

**Turing Pattern Formation in
the Chlorine Dioxide–Iodine–Malonic Acid
Reaction-Diffusion System**

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Abstract

The formation of localized structures in the chlorine dioxide-iodine-malonic acid (CDIMA) reaction-diffusion system is investigated numerically using a realistic model of this system. We analyze the one-dimensional patterns formed along the gradients imposed by boundary feeds, and study their linear stability to symmetry-breaking perturbations (the Turing instability) in the plane transverse to these gradients. We establish that an often-invoked simple local linear analysis which neglects longitudinal diffusion is inappropriate for predicting the linear stability of these patterns. Using a fully nonuniform analysis, we investigate the structure of the patterns formed along the gradients and their stability to transverse Turing pattern formation as a function of the values of two control parameters: the malonic acid feed concentration and the size of the reactor in the dimension along the gradients. The results from this investigation are compared with existing experimental results. We also verify that the two-variable reduction of the chemical model employed in the linear stability analysis is justified. Finally, we present numerical solution of the CDIMA system in two dimensions which is in qualitative agreement with experiments. This result also confirms our linear stability analysis, while demonstrating the feasibility of numerical exploration of realistic chemical models.

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Chapter 1 Introduction

Recent experimental developments have made possible the study of asymptotic spatiotemporal behavior in chemical systems in a controlled and reproducible manner, allowing predictions from theoretical and numerical studies of these systems to be compared quantitatively with experiments, in the same way that fluid systems have been studied. Indeed, the understanding of spatial pattern formation in nonequilibrium systems has greatly benefited from careful and controlled experiments on fluid systems [1]. Unlike fluid systems in which at high nonlinearity the term $\vec{u} \cdot \vec{\nabla} \vec{u}$ results in the break down of the velocity field to a turbulent state characterized by a wide range of spatial scales, spatial patterns in chemical systems can be studied at high nonlinearity [2]. Thus, chemical systems provide an opportunity to study rich and new phenomena that complement our knowledge from pattern formation in fluid systems.

The symmetry-breaking instability of a system from a homogeneous state to a patterned state was predicted in 1952 by Alan Turing [3], and has been observed for the first time only recently, nearly 40 years later, in the chlorite-iodide-malonic acid (CIMA) reaction-diffusion system [4, 25, 6]. The Turing instability, characterized by an intrinsic wavelength resulting solely from reaction and diffusion processes, has particular relevance to pattern formation in biological systems. Indeed, this instability mechanism and its possible application to morphogenesis is considered to be one of Turing's many and varied seminal scientific contributions, along with his work in founding modern digital computers [7]. The recent experiments have sparked a renewed interest in Turing patterns, with the possibility of comparing quantitative predictions from theoretical and numerical studies of chemical reaction-diffusion systems with experimental observation. Chemical systems are attractive laboratories for studying biological pattern formation since direct studies of biological systems are not always possible due to the difficulty of performing *in vivo* experiments.

Unlike hydrodynamic systems in which the governing equations and parameter values are well understood, the modeling of complex chemical systems is often not well known [1]. The success of the Belousov-Zhabotinsky chemical reaction as a physical system for studying nonlinear dynamics is derived in part from the existence of an accurate model in a few variables [8]. A realistic model of the CIMA reaction, based on the simpler chlorine dioxide-iodine-malonic acid (CDIMA) reaction, has been proposed [9, 10]. Hence, the CDIMA reaction-diffusion system has also become an archetype for the study of nonequilibrium pattern formation [11], in principle allowing numerical and theoretical investigations to be compared directly with experiments.

In practice, however, this has not been fully realized for two reasons. First, numerical investigations of reaction-diffusion equations using realistic chemical parameters is a demanding computational task. In addition, the algebraic complexity of the realistic nonlinear reaction terms renders these models unsuitable for analysis by standard analytical tools. As a result, the theoretical work on reaction-diffusion systems has been mostly based on abstract models. Second, despite the existence of the realistic CDIMA chemical model which has similar pattern-forming and dynamical properties to the related CIMA system, experimental work has continued to be based on the CIMA reaction, making direct comparisons of numerical and analytical work with experiments difficult. Consequently, unlike in fluid systems, experiment and theory in chemical systems have not been closely coupled, and there has been little motivation for experimenters to focus on making quantitative measurements.

