\)

Defining \( m_z = \frac{-U_0 \pm \sqrt{U_0^2 + 4k^2}}{2} \), a solution to Eqs. (6.29-6.33, 6.35, 6.36) is given by
\[
\hat{T}_i(z) = A_1 \left[ e^{m_z z} - e^{[m_z - m_\mu]z} e^{m_\mu z} \right] = \left[ \frac{\mathcal{A}k^2 - \frac{dT_0}{dz}(z = 0)}{1 - e^{[m_z - m_\mu]z}} \right] \left[ e^{m_z z} - e^{[m_z - m_\mu]z} e^{m_\mu z} \right] Z_1
\]  \(6.37\)

and
\[
\hat{T}_i^*(z) = A_1' \left[ e^{m_z z} - e^{[m_z - m_\mu]z} e^{m_\mu z} \right] = \left[ \frac{\mathcal{A}k^2 - \frac{dT_0^*}{dz}(z = 0)}{1 - e^{[m_z - m_\mu]z}} \right] \left[ e^{m_z z} - e^{[m_z - m_\mu]z} e^{m_\mu z} \right] Z_1
\]  \(6.38\)

We can then turn to Eq. (6.34), which gives us
\[
-\left[ \mathcal{A}k^2 \right] M - \left[ -\mathcal{A}k^2 + U_0 \right] N - U_0^2 = 0
\]  \(6.39\)

where \( M = \frac{m_\mu - m e^{m_\mu}}{1 - e^{m_\mu}} > 0 \) and \( N = \frac{m_\mu - m e^{[m_\mu - m_\mu]z}}{1 - e^{[m_\mu - m_\mu]z}} < 0 \). Figure 6.2 shows the corresponding neutral curve. The graph of \( U_0 \) versus \( k^2 \) is nearly a straight line. In fact it is easy to prove the following asymptotic limits for small values of \( k^2 \): For small \( k^2 \), Eq. (6.39) may be simplified to
get $U_0 = \mathcal{A}k^2[1 + L]$ at neutral while for large values of $k^2$, we get $U_0 = 2\mathcal{A}k^2$. This gives us some idea about the shape of the curve without having to actually plot it.

![Diagram of a typical neutral curve](image)

Figure 6.2 – Typical neutral curve for solidification when the latent heat is rejected only through the subcooled liquid

Now given $W$, and hence $k^2$, Eq. (6.39) determines the critical value of the interface speed, $U_0$. The most dangerous value of $n$ is one, which corresponds to $k = \pi/W$, giving only one crest and one trough at critical. As the control variable $T_L$ increases upward from zero, the output variable $U_0$ increases from zero, until there comes a point when Eq. (6.39) is satisfied. The corresponding value of $U_0$ will be referred as its critical value. Henceforth the subscript zero will refer to this critical state. At values of $U$ higher than $U_0$, the base solution loses its stability.

Now on increasing $T_L$ to its critical value $T_{L_0}$, and then slightly beyond, it might be thought that the branching to the new steady solution would be a forward pitchfork. Hence we now introduce $\frac{1}{2}\varepsilon^2$ as an input giving the amount by which $T_L$ is increased from its critical value. Observe that $\varepsilon$ takes on a different meaning from earlier.
Now the new supercritical solution will not have the speed of the corresponding base solution, hence we first find the change in $U$ corresponding to a given change in $T_L$. Eq. (6.16) indicates that for a small increase in $T_L$ from $T_{L_0}$, the corresponding change in $U$ from $U_0$, per unit change in $T_L$ is given by $\frac{1}{L} e^{U_0 T_L}$.

Before moving on to higher order problems, observe that neither $T_i$ nor $T_i^*$ is zero. It is worth noticing here that in the analogous precipitation problem in Chapter 5, the variable $c_i$ was found to be zero. This, in turn, was due to the fact that there were several cancellations of mappings in the interfacial mass balance equation, viz., $n.\nabla c = [1 - c] U k \cdot n$. The corresponding cancellations do not occur in solidification in the interfacial energy balance equation, viz., $\nabla T - \nabla T^* = \nabla U k \cdot n$. Not only does this make the analysis more cumbersome in solidification, but it also leads to a very fundamental difference between the two problems: Once the instability sets in, the front slows down in precipitation, while it speeds up in solidification. And to prove the fact of a “speed-up” in solidification, we move on to solve the higher order problems in $\varepsilon$.

**The First and Higher Order Problems**

We begin by making a guess as to how the steady states emanate from the planar morphology, i.e., how do the steady branches leave the critical point. Thus, to find the steady forward branches, we write

$$T_L = T_{L_0} + \frac{1}{2} \varepsilon^2$$

(6.40)
\[ \frac{1}{2} \varepsilon^2 = T_L - T_0 \]  
\hfill (6.41) 
is an input. We then expand \( U \) and \( Z \) as 
\[ U = U_0 + \varepsilon U_1 + \frac{1}{2} \varepsilon^2 U_2 + \frac{1}{6} \varepsilon^3 U_3 + \ldots \]  
\hfill (6.42) 
and 
\[ Z = Z_0 + \varepsilon Z_1 + \frac{1}{2} \varepsilon^2 Z_2 + \frac{1}{6} \varepsilon^3 Z_3 + \ldots \]  
\hfill (6.43) 
This guess is known to be correct in some other phase change problems (cf., Q. Buali, L.E. Johns and R. Narayanan) \[30\] and we begin by seeing if it works here. Using the formula for the surface normal vector given in Figure 6.1, and observing that the factor \( \sqrt{Z_\varepsilon^2 + 1} \) in the denominator cancels from both sides of Eq. (6.4), only the numerator of \( \vec{n} \vec{U} \) is needed, where \( \vec{U} = U \vec{k} \). The expansion of \( \vec{n} \vec{U} \) is given by Eq. (6.42). This and the other expansions (cf., Appendix B.2) lead to the respective problems at first and higher orders in \( \varepsilon \).

### The First Order Problem

The first order problem differs from the eigenvalue problem in that the system now responds to a change in \( T_L \), and this may require a change in \( U \) at first order, whence, at first order, we must determine \( T_1, T_1^*, Z_1 \) and also \( U_1 \). The first order problem is given by

\[ \nabla^2 T_1 + U_0 \frac{\partial T_1^*}{\partial z} = -U_1 \frac{dT_0^*}{dz} \]  
\hfill (6.44) 
on the domain, \(-1 < z < 0\), \(0 < x < W\), and 

\[ \nabla^2 T_1^* + U_0 \frac{\partial T_1^*}{\partial z} = -U_1 \frac{dT_0^*}{dz} \]  
\hfill (6.45) 
on the domain, \(0 < z < L\), \(0 < x < W\),

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\[ T_i = -\mathcal{A} \frac{d^2 Z_i}{dx^2} - Z_i \frac{dY_i}{dz} \]  

(6.46)

\[ \left[ T_i - T_i^* \right] + Z_i \left[ \frac{dT_i^*}{dz} - \frac{dT_i}{dz} \right] = 0 \]  

(6.47)

\[ \frac{\partial T_i}{\partial z} - \frac{\partial T_i^*}{\partial z} \]  

\[ + Z_i \left[ \frac{d^2 T_i^*}{dz^2} - \frac{d^2 T_i}{dz^2} \right] = -U \]  

(6.48)

at \( z = 0 \),

\[ T_i (z = -1) = 0 \]  

(6.49)

and

\[ T_i^* (z = L) = 0 \]  

(6.50)

The volume condition is given by

\[ \int_{0}^{w} Z_i dx = 0 \]  

(6.51)

The sidewall conditions are Neumann. Now Eqs. (6.44, 6.45, 6.47-51) have a particular solution depending only on \( z \), and the corresponding homogeneous problem is just the eigenvalue problem. Hence we have solutions of the form

\[ T_i (x, z) = T_{10} (z) + T_{11} (z) \cos(kx) \]  

(6.52)

\[ T_i^* (x, z) = T_{10}^* (z) + T_{11}^* (z) \cos(kx) \]  

(6.53)

\[ Z_i (x) = A \cos(kx) = \hat{Z}_i \cos(kx) = Z_{11} \cos(kx) \]  

(6.54)

where the notation for the subscript indices needs some clarification. The first index of a subscript will be used to represent the order of the problem and the second index will denote the
harmonic of which the variable in question is a coefficient. For example, $T_{11}$ represents a first order variable, and it is the coefficient of the first harmonic, viz., $\cos(\kappa x)$. Next, the expansions presented above are used to obtain the \{10\} and \{11\} problems.

The \{10\} problem

The \{10\} problem is given by

$$\frac{d^2T_{10}}{dz^2} + U_0 \frac{dT_{10}}{dz} = -U_1 \frac{dT_0}{dz}$$  \hspace{1cm} (6.55)

in the solid phase, $-1 < z < 0$, $0 < x < W$, and

$$\frac{d^2T^*_{10}}{dz^2} + U_0 \frac{dT^*_{10}}{dz} = -U_1 \frac{dT^*_0}{dz}$$  \hspace{1cm} (6.56)

in the liquid phase, $0 < z < L$, $0 < x < W$,

$$T_{10} - T^*_{10} = 0$$  \hspace{1cm} (6.57)

and

$$\frac{dT_{10}}{dz} - \frac{dT^*_{10}}{dz} = -U_1$$  \hspace{1cm} (6.58)

at $z = 0$,

$$T_{10}(z = -1) = 0$$  \hspace{1cm} (6.59)

and

$$T^*_{10}(z = L) = 0$$  \hspace{1cm} (6.60)

The general solution to Eqs. (6.55, 6.56) is given by

$$T_{10}(z) = A_{10} e^{-U_0 z} + e^{-U_0 z} \int_0^z e^{U_0 \xi} B_{10} d\xi$$  \hspace{1cm} (6.61)

$$T^*_{10}(z) = A^*_{10} e^{-U_0 z} + e^{-U_0 z} \int_0^z e^{U_0 \xi} \left[ B^*_{10} - U_1 \left[ 1 - e^{-U_0 \xi} \right] \right] d\xi$$  \hspace{1cm} (6.62)
and their derivatives are given by \( \frac{dT_{10}}{dz}(z = 0) = B_{10} - U_0 A_{10} \), and \( \frac{dT_{10}^{*}}{dz}(z = 0) = B_{10}^{*} - U_0 A_{10}^{*} \),

whereupon using Eqs. (6.57-6.59) to eliminate \( B_{10}, A_{10}^{*} \) and \( B_{10}^{*} \), there obtains

\[
T_{10}(z) = A_{10} \left[ e^{-U_{10}z} - \frac{e^{U_{0}}}{1 - e^{U_{0}}} \left[ 1 - e^{-U_{10}z} \right] \right]
\]

\[ (6.63) \]

\[
T_{10}^{*}(z) = A_{10} \left[ e^{-U_{10}z} - \frac{e^{U_{0}}}{1 - e^{U_{0}}} \left[ 1 - e^{-U_{10}z} \right] \right] + U_1 z e^{-U_{10}z}
\]

\[ (6.64) \]

where \( A_{10} \) is found by using Eq. (6.60) as

\[
A_{10} = \frac{-U_1 L}{1 + \frac{e^{U_{0}}}{e^{U_{0}} - 1} \left[ e^{U_{10}L} - 1 \right]}.
\]

The \{11\} problem

The \{11\} problem is similar to the eigenvalue problem. It is given by

\[
\left[ \frac{d^2}{dz^2} - k^2 \right] T_{11} + U_0 \frac{dT_{11}}{dz} = 0
\]

in the solid phase, \(-1 < z < 0, 0 < x < W\), and

\[
\left[ \frac{d^2}{dz^2} - k^2 \right] T_{11}^{*} + U_0 \frac{dT_{11}^{*}}{dz} = 0
\]

in the liquid phase, \(0 < z < L, 0 < x < W\),

\[
\left[ T_{11} - T_{11}^{*} \right] + Z_{11} \left[ \frac{dT_{10}}{dz} - \frac{dT_{10}^{*}}{dz} \right] = 0
\]

\[ (6.67) \]

and

\[
\left[ \frac{dT_{11}}{dz} - \frac{dT_{11}^{*}}{dz} \right] + Z_{11} \left[ \frac{d^2 T_{10}}{dz^2} - \frac{d^2 T_{10}^{*}}{dz^2} \right] = 0
\]

\[ (6.68) \]

at \( z = 0 \),

\[
T_{11}(z = -1) = 0
\]

\[ (6.69) \]
and
\[ T_{11}^*(z = L) = 0 \] (6.70)

Finally we turn to Eq. (6.46), which is a differential equation for \( Z_1 \). Using Eq. (6.51) and \( dZ_1/dx = 0 \) at \( x = 0, W \), and integrating Eq. (6.46) over \( 0 < x < W \), we find that \( U_1 \) must be zero, and therefore \( T_{i0} \) and \( T_{0i}^* \) must both be identically zero. Then the first order problem is exactly like the eigenvalue problem, and the condition at neutrality is given by Eq. (6.39), viz.,
\[-[\mathcal{A}k^2]M - [-\mathcal{A}k^2 + U_0]N - U_0^2 = 0.\]
What we have so far is this: \( U_1 = 0 \),
\[ T_i(x, z) = T_{1i}(z) \cos(kx) = \hat{T}_i(z) \cos(kx), \quad T_i^*(x, z) = T_{1i}^*(z) \cos(kx) = \hat{T}_i^*(z) \cos(kx), \text{ and} \]
\[ Z_i(x) = A \cos(kx) = \hat{Z}_i \cos(kx). \]
And we go on to the second order problem to find the value of \( A \). The speed of the surface does not change at order \( \varepsilon \) upon increasing \( T_L \) from \( T_{L_0} \) by \( \frac{1}{2} \varepsilon^2 \).

The Second Order Problem

At second order, the new unknowns to be determined are \( T_2, T_2^*, Z_2 \) and \( U_2 \), and the unknown \( A \) comes over from first order. The second order problem is
\[ \nabla^2 T_2 + U_0 \frac{\partial T_2}{\partial z} = -U_2 \frac{dT_0^*}{dz} \] (6.71)
on the domain, \(-1 < z < 0, \quad 0 < x < W\), and
\[ \nabla^2 T_2^* + U_0 \frac{\partial T_2^*}{\partial z} = -U_2 \frac{dT_0^*}{dz} \] (6.72)
on the domain, \( 0 < z < L, \quad 0 < x < W\),
\[ T_2 + 2Z_1 \frac{\partial T_1}{\partial z} + Z_1^2 \frac{d^2 T_0^*}{dz^2} = -A \frac{d^2 Z_1}{dx^2} - Z_2 \frac{dT_0^*}{dz} \] (6.73)
\[ [T_2 - T_2^*] + 2Z_1\left(\frac{\partial T_1^*}{\partial z} - \frac{\partial T_1^*}{\partial z}\right) + Z_1\left(\frac{d^2 T_0}{dz^2} - \frac{d^2 T_0^*}{dz^2}\right) + Z_2\left(\frac{d T_0^*}{dz} - \frac{d T_0^*}{dz}\right) = 0 \]  
(6.74)

and

\[ \left[\frac{\partial T_2}{\partial z} - \frac{\partial T_2^*}{\partial z}\right] + 2Z_1\left[\frac{\partial^2 T_0}{\partial z^2} - \frac{\partial^2 T_0^*}{\partial z^2}\right] + Z_1\left[\frac{d^3 T_0}{dz^3} - \frac{d^3 T_0^*}{dz^3}\right] + Z_2\left[\frac{d^2 T_0}{dz^2} - \frac{d^2 T_0^*}{dz^2}\right] \]
\[ -2Z_{1s}\left[\frac{\partial T_1}{\partial x} - \frac{\partial T_1^*}{\partial x}\right] = -U_2 \]

at \( z = 0 \),

\[ T_2(z = -1) = 0 \]  
(6.76)

and

\[ T_2^*(z = L) = 1 \]  
(6.77)

The volume condition is given by

\[ w \int_0^w Z_2 dx = 0 \]  
(6.78)

Observing the nature of the above equations, we assume the following form for the solution

\[ T_2(x, z) = T_{20}(z) + T_{21}(z) \cos(kx) + T_{22}(z) \cos(2kx) \]  
(6.79)

\[ T_2^*(x, z) = T_{20}^*(z) + T_{21}^*(z) \cos(kx) + T_{22}^*(z) \cos(2kx) \]  
(6.80)

\[ Z_2(x) = Z_{21} \cos(kx) + Z_{22} \cos(2kx) \]  
(6.81)

And again, we use these expansions to deduce the \{20\} and \{21\} and \{22\} problems. At \( z = 0 \), the following formulae may be useful:

\[ 2Z_1\left[\frac{\partial^2 T_1}{\partial z^2} - \frac{\partial^2 T_1^*}{\partial z^2}\right] = U_0\left[k^2 U_0^2\right] Z_1^2\left[1 + \cos(2kx)\right] \]

\[-2Z_{1s}\left[\frac{\partial T_1}{\partial x} - \frac{\partial T_1^*}{\partial x}\right] = -k^2 U_0 Z_1^2\left[1 - \cos(2kx)\right] \]
The \{20\} problem

The \{20\} problem is given by

\[
\frac{d^2 T_{20}}{dz^2} + U_0 \frac{dT_{20}}{dz} = -U_0 \frac{dT_0}{dz}
\]  

(6.82)

in the solid phase, \(-1 < z < 0\), \(0 < x < W\), and

\[
\frac{d^2 T_{20}^*}{dz^2} + U_0 \frac{dT_{20}^*}{dz} = -U_2 \frac{dT_0^*}{dz}
\]  

(6.83)

in the liquid phase, \(0 < z < L\), \(0 < x < W\),

\[
T_{20} - T_{20}^* = \frac{1}{2} U_0^2 \hat{Z}_1^2
\]  

(6.84)

and

\[
\left[ \frac{dT_{20}}{dz} - \frac{dT_{20}^*}{dz} \right] = -U_2 - \frac{1}{2} U_0 \hat{Z}_1^2
\]  

(6.85)

at \(z = 0\),

\[
T_{20} (z = -1) = 0
\]  

(6.86)

and

\[
T_{20}^* (z = L) = 1
\]  

(6.87)

A general solution to Eqs. (6.82, 6.83) is given by

\[
T_{20} (z) = A_{20} e^{-U_0 \hat{z}} + e^{U_0 \hat{z}} \int_0^z e^{U_0 \hat{\xi}} B_{20} d \hat{\xi}
\]  

(6.88)

\[
T_{20}^* (z) = A_{20}^* e^{-U_0 \hat{z}} + e^{U_0 \hat{z}} \int_0^z e^{U_0 \hat{\xi}} \left[ B_{20}^* - U_2 \left( 1 - e^{-U_0 \hat{\xi}} \right) \right] d \hat{\xi}
\]  

(6.89)

and their derivatives are given by \(\frac{dT_{20}}{dz}(z = 0) = B_{20} - U_0 A_{20}\), and \(\frac{dT_{20}^*}{dz}(z = 0) = B_{20}^* - U_0 A_{20}^*\),
whereupon using Eqs. (6.84-6.86) to eliminate $B_{20}$, $A_{20}^*$ and $B_{20}^*$, we get

$$T_{20}(z) = A_{20} e^{-U_0 z} - \frac{e^{U_0}}{1 - e^{U_0}} \left[ 1 - e^{-U_0 z} \right]$$

(6.90)

$$T_{20}^*(z) = A_{20} e^{-U_0 z} - \frac{e^{U_0}}{1 - e^{U_0}} \left[ 1 - e^{-U_0 z} \right] - \frac{1}{2} U_0^2 e^{-U_0 z} \hat{Z}_1^2 + U_2 z e^{-U_0 z}$$

(6.91)

where $A_{20}$ is found by using Eq. (6.87) as

$$A_{20} = \frac{-U_2 L + \frac{1}{2} U_0^2 \hat{Z}_1^2 + e^{U_0 L}}{1 + \left( \frac{e^{U_0}}{e^{U_0} - 1} \right)}.$$  

(6.92)

**The \{21\} problem**

The \{21\} problem is similar to the eigenvalue problem. It is given by

$$\left[ \frac{d^2}{dz^2} - k^2 \right] T_{21} + U_0 \frac{dT_{21}}{dz} = 0$$

(6.93)

in the solid phase, $-1 < z < 0$, $0 < x < W$, and

$$\left[ \frac{d^2}{dz^2} - k^2 \right] T_{21}^* + U_0 \frac{dT_{21}^*}{dz} = 0$$

(6.94)

in the liquid phase, $0 < z < L$, $0 < x < W$,

$$\left[ T_{21} - T_{21}^* \right] + Z_{21} \left( \frac{dT_0}{dz} - \frac{dT_0^*}{dz} \right) = 0$$

(6.95)

and

$$\left( \frac{dT_{21}}{dz} - \frac{dT_{21}^*}{dz} \right) + Z_{21} \left( \frac{d^2 T_0}{dz^2} - \frac{d^2 T_0^*}{dz^2} \right) = 0$$

(6.96)

at $z = 0$,

$$T_{21}(z = -1) = 0$$

(6.97)
T_{21}^*(z = L) = 0 \quad (6.98)

Defining \( m_{221} = \frac{-U_0 \pm \sqrt{U_0^2 + 4k^2}}{2} = m_z \), a solution to Eqs. (6.93-6.98) is given by

\[
T_{21}(z) = A_{21} \left[ e^{m_{21}z} - e^{[m_{21} - m_{21}]z} \right] \quad (6.99)
\]

\[
T_{21}^*(z) = A_{21}^* \left[ e^{m_{21}z} - e^{[m_{21} - m_{21}]z} \right] \quad (6.100)
\]

where

\[
A_{21} = \frac{\mathcal{A}k^2}{\left[1 - e^{m_{21} - m_{21}}\right]} Z_{21} \quad (6.101)
\]

\[
A_{21}^* = \frac{\mathcal{A}k^2 - U_0}{\left[1 - e^{m_{21} - m_{21}}\right]} Z_{21} \quad (6.102)
\]

The \{22\} problem

The \{22\} problem is given by

\[
\left[ \frac{d^2}{dz^2} - 4k^2 \right] T_{22} + U_0 \frac{dT_{22}}{dz} = 0 \quad (6.103)
\]

in the solid phase, \(-1 < z < 0\), \(0 < x < W\), and

\[
\left[ \frac{d^2}{dz^2} - 4k^2 \right] T_{22}^* + U_0 \frac{dT_{22}^*}{dz} = 0 \quad (6.104)
\]

in the liquid phase, \(0 < z < L\), \(0 < x < W\),

\[
T_{22} - T_{22}^* = \frac{1}{2} U_0^2 Z_1^2 + U_0 Z_{22} \quad (6.105)
\]

and

\[
\left[ \frac{dT_{22}}{dz} - \frac{dT_{22}^*}{dz} \right] + 2U_0 k^2 Z_1^2 + \frac{1}{2} U_0^3 Z_1^3 + U_0^2 Z_{22} = 0 \quad (6.106)
\]
at \( z = 0 \),

\[ T_{22}(z = -1) = 0 \tag{6.107} \]

and

\[ T_{22}^*(z = L) = 0 \tag{6.108} \]

Defining \( m_{122} = \frac{-U_0 \pm \sqrt{U_0^2 + 16k^2}}{2} \), a solution to Eqs. (6.103-6.108) is given by

\[ T_{22}(z) = A_{22} \left( e^{m_{22}z} - e^{m_{22}-m_{22}} e^{m_{22}z} \right) \tag{6.109} \]

\[ T_{22}^*(z) = A_{22}^* \left( e^{m_{22}z} - e^{[m_{22}-m_{22}]L} e^{m_{22}z} \right) \tag{6.110} \]

where

\[
A_{22} = \left[ \frac{1}{2} U_0 N_{22} + 2U_0 k^2 + \frac{1}{2} U_0^3 \right] Z_1^2 + \left[ U_0 N_{22} + U_0^2 \right] Z_2 \left[ 1 - e^{m_{22}-m_{22}} \right] \tag{6.111} \]

\[
A_{22}^* = \left[ \frac{1}{2} U_0 M_{22} + 2U_0 k^2 + \frac{1}{2} U_0^3 \right] Z_1^2 + \left[ U_0 M_{22} + U_0^2 \right] Z_2 \left[ 1 - e^{m_{22}-m_{22}} \right] \tag{6.112} \]

and where \( M_{22} = \frac{m_{22} - m_{22} e^{m_{22}-m_{22}}}{1 - e^{m_{22}-m_{22}}} \) and \( N_{22} = \frac{m_{22} - m_{22} e^{[m_{22}-m_{22}]L}}{1 - e^{m_{22}-m_{22}}} \).

Using the curvature equation

Finally we turn to Eq. (6.73), which is a differential equation for \( Z_2 \). Using Eq. (6.78) and \( dZ_2 / dx = 0 \) at \( x = 0, W \), and integrating Eq. (6.73) over \( 0 < x < W \), we find

\[ T_{20}(z = 0) + Z_1 \frac{d \hat{T}_1}{dz}(z = 0) + \frac{1}{2} Z_1^2 \frac{d^2 \hat{T}_1}{dz^2}(z = 0) = 0 \tag{6.113} \]

Using \( \frac{d \hat{T}_1}{dz}(z = 0) = \mathcal{A} k M \hat{Z}_1 \) and \( T_{20}(z = 0) = A_{20} \), we get \( A_{20} = -\mathcal{A} k^2 M \hat{Z}_1^2 \). Comparing with
Eq. (6.92), there obtains

\[
U_2 = \frac{1}{L} e^{u_2L} + \frac{1}{L} \left[ \frac{1}{2} U_0^2 + A k^2 M \left[ 1 + \left( e^{\frac{U_1}{k}} - 1 \right) \right] \right] Z_1^2
\]

(6.114)

where the first term is what \( U_2 \) would be if the base solution obtains at the new value of \( T_L \), and this term was derived earlier. The second term is the correction corresponding to a curved front. It is always positive. Hence the mean speed of a curved front would be faster than that of the corresponding planar front. In other words, the mean speed of the interface runs ahead of its base value.

To go to third order, we need to solve Eq. (6.73) for \( Z_2 \). To find \( Z_2 \), a solvability condition must be satisfied. It is

\[
\int_0^w T_2 (z = 0) + 2Z_1 \frac{dT_1}{dZ} (z = 0) Z_2 dx - \int_0^w T_1 (z = 0) Z_2 dx = 0
\]

(6.115)

It is easy to verify that this condition is automatically satisfied, whence we cannot learn the value of \( A \) at this order. Finally, substituting the expansions from Eqs. (6.79, 6.81) into Eq. (6.73), the constant term disappears due to the result obtained earlier using integrability, viz., due to Eq. (6.113). The coefficient of the first harmonic vanishes due to solvability, and there obtains by equating the coefficients of the second harmonic

\[
T_{22} (z = 0) + \frac{d}{dz} \frac{T_1}{Z} (z = 0) Z_1 - 4 A k^2 Z_{22} = 0
\]

(6.116)

Substituting for \( T_{22} (z = 0) = A_{22} \left[ 1 - e^{m_{22} z} \right] \) and using \( \frac{d}{dz} \frac{T_1}{Z} (z = 0) = A k^2 M Z_1 \), there obtains

\[
A_{22} = \frac{-\left[ A k^2 M \right] Z_1^2 + \left[ 4 A k^2 \right] Z_{22}}{\left[ 1 - e^{m_{22} z} \right]}
\]

(6.117)
Comparing with Eq. (6.111), and simplifying, we get

\[ Z_{22} = \left[ \frac{P}{Q} \right] Z_1^2 \]  

(6.118)

where

\[
\frac{P}{Q} = \frac{\left[ \frac{1}{2} U_0^2 N_{22} + 2U_0 k^2 + \frac{1}{2} U_0^3 \right] + \mathcal{A}k^2 M \left[ N_{22} - M_{22} \right]}{4\mathcal{A}k^2 \left[ N_{22} - M_{22} \right] - \left[ U_0 N_{22} + U_0^2 \right]} 
\]  

(6.119)

Hence, \( Z_{21} \) and \( A \) carry on to third order.

**The Third Order Problem**

The equations at the third order are given by

\[
\nabla^2 T_3 + U_0 \frac{\partial T_3}{\partial z} = -3U_2 \frac{\partial T_1}{\partial z} - U_3 \frac{dT_0}{dz} 
\]  

(6.120)

on the domain, \(-1 < z < 0\), \(0 < x < W\), and

\[
\nabla^2 T_3^* + U_0 \frac{\partial T_3^*}{\partial z} = -3U_2 \frac{\partial T_1^*}{\partial z} - U_3 \frac{dT_0^*}{dz} 
\]  

(6.121)

on the domain, \(0 < z < L\), \(0 < x < W\),

\[
-9\mathcal{A} \left( \frac{dZ_1}{dx} \right) \frac{d^2 Z_1}{dx^2} + \left[ T_3 + 3Z_1 \frac{\partial T_2}{\partial z} + 3Z_1^2 \frac{\partial^2 T_1}{\partial z^2} + 3Z_2 \frac{\partial T_1}{\partial z} + 3Z_1 \frac{d^2 T_0}{dz^2} + Z_1 \frac{d^3 T_0}{dz^3} \right] 
\]  

\[
= -\mathcal{A} \frac{d^2 Z_3}{dx^2} - \frac{d\phi}{dz} \]  

(6.122)

\[
\left[ T_3 - T_3^* \right] + 3Z_1 \left[ \frac{\partial T_2}{\partial z} - \frac{\partial T_2^*}{\partial z} \right] + 3Z_1^2 \left[ \frac{\partial^2 T_1}{\partial z^2} - \frac{\partial^2 T_1^*}{\partial z^2} \right] + 3Z_2 \left[ \frac{\partial T_1}{\partial z} - \frac{\partial T_1^*}{\partial z} \right] 
\]  

\[
+ 3Z_1Z_2 \left[ \frac{d^2 \phi}{dz^2} - \frac{d^2 \phi^*}{dz^2} \right] + Z_1 \left[ \frac{d^3 \phi}{dz^3} - \frac{d^3 \phi^*}{dz^3} \right] + Z_3 \left[ \frac{dT_0}{dz} - \frac{dT_0^*}{dz} \right] = 0 
\]  

(6.123)

and
\[
\begin{bmatrix}
\frac{\partial T_1}{\partial z} & \frac{\partial T_1}{\partial z} \\
\frac{\partial T_2}{\partial z^2} & \frac{\partial T_2}{\partial z^2} \\
\frac{\partial T_3}{\partial z^3} & \frac{\partial T_3}{\partial z^3} \\
\end{bmatrix}
+ 3Z_1 \begin{bmatrix}
\frac{\partial^2 T_1}{\partial z^2} & \frac{\partial^2 T_2}{\partial z^2} \\
\frac{\partial^2 T_2}{\partial z^2} & \frac{\partial^2 T_3}{\partial z^2} \\
\end{bmatrix}
+ 3Z_1 \begin{bmatrix}
\frac{\partial^3 T_1}{\partial z^3} & \frac{\partial^3 T_2}{\partial z^3} \\
\frac{\partial^3 T_2}{\partial z^3} & \frac{\partial^3 T_3}{\partial z^3} \\
\end{bmatrix}
+ 3Z_2 \begin{bmatrix}
\frac{\partial^2 T_1}{\partial z^2} & \frac{\partial^2 T_2}{\partial z^2} \\
\frac{\partial^2 T_2}{\partial z^2} & \frac{\partial^2 T_3}{\partial z^2} \\
\end{bmatrix}
+ 3Z_2 \begin{bmatrix}
\frac{\partial^2 T_1}{\partial z^2} & \frac{\partial^2 T_2}{\partial z^2} \\
\frac{\partial^2 T_2}{\partial z^2} & \frac{\partial^2 T_3}{\partial z^2} \\
\end{bmatrix}
\]

\[= U_3 \] (6.124)

at \( z = 0 \),

\[ T_3(z = -1) = 0 \] (6.125)

and

\[ T_3^*(z = L) = 0 \] (6.126)

The volume condition is given by

\[ \int_{-W}^{W} Z_3 dx = 0 \] (6.127)

We assume the following form for the solution

\[ T_3(x, z) = T_{30}(z) + T_{31}(z) \cos(kx) + T_{32}(z) \cos(2kx) + T_{33}(z) \cos(3kx) \] (6.128)

\[ T_3^*(x, z) = T_{30}^*(z) + T_{31}^*(z) \cos(kx) + T_{32}^*(z) \cos(2kx) + T_{33}^*(z) \cos(3kx) \] (6.129)

\[ Z_3(x) = Z_{31} \cos(kx) + Z_{32} \cos(2kx) + Z_{33} \cos(3kx) \] (6.130)

Now this problem can be solved completely, but it suffices to solve the \{31\} problem to learn the nature of bifurcation and the value of \( A^2 \), and it is to this that we turn our attention next.

**The \{31\} problem**

The \{31\} problem is given by

\[ \left[ \frac{d^2}{dz^2} - k^2 \right] T_{31} + U_0 \frac{dT_{31}}{dz} + 3U_2 \frac{dT_{31}}{dz} = 0 \] (6.131)

in the solid phase, \(-1 < z < 0\), \(0 < x < W\), and
\[
\left[ \frac{d^2}{dz^2} - k^2 \right] T_{31}^\prime + U_0 \frac{dT_{31}^\prime}{dz} + 3 U_2 \frac{d T_1^\prime}{dz} = 0 \quad (6.132)
\]

in the liquid phase, \(0 < z < L\), \(0 < x < W\),

\[
\left[ T_{31} - T_{31}^\prime \right] + 3 \left[ \frac{dT_{31,0}^\prime - dT_{31,0}^\prime}{dz} + \frac{dT_{22}^\prime}{dz} - \frac{dT_{22}^\prime}{dz} \right] Z_{22} + \frac{9}{4} \left[ \frac{d^2 T_1^\prime - d^2 T_1^\prime}{dz^2} \right] Z_{12}^2
\]

\[
+ \frac{3}{2} \left[ \frac{dT_{31}^\prime}{dz} - \frac{dT_{31}^\prime}{dz} \right] Z_{31} = 0 \quad (6.133)
\]

and

\[
\left[ \frac{dT_{31} - dT_{31}^\prime}{dz} \right] + 3 \left[ \frac{d^2 T_{31,0}^\prime - d^2 T_{31,0}^\prime}{dz^2} + \frac{dT_{22}^\prime}{dz} - \frac{dT_{22}^\prime}{dz} \right] Z_{22} + \frac{9}{4} \left[ \frac{d^2 T_1^\prime - d^2 T_1^\prime}{dz^2} \right] Z_{12}^2
\]

\[
+ \frac{3}{2} \left[ \frac{d^2 T_{31}^\prime}{dz^2} - \frac{d^2 T_{31}^\prime}{dz^2} \right] Z_{31} - 3 k^2 \left[ T_{22}^\prime - T_{22}^\prime \right] \hat{Z}_{12} = 0 \quad (6.134)
\]

at \(z = 0\),

\[T_{31}(z = -1) = 0 \quad (6.135)\]

and

\[T_{31}^\prime(z = L) = 0 \quad (6.136)\]

A general solution to Eqs. (6.131, 6.132) is given by

\[T_{31}(z) = \left[ A_{31} e^{m_z z} + B_{31} e^{m_z z} \right] + \left[ Cze^{m_z z} + Dze^{m_z z} \right] \quad (6.137)\]

\[T_{31}^\prime(z) = \left[ A_{31}^* e^{m_z z} + B_{31}^* e^{m_z z} \right] + \left[ C^* ze^{m_z z} + D^* ze^{m_z z} \right] \quad (6.138)\]
where \( C = \left[ \frac{3U_2 \hat{A}_1}{m_\pm - m_\pm} \right] m_\pm \), \( D = \left[ \frac{3U_2 \hat{A}_1}{m_\pm - m_\pm} \right] m_\pm e^{(m_\pm - m_\pm)} \), \( C^* = \left[ \frac{3U_2 \hat{A}_1^*}{m_\pm - m_\pm} \right] m_\pm \) and

\[
D^* = \left[ \frac{3U_2 \hat{A}_1^*}{m_\pm - m_\pm} \right] m_\pm e^{(m_\pm - m_\pm)}.
\]

Eliminating \( B_{31} \) and \( B_{31}^* \) using Eqs. (6.135, 6.136), we get

\[
T_{31}(z) = A_{31} \left[ e^{m_\pm z} - e^{(m_\pm - m_\pm)z} \right] + \left[ Ce^{(m_\pm - m_\pm)} + D \right] e^{m_\pm z} + \left[ Cze^{m_\pm z} + Dze^{m_\pm z} \right]
\] (6.139)

\[
T_{31}^*(z) = A_{31}^* \left[ e^{m_\pm z} - e^{(m_\pm - m_\pm)z} \right] - L \left[ C^* e^{(m_\pm - m_\pm)} + D^* \right] e^{m_\pm z} + \left[ C^* e^{m_\pm z} + D^* e^{m_\pm z} \right]
\] (6.140)

Now Eqs. (6.133, 6.134) can be written as

\[
A_{31} \left[ 1 - e^{(m_\pm - m_\pm)} \right] - A_{31}^* \left[ 1 - e^{(m_\pm - m_\pm)} \right] = -R_1
\] (6.141)

\[
A_{31} \left[ m_\pm - m_\pm e^{(m_\pm - m_\pm)} \right] - A_{31}^* \left[ m_\pm - m_\pm e^{(m_\pm - m_\pm)} \right] = -R_2
\] (6.142)

where

\[
R_1 = \left[ Ce^{(m_\pm - m_\pm)} + D \right] + L \left[ C^* e^{(m_\pm - m_\pm)} + D^* \right]
\]

\[
+ 3 \left[ \frac{d^2 T_0}{dz^2} - \frac{d^2 T_0^*}{dz^2} \right] + \frac{1}{2} \left[ \frac{d^2 T_{22}}{dz^2} - \frac{d^2 T_{22}^*}{dz^2} \right] \hat{Z}_1 + \frac{9}{4} \left[ \frac{d^2 T_1}{dz^2} - \frac{d^2 T_1^*}{dz^2} \right] \hat{Z}_1^2 + \frac{3}{2} \left[ \frac{d T_1}{dz} - \frac{d T_1^*}{dz} \right] Z_{32} \] (6.143)

\[
+ \frac{3}{2} \left[ \frac{d^3 T_0}{dz^3} - \frac{d^3 T_0^*}{dz^3} \right] \hat{Z}_1 Z_{22} + \frac{3}{4} \left[ \frac{d^3 T_{00}}{dz^3} - \frac{d^3 T_{00}^*}{dz^3} \right] \hat{Z}_1^3 + \left[ \frac{dT_0}{dz} - \frac{dT_0^*}{dz} \right] Z_{31}
\]

and
\[ R_2 = \left[ m \left[ C e^{(m-n)} + D \right] + [C + D] \right] - \left[ -Lm \left[ C^* e^{(m-n)} + D^* \right] + [C^* + D^*] \right] \]

\[ + 3 \left[ \left( \frac{d^3 T_{20}}{dz^3} - \frac{d^3 T_{20}^*}{dz^3} \right) + \frac{1}{2} \left( \frac{d^3 T_{22}}{dz^3} - \frac{d^3 T_{22}^*}{dz^3} \right) \right] Z_1 + \frac{9}{4} \left( \frac{d^3 T_1}{dz^3} - \frac{d^3 T_1^*}{dz^3} \right) Z_1^2 \]

\[ + \frac{3}{2} \left( \frac{d^3 T_1}{dz^3} - \frac{d^3 T_1^*}{dz^3} \right) Z_{22} + \frac{3}{2} \left( \frac{d^3 T_0}{dz^3} - \frac{d^3 T_0^*}{dz^3} \right) Z_{22} + \frac{3}{4} \left( \frac{d^4 T_0}{dz^4} - \frac{d^4 T_0^*}{dz^4} \right) \]

\[ + \left[ \frac{d^2 \beta}{dz^2} - \frac{d^2 \beta^*}{dz^2} \right] Z_31 - 3k^2 \left[ T_{22} - T_{22}^* \right] Z_1 + \frac{3}{2} k^2 \left( \frac{d^2 \beta}{dz^2} - \frac{d^2 \beta}{dz^2} \right) Z_{22} - 3k^2 \left( \hat{T}_1 - \hat{T}_1^* \right) Z_{22} \]

(6.144)

where all terms in \( R_1 \) and \( R_2 \) are evaluated at \( z = 0 \). Now \( R_1 \) and \( R_2 \) can be simplified using results from previous orders. At \( z = 0 \), the following formulae may be helpful:

\[ \frac{dT_{20}}{dz} - \frac{dT_{20}^*}{dz} = -U_2 - \frac{1}{2} U_0 \frac{\hat{Z}_1}{Z_1^2} \]

\[ \frac{d^2 T_{20}}{dz^2} - \frac{d^2 T_{20}^*}{dz^2} = 2U_0 U_2 + \frac{1}{2} U_0^4 \frac{\hat{Z}_1^2}{Z_1^2} \]

\[ \frac{dT_1}{dz} - \frac{dT_1^*}{dz} = -U_0^2 \frac{\hat{Z}_1}{Z_1} \]

\[ \frac{d^2 T_1}{dz^2} - \frac{d^2 T_1^*}{dz^2} = U_0 \left[ k^2 + U_0^2 \right] \frac{\hat{Z}_1}{Z_1} \]

\[ \frac{d^3 T_1}{dz^3} - \frac{d^3 T_1^*}{dz^3} = -U_0^2 \left[ 2k^2 + U_0^2 \right] \frac{\hat{Z}_1}{Z_1} \]

\[ \frac{dT_{22}}{dz} - \frac{dT_{22}^*}{dz} = - \left[ 2U_0 k^2 + \frac{1}{2} U_0^3 \right] \frac{\hat{Z}_1}{Z_1} - U_0^2 Z_{22} \]

\[ \frac{d^2 T_{22}}{dz^2} - \frac{d^2 T_{22}^*}{dz^2} = \left[ 4k^2 U_0^2 + \frac{1}{2} U_0^4 \right] \frac{\hat{Z}_1^2}{Z_1^2} + U_0 \left[ U_0^2 + 4k^2 \right] Z_{22} \]

Hence
\begin{align}
R_1 &= \left[ Ce^{m-m_2} + D \right] + L \left[ C^{*} e^{m-m_2} + D^* \right] - 3U_2 Z_i - \frac{3}{4} U_0 \left[ k^2 + U_0^2 \right] Z_i - \frac{3}{2} U_0^2 \hat{Z}_i z_{22} \\
&\quad - U_0 Z_{31} \\
R_2 &= \left[ m \left[ Ce^{m-m_2} + D \right] + \left[ C + D \right] \right] - \left[ -Lm \left[ C^{*} e^{m-m_2} + D^* \right] + \left[ C^{*} + D^* \right] \right] \\
&\quad + 6U_0^2 U_2 Z_i + \left[ \frac{3}{2} U_0^2 k^2 + \frac{3}{4} U_0^4 \right] Z_i + \frac{3}{2} U_0 \left[ U_0^2 + k^2 \right] \hat{Z}_i Z_{22} + U_0^2 Z_{31} \\
\end{align}

Then solving Eqs. (6.141, 6.142) for \( A_{3i} \) and \( A'_{3i} \), there obtains

\begin{align}
A_{3i} &= \frac{\left[ R_{1N} - R_{2} \right]}{[1 - e^{m-m_2}]}[M - N] \\
A'_{3i} &= \frac{\left[ R_{1M} - R_{2} \right]}{[1 - e^{m-m_2}]}[M - N] \\
\end{align}

**Using the curvature equation**

Finally we turn to Eq. (6.122), which is a differential equation for \( Z_3 \). To find \( Z_3 \), a solvability condition must be satisfied. It is

\begin{align}
\int_0^w \left[ T_3 (z = 0) + 3Z_1 \frac{dT_3}{dz}(z = 0) + 3Z_1^2 \frac{d^2 T_3}{dz^2}(z = 0) + 3Z_2 \frac{dT_1}{dz}(z = 0) - 9A \left( \frac{dZ_1}{dx} \right)^2 \frac{d^2 Z_1}{dx^2} \right] Z_i dx \\
- \int_0^w T_1 (z = 0) Z_3 dx = 0 \\
\end{align}

Using

\begin{align}
\int_0^w T_1 (z = 0) Z_3 dx &= \frac{1}{2} W \hat{Z}_1 T_{31} (z = 0) \\
\int_0^w \left[ 3Z_1 \frac{dT_3}{dz}(z = 0) \right] Z_i dx &= \frac{1}{2} W \hat{Z}_1 3Z_1 \left[ \frac{dT_{20}}{dz}(z = 0) + \frac{1}{2} \frac{dT_{22}}{dz}(z = 0) \right] \\
\int_0^w \left[ 3Z_1^2 \frac{d^2 T_3}{dz^2}(z = 0) \right] Z_i dx &= \frac{1}{2} W \hat{Z}_1 9 \frac{Z_1^2}{4} \frac{d^2 T_3}{dz^2}(z = 0) \\
\end{align}
\[
\int_{0}^{w} \left[ 3Z_2 \frac{\partial T_i}{\partial z} (z = 0) \right] Z_i dx = \frac{1}{2} W \hat{T}_i \left[ -\frac{3}{2} Z_{22} \frac{d \hat{T}_i}{dz} (z = 0) \right]
\]

\[
\int_{0}^{w} T_i (z = 0) Z_j dx = \frac{1}{2} W \hat{T}_i \left[ -\mathcal{A}k^2 Z_{31} \right]
\]

\[
\int_{0}^{w} \left[ -9A \left( \frac{dZ_i}{dx} \right)^2 + \frac{d^2 Z_i}{dx^2} \right] Z_i dx = \frac{1}{2} W \hat{T}_i \left\{ \frac{9}{4} \mathcal{A}k^4 \hat{Z}_i^3 \right\}
\]

there obtains

\[
T_{31} (z = 0) + 3 \left[ \frac{dT_{20}}{dz} (z = 0) + \frac{1}{2} \frac{dT_{22}}{dz} (z = 0) \right] \hat{Z}_i + \frac{9}{4} \frac{d^2 \hat{T}_i}{dz^2} (z = 0) \hat{Z}_i^2 + \frac{3}{2} \frac{d \hat{T}_i}{dz} (z = 0) Z_{22}
\]

\[
+ \frac{9}{4} \mathcal{A}k^4 \hat{Z}_i^3 + \left[ -\mathcal{A}k^2 \right] Z_{31} = 0
\]

(6.150)

which can be written as

\[
A_{31} \left[ 1 - e^{m - m_i} \right] = -R_3
\]

(6.151)

where

\[
R_3 = \left[ Ce^{m - m_i} + D \right] + 3 \left[ \frac{dT_{20}}{dz} (z = 0) + \frac{1}{2} \frac{dT_{22}}{dz} (z = 0) \right] \hat{Z}_i + \frac{9}{4} \frac{d^2 \hat{T}_i}{dz^2} (z = 0) \hat{Z}_i^2
\]

\[
+ \frac{3}{2} \frac{d \hat{T}_i}{dz} (z = 0) Z_{22} + \frac{9}{4} \mathcal{A}k^4 \hat{Z}_i^3 + \left[ -\mathcal{A}k^2 \right] Z_{31}
\]

(6.152)

whence using

\[
\frac{dT_{20}}{dz} (z = 0) = U_0 \left[ \frac{1}{1 - e^{U_0}} \right] \mathcal{A}k^2 M \hat{Z}_i^3
\]

\[
\frac{dT_{22}}{dz} (z = 0) = M_{22} \left[ -\mathcal{A}k^2 M \hat{Z}_i^2 + 4 \mathcal{A}k^2 Z_{22} \right]
\]

\[
\frac{d \hat{T}_i}{dz} (z = 0) = \mathcal{A}k^2 M \hat{Z}_i
\]
\[
\frac{d^2 \hat{T}_1}{dz^2} (z = 0) = \mathcal{A}k^2\left[k^2 - U_0M\right]\hat{Z}_1
\]

there obtains

\[
R_3 = \left[ Ce^{[m,-m]} + D \right] + \left[ 3 \left( \frac{1}{1-U_0} \right) \mathcal{A}k^2M - \frac{3}{2} \mathcal{A}k^2MM_{22} + \frac{9}{4} \mathcal{A}k^2\left[2k^2 - U_0M\right] \right] \hat{Z}_1^3 \nonumber
\]

\[
+ \left[ 3\mathcal{A}k^2\left( \frac{1}{2}M + 2M_{22} \right) \right] \hat{Z}_1 Z_{22} + \left[ -\mathcal{A}k^2 \right] Z_{31}\nonumber
\]  

(6.153)

Comparing the value of \(A_{31}\) from Eq. (6.147) and Eq. (6.151), we get

\[
\left[ R_1N - R_2 \right] + R_3 \left[ M - N \right] = 0
\]

(6.154)

Next, we define: \(\bar{R}_1 = R_1 - \left[-U_0Z_{31}\right]\), \(\bar{R}_2 = R_2 - U_0^2Z_{31}\), and \(\bar{R}_3 = R_3 - \left[-\mathcal{A}k^2 \right] Z_{31}\).