The focus of this work has been to use the chemically realistic model of the CDIMA system to investigate the Turing instability. We show that numerical computation using realistic parameters and boundary conditions is feasible in one and two dimensions, and results are in good qualitative agreement with certain aspects of the existing experimental work on the CIMA system. The hope is that our work will encourage further explorations using this realistic chemical model, and we comment on some possibilities.

The outline is as follows: To introduce the subject, we briefly review the Turing instability mechanism in Chapter 2. Relevant experimental work on Turing pattern

formation in the CIMA system is reviewed in Chapter 3. The CDIMA reaction diffusion model is described in Chapter 4. In Chapter 5, we present our analyses using this model. In Section 5.1, we investigate the formation and linear stability of one-dimensional steady state structures along gradients of imposed boundary feeds. In Section 5.2, these are further explored as a function of two control parameters. A verification of the validity of the reduced CDIMA model is presented in Section 5.3. Results from our two-dimensional simulation of the CDIMA reaction-diffusion system are presented in Section 5.4. Details of the numerical methods are given in Appendix B. Finally, we summarize what has been done as well as future prospects in Chapter 6.

Chapter 2 The Turing Instability Mechanism

In a 1952 article entitled “The Chemical Basis of Morphogenesis,” Turing [3] showed that the interplay between chemical reaction and diffusion in a system maintained far from equilibrium could lead to a pattern-forming instability. He showed that under certain conditions if two substances diffuse at different rates and react with each other, the homogeneous steady state of the system, while stable to homogeneous perturbations, would be unstable to inhomogeneous ones. The concept of a diffusion-driven instability was a novel idea, since intuitively we associate diffusion with a smoothing of any local accumulation, not with creation of such maxima [12]. These stationary structures which originate solely from reaction and diffusion processes (in particular, any convection or hydrodynamic motion is excluded) are characterized by an intrinsic wavelength that does not depend on the geometrical parameters of the system, but only on input concentrations of reactants, reaction constants and diffusion constants. This feature distinguishes Turing patterns from other nonequilibrium structures, such as Rayleigh-Bénard convection rolls where the wavelength depends on the cell height.

As indicated by the title of Turing’s original paper, because of its supposed role in morphogenesis, this instability mechanism has been the subject of a large amount of theoretical and numerical study over the past 40 years. However, no experimental observation of a Turing instability in any system had been made until 1990. The main problems associated with these experimental observations were as follows: To maintain the system far from equilibrium, fresh reactants had to be injected continuously in the reactor, thereby interfering with formation of stationary patterns. Furthermore, the condition that the different species diffuse at different rates is rarely fulfilled in aqueous solutions. The design and development of open gel reactors made possible the first experimental observation of sustained steady state patterns in the chlorite-iodide-malonic acid or CIMA reaction. The choice of this particular reaction-diffusion system for use in these experiments was fortuitous, because the starch indicator used

to display the concentration patterns in the iodide species actually plays a crucial role in the pattern formation itself by causing the required difference in the effective diffusion coefficients of the two dynamical chemical species (chlorite and iodide). The role of the starch in this mechanism was not known until after the first experimental observations.

The purpose of this chapter is to introduce Turing patterns and the conditions which lead to their formation. First, a qualitative description is presented in Sec. 2.1. A brief summary of some possible applications of the Turing mechanism to biological systems is given in Sec. 2.2. The chapter concludes with the mathematical description of the Turing instability conditions in Sec. 2.3.

2.1 The Turing Mechanism in Words

The principle of *local activation and long-range inhibition* can be used to explain the mechanism of the Turing instability. This is described by Meinhardt [13] as follows: Suppose we have a substance u , called the activator, which stimulates its own production (autocatalysis) and the production of its antagonist, the inhibitor v . In an initially homogeneous system, any small elevation of the activator concentration will become amplified through activator autocatalysis. If the inhibitor, which is also produced with increased activator production, diffuses faster than the activator, then it cannot stop the local increased activator production. However, fast inhibitor diffusion into the surrounding area suppresses activator production outside the activation center. The locally increased activator concentration will continue to increase, and the maximum becomes progressively narrower (due to lateral inhibition) until the rate of diffusion of activator out of the narrow peak equals its rate of production. Thus, a stable activator-inhibitor profile is obtained, although both continue to be made, diffuse and break down.