Substituting in Eq. (6.154), and using the relation at neutrality, viz., Eq. (6.39), there obtains

\[
\left[ \bar{R}_1 N - \bar{R}_2 \right] + \bar{R}_3 \left[ M - N \right] = 0
\]

(6.155)

where now

\[
\bar{R}_1 = \left[ \left[ Ce^{[m,-m]} + D \right] + L \left[ C^*e^{[m,-m]}L + D^* \right] \right] - 3U_0^2 \hat{Z}_1 - \frac{3}{4}U_0 \hat{Z}_1^2 - 3U_0^2 \hat{Z}_1 Z_{22}\nonumber
\]

(6.156)

\[
\bar{R}_2 = \left[ m_1 \left[ Ce^{[m,-m]} + D \right] + \left[ C + D \right] - \left[-Lm_1 \left[C^*e^{[m,-m]}L + D^* \right] + \left[ C^* + D^* \right] \right] \right] + 6U_0 U_2 \hat{Z}_1 \nonumber
\]

\[
+ \left[ 3U_0^2 \hat{Z}_1^2 + \frac{3}{4}U_0^4 \right] \hat{Z}_1^3 + \frac{3}{2}U_0 \left[ U_0^2 + k^2 \right] \hat{Z}_1 Z_{22}\nonumber
\]

(6.157)

\[
\bar{R}_3 = \left[ Ce^{[m,-m]} + D \right] + \left[ 3 \left( \frac{1}{1-U_0} \right) \mathcal{A}k^2M - \frac{3}{2} \mathcal{A}k^2MM_{22} + \frac{9}{4} \mathcal{A}k^2\left[2k^2 - U_0M\right] \right] \hat{Z}_1^3 \nonumber
\]

\[
+ \left[ 3\mathcal{A}k^2\left( \frac{1}{2}M + 2M_{22} \right) \right] \hat{Z}_1 Z_{22}\nonumber
\]

(6.158)

Now Eq. (6.155) is an equation for \(\hat{Z}_1^2\), whence, upon combining terms, we get
\[ T_1 + T_2 U \dot{Z}_1 + T_3 \dot{Z}_1^2 + T_4 \dot{Z}_1 Z_{22} = 0 \] (6.159)

where

\[ T_1 = \left[ LN \left( C^* e^{[m_-, m_+]} L + D^* \right) \right] \left[ m_- \left( C e^{[m_-, m_+]} + D \right) + [C + D] \right] \\
+ \left[ -Lm_- \left( C^* e^{[m_-, m_+]} L + D^* \right) + [C^* + D^*] \right] + M \left[ C e^{[m_-, m_+]} + D \right] \] (6.160)

\[ = \left[ \frac{A k^2 - U_0}{1 - e^{[m_-, m_+]}} \right] \left[ m_+ e^{[m_-, m_+]} \left[ -U_0 L [N - m_-] + m_- \right] \right] \left[ \frac{3}{m_- - m_+} \right] U_2 \dot{Z}_1 \\
- \left[ \frac{A k^2}{1 - e^{[m_-, m_+]}} \right] \left[ m_+ e^{[m_-, m_+]} \left[ U_0 [M - m_-] + m_- \right] \right] \left[ \frac{3}{m_- - m_+} \right] U_2 \dot{Z}_1 \\
T_2 = -3N - 6U_0 \] (6.161)

\[ T_3 = -\frac{3}{4} N U_0 \left( k^2 + U_0^2 \right) - \left[ \frac{3}{2} k^2 U_0^2 + \frac{3}{4} U_0^4 \right] \]
\[ + \left[ M - N \right] \left[ \frac{3}{2} \frac{U_0}{1 - U_0} \right] A k^2 M - \frac{3}{2} A k^2 M M_{22} + \frac{9}{4} A k^2 \left[ 2k^2 - U_0 M \right] \] (6.162)

\[ T_4 = -\frac{3}{2} N U_0^2 - \frac{3}{2} U_0 \left[ k^2 + U_0^2 \right] + \left[ M - N \right] \left[ 3 A k^2 \left[ \frac{1}{2} M + 2M_{22} \right] \right] \] (6.163)

Hence

\[ \left[ \frac{T_1}{U_2 \dot{Z}_1} + T_2 \right] U_2 + T_3 \dot{Z}_1^2 + T_4 \dot{Z}_{22} = 0 \] (6.164)

or

\[ \left[ \frac{T_1}{U_2 \dot{Z}_1} + T_2 \right] U_{2 \text{planar}} + \left[ \frac{T_1}{U_2 \dot{Z}_1} + T_2 \right] \left[ \frac{U_{2 \text{correction}}}{Z_1^2} \right] + T_3 + T_4 \left[ \frac{P}{Q} \right] Z_1^2 = 0 \] (6.165)
\[ Z_1^2 = - \left[ \frac{T_1}{U_2 Z_1} + T_2 \right] U_{2,\text{planar}} + \left[ \frac{T_3 + T_4 \left[ \frac{P}{Q} \right]}{U_2 Z_1} \right] + T_3 + T_4 \left[ \frac{P}{Q} \right] \] (6.166)

Hence, using Eq. (6.114) to substitute for \( U_{2,\text{planar}} \) and \( U_{2,\text{correction}} \), and Eq. (6.119) for \( \frac{P}{Q} \), we finally obtain

\[
\hat{Z}_1^2 = - \left[ \frac{\mathcal{A}k^2 - U_0}{1 - e^{[m_\text{e} - m_-]L}} \right] \left[ m_+ + e^{[m_\text{e} - m_-]L} \left[ -U_0 L \left[ N - m_- \right] + m_- \right] \right] - \left[ 3 \frac{m_- - m_+}{m_\text{e} - m_-} \right] - \left[ 3N + 6U_0 \right] \cdot \frac{1}{L} e^{U_0 L} 
\]

\[
\hat{Z}_1^2 = - \left[ \frac{\mathcal{A}k^2 - U_0}{1 - e^{[m_\text{e} - m_-]L}} \right] \left[ m_+ + e^{[m_\text{e} - m_-]L} \left[ -U_0 L \left[ N - m_- \right] + m_- \right] \right] - \left[ 3 \frac{m_- - m_+}{m_\text{e} - m_-} \right] - \left[ 3N + 6U_0 \right] 
\]

\[
\frac{1}{L} \left[ \frac{1}{2} U_0^2 + \mathcal{A}k^2 M \left[ 1 + \left[ \frac{U_0}{e^{U_0} - 1} \right] - \left[ e^{U_0} - 1 \right] \right] \right] 
\]

\[
+ \left[ M - N \right] \left[ 3 \frac{U_0}{1 - U_0} \mathcal{A}k^2 M - \frac{3}{2} \mathcal{A}k^2 MM_{22} + \frac{9}{4} \mathcal{A}k^2 \left[ 2k^2 - U_0 M \right] \right] 
\]

\[
+ \left[ 3 \mathcal{A}k^2 \left[ \frac{1}{2} M + 2M_{22} \right] \right] 
\]

\[
\left[ \frac{1}{2} U_0^2 N_{22} + 2U_0 k^2 + \frac{1}{2} U_0^3 \right] + \mathcal{A}k^2 M \left[ N_{22} - M_{22} \right] 
\]

\[
4 \mathcal{A}k^2 \left[ N_{22} - M_{22} \right] - \left[ U_0 N_{22} + U_0^2 \right] 
\] (6.167)
Table 6.1 – Case 1 – Values of $U_0$ and $A^2$ for inputs $L = 1, 2$ and $k^2$

<table>
<thead>
<tr>
<th>$k^2$</th>
<th>$L = 1$</th>
<th></th>
<th>$L = 2$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$U_0$</td>
<td>$A^2$</td>
<td>$U_0$</td>
<td>$A^2$</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>$5 \times 10^{-11}$</td>
<td>$-5.99 \times 10^0$</td>
<td>$7.5 \times 10^{-11}$</td>
<td>$3.998 \times 10^0$</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>$5 \times 10^{-10}$</td>
<td>$-5.99 \times 10^0$</td>
<td>$7.5 \times 10^{-10}$</td>
<td>$3.987 \times 10^0$</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>$5 \times 10^{-9}$</td>
<td>$-5.94 \times 10^0$</td>
<td>$7.45 \times 10^{-9}$</td>
<td>$3.849 \times 10^0$</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td>$5 \times 10^{-8}$</td>
<td>$-5.41 \times 10^0$</td>
<td>$7.07 \times 10^{-8}$</td>
<td>$3.342 \times 10^0$</td>
</tr>
<tr>
<td>1</td>
<td>$5 \times 10^{-7}$</td>
<td>$-2.215 \times 10^0$</td>
<td>$5.66 \times 10^{-7}$</td>
<td>$-3.579 \times 10^0$</td>
</tr>
<tr>
<td>10</td>
<td>$5 \times 10^{-6}$</td>
<td>$-2.662 \times 10^0$</td>
<td>$5 \times 10^{-6}$</td>
<td>$-1.487 \times 10^0$</td>
</tr>
<tr>
<td>$10^2$</td>
<td>$5 \times 10^{-5}$</td>
<td>$-2.667 \times 10^2$</td>
<td>$5 \times 10^{-5}$</td>
<td>$-1.379 \times 10^2$</td>
</tr>
<tr>
<td>$10^3$</td>
<td>$5 \times 10^{-4}$</td>
<td>$-2.667 \times 10^4$</td>
<td>$5 \times 10^{-4}$</td>
<td>$-1.348 \times 10^4$</td>
</tr>
<tr>
<td>$10^4$</td>
<td>$5 \times 10^{-3}$</td>
<td>$-2.68 \times 10^2$</td>
<td>$5 \times 10^{-3}$</td>
<td>$-1.35 \times 10^2$</td>
</tr>
<tr>
<td>$10^5$</td>
<td>$5 \times 10^{-2}$</td>
<td>$-2.802 \times 10^4$</td>
<td>$5 \times 10^{-2}$</td>
<td>$-1.474 \times 10^4$</td>
</tr>
<tr>
<td>$10^6$</td>
<td>0.5</td>
<td>$-4.392 \times 10^6$</td>
<td>0.5</td>
<td>$-3.621 \times 10^6$</td>
</tr>
</tbody>
</table>

The sign of $\hat{Z}_1^2$ is of interest. If it is positive, the pitchfork is forward, as assumed, otherwise it is backward. In the latter case, $T_L$ must be expanded as $T_L = T_{L_0} - \frac{1}{2} \alpha^2$. Clearly it is a formidable task to determine the sign of $\hat{Z}_1^2$ and one can possibly not determine its sign by inspection. We will therefore have to do some calculations in order to learn the nature of the bifurcation. Table 6.1 gives the sign of $\hat{Z}_1^2$ for various input values of $k^2$, $L$. Clearly $\hat{Z}_1^2$ can have either sign, whence the pitchfork can be backward as well as forward depending on the input parameters. However, the formula given in Eq. (6.167) is not very useful if one wants to
learn how the sign of \( Z_1^2 \) depends upon the inputs. It is hard to figure out the point of crossover from a backward to a forward pitchfork. Hence we will consider a case later where we will look at a special case of case 1 where the model equations will not have \( U \) on the domain. We will obtain a formula for \( Z_1^2 \) which would be much simpler compared to Eq. (6.167). This case is deferred until the end of the chapter, where we will find out the analytical dependence of \( Z_1^2 \) on inputs \( k^2 \) and \( L \).

For now, we continue in the spirit of hoping to find the reason for a “speed-up” in pure solidification. So we consider a simplification of case 1 where the solid phase is of infinite extent. This case might indeed be more realistic in that solids of extent much greater than the capillary length ought to be considered infinite.

**Case 2: Latent Heat Rejected Only to the Subcooled Liquid, Solid Phase of Infinite Extent**

The notation remains the same as in case 1. Since the solid phase depth is of infinite extent, all lengths are scaled by \( L \), the depth of the liquid phase. All speeds are scaled by \( \alpha / L \).

The scaled temperature is given by \( T_{scaled} = \frac{T_u - T}{\alpha L W / \lambda} \). Then, the scaled temperature in the solid phase must satisfy

\[
\nabla^2 T + U \frac{\partial T}{\partial z} = 0
\]

(6.168)

for \(-\infty < z < Z\) and \(0 < x < W\), while in the liquid phase

\[
\nabla^2 T^* + U \frac{\partial T^*}{\partial z} = 0
\]

(6.169)

must hold for \( Z < z < 1 \) and \(0 < x < W\). The equations along the interface, viz., along \( z = Z(x) \) are
\[ T = -\mathcal{A}[2H] = T^* \]  \hspace{1cm} (6.170)

and

\[ \mathbf{n} \cdot \nabla T - \mathbf{n} \cdot \nabla T^* = -\mathbf{n} \cdot \mathbf{U} \cdot \mathbf{k} \]  \hspace{1cm} (6.171)

where \( \mathcal{A} \) denotes \( \begin{bmatrix} \frac{\gamma \lambda}{\alpha L_\mu L} \end{bmatrix} \). Far-field conditions are given by

\[ T(z = -\infty) = 0 \]  \hspace{1cm} (6.172)

and

\[ T(z = 1) = T_L \]  \hspace{1cm} (6.173)

Side wall conditions are Neumann. The volume of the subcooled liquid must be maintained fixed, whence

\[ \int_0^W Z(x) dx = 0 \]  \hspace{1cm} (6.174)

**The Base Solution**

A base state solution is given by

\[ T_0(z) = 0 \]  \hspace{1cm} (6.175)

\[ T_0^*(z) = 1 - e^{-U_0 z} \]  \hspace{1cm} (6.176)

where \( U_0 \) is given by

\[ U_0 = -\ln(1 - T_L) \]  \hspace{1cm} (6.177)

**The Perturbation Eigenvalue Problem**

Expanding \( Z, T, \) and \( T^* \), at \( z = Z(x) \) as in Eqs. (6.17-6.19), the perturbation eigenvalue problem is given by

\[ \nabla^2 T_i + U_0 \frac{\partial T_i}{\partial z} = 0 \]  \hspace{1cm} (6.178)
on the domain, $-\infty < z < 0$, $0 < x < W$, and

$$\nabla^2 T_1^* + U_0 \frac{\partial T_1^*}{\partial z} = 0$$

(6.179)
on the domain, $0 < z < 1$, $0 < x < W$, where, at the base surface $z = 0$,

$$T_1 = -A \frac{d^2 Z_1}{dx^2} - Z_1 \frac{dT_0}{dz}$$

(6.180)

$$\left[ T_1 - T_1^* \right] + Z_1 \left[ \frac{dT_0}{dz} - \frac{dT_0^*}{dz} \right] = 0$$

(6.181)
and

$$\left[ \frac{\partial T_1}{\partial z} - \frac{\partial T_1^*}{\partial z} \right] + Z_1 \left[ \frac{d^2 T_0}{dz^2} - \frac{d^2 T_0^*}{dz^2} \right] = 0$$

(6.182)
must hold, and where,

$$T_1(z = -\infty) = 0$$

(6.183)
and

$$T_1^*(z = 1) = 0$$

(6.184)
also hold. The sidewall conditions are Neumann. Thus the problem is homogeneous in $T_1$, $T_1^*$ and $Z_1$, and it has solutions of the form

$$T_1 = \hat{T}_1(z) \cos(kx), \quad T_1^* = \hat{T}_1^*(z) \cos(kx) \quad \text{and} \quad Z_1 = A \cos(kx)$$

(6.185)
which satisfy the side wall conditions so long as $k = n\pi/W$, $n = 1, 2, \ldots$, where $k$ is the wave number of the disturbance. $n = 0$ is ruled out by the condition

$$\int_0^W Z_1 \, dx = 0$$

(6.186)
The expansions presented above give the equations for \( \hat{T}_1, \hat{T}_1^* \) and \( \hat{Z}_1 \). They can be solved just as in case 1 to get

\[
\hat{T}_1(z) = A_1 e^{m_z z} = \mathcal{A} k^2 \left[ e^{m_z z} \right] \hat{Z}_1
\]

and

\[
\hat{T}_1^*(z) = A_1^* \left[ e^{m_z z} - e^{[m_z - m_z] z} \right] = \left[ \frac{\mathcal{A} k^2 - U_0}{1 - e^{[m_z - m_z] z}} \right] \left[ e^{m_z z} - e^{[m_z - m_z] z} \right] \hat{Z}_1
\]

where \( m_z = \frac{-U_0 \pm \sqrt{U_0^2 + 4k^2}}{2} \). We can then turn to Eq. (6.182), which gives us

\[
-\left[ \mathcal{A} k^2 \right] m_z - \left[ -\mathcal{A} k^2 + U_0 \right] N - U_0^2 = 0
\]

where \( N = \frac{m_z - m_z e^{[m_z - m_z] z}}{1 - e^{[m_z - m_z] z}} \). Notice that the neutrality relation given by Eq. (6.189) can be obtained from Eq. (6.39) of case 1 simply by observing that the asymptotic limit of \( M \) as the solid depth approaches infinity is given by \( m_z \). The neutral curve is again as shown in Figure 6.2 (for case 1) and only one crest is seen at critical. Now on increasing \( T_L \) to its critical value \( T_{L_0} \), and then slightly beyond, the branching to the new steady solution is expected be a forward pitchfork. So as before we write

\[
T_L = T_{L_0} + \frac{1}{2} \varepsilon^2
\]

and expand \( U \) and \( Z \) as in Eqs. (6.42, 6.43) to get the first and higher order problems. Eq. (6.177) indicates that for a small increase in \( T_L \) from \( T_{L_0} \), the corresponding change in \( U \) from \( U_0 \), per unit change in \( T_L \) is given by \( e^{U_0} \).
The First Order Problem

The first order problem is given by

\[ \nabla^2 T_1 + U_o \frac{\partial T_1}{\partial z} = -U \frac{dV_o}{dz} \]  

(6.191)
on the domain, \( -\infty < z < 0 \), \( 0 < x < W \), and

\[ \nabla^2 T_1^* + U_o \frac{\partial T_1^*}{\partial z} = -U_i \frac{dT_0^*}{dz} \]  

(6.192)
on the domain, \( 0 < z < 1 \), \( 0 < x < W \),

\[ T_i = -A \frac{d^2 Z}{dx^2} - Z_o \frac{dV_o}{dz} \]  

(6.193)
\[ \left[ T_i - T_i^* \right] + Z_1 \left[ \frac{dT_0^d}{dz} - \frac{dT_0^*}{dz} \right] = 0 \]  

(6.194)
and

\[ \left[ \frac{\partial T_1}{\partial z} - \frac{\partial T_1^*}{\partial z} \right] + Z_1 \left[ \frac{d^2 T_0^d}{dz^2} - \frac{d^2 T_0^*}{dz^2} \right] = -U_i \]  

(6.195)
at \( z = 0 \),
\[ T_i (z = -\infty) = 0 \]  

(6.196)
and
\[ T_i^* (z = 1) = 0 \]  

(6.197)
The volume condition is given by

\[ \int_0^W Z_o dx = 0 \]  

(6.198)
The sidewall conditions are Neumann. Hence we have solutions of the form

\[ T_i (x, z) = T_{10} (z) + T_{11} (z) \cos(kx) \]  

(6.199)
\[ T_1^* (x, z) = T_{10}^* (z) + T_{11}^* (z) \cos(kx) \]  
(6.200)

\[ Z_1(x) = A \cos(kx) = Z_i \cos(kx) \]  
(6.201)

The expansions presented above are used to obtain the \{10\} and \{11\} problems. Again, as in case 1, \(U_1\) turns out to be zero, and therefore \(T_{10}\) and \(T_{10}^*\) must both be zero. Then the first order problem is exactly like the eigenvalue problem, and the condition at neutrality is given by Eq. (6.189), viz., \(-\lambda k^2 m + -\lambda k^2 + U_0 \) \(N - U_0^2 = 0\). And we go on to the second order problem to find the value of \(A\).

**The Second Order Problem**

The second order problem is

\[ \nabla^2 T_2 + U_0 \frac{\partial T_2}{\partial z} = -U_0 \frac{d\Psi_0}{dz} \]  
(6.202)

on the domain \(-\infty < z < 0\), \(0 < x < W\), and

\[ \nabla^2 T_{2}^* + U_0 \frac{\partial T_{2}^*}{\partial z} = -U_0 \frac{dT_{2}^*}{dz} \]  
(6.203)

on the domain \(0 < z < 1\), \(0 < x < W\),

\[ T_2 + 2Z_i \frac{\partial T_2}{\partial z} + Z_i^2 \frac{d^2 \Psi_0}{dz^2} = -A \frac{d^2 Z_2}{dx^2} - Z_i \frac{d\Psi_0}{dz} \]  
(6.204)

\[ [T_2 - T_{2}^*] + 2Z_i \left[ \frac{\partial T_1}{\partial z} - \frac{\partial T_{1}^*}{\partial z} \right] + Z_i^2 \left[ \frac{d^2 \Psi_0}{dz^2} - \frac{d^3 T_{1}^*}{dz^3} \right] + Z_i \left[ \frac{d \Psi_0}{dz} - \frac{dT_{1}^*}{dz} \right] = 0 \]  
(6.205)

and

\[ \left[ \frac{\partial T_{1}}{\partial z} - \frac{\partial T_{1}^*}{\partial z} \right] + 2Z_i \left[ \frac{\partial^2 T_1}{\partial z^2} - \frac{\partial^2 T_{1}^*}{\partial z^2} \right] + Z_i^2 \left[ \frac{d^3 \Psi_0}{dz^3} - \frac{d^3 T_{1}^*}{dz^3} \right] + Z_i \left[ \frac{d^2 \Psi_0}{dz^2} - \frac{d^2 T_{1}^*}{dz^2} \right] \]  
(6.206)

\[ -2Z_{1x} \left[ \frac{\partial T_1}{\partial x} - \frac{\partial T_{1}^*}{\partial x} \right] = -U_2 \]
at \( z = 0 \),

\[ T_2(z = -\infty) = 0 \tag{6.207} \]

and

\[ T_2^*(z = 1) = 1 \tag{6.208} \]

The volume condition is given by

\[ \int_0^w Z_2 dx = 0 \tag{6.209} \]

Again, assuming the solution has the form

\[ T_2(x, z) = T_{20}(z) + T_{21}(z) \cos(kx) + T_{22}(z) \cos(2kx) \tag{6.210} \]

\[ T_2^*(x, z) = T_{20}^*(z) + T_{21}^*(z) \cos(kx) + T_{22}^*(z) \cos(2kx) \tag{6.211} \]

\[ Z_2(x) = Z_{21} \cos(kx) + Z_{22} \cos(2kx) \tag{6.212} \]

we deduce the solutions to the \{20\} and \{21\} and \{22\} problems. At \( z = 0 \), the following formulae may be useful:

\[ 2Z_1 \left[ \frac{\partial^2 T_1}{\partial z^2} - \frac{\partial^2 T_1^*}{\partial z^2} \right] = U_0 \left[ k^2 + U_0^2 \right] Z_1 \left[ 1 + \cos(2kx) \right] \]

\[ -2Z_{1x} \left[ \frac{\partial T_1}{\partial x} - \frac{\partial T_1^*}{\partial x} \right] = -k^2 U_0 Z_1 \left[ 1 - \cos(2kx) \right] \]

**The \{20\} problem**

The \{20\} problem is given by

\[ \frac{d^2 T_{20}}{dz^2} + U_0 \frac{dT_{20}}{dz} = -U_2 \frac{dT_0^*}{dz} \tag{6.213} \]

in the solid phase, \( -\infty < z < 0 \), \( 0 < x < W \), and
\[
\frac{d^2 T_{20}^*}{dz^2} + U_0 \frac{dT_{20}^*}{dz} = -U_2 \frac{dT_{10}^*}{dz}
\]  
(6.214)

in the liquid phase, \(0 < z < 1\), \(0 < x < W\),

\[
T_{20} - T_{20}^* = \frac{1}{2} U_0^2 Z_{11}^2
\]  
(6.215)

and

\[
\left[ \frac{dT_{20}}{dz} - \frac{dT_{20}^*}{dz} \right] = -U_2 - \frac{1}{2} U_0^3 Z_{11}^2
\]  
(6.216)

at \(z = 0\),

\[
T_{20} (z = -\infty) = 0
\]  
(6.217)

and

\[
T_{20}^* (z = 1) = 1
\]  
(6.218)

A solution to Eqs. (6.213, 6.214), subject to the far field condition at the solid sink is given by

\[
T_{20} (z) = A_{20}
\]  
(6.219)

and

\[
T_{20}^* (z) = A_{20}^* e^{-U_0z} + e^{-U_0z} \int_0^z e^{U_0\xi} \left[ B_{20} - U_2 \left[ 1 - e^{-U_0\xi} \right] \right] d\xi
\]  
(6.220)

where \(A_{20}\) is some negative constant. Noticing that \(\frac{dT_{20}^*}{dz}(z = 0) = B_{20}^* - U_0 A_{20}^*\), and using Eqs. (6.215, 6.216) to eliminate \(A_{20}^*\) and \(B_{20}^*\), we get

\[
T_{20} (z) = A_{20}
\]  
(6.221)

\[
T_{20}^* (z) = A_{20} - \frac{1}{2} U_0^2 e^{-U_0z} Z_{11}^2 + U_2 z e^{-U_0z}
\]  
(6.222)

where \(A_{20}\) is found by using Eq. (6.218) as
Now the \( \{21\} \) and \( \{22\} \) problems can be solved entirely, but it is sufficient to solve the \( \{20\} \) problem to learn whether the front speeds up or slows down. To do this, we integrate Eq. (6.204) over \( 0 < x < W \), whence

\[
T_{20}(z = 0) + Z_1 \frac{d T_1}{dz}(z = 0) + \frac{1}{2} Z_1^2 \frac{d^2 T_0}{dz^2}(z = 0) = 0
\]  

(6.224)

Using \( \frac{d T_1}{dz}(z = 0) = \mathcal{A} k^2 m \hat{Z}_1 \), and \( T_{20}(z = 0) = A_{20} \), there obtains \( A_{20} = -\mathcal{A} k^2 m \hat{Z}_1^2 \).

Comparing with Eq. (6.223), there obtains

\[
U_2 = \frac{e^{U_0}}{U_{2,\text{planar}}} \left[ \frac{1}{2} U_0^2 + \mathcal{A} k^2 m e^{U_0} \right] \hat{Z}_1^2
\]

(6.225)

The correction term is always positive, whence the mean speed of the interface runs ahead of its base value, and our hypothesis of a "speed-up" in solidification is again confirmed. But one might ask: Is this result limited to cases where the latent heat is rejected only to the subcooled liquid? It is to this question that we turn next. Hence we consider a third case where the latent heat is rejected to the subcooled liquid as well as to the frozen solid, and both phases are taken to be finite. Indeed, one might intuitively expect that as rejecting the latent heat to the solid phase is stabilizing in contrast to rejecting heat to the liquid, it might also have an opposite effect in regard to the front speed correction, i.e., a large enough \( T_s \) might be expected to slow down the front compared to its base value. However, it will be shown in the next section that this is not so, and that once the instability sets in, the front speeds up, no matter the value of \( T_s \).
Case 3: Latent Heat Rejected to the Frozen Solid as Well as to the Subcooled Liquid, Both Phases of Finite Extent

The notation, including all scales and references, remains the same as in case 1. Then in the solid phase, the equation for the scaled temperature is given by

$$\nabla^2 T + U \frac{\partial T}{\partial z} = 0$$  \hspace{1cm} (6.226)

for $-1 < z < Z$ and $0 < x < W$, while in the liquid phase

$$\nabla^2 T^* + U \frac{\partial T^*}{\partial z} = 0$$  \hspace{1cm} (6.227)

must hold for $Z < z < L$ and $0 < x < W$. The equations along the interface, viz., along $z = Z(x)$ are

$$T = -\mathcal{A}[2H] = T^*$$  \hspace{1cm} (6.228)

and

$$\mathbf{n} \cdot \nabla T - \mathbf{n} \cdot \nabla T^* = -U \mathbf{k} \cdot \mathbf{n}$$  \hspace{1cm} (6.229)

where $\mathcal{A}$ denotes $\left[ \frac{\gamma^2}{\alpha L_\gamma^2 S} \right] T_M$. Far-field conditions are given by

$$T(z = -1) = T_s$$  \hspace{1cm} (6.230)

and

$$T^*(z = L) = T_l$$  \hspace{1cm} (6.231)

Side wall conditions are Neumann. The volume of the subcooled liquid must be maintained fixed, whence

$$\int_{-W}^{W} Z(x) dx = 0$$  \hspace{1cm} (6.232)
The Base Solution

A base state solution is given by

\[ T_0(z) = A_0 \left[ 1 - e^{-U_0 z} \right] = -\left[ \frac{T_S}{e^{U_0} - 1} \right] \left[ 1 - e^{-U_0 z} \right] \]  \hspace{1cm} (6.233) 

and

\[ T_0^*(z) = A_0^* \left[ 1 - e^{-U_0^* z} \right] = -\left[ \frac{T_L}{1 - e^{-U_0^* z}} \right] \left[ 1 - e^{-U_0^* z} \right] \]  \hspace{1cm} (6.234) 

where \( U_0 \) is given by

\[ \frac{T_S}{e^{U_0} - 1} + \frac{T_L}{1 - e^{-U_0^* z}} = 1 \]  \hspace{1cm} (6.235) 

Some useful derivatives and their differences are given in Table 6.2.

<table>
<thead>
<tr>
<th>Case</th>
<th>Derivative</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>( d^2T_0 / dz^2 )</td>
<td>( U_0 A_0 \left[ \frac{T_S}{e^{U_0} - 1} \right] &gt; 0 )</td>
</tr>
<tr>
<td>3</td>
<td>( d^3T_0 / dz^3 )</td>
<td>( U_0 A_0 \left[ \frac{T_S}{e^{U_0} - 1} \right] &lt; 0 )</td>
</tr>
<tr>
<td>4</td>
<td>( d^4T_0 / dz^4 )</td>
<td>( U_0 A_0 \left[ \frac{T_S}{e^{U_0} - 1} \right] &gt; 0 )</td>
</tr>
<tr>
<td>5</td>
<td>( d^2T_0^* / dz^2 )</td>
<td>( U_0^* A_0^* \left[ \frac{T_L}{1 - e^{-U_0^* z}} \right] &lt; 0 )</td>
</tr>
<tr>
<td>5</td>
<td>( d^3T_0^* / dz^3 )</td>
<td>( U_0^* A_0^* \left[ \frac{T_L}{1 - e^{-U_0^* z}} \right] &gt; 0 )</td>
</tr>
<tr>
<td>5</td>
<td>( d^4T_0^* / dz^4 )</td>
<td>( U_0^* A_0^* \left[ \frac{T_L}{1 - e^{-U_0^* z}} \right] &lt; 0 )</td>
</tr>
</tbody>
</table>

The Perturbation Eigenvalue Problem

Expanding \( Z \), \( T \), and \( T^* \), at \( z = Z(x) \) as in Eqs. (6.17-6.19), the perturbation eigenvalue problem is given by
\[ \nabla^2 T_i + U_0 \frac{\partial T_i}{\partial z} = 0 \quad (6.236) \]

on the domain, \(-1 < z < 0\), \(0 < x < W\), and

\[ \nabla^2 T_i^* + U_0 \frac{\partial T_i^*}{\partial z} = 0 \quad (6.237) \]

on the domain, \(0 < z < L\), \(0 < x < W\), where, at the base surface \(z = 0\),

\[
T_i = -A \frac{d^2 Z_1}{dx^2} - Z_1 \frac{dT_0}{dz} \quad (6.238)
\]

\[
\left[ T_i - T_i^* \right] + Z_1 \left[ \frac{dT_0}{dz} - \frac{dT_0^*}{dz} \right] = 0 \quad (6.239)
\]

and

\[
\left[ \frac{\partial T_i}{\partial z} - \frac{\partial T_i^*}{\partial z} \right] + Z_1 \left[ \frac{d^2 T_0}{dz^2} - \frac{d^2 T_0^*}{dz^2} \right] = 0 \quad (6.240)
\]

must hold, and where,

\[ T_i (z = -1) = 0 \quad (6.241) \]

and

\[ T_i^* (z = L) = 0 \quad (6.242) \]

The sidewall conditions are Neumann. Thus the problem is homogeneous in \(T_i\), \(T_i^*\) and \(Z_1\), and

it has solutions of the form

\[ T_i = \hat{T}_i (z) \cos(kx) \quad T_i^* = \hat{T}_i^* (z) \cos(kx) \quad \text{and} \quad Z_1 = A \cos(kx) \quad (6.243) \]

which satisfy the side wall conditions so long as \(k = n\pi/W\), \(n = 1, 2, \ldots\), where \(k\) is the wave

number of the disturbance. \(n = 0\) is ruled out by the condition

\[ \int_{0}^{W} Z_1 dx = 0 \quad (6.244) \]
The expansions presented above give the equations for \( \hat{T}_i \), \( \hat{T}_i^* \) and \( \hat{Z}_i \). They are

\[
\left[ \frac{d^2}{dz^2} - k^2 \right] \hat{T}_i + U_0 \frac{d}{dz} \hat{T}_i = 0
\]  
(6.245)

in the solid phase, \(-1 < z < 0\), \(0 < x < W\), and

\[
\left[ \frac{d^2}{dz^2} - k^2 \right] \hat{T}_i^* + U_0 \frac{d}{dz} \hat{T}_i^* = 0
\]  
(6.246)

in the liquid phase, \(0 < z < L\), \(0 < x < W\),

\[
\hat{T}_i = \left[ \mathcal{A} k^2 - \frac{d T_0}{d z} \right] \hat{Z}_i
\]  
(6.247)

\[
\left[ \hat{T}_i - \hat{T}_i^* \right] + \hat{Z}_i \left[ \frac{d T_0}{d z} - \frac{d T_0^*}{d z} \right] = 0
\]  
(6.248)

and

\[
\left[ \frac{d \hat{T}_i}{d z} - \frac{d \hat{T}_i^*}{d z} \right] + \hat{Z}_i \left[ \frac{d^2 T_0}{d z^2} - \frac{d^2 T_0^*}{d z^2} \right] = 0
\]  
(6.249)

at \(z = 0\),

\[
\hat{T}_i(z = -1) = 0
\]  
(6.250)

and

\[
\hat{T}_i^*(z = L) = 0
\]  
(6.251)

Defining \( m_{\pm} = \frac{-U_0 \pm \sqrt{U_0^2 + 4k^2}}{2} \), a solution to Eqs. (6.245-6.248, 6.250, 6.251) is given by
\[ \hat{T}_1(z) = A_1 \left[ e^{m_z} - e^{(m_z - m_\mu)} e^{m_z} \right] \left( \frac{\mathcal{A} k^2 - \frac{dT_0}{dz}(z = 0)}{1 - e^{(m_z - m_\mu)}} \right) \left[ e^{m_z} - e^{(m_z - m_\mu)} e^{m_z} \right] \hat{Z}_1 \] (6.252)

\[ \hat{T}_1^*(z) = A_1^* \left[ e^{m_z} - e^{(m_z - m_\mu)} e^{m_z} \right] \left( \frac{\mathcal{A} k^2 - \frac{dT_0^*}{dz}(z = 0)}{1 - e^{(m_z - m_\mu)}} \right) \left[ e^{m_z} - e^{(m_z - m_\mu)} e^{m_z} \right] \hat{Z}_1 \] (6.253)

We can then turn to Eq. (6.249), which gives us

\[ \begin{bmatrix} -\mathcal{A} k^2 + \frac{dT_0}{dz} \end{bmatrix} M - \begin{bmatrix} -\mathcal{A} k^2 + \frac{dT_0^*}{dz} \end{bmatrix} N = U_0^2 \] (6.254)

or

\[ \begin{bmatrix} -\mathcal{A} k^2 + \frac{U_0 T_S}{e^{U_0} - 1} \end{bmatrix} M + \begin{bmatrix} -\mathcal{A} k^2 + \frac{U_0 T_S}{e^{U_0} - 1} - U_0 \end{bmatrix} N = U_0^2 \] (6.255)

where \( M = \left[ \frac{m_z - m_\mu e^{(m_z - m_\mu)}}{1 - e^{(m_z - m_\mu)}} \right] \) and \( N = \left[ \frac{m_z - m_\mu e^{(m_z - m_\mu)}}{1 - e^{(m_z - m_\mu)}} \right] \).

Figures 6.3 and 6.4 show the corresponding neutral curves. As the control variable \( T_L \) increases upward from zero, the output variable \( U_0 \) increases from zero, until there comes a point when a line of constant \( U_0 \) first crosses the neutral curve at an admissible value of \( k \). The corresponding value of \( U_0 \) will be referred as its critical value. Henceforth the subscript zero will refer to this critical state. At values of \( U \) higher than \( U_0 \), the base solution loses its stability. The “dip” is present in both kinds of neutral curves and this implies that the critical value of \( U \) need not correspond to the least allowable value of \( k^2 \). In fact, \( n \) might be any of the numbers: 1, 2, 3... , and hence multiple crests might be seen.
Figure 6.3 – An unusual neutral curve in solidification when the latent heat is rejected through both phases

Figure 6.4 – Typical neutral curve in solidification when the latent heat is rejected through both phases

Now on increasing $T_L$ to its critical value $T_{L_0}$, and then slightly beyond, the branching to the new steady solution is expected be a forward pitchfork. Hence we write

$$T_L = T_{L_0} + \frac{1}{2} e^2$$  \hspace{1cm} (6.256)

and expand $U$ and $Z$ as in Eqs. (6.42, 6.43) to get the first and higher order problems. Eq.
(6.235) indicates that for a small increase in $T_L$ from $T_{L_0}$, the corresponding change in $U$ from $U_0$, per unit change in $T_L$ is given by

$$
\frac{e^{U_0 L}}{[e^{U_0 L} - 1]^2} \frac{T_{L_0}}{e^{U_0 L} - 1} L e^{U_0 L} + \frac{T_S}{e^{U_0 L} - 1} e^{U_0} \frac{e^{U_0 L}}{[e^{U_0 L} - 1]^2} \frac{T_{L_0}}{e^{U_0 L} - 1} L e^{U_0 L}
$$

**The First Order Problem**

The first order problem is given by

$$\nabla^2 T_i + U_0 \frac{\partial T_i}{\partial z} = -U_1 \frac{dT_0}{dz} \quad (6.257)
$$

on the domain, $-1 < z < 0, \ 0 < x < W$, and

$$\nabla^2 T_i^* + U_0 \frac{\partial T_i^*}{\partial z} = -U_1 \frac{dT_0^*}{dz} \quad (6.258)
$$

on the domain, $0 < z < L, \ 0 < x < W$, where, at the base surface $z = 0$,

$$T_i + Z_1 \frac{dT_0}{dz} = -\mathcal{A} \frac{d^2 Z_1}{dx^2} \quad (6.259)
$$

$$[T_i - T_i^*] + Z_i \left[\frac{dT_0}{dz} - \frac{dT_0^*}{dz}\right] = 0 \quad (6.260)
$$

and

$$\left[\frac{\partial T_i}{\partial z} - \frac{\partial T_i^*}{\partial z}\right] + Z_i \left[\frac{d^2 T_0}{dz^2} - \frac{d^2 T_0^*}{dz^2}\right] = -U_1 \quad (6.261)
$$

must hold, and where

$$T_i(z = -1) = 0 \quad (6.262)$$

and

$$T_i^*(z = L) = 0 \quad (6.263)$$

The volume condition is given by
\[ \int_0^w Z_i dx = 0 \quad (6.264) \]

The sidewall conditions are Neumann, and Eqs. (6.257, 6.258, 6.260-6.264) can be solved by writing

\[ T_i(x, z) = T_{10}(z) + T_{11}(z) \cos(ka) \quad (6.265) \]

\[ T_{1i}^*(x, z) = T_{10}^*(z) + T_{11}^*(z) \cos(ka) \quad (6.266) \]

\[ Z_1(x) = A \cos(ka) \]

The expansions presented above are used to deduce the \{10\} and \{11\} problems.

**The \{10\} problem**

The \{10\} problem is given by

\[ \frac{d^2 T_{10}}{dz^2} + U_0 \frac{dT_{10}}{dz} = -U_1 \frac{dT_0^*}{dz} \quad (6.268) \]

in the solid phase, \(-1 < z < 0\), \(0 < x < W\), and

\[ \frac{d^2 T_{10}^*}{dz^2} + U_0 \frac{dT_{10}^*}{dz} = -U_1 \frac{dT_0^*}{dz} \quad (6.269) \]

in the liquid phase, \(0 < z < L\), \(0 < x < W\),

\[ T_{10} - T_{10}^* = 0 \quad (6.270) \]

and

\[ \frac{dT_{10}}{dz} - \frac{dT_{10}^*}{dz} = -U_1 \quad (6.271) \]

at \(z = 0\),

\[ T_{10}^*(z = -1) = 0 \quad (6.272) \]

and
The general solution to Eqs. (6.268, 6.269) is given by:

\[
T_{10}(z) = A_{10}e^{-U_0z} + e^{-U_0\xi_0} \int_0^z e^{U_0\xi} \left[ B_{10} - U_1A_0 \left( 1 - e^{-U_0\xi} \right) \right] d\xi
\]

\[
T_{10}^*(z) = A_{10}^*e^{-U_0z} + e^{-U_0\xi_0} \int_0^z e^{U_0\xi} \left[ B_{10}^* - U_1A_0^* \left( 1 - e^{-U_0\xi} \right) \right] d\xi
\]

and their derivatives are given by \( \frac{dT_{10}}{dz}(z = 0) = B_{10} - U_0A_{10} \), and \( \frac{dT_{10}^*}{dz}(z = 0) = B_{10}^* - U_0A_{10}^* \),

whereupon using Eqs. (6.270-6.272) to eliminate \( B_{10}, A_{10}^* \) and \( B_{10}^* \), we get

\[
T_{10}(z) = A_{10}e^{-U_0z} + \left[ U_1A_0 - A_{10} \right] \frac{e^{U_0\xi}}{1 - e^{U_0\xi}} \left[ 1 - e^{-U_0\xi} \right] + U_1A_0ze^{-U_0z}
\]

\[
T_{10}^*(z) = A_{10}e^{-U_0z} + \left[ U_1A_0 - A_{10} \right] \frac{e^{U_0\xi}}{1 - e^{U_0\xi}} \left[ 1 - e^{-U_0\xi} \right] + U_1ze^{-U_0z}
\]

where \( A_{10} \) is found by using Eq. (6.273) as \( A_{10} = U_1 \left[ \frac{A_0 \left( \frac{e^{U_0}}{e^{U_0} - 1} \right) \left[ e^{U_{0L}} - 1 \right] - A_0L - L}{1 + \left[ \frac{e^{U_0}}{e^{U_0} - 1} \right] \left[ e^{U_{0L}} - 1 \right]} \right] \).

The \{11\} problem

The \{11\} problem is similar to the eigenvalue problem. It is given by

\[
\left[ \frac{d^2}{dz^2} - k^2 \right] T_{11} + U_0 \frac{dT_{11}}{dz} = 0
\]

in the solid phase, \(-1 < z < 0\), \(0 < x < W\), and

\[
\left[ \frac{d^2}{dz^2} - k^2 \right] T_{11}^* + U_0 \frac{dT_{11}^*}{dz} = 0
\]

in the liquid phase, \(0 < z < L\), \(0 < x < W\),

\[171\]
\[
\left[ T_{11} - T_{11}^* \right] + Z_{11} \left[ \frac{dT_0}{dz} - \frac{dT'_0}{dz} \right] = 0 \quad (6.280)
\]

and
\[
\left[ \frac{dT_{11}}{dz} - \frac{dT'_{11}}{dz} \right] + Z_{11} \left[ \frac{d^2T_0}{dz^2} - \frac{d^2T'_0}{dz^2} \right] = 0 \quad (6.281)
\]

at \( z = 0 \),
\[
T_{11}(z = -1) = 0 \quad (6.282)
\]

and
\[
T_{11}^*(z = L) = 0 \quad (6.283)
\]

Finally using Eq. (6.264) and \( dZ_1/dx = 0 \) at \( x = 0, W \), and integrating Eq. (6.259) over \( 0 < x < W \), we find that the constant \( A_{10} \) must be zero. Hence \( U_1 \) must be zero, and therefore \( T_{10} \) and \( T_{10}^* \) must both be identically zero. Then the first order problem is exactly like the eigenvalue problem, and the condition at neutrality is given by Eq. (6.255), viz.,
\[
- \left[ \mathcal{A}k^2 + \frac{U_0 T_5}{e^{U_0} - 1} \right] M + \left[ \mathcal{A}k^2 + \frac{U_0 T_5}{e^{U_0} - 1} - U_0 \right] N = U_0^2 . \]

What we have so far is this: \( U_1 = 0 \),
\[
T_i(x, z) = T_{1i}(z) \cos(kx) = \hat{T}_i(z) \cos(kx), \quad T_{1i}^*(x, z) = T_{1i}^*(z) \cos(kx) = \hat{T}_i^*(z) \cos(kx), \quad \text{and}
\]
\[
Z_i(x) = A \cos(kx) = \hat{Z}_i \cos(kx) . \quad \text{And we go on to the second order problem to find the value of} \ A .
\]

The Second Order Problem

The second order problem is
\[
\nabla^2 T_2 + U_0 \frac{\partial T_2}{\partial z} = -U_2 \frac{dT_0}{dz} \quad (6.284)
\]
on the domain, \(-1 < z < 0\), \(0 < x < W\), and
\[ \nabla^2 T_2 + U_0 \frac{\partial T_2}{\partial z} = -U_2 \frac{dT_0}{dz} \]  

(6.285)

on the domain, \(0 < z < L\), \(0 < x < W\),

\[ T_2 + 2Z_1 \frac{\partial T_1}{\partial z} + Z_2 \frac{d^2 T_0}{dz^2} = - \mathcal{A} \frac{d^2 Z_2}{dx^2} - Z_2 \frac{dT_0}{dz} \]  

(6.286)

\[ \left[ T_2 - T_2^* \right] + 2Z_1 \left[ \frac{\partial T_1}{\partial z} - \frac{\partial T_1^*}{\partial z} \right] + Z_2^2 \left[ \frac{d^2 T_0}{dz^2} - \frac{d^2 T_0^*}{dz^2} \right] + Z_2 \left[ \frac{dT_0}{dz} - \frac{dT_0^*}{dz} \right] = 0 \]  

(6.287)

and

\[ \left[ \frac{\partial T_1}{\partial z} - \frac{\partial T_1^*}{\partial z} \right] + 2Z_1 \left[ \frac{\partial^2 T_1}{\partial z^2} - \frac{\partial^2 T_1^*}{\partial z^2} \right] + Z_2 \left[ \frac{d^3 T_0}{dz^3} - \frac{d^3 T_0^*}{dz^3} \right] + Z_2 \left[ \frac{d^2 T_0}{dz^2} - \frac{d^2 T_0^*}{dz^2} \right] = 0 \]  

(6.288)

\[ -2Z_{1x} \left[ \frac{\partial T_1}{\partial x} - \frac{\partial T_1^*}{\partial x} \right] = -U_2 \]

at \( z = 0 \),

\[ T_2 (z = -1) = 0 \]  

(6.289)

and

\[ T_2^* (z = L) = 1 \]  

(6.290)

The volume condition is given by

\[ \int_0^L Z_2 \, dx = 0 \]  

(6.291)

Assuming the solution to be of the form

\[ T_2 (x, z) = T_{20}(z) + T_{21}(z) \cos(kx) + T_{22}(z) \cos(2kx) \]  

(6.292)

\[ T_2^* (x, z) = T_{20}^*(z) + T_{21}^*(z) \cos(kx) + T_{22}^*(z) \cos(2kx) \]  

(6.293)

\[ Z_2 (x) = Z_{21} \cos(kx) + Z_{22} \cos(2kx) \]  

(6.294)

we deduce the \{20\} and \{21\} and \{22\} problems. At \( z = 0 \), the following formulae may be
useful:

\[ 2Z_1 \left[ \frac{\partial^2 T_1}{\partial z^2} - \frac{\partial^2 T_1^*}{\partial z^2} \right] = U_0 \left[ k^2 + U_0^2 \right] \hat{Z}_1^2 \left[ 1 + \cos(2kx) \right] \]

\[ -2Z_{1*} \left[ \frac{\partial T_{1*}}{\partial x} - \frac{\partial T_{1*}}{\partial x} \right] = -k^2 U_0 \hat{Z}_1^2 \left[ 1 - \cos(2kx) \right] \]

The \{20\} problem

The \{20\} problem is given by

\[ \frac{d^2 T_{20}}{dz^2} + U_0 \frac{dT_{20}}{dz} = -U_2 \frac{dT_0}{dz} \quad (6.295) \]

in the solid phase, \(-1 < z < 0\), \(0 < x < W\), and

\[ \frac{d^2 T_{20}^*}{dz^2} + U_0 \frac{dT_{20}^*}{dz} = -U_2 \frac{dT_{0}^*}{dz} \quad (6.296) \]

in the liquid phase, \(0 < z < L\), \(0 < x < W\),

\[ T_{20} - T_{20}^* = \frac{1}{2} U_0 \hat{Z}_1^2 \quad (6.297) \]

and

\[ \left[ \frac{dT_{20}}{dz} - \frac{dT_{20}^*}{dz} \right] = -U_2 - \frac{1}{2} U_0 \hat{Z}_1^2 \quad (6.298) \]

at \(z = 0\),

\[ T_{20} (z = -1) = 0 \quad (6.299) \]

and

\[ T_{20}^* (z = L) = 1 \quad (6.300) \]

A general solution to Eqs. (6.295, 6.296) is given by

\[ T_{20} (z) = A_{20} e^{-U_{1*}z} + e^{-U_{1*}z} \int_0^z e^{U_{1*}\zeta} \left[ B_{20} - U_2 A_0 \left[ 1 - e^{-U_{1*}\zeta} \right] \right] d\zeta \quad (6.301) \]
\[ T_{20}^* (z) = A_{20} e^{-U_{0}z} + e^{-U_{0}z} \int_{0}^{z} B_{20}^* - U_{2} A_{20} \left[ 1 - e^{-U_{0}z} \right] d\xi \]  \hspace{1cm} (6.302)

and their derivatives are given by \[ \frac{dT_{20}}{dz} (z = 0) = B_{20} - U_{0} A_{20} , \text{ and } \frac{dT_{20}^*}{dz} (z = 0) = B_{20}^* - U_{0} A_{20}^* \],

whereupon using Eqs. (6.297-6.299) to eliminate \( B_{20} \), \( A_{20}^* \) and \( B_{20}^* \), we get

\[ T_{20} (z) = A_{20} e^{-U_{0}z} + \left[ U_{2} A_{0} - A_{20} \right] \left[ \frac{e^{U_{0}}}{1 - e^{U_{0}}} \left[ 1 - e^{U_{0}z} \right] + U_{2} A_{0} z e^{-U_{0}z} \right] \]  \hspace{1cm} (6.303)

\[ T_{20}^* (z) = A_{20} e^{-U_{0}z} + \left[ U_{2} A_{0} - A_{10} \right] \left[ \frac{e^{U_{0}}}{1 - e^{U_{0}}} \left[ 1 - e^{U_{0}z} \right] + U_{2} A_{0} z e^{-U_{0}z} \right] \]
\[-\frac{1}{2} U_{0}^{2} Z_{1} e^{-U_{0}z} + U_{2} z e^{-U_{0}z} \]  \hspace{1cm} (6.304)

where \( A_{20} \) is found by using Eq. (6.300) as

\[ A_{20} = U_{2} \left[ \frac{e^{U_{0}}}{e^{U_{0}L} - 1} \right] \left[ \frac{e^{U_{0}L} - 1}{1 + \frac{e^{U_{0}}}{e^{U_{0}L} - 1}} \right] - A_{0} \left[ \frac{1}{2} U_{0}^{2} Z_{1} e^{U_{0}L} + e^{U_{0}L} \right] \]  \hspace{1cm} (6.305)

**The \{21\} problem**

The \{21\} problem is similar to the eigenvalue problem. It is given by

\[ \left[ \frac{d^{2}}{dz^{2}} - k^{2} \right] T_{21} + U_{0} \frac{dT_{21}}{dz} = 0 \]  \hspace{1cm} (6.306)

in the solid phase, \(-1 < z < 0 , \ 0 < x < W \), and

\[ \left[ \frac{d^{2}}{dz^{2}} - k^{2} \right] T_{21}^* + U_{0} \frac{dT_{21}^*}{dz} = 0 \]  \hspace{1cm} (6.307)

in the liquid phase, \( 0 < z < L , \ 0 < x < W \),

\[ \left[ T_{21}^* - T_{21} \right] + Z_{21} \left[ \frac{dT_{0}}{dz} - \frac{dT_{0}^*}{dz} \right] = 0 \]  \hspace{1cm} (6.308)
and
\[
\left[ \frac{dT_{21}}{dz} - \frac{dT'_{21}}{dz} \right] + Z_{21} \left[ \frac{d^2T_0}{dz^2} - \frac{d^2T'_0}{dz^2} \right] = 0
\] (6.309)

at \( z = 0 \),
\[
T_{21}(z = -1) = 0 \tag{6.310}
\]
and
\[
T'_{21}(z = L) = 0 \tag{6.311}
\]