An example put forth by Murray [14], though unrealistic, is amusing and illustrates this mechanism. Consider a (uniform) field of dry grass, in which a local patch of wild fire is started. In the absence of a mechanism inhibiting the spread of the fire, a

homogeneously charred field will result. However, consider the field being populated by grasshoppers. Those in the vicinity of the fire, travel faster than the fire through the field to escape. In the process, they sweat profusely from the heat, and this moisture prevents the spread of the fire into those regions. The final finite area of the charred region will depend on the diffusion constants of the reactants, the fire and the grasshopper, and various reaction parameters. Therefore, one can imagine how an initial random scattering of local patches of fire can lead to an inhomogeneous distribution of charred and uncharred regions.

2.2 Biological Applications

Morphogenesis is the development of pattern and form from the initially homogeneous ball of cells that come to be after fertilization. The mechanism by which these cells, all with identical DNA coding, differentiate into specialized cells, such as cartilage and epidermal cells, for example, is not well understood. The concept of *positional information* asserts that cells are preprogrammed to react to a certain chemical (or morphogen) by expressing part of their gene sequence and thereby differentiating accordingly, or moving around in the embryo (see Ref. [14] and references therein). The first step of this process is the formation of the morphogen concentration spatial pattern. Then, each cell can read its position in the coordinates of chemical concentration, and differentiate, undergo appropriate cell change, or migrate accordingly. Reaction-diffusion models have been proposed as the possible mechanism for generating the spatial *prepattern* of morphogen concentration, this idea being put forth by Turing in 1952. The difficulty of clearly identifying the chemical species that act as prepattern morphogens, coupled with unavailability of *in vivo* experiments, has proven to be a drawback in the acceptance of a chemical theory of morphogenesis [14].

The most striking application of the Turing mechanism is to the formation of mammalian and fish coat patterns, as well as insect wing patterns. Detailed discussions are given in the text by Murray [14]. Recently, an interesting set of experiments

on the marine angelfish *Pomacanthus* [15] strongly suggests a reaction-diffusion mechanism to be viable in the stripe formation. This example is particularly interesting, since unlike mammal skin patterns which enlarge proportionally during their body growth, the stripes of the angelfish possess a constant wavelength that is maintained as the fish matures. In addition to the development of patterns observed on macroscopic scales, the Turing mechanism has been shown to produce structures on the mesoscopic scale of the cell cytoplasm [16], as well as the cell membrane [17].

2.3 Turing Instability Conditions

In his original paper [3], Turing suggested that the reaction and diffusion of chemicals could account for the instability of an originally homogeneous steady state to a stable steady pattern when triggered by random disturbances. Consider the general governing equations for the reaction-diffusion mechanism of two chemical species:

$$\sigma \frac{\partial u}{\partial t} = f(u, v; \vec{\mu}) + \nabla^2 u \quad (2.1)$$

$$\frac{\partial v}{\partial t} = g(u, v; \vec{\mu}) + c \nabla^2 v, \quad (2.2)$$

where f and g represent the (nonlinear) reaction kinetics, u and v are chemical concentrations, $\vec{\mu}$ is a set of reaction parameters that may include concentrations of other chemical species, $c = D_v/D_u$ is the ratio of diffusion constants, and $\sigma \geq 1$ is a constant separating the characteristic time scales for changes in the concentrations of the u and v species. Turing's idea was as follows [14]: if in the absence of diffusion ($u(\vec{r}, t), v(\vec{r}, t)$) tend to a linearly stable uniform steady state, then under certain conditions, the addition of diffusion leads to the development of spatially inhomogeneous patterns. Although these conditions were originally considered for a spatially uniform system, where the parameters $\vec{\mu}$ are constant, the actual experimental realization of the Turing instability occurs in the presence of externally imposed feed gradients, where $\vec{\mu} = \vec{\mu}(z)$. We will investigate the Turing instability conditions for uniform and nonuniform parameters, $\vec{\mu}$.

2.3.1 Uniform background

The uniform background case is realized experimentally in batch reactors where there are no externally imposed gradients from continuous feed of chemical reactants, and Turing patterns are necessarily transient. The parameters $\vec{\mu}$ are constants independent of position, The homogeneous steady state $\vec{c}_s = (u_s^o, v_s^o)$ is obtained as the solution to:

$$f(u, v; \vec{\mu}) = g(u, v; \vec{\mu}) = 0. \quad (2.3)$$

The linear stability of this state is obtained by substituting the following into the governing reaction-diffusion equations:

$$\vec{c}(\vec{r}, t) = \vec{c}_s + \vec{\delta c}(\vec{r}, t), \quad \vec{\delta c}(\vec{r}, t) = \sum_k (\delta u_k^o, \delta v_k^o) e^{i\vec{k} \cdot \vec{r}} e^{\lambda_k t}, \quad (2.4)$$