Defining \( m_{21} = \frac{-U_0 \pm \sqrt{U_0^2 + 4k^2}}{2} = m_z \), a solution to Eqs. (6.306-6.311) is given by
\[
T_{21}(z) = A_{21} \left[ e^{m_{21}z} - e^{[m_{21} - m_{21}]} e^{m_{21}z} \right] \tag{6.312}
\]
\[
T'_{21}(z) = A'_{21} \left[ e^{m_{21}z} - e^{[m_{21} - m_{21}]} e^{m_{21}z} \right] \tag{6.313}
\]

where
\[
A_{21} = \left[ \mathcal{A} k^2 - \frac{dT_0}{dz}(z = 0) \right] \left[ 1 - e^{m_{21} - m_{21}} \right] Z_{21} \tag{6.314}
\]
\[
A'_{21} = \left[ \mathcal{A} k^2 - \frac{dT'_0}{dz}(z = 0) \right] \left[ 1 - e^{m_{21} - m_{21}} e^{m_{21}z} \right] Z_{21} \tag{6.315}
\]

The \{22\} problem

The \{22\} problem is given by
\[
\left[ \frac{d^2}{dz^2} - 4k^2 \right] T_{22} + U_0 \frac{dT_{22}}{dz} = 0 \tag{6.316}
\]
in the solid phase, \(-1 < z < 0\), \(0 < x < W\), and
\[
\left[ \frac{d^2}{dz^2} - 4k^2 \right] T_{22}^* + U_0 \frac{dT_{22}^*}{dz} = 0
\]  \quad (6.317)

in the liquid phase, \(0 < z < L, 0 < x < W\),

\[
\left[ T_{22} - T_{22}^* \right] = \frac{1}{2} U_0^2 \hat{Z}_1^2 + U_0 Z_{22}
\]  \quad (6.318)

and

\[
\left[ \frac{dT_{22}}{dz} - \frac{dT_{22}^*}{dz} \right] + 2U_0 k^2 \hat{Z}_1^2 + \frac{1}{2} U_0^3 \hat{Z}_1^3 + U_0^2 Z_{22} = 0
\]  \quad (6.319)

at \(z = 0\),

\[T_{22}(z = -1) = 0\]  \quad (6.320)

and

\[T_{22}^*(z = L) = 0\]  \quad (6.321)

Defining \(m_{22} = \frac{-U_0 \pm \sqrt{U_0^2 + 16k^2}}{2}\), a solution to Eqs. (6.316-6.321) is given by

\[
T_{22}(z) = A_{22} \left[ e^{m_{22} z} - e^{m_{22} - m_{22} - m_{22}} e^{m_{22} z} \right]
\]  \quad (6.322)

\[
T_{22}^*(z) = A_{22}^* \left[ e^{m_{22} z} - e^{m_{22} - m_{22}} e^{m_{22} z} \right]
\]  \quad (6.323)

where

\[
A_{22} = \frac{\left[ \frac{1}{2} U_0^2 N_{22} + 2U_0 k^2 + \frac{1}{2} U_0^3 \right] Z_1^2 + \left[ U_0^2 N_{22} + U_0^2 \right] Z_{22}}{\left[ 1 - e^{m_{22} - m_{22}} \right] \left[ N_{22} - M_{22} \right]}
\]  \quad (6.324)
\[ A'_{22} = \left[ \frac{1}{2} U_0^2 M_{22} + 2 U_0 k^2 + \frac{1}{2} U_0^3 \right] \left[ \tilde{Z}_{1}^2 + \left[ U_0 M_{22} + U_0^2 \right] Z_{22} \right] \left[ 1 - e^{m_{22} - m_{22}} \right] \left[ N_{22} - M_{22} \right] \]  

(6.325)

and where

\[ M_{22} = \frac{m_{22} - m_{22} e^{m_{22} - m_{22}}}{1 - e^{m_{22} - m_{22}}} \quad \text{and} \quad N_{22} = \frac{m_{22} - m_{22} e^{m_{22} - m_{22}}}{1 - e^{m_{22} - m_{22}}} \]

Using the curvature equation

Finally, using Eq. (6.291) and \( dZ_2/\,dx = 0 \) at \( x = 0, W \), and integrating Eq. (6.286) over \( 0 < x < W \), we find

\[ T_{20}(z = 0) + \tilde{Z}_1 \frac{dT_1}{dz}(z = 0) + \frac{1}{2} \tilde{Z}_1^2 \frac{d^2 T_0}{dz^2}(z = 0) = 0 \]  

(6.326)

Using \( \frac{dT_1}{dz}(z = 0) = \left[ \mathcal{A} k^2 - \frac{dT_0}{dz}(z = 0) \right] M Z_1 \), and \( T_{20}(z = 0) = A_{20} \), there obtains

\[ A_{20} = \left[ -\mathcal{A} k^2 M + M \frac{dT_0}{dz}(z = 0) - \frac{1}{2} \frac{d^2 T_0}{dz^2}(z = 0) \right] \tilde{Z}_1^2 \]  

(6.327)

Comparing with Eq. (6.305), and simplifying, there obtains

\[
U_2 = \left[ \begin{array}{c}
\frac{e^{U_0 L}}{e^{U_0 L} - 1} \\
\frac{T_{k_0}}{\left[ e^{U_0 L} - 1 \right]^2} \left[ e^{U_0 L} - 1 \right] + \frac{T_S}{\left[ e^{U_0} - 1 \right]^2} e^{U_0} \\
\end{array} \right]_{U_2,\text{planar}} \]  

(6.328)
where the correction term is always positive, whence the mean speed of the interface runs ahead of its base value.

We have learned that in pure solidification, once the front becomes unstable, its mean speed is higher than its base value. Hence the result of a “speed up” in pure solidification is unconditional, viz., the front always speeds up regardless of whether or not the latent heat is being rejected to the solid phase. Also, the reader is encouraged to verify that as \( T_s \) goes to zero, the limiting value of \( U_2 \) is given by

\[
\lim_{T_s \to 0} U_2 = \frac{1}{L} e^{U_0 L} + \frac{1}{L} \left[ \frac{1}{2} U_0^2 + \mathcal{A} k^2 M \left[ 1 + \left( \frac{e^{U_0}}{e^{U_0} - 1} \right) \left( e^{U_0 L} - 1 \right) \right] \right] \left( \begin{array}{c} \hat{V}_1 \\ \hat{V}_2 \end{array} \right)
\]

which is the same expression as what was obtained in Eq. (6.114) for case 1 where the latent heat was rejected only through the subcooled liquid.

For this case then, the only other information that one might be interested in seeking is the nature of the branching to the new steady solution, i.e., whether the bifurcation is a forward or a backward pitchfork. To that end, we need to go to third order, but before that, we need to solve Eq. (6.286) for \( Z_2 \). Now to find \( Z_2 \), a solvability condition must be satisfied. It is

\[
\int_0^\infty \left[ T_2 (z = 0) + 2Z_1 \frac{\partial T_1}{\partial z} (z = 0) + Z_1^2 \frac{d^2 T_0}{dz^2} (z = 0) \right] Z_1 dz - \int_0^\infty T_1 (z = 0) Z_2 dx = 0
\]

It is easy to verify that this condition is automatically satisfied. Hence, Eq. (6.286) can be solved for \( Z_2 \). Substituting the expansions from Eqs. (6.292-6.294), the constant term disappears due to the result obtained earlier using integrability, viz., Eq. (6.326). The coefficient of the first harmonic vanishes due to solvability, and there obtains by equating the coefficients of the second harmonic
\( T_{22} (z = 0) + \frac{dT^\wedge_1}{dz} (z = 0) Z_1 + \frac{1}{2} \frac{d^2 T_0}{dz^2} (z = 0) Z_i^2 + \frac{dT_0}{dz} (z = 0) Z_{22} - 4 \mathcal{A} k^2 Z_{22} = 0 \)  \hfill (6.331) 

Substituting \( T_{22} (z = 0) = A_{22} \left[ 1 - e^{[m_{22} - n_{22}]} \right] \), and using \( \frac{dT^\wedge_1}{dz} (z = 0) = \left[ \mathcal{A} k^2 - \frac{dT_0}{dz} (z = 0) \right] M Z_1, \) there obtains

\[ A_{22} = \frac{-Z_1^2 \left[ \mathcal{A} k^2 M + \frac{1}{2} \frac{d^2 T_0}{dz^2} (z = 0) - M \frac{dT_0}{dz} (z = 0) \right] - Z_{22} \left[ \frac{dT_0}{dz} (z = 0) - 4 \mathcal{A} k^2 \right]}{1 - e^{[m_{22} - n_{22}]} \right] \]  \hfill (6.332) 

Comparing with Eq. (6.324), and simplifying, we learn that \( Z_{22} \) can be found in terms of \( Z_1^2 \) as

\[ Z_{22} = \left[ \frac{P}{Q} \right] Z_1^2 \]  \hfill (6.333) 

where

\[ \frac{P}{Q} = \left[ \frac{1}{2} U_0^2 N_{22} + 2 U_0 k^2 + \frac{1}{2} U_0^3 \right] + \left[ \mathcal{A} k^2 M + \frac{1}{2} \frac{d^2 T_0}{dz^2} (z = 0) - M \frac{dT_0}{dz} (z = 0) \right] \left[ N_{22} - M_{22} \right] \]  \hfill (6.334) 

Hence, \( Z_{21} \) and \( A \) carry on to third order.

**The Third Order Problem**

The equations at the third order are given by

\[ \nabla^2 T_3 + U_0 \frac{\partial \overline{T_3}}{\partial z} = -3 U_2 \frac{\partial \overline{T_1}}{\partial z} - U_3 \frac{dT_0}{dz} \]  \hfill (6.335) 

on the domain \(-1 < z < 0, \ 0 < x < W\), and

\[ \nabla^2 T_3^* + U_0 \frac{\partial \overline{T_3}^*}{\partial z} = -3 U_2 \frac{\partial \overline{T_1}^*}{\partial z} - U_3 \frac{dT_0}{dz} \]  \hfill (6.336) 

on the domain \(0 < z < L, \ 0 < x < W,\)
\[-9A \left( \frac{dz}{dx} \right)^2 \frac{d^2 Z}{d x^2} + \left[ T_3 + 3Z_1 \frac{\partial T_3}{\partial z} + 3Z_1^2 \frac{\partial^2 T_3}{\partial z^2} + 3Z_2 \frac{\partial T_3}{\partial z} + 3Z_2^2 \frac{\partial^2 T_3}{\partial z^2} + Z_3 \frac{d^2 T_0}{dz^2} + Z_3 \frac{d^3 T_0}{dz^3} \right] \]

\[= -A \frac{d^2 Z_3}{dx^2} - Z_3 \frac{dT_0}{dz} \]

\[\left[ T_3 - T_3^* \right] + 3Z_1 \left[ \frac{\partial T_2}{\partial z} - \frac{\partial T_2^*}{\partial z} \right] + 3Z_1^2 \left[ \frac{\partial^2 T_2}{\partial z^2} - \frac{\partial^2 T_2^*}{\partial z^2} \right] + 3Z_2 \left[ \frac{\partial T_1}{\partial z} - \frac{\partial T_1^*}{\partial z} \right] \]

\[+ 3Z_1Z_2 \left[ \frac{d^2 T_0}{dz^2} - \frac{d^2 T_0^*}{dz^2} \right] + Z_3 \left[ \frac{d^3 T_0}{dz^3} - \frac{d^3 T_0^*}{dz^3} \right] + Z_3 \left[ \frac{dT_0}{dz} - \frac{dT_0^*}{dz} \right] = 0 \]

\[= U_3 \] (6.338)

\[\left[ \begin{array}{l} \frac{\partial T_1}{\partial z} - \frac{\partial T_1^*}{\partial z} \\ \frac{\partial^2 T_2}{\partial z^2} - \frac{\partial^2 T_2^*}{\partial z^2} \\ \frac{\partial^3 T_1}{\partial z^3} - \frac{\partial^3 T_1^*}{\partial z^3} \\ \frac{\partial T_1}{\partial z} \end{array} \right] + 3Z_1 \left[ \begin{array}{l} \frac{\partial^2 T_2}{\partial z^2} - \frac{\partial^2 T_2^*}{\partial z^2} \\ \frac{\partial^3 T_1}{\partial z^3} - \frac{\partial^3 T_1^*}{\partial z^3} \end{array} \right] + 3Z_2 \left[ \begin{array}{l} \frac{\partial^2 T_2}{\partial z^2} - \frac{\partial^2 T_2^*}{\partial z^2} \end{array} \right] \]

\[+ 3Z_1Z_2 \left[ \begin{array}{l} \frac{d^2 T_0}{dz^2} - \frac{d^2 T_0^*}{dz^2} \end{array} \right] + Z_3 \left[ \begin{array}{l} \frac{d^3 T_0}{dz^3} - \frac{d^3 T_0^*}{dz^3} \end{array} \right] + Z_3 \left[ \begin{array}{l} \frac{dT_0}{dz} - \frac{dT_0^*}{dz} \end{array} \right] = -U_3 \]

at \( z = 0 \),

\[T_3(z = -1) = 0 \]

(6.340)

and

\[T_3^*(z = L) = 0 \]

(6.341)

The volume condition is given by

\[\int_0^W Z_3 \, d\chi = 0 \]

(6.342)

We assume the following form for the solution

\[T_3(x, z) = T_{30}(z) + T_{31}(z) \cos(k\chi) + T_{32}(z) \cos(2k\chi) + T_{33}(z) \cos(3k\chi) \] (6.343)
This problem can be solved completely, but it is sufficient to solve the \{31\} problem to learn the nature of bifurcation and the value of $A^2$. This can be done exactly as in case 1. However, the algebra is cumbersome and we will stop here as far as case 3 is concerned.

Up till now we have worked out three cases of pure solidification, and we have learned that the solidification front speeds up, no matter what. By contrast we learned in Chapter 5 that a precipitation front always slows down once the instability sets in. Now these two problems are closely related and their physics are very similar. Then one might ask: What is the reason for this fundamental difference? In other words, can we explain this basic difference of a “speed-up” in solidification versus a “slow-down” in precipitation? In our quest to answer this question, we go to a yet simpler model, where the solid phase is completely ignored. Nothing new will be learned, and we will again see that the front speeds up compared to its base value. But the model is now as close as one can get to the precipitation model, and we can therefore hope to learn the fundamental difference between the two problems.

**Case 4: Solid Phase Ignored, Latent Heat Rejected Only through the Subcooled Liquid**

The notation remains the same as in case 1. Since the solid phase is altogether ignored, all lengths are scaled by $L$, the depth of the liquid phase. All speeds are scaled by $\alpha / L$. The scaled temperature is given by $T_{\text{scaled}} = \frac{T_M - T}{\alpha L_H / \lambda}$. Then the equation for the scaled liquid side temperature is given by

$$\nabla^2 T^* + U \frac{\partial T^*}{\partial z} = 0$$

(6.346)

for $Z < z < 1$ and $0 < x < W$. The equations along the interface, viz., along $z = Z(x)$ are
$T^* = -\mathcal{A}[2H]$ \hfill (6.347)

and

$\nabla \cdot \mathbf{U} = U_k \mathbf{n}$ \hfill (6.348)

where $\mathcal{A}$ denotes $\left[ \frac{\nu}{\alpha \ell \mu} \right] T_m$. The temperature at the liquid side sink is given by

$T^*(z=1) = T_L$ \hfill (6.349)

Side wall conditions are Neumann. The volume of the subcooled liquid must be maintained fixed, whence

$\int_0^w Z(x) \, dx = 0$ \hfill (6.350)

**The Base Solution**

A base state solution is given by

$T_0^*(z) = 1 - e^{-U_0 z}$ \hfill (6.351)

where $U_0$ is given by

$U_0 = -\ln(1 - T_L)$ \hfill (6.352)

whence

$\frac{dT_0^*}{dz}(z = 0) = U_0$, $\frac{dT_0^*}{dz^2}(z = 0) = -U_0^2$, $\frac{dT_0^*}{dz^3}(z = 0) = U_0^3$, $\frac{dT_0^*}{dz^4}(z = 0) = -U_0^4$.

**The Perturbation Eigenvalue Problem**

Expanding $Z$, $T$, and $T^*$, at $z = Z(x)$ as in Eqs. (6.17, 6.19), the perturbation eigenvalue problem is given by

$\nabla^2 T^*_i + U_0 \frac{\partial T^*_i}{\partial z} = 0$ \hfill (6.353)

on the domain, $0 < z < 1$, $0 < x < W$, where, at $z = 0$,
\[ T_1^* = -A \frac{d^2 Z_1}{dx^2} - Z_1 \frac{dT_0^*}{dz} \]  
\hfill (6.354)

and

\[ \frac{\partial T_1^*}{\partial z} + Z_1 \frac{d^2 T_0^*}{dz^2} = 0 \]  
\hfill (6.355)

must hold, and where,

\[ T_1^* (z = 1) = 0 \]  
\hfill (6.356)

must hold. The sidewall conditions are Neumann. Then the problem has solutions of the form

\[ T_1^* = \hat{T}_1^* (z) \cos(kx) \quad \text{and} \quad Z_1 = A \cos(kx) \]  
\hfill (6.357)

which satisfy the side wall conditions so long as \( k = n\pi/W, n = 1, 2, \ldots \), where \( k \) is the wave number of the disturbance and \( n = 0 \) is ruled out by the condition

\[ \int_0^W Z_1 dx = 0 \]  
\hfill (6.358)

The expansions presented above give the equations for \( \hat{T}_1^* \) and \( \hat{Z}_1 \). They are

\[ \left[ \frac{d^2}{dz^2} - k^2 \right] \hat{T}_1 + U_0 \frac{d \hat{T}_1}{dz} = 0 \]  
\hfill (6.359)

on the domain, \( 0 < z < 1, \ 0 < x < W \),

\[ \hat{T}_1^* = \left[ AK^2 - \frac{dT_0}{dz} \right] \hat{Z}_1 \]  
\hfill (6.360)

and

\[ \frac{d \hat{T}_1}{dz} + \hat{Z}_1 \frac{d^2 T_0^*}{dz^2} = 0 \]  
\hfill (6.361)

at \( z = 0 \), and
\[ T'_1 (z = 1) = 0 \] (6.362)

Defining \( m_z = \frac{-U_0 \pm \sqrt{U_0^2 + 4k^2}}{2} \), a solution to Eqs. (6.359, 6.361, 6.362) is given by

\[ T^*_1 (z) = \left[ \frac{\mathcal{A} k^2 - U_0}{1 - e^{m_z - m_{-1}}} \right] \left[ e^{m_z} - e^{m_{-1}} \right] Z_1 \] (6.363)

We can then turn to Eq. (6.361), which gives us

\[ \left[ \mathcal{A} k^2 - U_0 \right] N = U_0^2 \] (6.364)

where \( N = \left[ \frac{m_z - m_{-1} e^{m_{-1}}}{1 - e^{m_{-1}}} \right] \).

The neutral curve is as shown in Figure 6.2, whence only one crest is seen at critical. Now on increasing \( T_L \) to its critical value \( T_{L_0} \), and then slightly beyond, the branching to the new steady solution is expected be a forward pitchfork. Hence we write

\[ T_L = T_{L_0} + \frac{1}{2} \varepsilon^2 \] (6.365)

and expand \( U \) and \( Z \) as in Eqs. (6.42, 6.43) to get the first and higher order problems. Eq. (6.352) indicates that for a small increase in \( T_L \) from \( T_{L_0} \), the corresponding change in \( U \) from \( U_0 \), per unit change in \( T_L \) is given by \( e^{U_0} \).

Before moving on to solve the higher order problems, observe that even for this simple case where the solid phase has been completely ignored, \( \hat{T}_1 \) turns out to be nonzero. Now in Chapter 5, the variable \( c_1 \) was found to be zero due to cancellations of mappings in the mass balance equation at the interface, viz., \( \hat{n} \cdot \nabla c = \left[ 1 - c \right] \hat{k} \cdot \hat{n} \). The corresponding cancellations are
not seen in the interfacial energy balance equation in solidification. And mathematically, this is
what leads to the key difference between the two problems.

**The First Order Problem**

The first order problem is given by

\[
\nabla^2 T_1^* + U_0 \frac{\partial T_1^*}{\partial z} = -U_1 \frac{dT_0^*}{dz} \tag{6.366}
\]

on the domain, \(0 < z < 1, \ 0 < x < W\),

\[
T_1^* = -A \frac{d^2 Z_1}{dx^2} - Z_1 \frac{dT_0^*}{dz} \tag{6.367}
\]

and

\[
\frac{\partial T_1^*}{\partial z} + Z_1 \frac{d^2 T_0^*}{dz^2} = U_1 \tag{6.368}
\]

at \(z = 0\),

\[
T_1^* (z = 1) = 0 \tag{6.369}
\]

and

\[
\int_0^W Z_1 dx = 0 \tag{6.370}
\]

The sidewall conditions are Neumann, and Eqs. (6.366, 6.368-6.370) can be solved by writing

\[
T_1^* (x, z) = T_{10}^* (z) + T_{11}^* (z) \cos(kx) \tag{6.371}
\]

\[
Z_1 (x) = A \cos(kx) = Z_1 \cos(kx) \tag{6.372}
\]

**The \{10\} problem**

The \{10\} problem is given by

\[
\frac{d^2 T_{10}^*}{dz^2} + U_0 \frac{dT_{10}^*}{dz} = -U_1 \frac{dT_0^*}{dz} \tag{6.373}
\]
on the domain, $0 < z < 1$, $0 < x < W$,

$$\frac{dT_{10}^*}{dz} = U_1$$  \hspace{1cm} (6.374)

at $z = 0$, and

$$T_{10}^*(z = 1) = 0$$  \hspace{1cm} (6.375)

A general solution to Eq. (6.373) is given by

$$T_{10}^*(z) = A_{10}^* e^{-U_0 z} + \int_0^z e^{U_0 \xi} \left[ B_{10}^* - U_1 \left[ 1 - e^{-U_0 \xi} \right] \right] d\xi$$  \hspace{1cm} (6.376)

whence $\frac{dT_{10}^*}{dz} (z = 0) = B_{10}^* - U_0 A_{10}^*$. Using Eqs. (6.374, 6.375) to eliminate $A_{10}^*$ and $B_{10}^*$, we get

$$T_{10}^*(z) = U_1 \left[ z e^{-U_0 z} - e^{-U_0 z} \right]$$  \hspace{1cm} (6.377)

The \{11\} problem

The \{11\} problem is similar to the eigenvalue problem. It is given by

$$\left[ \frac{d^2}{dz^2} - k^2 \right] T_{11}^* + U_0 \frac{dT_{11}^*}{dz} = 0$$  \hspace{1cm} (6.378)

on the domain, $0 < z < 1$, $0 < x < W$,

$$\frac{dT_{11}^*}{dz} + Z_{11} \frac{d^2 T_{11}^*}{dz^2} = 0$$  \hspace{1cm} (6.379)

at $z = 0$, and

$$T_{11}^*(z = 1) = 0$$  \hspace{1cm} (6.380)

Finally using Eq. (6.370) and $dZ_1/dx = 0$ at $x = 0, W$, and integrating Eq. (6.367) over $0 < x < W$, we find that $U_1$ must be zero, and therefore $T_{10}^*$ must be identically zero. Then the first order problem is exactly like the eigenvalue problem, and the condition at neutrality is given
by Eq. (6.364), viz., \[ AK^2 - U_0 \] \( N = U_0^2 \). What we have so far is this: \( U_1 = 0 \),

\[ T_1^*(x,z) = T_{11}^*(z) \cos(kx) = \hat{T}_1^*(z) \cos(kx) \text{, and } Z_1(x) = A \cos(kx) = \hat{Z}_1 \cos(kx) \text{. And we go on to } \\
\text{the second order problem to find the value of } A. \\
\textbf{The Second Order Problem }

The second order problem is

\[ \nabla^2 T_2^* + U_0 \frac{\partial T_2^*}{\partial z} = -U_2 \frac{dT_0^*}{dz} \] (6.381)

on the domain, \( 0 < z < 1, \ 0 < x < W \),

\[ T_2^* + 2Z_1 \frac{\partial T_1^*}{\partial z} + Z_2 \frac{d^2 T_0^*}{dz^2} = -A \frac{d^2 Z_2}{dx^2} - Z_2 \frac{dT_0^*}{dz} \] (6.382)

and

\[ \frac{\partial T_2^*}{\partial z} + 2Z_1 \frac{\partial^2 T_1^*}{\partial z^2} + Z_1 \frac{d^2 T_0^*}{dz^2} + Z_2 \frac{d^2 T_0^*}{dz^2} - 2Z_{1x} \frac{\partial T_1^*}{\partial x} = U_2 \] (6.383)

at \( z = 0 \), and

\[ T_2^*(z = 1) = 1 \] (6.384)

and

\[ \int_0^W Z_2 dx = 0 \] (6.385)

Then, we assume the following form for the solution:

\[ T_2^*(x,z) = T_{20}^*(z) + T_{21}^*(z) \cos(kx) + T_{22}^*(z) \cos(2kx) \] (6.386)

\[ Z_2(x) = Z_{21} \cos(kx) + Z_{22} \cos(2kx) \] (6.387)

And again, we use these expansions to deduce the \{20\} and \{21\} and \{22\} problems.
The $\{20\}$ problem

The $\{20\}$ equations are given by

$$
\frac{d^2 T^*_{20}}{dz^2} + U_0 \frac{dT^*_{20}}{dz} = -U_2 \frac{dT^*_{0}}{dz}
$$

(6.388)

on the domain, $0 < z < 1$, $0 < x < W$,

$$
\frac{dT^*_{20}}{dz} = U_2 + \frac{1}{2} U_0^3 \hat{Z}_1^2
$$

(6.389)

at $z = 0$, and

$$
T^*_{20}(z = 1) = 1
$$

(6.390)

A general solution to Eq. (6.388) is given by

$$
T^*_{20}(z) = A_{20} e^{-U_0 z} + e^{-U_0 z} \int_0^z e^{U_0 \xi} \left[ B_{20} - U_2 \left[ 1 - e^{-U_0 \xi} \right] \right] d\xi
$$

(6.391)

whence

$$
\frac{dT^*_{20}}{dz}(z = 0) = B_{20} - U_0 A_{20}.
$$

Using Eqs. (6.389, 6.390) to eliminate $A_{20}$ and $B_{20}$, we get

$$
T^*_{20}(z) = 1 + \frac{1}{2} U_0^2 \left[ e^{-U_0} - e^{-U_0 z} \right] \hat{Z}_1^2 - U_2 \left[ e^{-U_0} - ze^{-U_0 z} \right]
$$

(6.392)

whence

$$
T^*_{20}(z = 0) = -\frac{1}{2} U_0 \hat{Z}_1^2 + 1 + e^{-U_0} \left[ \frac{1}{2} U_0^2 \hat{Z}_1^2 - U_2 \right]
$$

(6.393)

The $\{21\}$ problem

The $\{21\}$ problem is given by

$$
\left[ \frac{d^2}{dz^2} - k^2 \right] T^*_{21} + U_0 \frac{dT^*_{21}}{dz} = 0
$$

(6.394)

on the domain, $0 < z < 1$, $0 < x < W$,
\[
\frac{dT_21^*}{dz} + Z_{21} \frac{d^2 T_0^*}{dz^2} = 0 \tag{6.395}
\]

at \( z = 0 \), and

\( T_{21}^*(z = 1) = 0 \) \tag{6.396}

**The \{22\} problem**

The \{22\} problem is given by

\[
\left[ \frac{d^2}{dz^2} - 4k^2 \right] T_{22}^* + U_0 \frac{d T_{22}^*}{dz} = 0 \tag{6.397}
\]

on the domain, \( 0 < z < 1, \ 0 < x < W \),

\[
\frac{dT_{22}^*}{dz} = \left[ 2k^2 \left[ U_0 - \mathcal{A}k^2 \right] + \frac{1}{2} U_0^3 \right] Z_1^2 + U_0^2 Z_{22} \tag{6.398}
\]

at \( z = 0 \), and

\( T_{22}^*(z = 1) = 0 \) \tag{6.399}

**Using the curvature equation**

Finally using Eq. (6.385) and \( dZ_2/dx = 0 \) at \( x = 0, W \), and integrating Eq. (6.367) over

\( 0 < x < W \), we find

\[
T_{20}^*(z = 0) + Z_1 \frac{dT_{20}^*}{dz} (z = 0) + \frac{1}{2} Z_1^2 \frac{d^2 T_{20}^*}{dz^2} (z = 0) = 0 \tag{6.400}
\]

Using \( \frac{dT_{20}^*}{dz} (z = 0) = U_0^2 \hat{Z}_1 \) and \( \frac{d^2 T_{20}^*}{dz^2} (z = 0) = -U_0^2 \), there obtains

\[
T_{20}^*(z = 0) = -\frac{1}{2} U_0^2 \hat{Z}_1^2 \tag{6.401}
\]
Comparing with Eq. (6.393), we get

\[
U_2 = \frac{e^{U_0}}{U_{2,\text{plane}}} + \frac{1}{2} U_0^2 Z_1^2 \quad \quad (6.402)
\]

The correction term is always positive, whence the mean speed of the interface runs ahead of its base value. Now the model given in case 4 is the closest that one can get to the model of precipitation. Yet, we find a “speed-up” in case 4 while the precipitation problem exhibits an unconditional “slow-down” once the instability sets in. The only difference between the two models is that the energy balance equation in the present solidification model is different from the mass balance equation of the precipitation model. Hence we have learned that the key disparity between the two problems is that mass is fundamentally different from heat. In the most basic terms, there is no such thing as a hidden mass or latent mass.

Now notice that the result of a “speed-up” in solidification is obtained at second order, and this result holds regardless of the values of the input parameters \( k^2 \) and \( L \). But recall from the third order derivations for case 1, that the sign of \( A^2 \) depends strongly on the inputs \( k^2 \) and \( L \) and hence the nature of the bifurcation is a function of the input variables. Although this was clear from Table 6.1, we had to cater to numerical calculations and it was hard to tell the functional dependence of \( A^2 \) on the inputs simply by inspection. In our quest to delineate this dependence, we move on to the next case where the latent heat is rejected to the frozen solid as well as to the subcooled liquid, as in case 3, but now we drop \( U \) from the domain equations. It will be seen that this simplifies the model equations and also the formula for \( A^2 \).

**Case 5: Latent Heat Rejected to Frozen Solid as Well as to the Subcooled Liquid, Both Phases of Finite Extent, \( U \) Dropped from Domain Equations**

In this section we work out a special case of case 3 where \( U \) has been dropped from the domain regardless of whether or not it is small. For small values of growth speed \( U \), this is a
reasonable approximation. This is done solely with the purpose of making the algebra more tractable. Once again, we will learn that the front speeds up at the onset of instability. What we also wish to learn is whether \( A^2 \) is found to be positive or negative at third order. In other words, we wish to find whether the pitchfork bifurcation is forward or backward. We will find that \( A^2 \) can have either sign, whence the bifurcation can be forward as well as backward depending on the inputs \( k^2 \) and the ratio of the depth of the two phases. To see this, we start by rewriting the nonlinear model. All scales remain the same as in case 3. Then, the scaled temperature in the solid phase must satisfy

\[
\nabla^2 T = 0 \quad (6.403)
\]

for \(-1 < z < Z\) and \(0 < x < W\), while in the liquid phase

\[
\nabla^2 T^* = 0 \quad (6.404)
\]

must hold for \(Z < z < L\) and \(0 < x < W\). The equations along the interface, viz., along \(z = Z(x)\) are

\[
T = -A[2H] = T^* \quad (6.405)
\]

and

\[
\mathbf{n}\nabla T - \mathbf{n}\nabla T^* = -\mathbf{n}\mathbf{U}k \quad (6.406)
\]

where \( A \) denotes \( \left[ \frac{\gamma\lambda}{\alpha L_H S} \right] T_m \). Far-field conditions are given by

\[
T(z = -1) = T_s \quad (6.407)
\]

and

\[
T(z = L) = T_L \quad (6.408)
\]

Side wall conditions are Neumann. The volume of the subcooled liquid must be maintained
fixed, whence

\[ \int_{0}^{W} Z(x) \, dx = 0 \]  
\[ (6.409) \]

**The Base Solution**

A base state solution is given by

\[ T_0(z) = -T_S z \]  
\[ (6.410) \]

and

\[ T_0^*(z) = \frac{T_L}{L} z \]  
\[ (6.411) \]

where \( U_0 \) is given by

\[ U_0 = T_S + \frac{T_L}{L} \]  
\[ (6.412) \]

Notice that both phases have linear base temperature gradients, and this leads to a lot of simplification at higher orders as all second and higher derivatives of \( T_0 \) and \( T_0^* \) vanish.

**The Perturbation Eigenvalue Problem**

Expanding \( Z, T, \) and \( T^* \), at \( z = Z(x) \) as in Eqs. (6.17-6.19), the perturbation eigenvalue problem is given by

\[ \nabla^2 T_i = 0 \]  
\[ (6.413) \]

on the domain, \(-1 < z < 0, 0 < x < W\), and

\[ \nabla^2 T_i^* = 0 \]  
\[ (6.414) \]

on the domain, \(0 < z < L, 0 < x < W\), where, at the base surface \( z = 0\),

\[ T_i = -\mathcal{A} \frac{d^2 Z_1}{dx^2} - Z_1 \frac{dT_0}{dz} \]  
\[ (6.415) \]
\[
[T_i - T_i^*] + Z_i \left[ \frac{d T_0}{d z} - \frac{dT_0^*}{d z} \right] = 0
\]  
(6.416)

and

\[
\frac{\partial T_i}{\partial z} - \frac{\partial T_i^*}{\partial z} = 0
\]  
(6.417)

must hold, and where,

\[
T_i (z = -1) = 0
\]  
(6.418)

and

\[
T_i^* (z = L) = 0
\]  
(6.419)

The sidewall conditions are Neumann. Thus the problem is homogeneous in \( T_i, T_i^* \) and \( Z_i \), and it has solutions of the form

\[
T_i = \hat{T}_i (z) \cos(kx), \quad T_i^* = \hat{T}_i^* (z) \cos(kx) \quad \text{and} \quad Z_i = A \cos(kx)
\]  
(6.420)

which satisfy the side wall conditions so long as \( k = n\pi/W, \ n = 1,2..., \) where \( k \) is the wave number of the disturbance. \( n = 0 \) is ruled out by the condition

\[
\int_{-W}^{W} Z_i dx = 0
\]  
(6.421)

The expansions presented above give the equations for \( \hat{T}_i, \hat{T}_i^* \) and \( \hat{Z}_i \). They are

\[
\left[ \frac{d^2}{dz^2} - k^2 \right] \hat{T}_i = 0
\]  
(6.422)

in the solid phase, \(-1 < z < 0, \ 0 < x < W\), and

\[
\left[ \frac{d^2}{dz^2} - k^2 \right] \hat{T}_i^* = 0
\]  
(6.423)

in the liquid phase, \( 0 < z < L, \ 0 < x < W\),

194
\[ \hat{T}_1 = \left[ \mathcal{A} k^2 - dT_0 \right] Z_1 \]  
(6.424)

\[ \left[ \hat{T}_1 - \hat{T}_1^* \right] + \hat{Z}_1 \left[ \frac{dT_0}{dz} - \frac{dT_0^*}{dz} \right] = 0 \]  
(6.425)

and

\[ \frac{d \hat{T}_1^*}{dz} - \frac{d \hat{T}_1}{dz} = 0 \]  
(6.426)

at \( z = 0 \),

\[ \hat{T}_1 (z = -1) = 0 \]  
(6.427)

and

\[ \hat{T}_1^* (z = L) = 0 \]  
(6.428)

A solution to Eqs. (6.422-6.425, 6.427, 6.428) is given by

\[ \hat{T}_1 (z) = A_1 \left[ e^{kz} - e^{-2k} e^{-kz} \right] \left[ \mathcal{A} k^2 \frac{dT_0}{dz} \left( z = 0 \right) \right] \left[ e^{kz} - e^{-2k} e^{-kz} \right] Z_1 \]  
(6.429)

and

\[ \hat{T}_1^* (z) = A_1 \left[ e^{kz} - e^{-2kL} e^{-kz} \right] \left[ \mathcal{A} k^2 \frac{dT_0^*}{dz} \left( z = 0 \right) \right] \left[ e^{kz} - e^{-2k} e^{-kz} \right] Z_1 \]  
(6.430)

We can then turn to Eq. (6.426) which gives us

\[ U_0 = \left[ -\mathcal{A} k^2 + T_s \right] \left[ 1 + \frac{\tanh kL}{\tanh k} \right] \]  
(6.431)

The following formulae might be helpful while drawing a curve of \( U_0 \) versus \( k^2 \):
\[ \tanh k = \frac{e^k - e^{-k}}{e^k + e^{-k}} \]

\[
\lim_{k^2 \to \text{small}} \tanh k = k - \frac{1}{3} k^3
\]

\[
\lim_{k^2 \to \text{large}} \tanh k = 1
\]

\[
\lim_{k^2 \to \text{small}} \left( 1 + \frac{\tanh k L}{\tanh k} \right) = [1 + L] + k^2 \left[ \frac{1}{3} L [1 - L][1 + L] \right]
\]

\[
\lim_{k^2 \to \text{small}} U_0 = \lim_{k^2 \to \text{small}} \left[ \mathcal{A}k^2 + T_S \right] \left[ 1 + \frac{\tanh k L}{\tanh k} \right] = \left[ \mathcal{A}k^2 + T_S \right] \left[ 1 + L \right] + k^2 \left[ \frac{1}{3} L [1 - L][1 + L] \right]
\]

\[
\lim_{k^2 \to 0} U_0 = T_S [1 + L]
\]

\[
\frac{dU_0}{dk^2} (k^2 = 0) = \frac{1}{3} L [1 - L][1 + L] T_S + \mathcal{A} [1 + L]
\]

\[
\lim_{k^2 \to \text{large}} U_0 = \lim_{k^2 \to \text{large}} \left[ \mathcal{A}k^2 + T_S \right] \left[ 1 + \frac{\tanh k L}{\tanh k} \right] = 2 \left[ \mathcal{A}k^2 + T_S \right] \text{ for all values of } L.
\]

Figure 6.5 – Typical neutral curve for solidification when the latent heat is rejected through both phases; \( U \) is dropped from the domain equations.
Figure 6.5 shows the corresponding neutral curve. Given \( W \), and hence \( k^2 \), Eq. (6.431) determines the critical value of the interface speed, \( U_0 \). For \( L \leq 1 \) the curve is monotonically increasing, hence the most dangerous value of \( n \) is one, which corresponds to \( k = \pi/W \), giving only one crest at critical. For \( L > 1 \), the curve must show a dip whence multiple crests are possible. As the control variable \( T_L \) increases upward from zero, the output variable \( U_0 \) increases from zero, until there comes a point when Eq. (6.431) is satisfied. The corresponding value of \( U_0 \) will be referred as its critical value. Henceforth the subscript zero will refer to this critical state. At values of \( U \) higher than \( U_0 \), the base solution loses its stability.

Now on increasing \( T_L \) to its critical value \( T_{L_0} \), and then slightly beyond, the branching to the new steady solution is expected be a forward pitchfork. As before, we write

\[
T_L = T_{L_0} + \frac{1}{2} \varepsilon^2 \tag{6.432}
\]

and expand \( U \) and \( Z \) as in Eqs. (6.42, 6.43) to get the first and higher order problems. Eq. (6.412) indicates that for a small increase in \( T_L \) from \( T_{L_0} \), the corresponding change in \( U \) from \( U_0 \), per unit change in \( T_L \) is given by \( \frac{1}{L} \).

**The First Order Problem**

The first order problem is given by

\[
\nabla^2 T_1 = 0 \tag{6.433}
\]

on the domain, \( -1 < z < 0 \), \( 0 < x < W \), and

\[
\nabla^2 T_1^* = 0 \tag{6.434}
\]

on the domain, \( 0 < z < L \), \( 0 < x < W \).
\[ T_i = -A \frac{d^2Z_i}{dx^2} - Z_i \frac{dT_0}{dz} \]  
(6.435)

\[ \left[ T_i - T_i^* \right] + Z_i \left[ \frac{dT_0}{dz} - \frac{dT_0^*}{dz} \right] = 0 \]  
(6.436)

and

\[ \left[ \frac{\partial T_i}{\partial z} - \frac{\partial T_i^*}{\partial z} \right] = -U_i \]  
(6.437)

at \( z = 0 \), and

\[ T_i (z = -1) = 0 \]  
(6.438)

and

\[ T_i^* (z = L) = 0 \]  
(6.439)

The volume condition is given by

\[ \int_0^W Z_i dx = 0 \]  
(6.440)

The sidewall conditions are Neumann. Hence we have solutions of the form

\[ T_i (x, z) = T_{i0} (z) + T_{i1} (z) \cos(kx) \]  
(6.441)

\[ T_i^* (x, z) = T_{i0}^* (z) + T_{i1}^* (z) \cos(kx) \]  
(6.442)

\[ Z_i (x) = A \cos(kx) = \hat{Z}_i \cos(kx) \]  
(6.443)

The expansions presented above are used to deduce the \{10\} and \{11\} problems.

**The \{10\} problem**

The \{10\} problem is given by

\[ \frac{d^2T_{10}}{dz^2} = 0 \]  
(6.444)
in solid phase, \(-1 < z < 0\), \(0 < x < W\), and

$$\frac{d^2 T_{10}^*}{dz^2} = 0$$  \hspace{1cm} (6.445)

in liquid phase, \(0 < z < L\), \(0 < x < W\),

$$T_{10} - T_{10}^* = 0$$  \hspace{1cm} (6.446)

and

$$\left[ \frac{dT_{10}}{dz} - \frac{dT_{10}^*}{dz} \right] = -U_1$$  \hspace{1cm} (6.447)

at \(z = 0\),

$$T_{10}(z = -1) = 0$$  \hspace{1cm} (6.448)

and

$$T_{10}^*(z = L) = 0$$  \hspace{1cm} (6.449)

A solution to Eqs. (6.444-6.449) is given by

$$T_{10}(z) = -U_1 \left[ \frac{L}{L+1} \right] [z+1]$$  \hspace{1cm} (6.450)

$$T_{10}^*(z) = U_1 \left[ \frac{1}{L+1} \right] [z-L]$$  \hspace{1cm} (6.451)

The \{11\} problem

The \{11\} problem is similar to the eigenvalue problem. It is given by

$$\left[ \frac{d^2}{dz^2} - k^2 \right] T_{11} = 0$$  \hspace{1cm} (6.452)

in the solid phase, \(-1 < z < 0\), \(0 < x < W\), and

$$\left[ \frac{d^2}{dz^2} - k^2 \right] T_{11}^* = 0$$  \hspace{1cm} (6.453)
in the liquid phase, \( 0 < z < L \), \( 0 < x < W \),

\[
\left[ T_{i1} - T_{i1}^* \right] + Z_{i1} \left[ \frac{dT_0}{dz} - \frac{dT_0^*}{dz} \right] = 0 \tag{6.454}
\]

and

\[
\frac{dT_{i1}}{dz} - \frac{dT_{i1}^*}{dz} = 0 \tag{6.455}
\]

at \( z = 0 \),

\[ T_{i1}(z = -1) = 0 \tag{6.456} \]

and

\[ T_{i1}^*(z = L) = 0 \tag{6.457} \]

Finally we can turn to Eq. (6.435), which is a differential equation for \( Z \). Using Eq. (6.440) and \( dZ_i/dx = 0 \) at \( x = 0, W \), and integrating Eq. (6.435) over \( 0 < x < W \), we find that \( U_i \) must be zero, and therefore \( T_{i0} \) and \( T_{i0}^* \) must both be identically zero. Then the first order problem is exactly like the eigenvalue problem, and the condition at neutrality is given by Eq. (6.431), viz., \( U_0 = \left[ \mathcal{A} k^2 + T_s \right] \left[ 1 + \frac{\tanh kL}{\tanh k} \right] \). What we have so far is this:

\[ T_i = T_{i1}(z) \cos(kx) = T_i^* \cos(kx) , \quad T_{i1}(z) \cos(kx) = T_{i1}^*(z) \cos(kx) , \quad U_i = 0 \]

\[ Z_i(x) = A \cos(kx) = Z_i^* \cos(kx) . \]

And we go on to the second order problem to find the value of \( A \).

**The Second Order Problem**

The second order problem is

\[ \nabla^2 T_2 = 0 \tag{6.458} \]
on the domain, \(-1 < z < 0\), \(0 < x < W\), and

\[ \nabla^2 T^*_2 = 0 \]  \hspace{1cm} (6.459)

on the domain, \(0 < z < L\), \(0 < x < W\),

\[ T_2 + 2Z_1 \frac{\partial T_1}{\partial z} = -A \frac{d^2 Z_2}{dx^2} - Z_2 \frac{dT_0}{dz} \]  \hspace{1cm} (6.460)

\[ \left[T_2 - T_2^*\right] + 2Z_1 \left[\frac{\partial T_1}{\partial z} - \frac{\partial T_1^*}{\partial z}\right] + Z_2 \left[\frac{dT_0}{dz} - \frac{dT_0^*}{dz}\right] = 0 \]  \hspace{1cm} (6.461)

and

\[ \left[\frac{\partial T_2}{\partial z} - \frac{\partial T_2^*}{\partial z}\right] + 2Z_1 \left[\frac{\partial^2 T_1}{\partial z^2} - \frac{\partial^2 T_1^*}{\partial z^2}\right] - 2Z_{1x} \left[\frac{\partial T_1}{\partial x} - \frac{\partial T_1^*}{\partial x}\right] = -U_2 \]  \hspace{1cm} (6.462)

at the base surface \(z = 0\). The far-field conditions are given by

\[ T_2(z = -1) = 0 \]  \hspace{1cm} (6.463)

and

\[ T_2^*(z = L) = 1 \]  \hspace{1cm} (6.464)

The volume condition is given by

\[ \int_{0}^{W} Z_d x = 0 \]  \hspace{1cm} (6.465)

The stricken terms are zero because of results from previous orders. Assuming that the above equations have a solution of the form

\[ T_2(x, z) = T_{20}(z) + T_{21}(z) \cos(kx) + T_{22}(z) \cos(2kx) \]  \hspace{1cm} (6.466)

\[ T_2^*(x, z) = T_{20}^*(z) + T_{21}^*(z) \cos(kx) + T_{22}^*(z) \cos(2kx) \]  \hspace{1cm} (6.467)

\[ Z_2(x) = Z_{21} \cos(kx) + Z_{22} \cos(2kx) \]  \hspace{1cm} (6.468)

we deduce the \{20\} and \{21\} and \{22\} problems. At \(z = 0\), the following formulae may be
useful:

\[
2Z_1 \left[ \frac{\partial^2 T_i}{\partial z^2} - \frac{\partial^2 T_1^*}{\partial z^2} \right] = k^2 U_0 \hat{Z}_1^2 \left[ 1 + \cos(2kx) \right]
\]

\[
-2Z_1 \left[ \frac{\partial T_i}{\partial x} - \frac{\partial T_1^*}{\partial x} \right] = -k^2 U_0 \hat{Z}_1^2 \left[ 1 - \cos(2kx) \right]
\]

The \{20\} problem

The \{20\} problem is given by

\[
\frac{d^2 T_{20}}{dz^2} = 0
\]

in the solid phase, \(-1 < z < 0\), \(0 < x < W\), and

\[
\frac{d^2 T_{20}^*}{dz^2} = 0
\]

in the liquid phase, \(0 < z < L\), \(0 < x < W\),

\[
T_{20} - T_{20}^* = 0
\]

and

\[
\frac{dT_{20}}{dz} - \frac{dT_{20}^*}{dz} = -U_2
\]

at \(z = 0\),

\[
T_{20} (z = -1) = 0
\]

and

\[
T_{20}^* (z = L) = 1
\]

A solution to Eqs. (6.469-6.474) is given by
\[ T_{20}(z) = \left[ \frac{-U_z L + 1}{L + 1} \right] [z + 1] \quad (6.475) \]

\[ T_{20}^*(z) = \left[ \frac{U_z + 1}{L + 1} \right] [z - L] + 1 \quad (6.476) \]

**The \{21\} problem**

The \{21\} problem is similar to the eigenvalue problem. It is given by

\[
\left[ \frac{d^2}{dz^2} - k^2 \right] T_{21} = 0
\]

in the solid phase, \(-1 < z < 0\), \(0 < x < W\), and

\[
\left[ \frac{d^2}{dz^2} - k^2 \right] T_{21}^* = 0
\]

in the liquid phase, \(0 < z < L\), \(0 < x < W\),

\[
[T_{21} - T_{21}^*] + Z_{21} \left[ \frac{dT_0}{dz} - \frac{dT_0^*}{dz} \right] = 0
\]

and

\[
\frac{dT_{21}}{dz} - \frac{dT_{21}^*}{dz} = 0
\]

at \(z = 0\),

\[ T_{21}(z = -1) = 0 \quad (6.481) \]

and

\[ T_{21}^*(z = L) = 0 \quad (6.482) \]

A solution to Eqs. (6.477-6.482) is given by

\[
T_{21}(z) = A_{21} \left[ e^{kz} - e^{-2k} e^{-kz} \right] = \left[ \frac{Ak^2 - \frac{dT_0}{dz}(z = 0)}{1 - e^{-2k}} \right] \left[ e^{kz} - e^{-2k} e^{-kz} \right] Z_{21}
\]

\[ (6.483) \]
The \{22\} problem

The \{22\} problem is given by

\[
T_{21}^* (z) = A_{21}^* \left( e^{kz} - e^{2kz} e^{-kz} \right) = \left[ \frac{A k^2 - \frac{dT_0^*}{dz} (z = 0)}{1 - e^{2kL}} \right] \left[ e^{kz} - e^{2kL} e^{-kz} \right] Z_{21} \tag{6.484}
\]

and

\[
T_{22}^* (z) = A_{22}^* \left( e^{2kz} - e^{-4kz} e^{-2kz} \right) = \left[ \frac{A k^2 - \frac{dT_0^*}{dz} (z = 0)}{1 - e^{2kL}} \right] \left[ e^{kz} - e^{2kL} e^{-kz} \right] Z_{22} \tag{6.491}
\]

in the solid phase, \(-1 < z < 0, 0 < x < W\), and

\[
T_{22} - T_{22}^* = U_0 Z_{22} \tag{6.487}
\]

and

\[
\frac{dT_{22}}{dz} - \frac{dT_{22}^*}{dz} = -2U_0 k^2 \hat{Z}_1^2 \tag{6.488}
\]

at \( z = 0 \),

\[
T_{22} (z = -1) = 0 \tag{6.489}
\]

and

\[
T_{22}^* (z = L) = 0 \tag{6.490}
\]

A solution to Eqs. (6.485-6.490) is given by

\[
T_{22} (z) = A_{22} \left( e^{2kz} - e^{-4kz} e^{-2kz} \right) \tag{6.491}
\]

\[
T_{22}^* (z) = A_{22}^* \left( e^{2kz} - e^{4kL} e^{-2kz} \right) \tag{6.492}
\]
where

\[
A_{22} = \left[ \frac{1}{1-e^{-4kL}} \right] \left[ \frac{\tanh 2k}{\tanh 2k + \tanh 2kL} \right] U_0 \left[ Z_{22} - k \tanh 2kL \hat{Z}_1^2 \right]
\] (6.493)

\[
A_{22}^* = -\left[ \frac{1}{1-e^{-4kL}} \right] \left[ \frac{\tanh 2kL}{\tanh 2k + \tanh 2kL} \right] U_0 \left[ Z_{22} + k \tanh 2k \hat{Z}_1^2 \right]
\] (6.494)

**Using the curvature equation**

Finally we can turn to Eq. (6.460), which is a differential equation for \(Z_2\). Using Eq. (6.465) and \(dZ_2/dx = 0\) at \(x = 0, W\), and integrating Eq. (6.460) over \(0 < x < W\), we find

\[
T_20(z = 0) + Z_1 \frac{d\hat{T}_1}{dz}(z = 0) = 0
\] (6.495)

Using \(d\hat{T}_1/dz(z = 0) = \left[ \frac{k}{\tanh k} \right] [\mathcal{A}k^2 + T_S] \hat{Z}_1\), and \(T_20(z = 0) = \left[ -\frac{U_2L+1}{L+1} \right] \), there obtains

\[
U_2 = \frac{1}{L_{U_2,\text{plane}}} + \left[ \frac{k}{\tanh k} \right] [\mathcal{A}k^2 + T_S] \left[ 1 + \frac{1}{L} \right] \hat{Z}_1^2
\] (6.496)

where the correction term is again seen to be always positive, whence the mean speed of the interface runs ahead of its base value.

To go to third order, we need to solve Eq. (6.460) for \(Z_2\). To find \(Z_2\), a solvability condition must be satisfied. It is

\[
\int_0^w \left[ T_2(z = 0) + 2Z_1 \frac{\partial T_1}{\partial Z}(z = 0) \right] Z_1 dx - \int_0^w T_1(z = 0) Z_2 dx = 0
\] (6.497)

Again this condition is automatically satisfied, whence Eq. (6.460) can be solved for \(Z_2\).

Substituting the expansions from Eqs. (6.466-6.468) into Eq. (6.460), the constant term disappears due to the result obtained earlier using integrability, viz., Eq. (6.495). The coefficient
of the first harmonic vanishes due to solvability, and there obtains by equating the coefficients of
the second harmonic
\[ T_{22}(z = 0) + \frac{dT_0}{dz}(z = 0) Z_1 + \left[ \frac{dT_0}{dz}(z = 0) - 4AK^2 \right] Z_{22} = 0 \] (6.498)

Substituting \( T_{22}(z = 0) = A_{22}[1 - e^{-4k}] \) and using \( \frac{dT_0}{dz}(z = 0) = \left[ \frac{k}{\tanh k} \right] [AK^2 + T_s] \hat{Z}_1 \), we get
\[ A_{22} = \left[ \frac{1}{1 - e^{-4k}} \right] [4AK^2 + T_s] Z_{22} - \left[ \frac{k}{\tanh k} \right] [AK^2 + T_s] \hat{Z}_1^2 \] (6.499)

Comparing with Eq. (6.493) and simplifying, there obtains
\[ Z_{22} = \left[ \frac{P}{Q} \right] \hat{Z}_1^2 \] (6.500)

where
\[ \frac{P}{Q} = \left[ \frac{k}{\tanh k} \right] [AK^2 + T_s] - kU_o \tanh 2kL \left[ \frac{\tanh 2k}{\tanh 2k + \tanh 2kL} \right] \]
\[ - U_0 \left[ \frac{\tanh 2k}{\tanh 2k + \tanh 2kL} \right] \] (6.501)

Hence, \( Z_{21} \) and \( A \) carry on to third order.

**The Third Order Problem**

The equations at the third order are given by
\[ \nabla^2 T_3 = 0 \] (6.502)
on the domain, \(-1 < z < 0 \), \( 0 < x < W \), and
\[ \nabla^2 T_3^* = 0 \] (6.503)
on the domain, \( 0 < z < L \), \( 0 < x < W \),
\[ -9\mathcal{A} \left( \frac{dZ_1}{dx} \right)^2 \frac{d^2Z_1}{dx^2} + \left[ T_3 + 3Z_1 \frac{\partial T_2}{\partial z} + 3Z_1^2 \frac{\partial^2 T_1}{\partial z^2} + 3Z_2 \frac{\partial T_1}{\partial z} \right] = -\mathcal{A} \frac{d^2Z_3}{dx^2} - Z_3 \frac{dT_0}{dz} \] (6.504)
\[
\left[ T_3 - T_3^* \right] + 3Z_1 \left[ \frac{\partial T_1}{\partial z} - \frac{\partial T_1^*}{\partial z} \right] + 3Z_1^2 \left[ \frac{\partial^2 T_2}{\partial z^2} - \frac{\partial^2 T_2^*}{\partial z^2} \right] + 3Z_2 \left[ \frac{\partial T_1}{\partial z} - \frac{\partial T_1^*}{\partial z} \right] \\
+ Z_3 \left[ \frac{dT_0}{dz} - \frac{dT_0^*}{dz} \right] = 0
\]

\[ (6.505) \]

and

\[
\left[ \frac{\partial T_3}{\partial z} - \frac{\partial T_3^*}{\partial z} \right] + 3Z_1 \left[ \frac{\partial^2 T_2}{\partial z^2} - \frac{\partial^2 T_2^*}{\partial z^2} \right] + 3Z_1^2 \left[ \frac{\partial^3 T_1}{\partial z^3} - \frac{\partial^3 T_1^*}{\partial z^3} \right] + 3Z_2 \left[ \frac{\partial T_1}{\partial z} - \frac{\partial T_1^*}{\partial z} \right] \\
- 3Z_1 \left[ \frac{\partial T_2}{\partial x} - \frac{\partial T_2^*}{\partial x} \right] + 2Z_1 \left[ \frac{\partial^2 T_1}{\partial x \partial z} - \frac{\partial^2 T_1^*}{\partial x \partial z} \right] - 3Z_2 \left[ \frac{\partial T_1}{\partial x} - \frac{\partial T_1^*}{\partial x} \right] = -U_3
\]

\[ (6.506) \]

at \( z = 0 \),

\[ T_3 (z = -1) = 0 \]

\[ (6.507) \]

and

\[ T_3^* (z = L) = 0 \]

\[ (6.508) \]

The volume condition is given by

\[
\int_0^W Z_3 dx = 0
\]

\[ (6.509) \]

The stricken terms vanish at \( z = 0 \) on account of results from previous orders. We assume the following form for the solution

\[
T_3 (x, z) = T_{30} (z) + T_{31} (z) \cos(kx) + T_{32} (z) \cos(2kx) + T_{33} (z) \cos(3kx)
\]

\[ (6.510) \]

\[
T_3^* (x, z) = T_{30}^* (z) + T_{31}^* (z) \cos(kx) + T_{32}^* (z) \cos(2kx) + T_{33}^* (z) \cos(3kx)
\]

\[ (6.511) \]

\[
Z_3 (x) = Z_{31} \cos(kx) + Z_{32} \cos(2kx) + Z_{33} \cos(3kx)
\]

\[ (6.512) \]

This problem can be solved completely but it is sufficient to solve the \{31\} problem to learn the nature of bifurcation and the value of \( A^2 \).
The \{31\} problem

The \{31\} problem is given by

\[
\left[ \frac{d^2}{dz^2} - k^2 \right] T_{31} = 0 \tag{6.513}
\]

in the solid phase, \(-1 < z < 0\), \(0 < x < W\), and

\[
\left[ \frac{d^2}{dz^2} - k^2 \right] T_{31}^* = 0 \tag{6.514}
\]

in the liquid phase, \(0 < z < L\), \(0 < x < W\),

\[
T_{31} - T_{31}^* = U_0 Z_{31} + 3U_2 \hat{Z}_1 + \frac{3}{4} k^2 U_0 \hat{Z}_1^3 \tag{6.515}
\]

and

\[
\left[ \frac{dT_{31}}{dz} - \frac{dT_{31}^*}{dz} \right] = -\frac{3}{2} k^2 U_0 \hat{Z}_1 Z_{22} \tag{6.516}
\]

at \(z = 0\),

\[
T_{31}(z = -1) = 0 \tag{6.517}
\]

and

\[
T_{31}^*(z = L) = 0 \tag{6.518}
\]

A solution to Eqs. (6.513-6.518) is given by

\[
T_{31}(z) = A_{21} \left[ e^{kz} - e^{-2k} e^{-kz} \right] \tag{6.519}
\]

and

\[
T_{31}^*(z) = A_{31}^* \left[ e^{kz} - e^{2k} e^{-kz} \right] \tag{6.520}
\]

where
\[ A_{31} = \left[ \frac{1}{1-e^{-2k}} \right] \left[ \frac{\tanh k}{\tanh k + \tanh kL} \right] \left[ U_0 Z_{31} + 3U_2 \hat{Z}_1 + \frac{3}{4} k^2 U_0 \hat{Z}_1^2 - \frac{3}{2} k U_0 \tanh kL \hat{Z}_1 Z_{22} \right] \] (6.521)

and

\[ A_{31}' = -\left[ \frac{1}{1-e^{2Uk}} \right] \left[ \frac{\tanh kL}{\tanh k + \tanh kL} \right] \left[ U_0 Z_{31} + 3U_2 \hat{Z}_1 + \frac{3}{4} k^2 U_0 \hat{Z}_1^2 + \frac{3}{2} k U_0 \tanh k \hat{Z}_1 Z_{22} \right] \] (6.522)

**Using the curvature equation**

Finally we turn to Eq. (6.504), which is a differential equation for \( Z_3 \). To find \( Z_3 \), a solvability condition must be satisfied. It is

\[ \int_0^w T_3 (z = 0) + 3Z_1 \frac{\partial T_1}{\partial z}(z = 0) + 3Z_1^2 \frac{\partial^2 T_1}{\partial z^2}(z = 0) + 3Z_2 \frac{\partial T_1}{\partial z}(z = 0) - 9A \left( \frac{dZ_1}{dx} \right)^2 \frac{d^2 Z_1}{dx^2} Z_3dx = 0 \] (6.523)

whence

\[ T_{31} (z = 0) + 3 \left[ \frac{dT_{20}}{dz}(z = 0) + \frac{1}{2} \frac{dT_{22}}{dz}(z = 0) \right] \hat{Z}_1 + 9 \frac{d^2 T_1}{dz^2}(z = 0) \hat{Z}_1^2 + \frac{3}{2} \frac{d T_1}{dz}(z = 0) Z_{22} + \frac{9}{4} \mathcal{A} k^4 \hat{Z}_1^3 - \left[ \mathcal{A} k^2 + T_5 \right] Z_{31} = 0 \] (6.524)

which can be written as

\[ A_{31} \left[ 1 - e^{-2k} \right] = -R_3 \] (6.525)

where

\[ R_3 = 3 \left[ \frac{dT_{20}}{dz}(z = 0) + \frac{1}{2} \frac{dT_{22}}{dz}(z = 0) \right] \hat{Z}_1 + 9 \frac{d^2 T_1}{dz^2}(z = 0) \hat{Z}_1^2 + \frac{3}{2} \frac{d T_1}{dz}(z = 0) Z_{22} + \frac{9}{4} \mathcal{A} k^4 \hat{Z}_1^3 - \left[ \mathcal{A} k^2 + T_5 \right] Z_{31} \] (6.526)

which can be simplified to get
Comparing the value of \( A_{31} \) from Eq. (6.521) and (6.525), and using Eq. (6.527), we get after some simplification

\[
R_3 = 3 \hat{Z}_1 \left[ \left( -\frac{U_r L + 1}{L + 1} \right) + \left( \frac{k}{\tanh 2k} \right) \left[ 4 \mathcal{A} k^2 + T_s \right] \hat{Z}_{22} - \left( \frac{k}{\tanh k} \right) \left[ \mathcal{A} k^2 + T_s \right] \hat{Z}_1^2 \right] \\
+ \frac{9}{4} k^2 \left[ \mathcal{A} k^2 + T_s \right] \hat{Z}_1^3 + \frac{3}{2} \left( \frac{k}{\tanh k} \right) \left[ \mathcal{A} k^2 + T_s \right] \hat{Z}_1 \hat{Z}_{22} + \frac{9}{4} \mathcal{A} k^4 \hat{Z}_1^3 - \left( \mathcal{A} k^2 + T_s \right) \hat{Z}_{31}
\]

(6.527)

where \( P \) is given by Eq. (6.501). Again, the sign of \( A^2 \) is of interest. If it is positive, the pitchfork is forward. On doing calculations it will be learned that \( A^2 \) can be positive as well as negative depending upon the input parameters. But in order to make our analysis yet simpler, let us put \( T_s = 0 \) in our results for this case.

**Case 6: Latent Heat Rejected to the Subcooled Liquid Only, Both Phases of Finite Extent, \( U \) Dropped From Domain Equations**

Putting \( T_s = 0 \) in the results of case 5, there obtains at the base

\[ T_0(z) = 0 \]  
(6.529)

and

\[ T_0^*(z) = \frac{T_L}{L} z \]  
(6.530)

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where $U_0$ is given by

$$U_0 = \frac{T}{L}$$  \hspace{1cm} (6.531)

The condition at neutrality is given by

$$U_0 = \mathcal{A} k^2 \left[ 1 + \frac{\tanh k L}{\tanh k} \right]$$  \hspace{1cm} (6.532)

Figure 6.6 shows the corresponding neutral curve. The curve is monotonically increasing for all values of $L$. Hence the most dangerous value of $n$ is one, which corresponds to $k = \pi/W$, giving only one crest at critical.

![Figure 6.6](image)

Figure 6.6 – Typical neutral curve for solidification when the latent heat is rejected through the subcooled liquid only; $U$ is dropped from the domain equations

At second order, we will find a “speed-up” and $U_2$ is given by the formula

$$U_2 = \frac{1}{L} \left[ \frac{k}{\tanh k} \right] \mathcal{A} k^2 \left[ 1 + \frac{1}{L} \right] Z_i^2$$  \hspace{1cm} (6.533)

$Z_{22}$ is found as $Z_{22} = \left[ \frac{P}{Q} \right] Z_i^2$, where
And at third order we find $A^2$ as

$$
\left[ \frac{P}{Q} \right] \left[ \frac{1}{2} k \tanh k L - 4 \left( \frac{k}{\tanh 2k} \right) - \frac{1}{2} \left( \frac{k}{\tanh k} \right) \right] \\
- \frac{1}{U_0} \left[ \frac{k}{\tanh k} \right] \mathcal{A} k^2 \left[ 1 + \frac{1}{L} \right] \\
+ \left[ \frac{k}{\tanh k} \right] + \left[ \frac{k}{\tanh k} \right] \left[ \frac{k}{\tanh 2k} \right] - \frac{7}{4} k^2
$$

$$
A^2 = \frac{1}{LU_0}
$$

Our job then is to find the sign of $A^2$. To accomplish this, we will consider two sub-cases: one where $k^2$ is large, and another where $k^2$ is small.

**Analysis for Large $k^2$:**

Since $\tanh k$ approaches 1 for large values of $k^2$, we have $\lim_{k^2 \to \text{large}} U_0 = 2\mathcal{A}k^2$ and

$$
\lim_{k^2 \to \text{large}} \frac{P}{Q} = 0
$$

hence using Eq. (6.535), we get

$$
A^2 = \frac{1}{LU_0} = \frac{1}{L} \frac{1}{2\mathcal{A}k^2}
$$

whence neglecting the lower order terms in $k^2$ there obtains

$$
A^2 = -\frac{2}{3} \frac{1}{\mathcal{A} L k^4} < 0
$$

We learn that the bifurcation is always a backward pitchfork for large values of inputs $k^2$ no matter the value of $L$. Table 6.3 gives the value of the critical speed $U_0$ and $A^2$ for

$\mathcal{A} = 0.26 \times 10^6$ and for two different values of $L$. The value of $U_0$ is calculated using Eq. (6.532). The values of $A^2$ were obtained from Eq. (6.535) but they can be calculated directly.
from Eq.(6.536). Notice that since \( k^2 \) is large the value of the critical speed \( U_0 \) does not depend on \( L \).

Table 6.3 – Case 6 – Values of \( U_0 \) and \( A^2 \) for inputs \( L = 1, 2 \) and for large values of \( k^2 \)

<table>
<thead>
<tr>
<th>( k^2 )</th>
<th>( L = 1 )</th>
<th>( L = 2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( U_0 )</td>
<td>( A^2 )</td>
<td>( U_0 )</td>
</tr>
<tr>
<td>10^3</td>
<td>5 x 10^{-4}</td>
<td>-2.667</td>
</tr>
<tr>
<td>10^4</td>
<td>5 x 10^{-3}</td>
<td>-2.667 x 10^{-2}</td>
</tr>
<tr>
<td>10^5</td>
<td>5 x 10^{-2}</td>
<td>-2.667 x 10^{-4}</td>
</tr>
<tr>
<td>10^6</td>
<td>0.5</td>
<td>-2.667 x 10^{-6}</td>
</tr>
<tr>
<td>10^7</td>
<td>5</td>
<td>-2.667 x 10^{-8}</td>
</tr>
<tr>
<td>10^8</td>
<td>50</td>
<td>-2.667 x 10^{-10}</td>
</tr>
</tbody>
</table>

Analysis for Small \( k^2 \):

Since \( \tanh k \) approaches \( k \) for small values of \( k^2 \) we have
\[
\lim_{k^2 \to \text{small}} U_0 = \left[ 1 + L \right] A k^2
\]

and
\[
\lim_{k^2 \to \text{large}} \frac{P}{Q} = \frac{1}{3}
\]

hence using Eq. (6.535), we get

\[
A^2 = \frac{3}{2} \left[ \frac{1}{L + 1} \right] \left[ \frac{1}{L - 3/2} \right] \frac{1}{A} k^2
\]

(6.537)

Clearly the nature of the bifurcation depends on the ratio of the depths of the two phases. For \( L < \frac{3}{2} \) we have a backward pitchfork whereas the pitchfork is forward for \( L > \frac{3}{2} \). Table 6.4 gives the value of \( A^2 \) for \( A = 0.26 \times 10^6 \) and for two different values of \( L \). The values of \( A^2 \) were obtained from Eq. (6.535) but they can be calculated directly from Eq. (6.537).
Table 6.4 – Case 6 – Values of $U_0$ and $A^2$ for inputs $L = 1, 2$ and for small values of $k^2$

<table>
<thead>
<tr>
<th>$k^2$</th>
<th>$L = 1$</th>
<th>$L = 2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$U_0$</td>
<td>$A^2$</td>
</tr>
<tr>
<td>$10^{-8}$</td>
<td>$5 \times 10^{-15}$</td>
<td>$-6 \times 10^{-14}$</td>
</tr>
<tr>
<td>$10^{-7}$</td>
<td>$5 \times 10^{-14}$</td>
<td>$-6 \times 10^{-13}$</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>$5 \times 10^{-13}$</td>
<td>$-6 \times 10^{-12}$</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>$5 \times 10^{-12}$</td>
<td>$-6 \times 10^{-11}$</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>$5 \times 10^{-11}$</td>
<td>$-6 \times 10^{-10}$</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>$5 \times 10^{-10}$</td>
<td>$-6 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

Table 6.5 – Case 6 – Values of $U_0$ and $A^2$ for inputs $L = 1, 2$ and $k^2$

<table>
<thead>
<tr>
<th>$k^2$</th>
<th>$L = 1$</th>
<th>$L = 2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$U_0$</td>
<td>$A^2$</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>$5 \times 10^{-11}$</td>
<td>$-6 \times 10^{-10}$</td>
</tr>
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<td>$5 \times 10^{-9}$</td>
<td>$-5.94 \times 10^{-8}$</td>
</tr>
<tr>
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<td>$5 \times 10^{-8}$</td>
<td>$-5.41 \times 10^{-7}$</td>
</tr>
<tr>
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</tr>
<tr>
<td>10</td>
<td>$5 \times 10^{-6}$</td>
<td>$-2.66 \times 10^{-5}$</td>
</tr>
<tr>
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<td>$5 \times 10^{-5}$</td>
<td>$-2.66 \times 10^{-4}$</td>
</tr>
<tr>
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<td>$-2.66 \times 10^{-3}$</td>
</tr>
<tr>
<td>$10^4$</td>
<td>$5 \times 10^{-3}$</td>
<td>$-2.67 \times 10^{-2}$</td>
</tr>
<tr>
<td>$10^5$</td>
<td>$5 \times 10^{-2}$</td>
<td>$-2.67 \times 10^{-1}$</td>
</tr>
<tr>
<td>$10^6$</td>
<td>0.5</td>
<td>$-2.66 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
Then defining $L_{\text{crossover}} = \frac{3}{2}$, we have the following result: For $L < L_{\text{crossover}}$ the pitchfork is backward for small as well as for large values of $k^2$. For $L > L_{\text{crossover}}$, the pitchfork is forward for small values of $k^2$ while it is backward for large values of $k^2$. This is shown in Table 6.5 which shows the values of $A^2$ for $\mathcal{A} = 0.26 \times 10^6$ and for $L = 1, 2$ over a wide range of $k^2$. Observe that for $L > L_{\text{crossover}}$, $A^2$ flips sign for some intermediate value of $k^2$ and the bifurcation type changes from a forward to a backward pitchfork.

![Diagram](image)

Figure 6.7 – Transition diagram of $L$ versus $k^2$ showing regions corresponding to forward and backward pitchfork.

The reader might also be interested in comparing the results of Table 6.5 with those calculated in Table 6.1 where $U$ was not dropped from the domain equations. The two tables list the outputs $U_0$ and $A^2$ for the same values of inputs $k^2$ and $L$. Observe that the results are in excellent agreement unless $k^2$ is large enough that $U_0$ is not small anymore and dropping $U$ from the domain equations is not a good approximation.
Finally we show a transition diagram, cf., Figure 6.7 which shows windows in the parameter space \((L, k^2)\) where we have forward and backward pitchfork.

**Discussion**

We have identified regions where the bifurcation might be backward and regions where it might be a forward pitchfork. We obtain a backward pitchfork for most cases, unless \(L\) is greater than \(L_{\text{crossover}}\) and the input values of \(k^2\) are small. Hence a forward pitchfork is easy to get for experimentally realizable values of \(L\) and \(k^2\) if one just knows where to look.

A forward pitchfork is also called a supercritical bifurcation (pitchfork opening to the right) while a backward pitchfork is often termed as a subcritical bifurcation (pitchfork opening to the left). Figures 6.8 and 6.9 show schematics representing the two types of bifurcations.

In both these cartoons we plot the control parameter \(\lambda\) on the horizontal axis and the square of the amplitude of the non-planar solution \(A^2\) on the vertical axis. For the solidification problem our control parameter is the undercooling in the subcooled liquid, i.e., \(\lambda = T_\gamma\). One might study the stability of the new branches (new non-planar solutions) to prove that subcritical solutions are unstable while supercritical solutions are stable [6]. Hence the solid lines in Figures 6.8 and 6.9 signify a stable solution while the dotted lines are indicative of unstable solutions.

![Figure 6.8](image_url)  
*Figure 6.8 – A cartoon illustrating a forward/supercritical branching*
Figure 6.9 – A cartoon illustrating a backward/subcritical branching

In the case of a supercritical bifurcation, as we increase the control parameter, the instability will set in only after one crosses the critical value of the control parameter $\lambda_c$. Hence the supercritical case is in good agreement [31] with the predictions of the linear theory and gives us a solution when the planar solution is no longer stable to infinitesimal perturbations. And this corresponds to a smooth transition from a planar to a non-planar solution. In the case of a subcritical bifurcation however, the solution can jump discontinuously to the new non-planar steady state even before the critical point predicted by the linear theory [6]. However some other researchers [32] have emphasized that the prediction of a subcritical bifurcation should not be understood as evidence that finite amplitude solutions do not exist. Ordinarily then, the implication of a subcritical case is that the planar solution might be unstable to finite amplitude perturbations even though it is stable to infinitesimal perturbations according to the linear stability theory [10].
Now Wollkind and Segel [33] have argued that the occurrence of a forward pitchfork is related to the formation of stable bands and a periodic structure. Hence the region of a forward pitchfork is also referred as a cellular regime while the region of a subcritical bifurcation is ordinarily considered to physically correspond to dendritic growth.

Next, going back to the analysis of case 6, let us try to advance some arguments to relate the predictions of the linear and the nonlinear theory. The predictions of the linear theory are seen from the neutral curve, cf., Figure 6.6. It is clear that for small values of $k^2$ the curve is very sensitive to the value of $L$. A possible explanation is that for low values of $k^2$ the effect of surface tension cannot be significant. What is important is the diffusion in the two phases and hence the ratio of the depths of the two phases plays a key role. For large values of $k^2$ we see from Figure 6.6 that the neutral curve becomes asymptotic to $U_0 = 2A k^2$ for all values of $L$, hence the ratio of the depths of the two phases is not of much importance. This is reasonable as the effect of surface tension becomes dominating for large enough values of $k^2$.

Now the prediction of the nonlinear theory for large values of $k^2$ is that the nature of the branching is independent of $L$ and it is always a backward pitchfork. And this is consistent with the predictions of the linear theory in that the ratio of the depths of the two phases cannot possibly have a significant effect on the critical front speed if one is running an experiment in the large $k^2$ regime.

However, for small values of $k^2$, diffusion in the two phases is important compared to surface tension and hence the nature of branching depends on $L$. What is more interesting is this: We learned that for $L < \frac{3}{2}$ we have a backward pitchfork while for $L > \frac{3}{2}$ the branching is forward. Now the linear stability theory predicted (cf., Figure 6.6) that a larger value of $L$ ought
to give us more stability compared to a smaller $L$. Then the fact that the weak nonlinear analysis predicts a larger value of $L \left( L > \frac{3}{2} \right)$ (as opposed to a smaller value $L$) to give a forward bending pitchfork is interesting because a forward pitchfork is ordinarily associated with the formation of cellular patterns (as opposed to dendrites) which are in turn associated with a lesser degree of disorder. A backward pitchfork is, on the other hand, related to the formation of dendrites which certainly have a higher degree of disorder, and that is what we get for smaller values of $L \left( L < \frac{3}{2} \right)$ for small values of $k^2$.

**Concluding Remarks**

We have performed a weak nonlinear analysis for the problem of solidification of a pure material. We have found that once the instability sets in, the front speed always runs ahead of its base value regardless of the values of input parameters. We have also learned that the nature of the branching of the planar solution to the non-planar solution depends on the inputs $k^2$ and $L$. We have identified regions in the $(L, k^2)$ plane where the pitchfork is forward and regions where it is backward. It is possible to obtain both in physically realizable experiments.
CHAPTER 7
CONCLUSIONS AND RECOMMENDATIONS

In this chapter, we summarize the main results of this dissertation and propose relevant future work. This dissertation has focused on understanding the underlying physics and causes of morphological instability in two phase-change problems, namely precipitation and solidification. The theoretical methods involve linear stability calculations and weak nonlinear calculations.

The major findings of the linear stability analysis are these: First, the solidification instability can give rise to the possibility of a multiple-cell pattern at the onset of instability whereas for other growth problems involving solid-liquid interfaces, such as precipitation from a supersaturated solution, the onset of an instability from a planar state can result in at most a single crest and trough. Second, we have found that a solid-liquid front that grows on account of temperature gradients is the only one amongst all solid-liquid front growth problems where a critical wavelength, independent of surface energy, can occur. This critical wavelength which is of the order of the size of the container can be obtained for reasonable and measurable values of growth speed for most systems of practical interest. This fact alone sets solidification apart from any other growth problem involving a solid-liquid interface where the critical wavelength must obtain for unreasonably low values of growth speeds.

These conclusions demand that careful experiments be designed in order to validate the findings. The experiment must be run so that one is able to creep up on the instability by slowly increasing the value of the control parameter to its critical value. It would be valuable to demonstrate in an experiment that the pattern evolving at the onset of instability is indeed consistent with the theoretical predictions. If the prediction of the nonlinear results is a forward pitchfork, then one might want to confirm that the critical value of the control parameter seen in the experiment is consistent with the theoretical value predicted by the linear stability analysis.
Also, one might want to check in the case of a backward pitchfork if the critical value of the control parameter seen in an experiment is very different from the prediction of the linear analysis.

The main findings of the nonlinear calculations are these: First, a solidification front always moves ahead of its predicted base value upon becoming unstable. This is in contrast with other solid-liquid growth instability problems such as precipitation where an unstable front always slows down compared to its predicted base value. Second, the nature of the bifurcation in solidification may be a forward pitchfork, leading to cellular growth, or a backward pitchfork, leading to dendritic growth. In contrast, other growth problems such as precipitation and electrodeposition are ordinarily characterized by dendritic growth in the post onset region.

These findings raise several interesting questions that ought to be answered in future studies. One of the most important questions is this: Although the two phenomenon are very similar, why is the interfacial instability in solidification so different from that in precipitation? For instance, can we find out a physical reason as to why a solidification front always speeds up upon becoming unstable whereas a precipitation front slows down compared to its predicted base value? Why do we only see a backward pitchfork in a precipitation instability whereas a solidification instability gives rise to the possibility of a backward as well as a forward pitchfork? Then, one might investigate the question of cross-sectional dependence on the nature of bifurcation beyond the onset of instability. In other words, can we ascribe a physical reason as to why the nature of the branching should depend on the shape of the cross section of the container in which the growth takes place? One might also want to validate such a cross-sectional dependence in an experiment. Another important question that one might ask is whether we can specifically point out the algebraic terms in the nonlinear calculations that tend
to favor a backward bifurcation and terms that want to make the branching forward. Finally, one might want to trace out the stable steady state solution in the post onset regime in the case of a backward pitchfork, and one might wonder why the morphology of the interface changes in a discontinuous and abrupt fashion instead of changing slowly and continuously.
APPENDIX A
SURFACE VARIABLES

In this appendix, we give the formulas for three surface variables, namely the unit normal vector, the surface speed and the mean curvature. This is sufficient as far as the theoretical work in this dissertation is concerned. The reader is referred to the book by Johns and Narayanan [3] for further details.

A.1 The Unit Normal Vector

Let us define a free surface by \( z = Z(x,t) \) in Cartesian coordinates or \( z = Z(r,\theta,t) \) in cylindrical coordinates. Also we define a functional that vanishes on the surface as

\[
f = z - Z(x,t) = 0
\]

in Cartesian coordinates, and

\[
f = z - Z(r,\theta,t) = 0
\]

in cylindrical coordinates. Then the normal vector pointing into the region where \( f \) is positive is given by

\[
\vec{n} = \frac{\nabla f}{|\nabla f|}
\]

Here,

\[
\nabla f = \frac{\partial f}{\partial x} i_x + \frac{\partial f}{\partial z} i_z
\]

in Cartesian coordinates and

\[
\nabla f = \frac{\partial f}{\partial r} i_r + \frac{1}{r} \frac{\partial f}{\partial \theta} i_\theta + \frac{\partial f}{\partial z} i_z
\]

in cylindrical coordinates. Then the equation for the normal is given by
\[ \mathbf{n} = \frac{-\frac{\partial Z}{\partial x} \mathbf{i}_x + \mathbf{i}_z}{\left( \left( \frac{\partial Z}{\partial x} \right)^2 + 1 \right)^{\frac{1}{2}}} \]

in Cartesian coordinates, and

\[ \mathbf{n} = \frac{-\frac{\partial Z}{\partial r} \mathbf{i}_r + \mathbf{i}_z}{\left( \left( \frac{\partial Z}{\partial r} \right)^2 + 1 \right)^{\frac{1}{2}}} \]

in cylindrical coordinates, if $$\theta$$-independence is assumed.

### A.2 The Surface Speed

Let a surface be denoted by

\[ f(\mathbf{r}, t) = 0 \]

Let the surface move a small distance $$\Delta s$$ along its normal in time $$\Delta t$$. Then, \( f(\mathbf{r} \pm \Delta s \mathbf{n}, t + \Delta t) \) is given by

\[ f(\mathbf{r} \pm \Delta s \mathbf{n}, t + \Delta t) = f(\mathbf{r}, t) \pm \Delta s \mathbf{n} \cdot \nabla f(\mathbf{r}, t) + \Delta t \frac{\partial f(\mathbf{r}, t)}{\partial t} + \ldots \]

whence \( f(\mathbf{r} \pm \Delta s \mathbf{n}, t + \Delta t) = 0 = f(\mathbf{r}, t) \) requires

\[ \pm \Delta s \mathbf{n} \cdot \nabla f(\mathbf{r}, t) = -\Delta t \frac{\partial f(\mathbf{r}, t)}{\partial t} \]

The normal speed of the surface, \( u \), is then given by

\[ u = \pm \frac{\Delta s}{\Delta t} = - \frac{\frac{\partial f(\mathbf{r}, t)}{\partial t}}{\mathbf{n} \cdot \nabla f(\mathbf{r}, t)} \]

Hence, using the definition of the unit normal given earlier we get
\[ u = -\frac{\partial f}{\partial t} \left\| \nabla f \right\| . \]

For the problems concerned in this dissertation, the definition of \( u \) becomes

\[ u = \frac{\partial Z}{\partial t} \left[ \left( \frac{\partial Z}{\partial x} \right)^2 + 1 \right]^{1/2} \]

in Cartesian coordinates, and

\[ u = \frac{\partial Z}{\partial t} \left[ \left( \frac{\partial Z}{\partial r} \right)^2 + 1 \right]^{1/2} \]

in cylindrical coordinates, if \( \theta \)-independence is assumed.

### A.3 The Mean Curvature

The book by Johns and Narayanan [3] gives a detailed derivation of the curvature for a general surface. In this appendix, we simply provide the formulas used in this dissertation.

For a Cartesian surface defined as

\[ f = z - Z(x, t) = 0 \]

the mean curvature is given by

\[ 2H = \frac{Z_{xx}}{\left[ Z_x^2 + 1 \right]^{3/2}} \]

where the subscripts denote the derivative of \( Z \) with respect to that variable. For a Cartesian surface defined as

\[ f = z - Z(x, y, t) = 0 \]
the mean curvature is given by

$$2H = \frac{\left[1 + Z_y^2\right]Z_{xx} - 2Z_{,x}Z_{,y} + \left[1 + Z_x^2\right]Z_{yy}}{\left[1 + Z_x^2 + Z_y^2\right]^{3/2}}$$
APPENDIX B
THE PERTURBATION EQUATIONS AND THE MAPPINGS

In this appendix, we explain the perturbation equations and the mappings used in this dissertation. The reader is referred to the book by Johns and Narayanan [3] for further details. Higher order mappings are given in Appendix B.2.

B.1 The Expansion of a Domain Variable and its Derivatives along the Mapping

Let \( u \) denote the solution of a problem on a domain \( D \). Now the domain \( D \) might itself be inconvenient. It may not be specified and must be determined as a part of the solution. This becomes clear when we study a moving front problem such as precipitation or solidification where the shape of the interface is not known and it is a part of the solution.

It is however possible to obtain the solution \( u \) as well as to solve for the domain shape \( D \) by solving a new and easier problem defined on a regular and specified reference domain \( D_0 \). \( D_0 \) may be determined by the original problem or it may be chosen so as to simplify our work.

The key idea is to imagine a family of domains \( D_\varepsilon \) growing out of the reference domain \( D_0 \) and to imagine that \( u \) must be determined on each of these, one being the domain of interest, \( D \). Now imagine that the domain \( D \), being in the vicinity of the reference domain \( D_0 \), can be expressed in terms of the reference domain \( D_0 \) via a small parameter \( \varepsilon \). Therefore the solution \( u \) and the domain \( D \) are solved simultaneously in a series of companion problems. What needs to be done is to discover how to determine \( u \) in terms of the solutions to problems defined on \( D_0 \). Let the points on \( D_0 \) be denoted by the coordinate \( y_0 \) and those on \( D \) by the coordinate \( y \). The \( x \)-coordinate is assumed to remain unchanged.

Let \( u \) be a function of the spatial coordinate \( y \). Then \( u \) must be a function of \( \varepsilon \) directly because it lies on \( D \) and also because it is a function of \( y \). The point \( y \) of the domain \( D_\varepsilon \) is
then determined in terms of the point $y_0$ of the reference domain $D_0$ by the mapping

$$y = f(y_0, \varepsilon)$$

The function $f$ can be expanded in powers of $\varepsilon$ as

$$f(y, \varepsilon) = f(y_0, \varepsilon = 0) + \varepsilon \frac{\partial f(y_0, \varepsilon = 0)}{\partial \varepsilon} + \frac{1}{2} \varepsilon^2 \frac{\partial^2 f(y_0, \varepsilon = 0)}{\partial \varepsilon^2} + ...$$

where $f(y_0, \varepsilon = 0) = y_0$ and the derivatives of $f$ are evaluated holding $y_0$ fixed. Then in terms of the notation

$$y_1(y_0, \varepsilon) = \frac{\partial f(y_0, \varepsilon = 0)}{\partial \varepsilon}$$

$$y_2(y_0, \varepsilon) = \frac{\partial^2 f(y_0, \varepsilon = 0)}{\partial \varepsilon^2}$$

etc., the mapping can be written as

$$y = f(y_0, \varepsilon) = y_0 + \varepsilon y_1(y_0, \varepsilon = 0) + \frac{1}{2} \varepsilon^2 y_2(y_0, \varepsilon = 0) + ...$$

The boundary of the reference domain must be carried into the boundary of the present domain by the same mapping. At the boundary of the new domain, the function $y$ is replaced by $Y$ to point out the difference. Its expansion in powers of $\varepsilon$ can be written similarly as

$$Y = Y_0 + \varepsilon Y_1(Y_0, \varepsilon = 0) + \frac{1}{2} \varepsilon^2 Y_2(Y_0, \varepsilon = 0) + ...$$

Notice that it is the $Y_i$'s that need to be determined to specify the domain $D$ in terms of the domain $D_0$.

Finally, the variable $u(y, \varepsilon)$ can be expanded in powers of $\varepsilon$ along the mapping as

$$u(y, \varepsilon) = u(y = y_0, \varepsilon = 0) + \varepsilon \frac{du(y = y_0, \varepsilon = 0)}{d\varepsilon} + \frac{1}{2} \varepsilon^2 \frac{d^2 u(y = y_0, \varepsilon = 0)}{d\varepsilon^2} + ...$$
where \( \frac{du}{d\varepsilon} \) denotes the derivative of the function \( u \) depending on \( y \) and \( \varepsilon \) taken along the mapping. To obtain a formula for \( \frac{du(y = y_0, \varepsilon = 0)}{d\varepsilon} \), differentiate \( u \) along the mapping taking \( y \) to depend on \( \varepsilon \), holding \( y_0 \) fixed. Using the chain rule, this gives

\[
\frac{du(y, \varepsilon)}{d\varepsilon} = \frac{\partial u(y, \varepsilon)}{\partial \varepsilon} + \frac{\partial u(y, \varepsilon)}{\partial y} \frac{\partial f(y_0, \varepsilon)}{\partial \varepsilon}
\]

Evaluating the above equation at \( \varepsilon = 0 \), we get

\[
\frac{du(y = y_0, \varepsilon = 0)}{d\varepsilon} = \frac{\partial u(y_0, \varepsilon = 0)}{\partial \varepsilon} + \frac{\partial u(y_0, \varepsilon = 0)}{\partial y} y_1(y_0, \varepsilon)
\]

Then, introducing the definition of \( u_1 \) via

\[
u_1(y_0) = \frac{\partial u(y_0, \varepsilon = 0)}{\partial \varepsilon}
\]

and observing that

\[
\frac{\partial u(y_0, \varepsilon = 0)}{\partial y} = \frac{\partial u_0(y_0)}{\partial y_0}
\]

we get

\[
\frac{du(y = y_0, \varepsilon = 0)}{d\varepsilon} = u_1(y_0) + \frac{\partial u_0(y_0)}{\partial y_0} y_1(y_0, \varepsilon)
\]

All higher order derivatives of \( u \) can be determined the same way. If a domain variable needs to be specified at the boundary it is written similarly as

\[
\frac{du(y = Y_0, \varepsilon = 0)}{d\varepsilon} = u_1(Y_0) + \frac{\partial u_0(Y_0)}{\partial y_0} Y_1(Y_0, \varepsilon)
\]
When additional derivatives are obtained and substituted into the expansion of $u$, it becomes

$$u(y, \epsilon) = u_0 + \epsilon \left[ u_1 + \frac{\partial u_0}{\partial y_0} \right] + \frac{1}{2} \epsilon^2 \left[ u_2 + 2 y_1 \frac{\partial u_1}{\partial y_0} + y_1^2 \frac{\partial^2 u_0}{\partial y_0^2} + y_2 \frac{\partial u_0}{\partial y_0} \right] + ...$$

The reader might wonder that the mapping $y_1$ does not appear in the domain equations given in this dissertation. In fact, the mappings on the domain can not be determined and they are never required. This can be proved rigorously as done in the book by Johns and Narayanan [3], but in the interest of continuity, let us work out an example to show that one need not worry about the mappings on the domain. Once we have gone through this example, we can use this as a rule of thumb. Let $u$ satisfy

$$\frac{\partial u}{\partial y} = 0$$

in the inconvenient domain $D$. Using chain rule

$$\frac{\partial u}{\partial y} = \frac{\partial u}{\partial y_0} \frac{\partial y_0}{\partial y}$$

where, holding $\epsilon$ fixed, $\frac{\partial y_0}{\partial y}$ is given by

$$\frac{\partial y_0}{\partial y} = 1 - \epsilon \frac{\partial y_1}{\partial y} - \frac{1}{2} \epsilon^2 \frac{\partial y_2}{\partial y} - ...$$

Thus, up to the first order in $\epsilon$, the domain equation becomes

$$\frac{\partial u}{\partial y} = \frac{\partial u_0}{\partial y_0} + \epsilon \left[ \frac{\partial u_1}{\partial y_0} + y_1 \frac{\partial^2 u_0}{\partial y_0^2} \right] + ...$$

Therefore, the domain equation at the zeroth order in $\epsilon$ is

$$\frac{\partial u_0}{\partial y_0} = 0$$
whereas the domain equation at first order in $\varepsilon$, using $\frac{\partial^2 u_0}{\partial y^2_0} = 0$, becomes

$$\frac{\partial u}{\partial y_0} = 0$$

Notice that the mapping is lost from domain equations. If surface variables were considered the mapping would not be lost, as is evident from all the problems studied in this dissertation.

### B.2 The Higher Order Mappings

Up to the fourth order, the expansion of the domain variable $u$ along the mapping is

$$u = u_0 + \varepsilon \left[ u_1 + y_1 \frac{\partial u_0}{\partial y_0} + \frac{1}{2} \varepsilon^2 \left[ u_2 + 2y_1 \frac{\partial u_1}{\partial y_0} + y_1 \frac{\partial^2 u_0}{\partial y^2_0} + y_2 \frac{\partial u_0}{\partial y_0} \right] + \frac{1}{6} \varepsilon^3 \left[ u_3 + 3y_1 \frac{\partial u_2}{\partial y_0} + 3y_2 \frac{\partial u_1}{\partial y_0} + 3y_1^2 \frac{\partial^2 u_1}{\partial y^2_0} + 6y_1^2 \frac{\partial^2 u_0}{\partial y^2_0} + y_3 \frac{\partial u_0}{\partial y_0} \right] + \frac{1}{24} \varepsilon^4 \left[ u_4 + 10y_1y_2 \frac{\partial^3 u_1}{\partial y^3_0} + 6y_1^2 \frac{\partial^2 u_2}{\partial y^2_0} + 6y_1^2 \frac{\partial^2 u_1}{\partial y^2_0} + 3y_2 \frac{\partial^2 u_0}{\partial y^2_0} + 4y_1 \frac{\partial^3 u_0}{\partial y^3_0} + 4y_2 \frac{\partial^2 u_0}{\partial y_0} + 4y_1^3 \frac{\partial^3 u_1}{\partial y^3_0} + 4y_1y_3 \frac{\partial^2 u_0}{\partial y^2_0} \right] \right]$$

and the expansion of its derivative is given as

$$\frac{\partial u}{\partial y} = \frac{\partial u_0}{\partial y_0} + \varepsilon \left[ \frac{\partial u_1}{\partial y_0} + y_1 \frac{\partial^2 u_0}{\partial y^2_0} + \frac{1}{2} \varepsilon^2 \left[ \frac{\partial u_2}{\partial y_0} + 2y_1 \frac{\partial^2 u_1}{\partial y^2_0} + y_1 \frac{\partial^3 u_0}{\partial y^3_0} + y_2 \frac{\partial^2 u_0}{\partial y^2_0} \right] + \frac{1}{6} \varepsilon^3 \left[ \frac{\partial u_3}{\partial y_0} + 3y_1 \frac{\partial^2 u_2}{\partial y^2_0} + 3y_2 \frac{\partial^2 u_1}{\partial y^2_0} + 3y_1^2 \frac{\partial^3 u_1}{\partial y^3_0} + 3y_1y_2 \frac{\partial^3 u_0}{\partial y^3_0} + y_3 \frac{\partial^3 u_0}{\partial y^3_0} + y_4 \frac{\partial^2 u_0}{\partial y^2_0} \right] + \frac{1}{24} \varepsilon^4 \left[ \frac{\partial u_4}{\partial y_0} + 10y_1y_2 \frac{\partial^3 u_1}{\partial y^3_0} + 6y_1^2 \frac{\partial^2 u_2}{\partial y^2_0} + 6y_1^2 \frac{\partial^2 u_1}{\partial y^2_0} + 3y_2 \frac{\partial^2 u_0}{\partial y^2_0} + 4y_1 \frac{\partial^3 u_0}{\partial y^3_0} + 4y_2 \frac{\partial^2 u_0}{\partial y_0} + 4y_1^3 \frac{\partial^3 u_1}{\partial y^3_0} + 4y_1y_3 \frac{\partial^2 u_0}{\partial y^2_0} \right] \right]$$
APPENDIX C
EIGENFUNCTIONS OF AN EQUILATERAL TRIANGLE AND A REGULAR HEXAGON
SATISFYING NEUMANN BOUNDARY CONDITIONS

In this appendix, we give the function \( f(x, y) \) which is an eigenfunction of \( \nabla^2 \) on an arbitrary cross section \( S \), subject to Neumann sidewall conditions. It satisfies

\[
\nabla^2 f(x, y) = -k^2 f(x, y) \text{ on } S; \quad \bar{p}.\nabla f = 0 \text{ on } \partial S
\]

where \( \partial S \) denotes the boundary of \( S \) and \( \bar{p} \) denotes the outward normal to \( \partial S \). Appendix C.1 gives the eigenfunctions and eigenvalues corresponding to an equilateral triangle. Appendix C.2 gives the eigenfunctions and eigenvalues of a regular hexagon.

C.1 Eigenfunctions of an Equilateral Triangle

Consider an equilateral triangle of side \( h \), whose vertices are given by \((0, 0)\), \((h, 0)\) and \((h/2, \sqrt{3}h/2)\). The eigenfunction \( f(x, y) \) that satisfies \( \nabla^2 f(x, y) = -k^2 f(x, y) \) on \( S \);

\[
\bar{p}.\nabla f = 0 \text{ on } \partial S
\]

is given by [34] as

\[
f^{m,n}(x, y) = f^{m,n}_x(x, y) + f^{m,n}_a(x, y)
\]

where

\[
f^{m,n}_x(x, y) = \cos\left(\frac{\pi l}{3r}[3r - y]\right) \cos\left(\frac{\sqrt{3}\pi}{9r}[m-n][x-h/2]\right)
\]

\[
+ \cos\left(\frac{\pi m}{3r}[3r - y]\right) \cos\left(\frac{\sqrt{3}\pi}{9r}[n-l][x-h/2]\right)
\]

\[
+ \cos\left(\frac{\pi n}{3r}[3r - y]\right) \cos\left(\frac{\sqrt{3}\pi}{9r}[l-m][x-h/2]\right)
\]

and
The eigenfunction is given by

\[
f_{\mu,n}(x,y) = \cos\left(\frac{\pi l}{3r}[3r - y]\right)\sin\left(\frac{\sqrt{3}\pi[m-n]}{9r}[x-h/2]\right) + \cos\left(\frac{\pi m}{3r}[3r - y]\right)\sin\left(\frac{\sqrt{3}\pi[n-l]}{9r}[x-h/2]\right) + \cos\left(\frac{\pi n}{3r}[3r - y]\right)\sin\left(\frac{\sqrt{3}\pi[l-m]}{9r}[x-h/2]\right)
\]

where

\[l = -[m+n] \quad \text{and} \quad r = \frac{h}{2\sqrt{3}}\]

The corresponding eigenvalue is given by

\[
k^2 = \frac{4}{27}\left(\frac{\pi}{r}\right)^2 \left[m^2 + mn + n^2\right]
\]

### C.2 Eigenfunctions of a Regular Hexagon

Consider a regular hexagon of side \(L\), and centered at the origin \((0,0)\). The eigenfunction

\[f(x,y)\] that satisfies \(\nabla^2 f(x,y) = -k^2 f(x,y)\) on \(S\); \(\vec{p}.\nabla f = 0\) on \(\partial S\) is given by [7] as

\[
f(x,y) = 2\cos\left(\frac{2\pi x}{L\sqrt{3}}\right)\cos\left(\frac{2\pi y}{3L}\right) + \cos\left(\frac{4\pi y}{3L}\right)
\]

The corresponding eigenvalue is given by

\[
k^2 = \left(\frac{4\pi}{3L}\right)^2
\]
REFERENCES


BIOGRAPHICAL SKETCH

Saurabh Agarwal was born in 1980 in New Delhi, India. In 2002, he received a B.S. in chemical engineering from the Indian Institute of Technology, Kanpur. He joined the University of Florida as a graduate student in 2002. During his graduate studies, he worked under the supervision of Prof. Ranga Narayanan and Prof. Lewis E. Johns. In 2007, he graduated from the University of Florida with a Ph.D in chemical engineering.