where $\vec{c} = (u, v)$ is a vector of concentrations, k is the spatial wave number of the perturbation, λ_k is the growth rate of the k^{th} mode, and $(\delta u_k^o, \delta v_k^o)$ is the corresponding constant eigenvector. The resulting linear eigenvalue problem:

$$\begin{pmatrix} (a_{11} - k^2)/\sigma & a_{12}/\sigma \\ a_{21} & a_{22} - ck^2 \end{pmatrix} \begin{pmatrix} \delta u_k^o \\ \delta v_k^o \end{pmatrix} = \lambda_k \begin{pmatrix} \delta u_k^o \\ \delta v_k^o \end{pmatrix} \quad (2.5)$$

has a nontrivial solution for:

$$\sigma \lambda_k^2 + [(\sigma c + 1)k^2 - (a_{11} + \sigma a_{22})] \lambda_k + [(a_{22} - ck^2)(a_{11} - k^2) - a_{12}a_{21}] = 0, \quad (2.6)$$

with,

$$\lambda_k^{(\pm)} = -\frac{1}{2\sigma} [(\sigma c + 1)k^2 - (a_{11} + \sigma a_{22})] \pm \frac{1}{2\sigma} \sqrt{[(\sigma c + 1)k^2 - (a_{11} + \sigma a_{22})]^2 - 4h(k^2)}, \quad (2.7)$$

where,

$$h(k^2) = \sigma [ck^4 - (a_{22} + ca_{11})k^2 + (a_{11}a_{22} - a_{12}a_{21})]. \quad (2.8)$$

The quantities $a_{11} = f_u$, $a_{12} = f_v$, $a_{21} = g_u$, and $a_{22} = g_v$ are the elements of the Jacobian of the reaction terms with respect to the concentrations, evaluated at the uniform steady state. λ_k has a rich behavior depending on the values of σ , c , and a_{ij} parameters. The conditions for the Turing instability are that this uniform steady state be linearly: (i) stable to homogeneous perturbation, and (ii) unstable to inhomogeneous perturbations. Hence, this is a *symmetry-breaking* mechanism, since it breaks the homogenous spatial symmetry of the uniform state. For the general reaction-diffusion system given in Eqs. (2.1) and (2.2), these conditions are derived in Appendix A. Below, we refer to the relevant results for the purpose of discussion. Stability of the uniform steady state to homogeneous $k = 0$ perturbations requires the following inequalities to be satisfied:

$$a_{11} + \sigma a_{22} < 0, \quad (2.9)$$

$$a_{11}a_{22} - a_{12}a_{21} > 0. \quad (2.10)$$

In order for the uniform steady state to be simultaneously unstable to inhomogeneous $k \neq 0$ perturbations, we must have:

$$a_{22} + ca_{11} > 0. \quad (2.11)$$

$$(a_{22} + ca_{11})^2 - 4c(a_{11}a_{22} - a_{12}a_{21}) \geq 0. \quad (2.12)$$

Comparing Eqs. (2.9) and (2.11) we conclude that a_{11} and a_{22} must have opposite sign. In the standard terminology, the activator species has a positive sign and the inhibitor has a negative sign in the Jacobian. Thus, taking $a_{11} > 0$ and $a_{22} < 0$ identifies u as the activator and v as the inhibitor. If $\sigma = 1$, then Eqs. (2.9) and (2.11) are simultaneously satisfied only for $c > 1$. We will come to the physical implication of this result in the context of the role of the starch indicator in the pattern formation process later.

Equations (2.9)–(2.12) constitute the Turing conditions. The onset of this in-

stability occurs when the critical parameters satisfy Eq. (2.12) as an equality. The critical wave number k_c is given by:

$$k_c^2 = \frac{(a_{22} + ca_{11})}{2c}. \quad (2.13)$$

Beyond criticality, a band of linearly unstable modes lies in the range given by Eq. (A.9), while the fastest growing mode $k_{\max}$ is given by:

$$k_{\max}^2 = -\frac{(a_{11} - \sigma a_{22})}{\sigma c - 1} + \frac{(\sigma c + 1)}{\sigma c - 1} \sqrt{\frac{-a_{12}a_{21}}{c}}, \quad (2.14)$$

and is obtained by maximizing $\lambda_k^{(+)}$.

It will be useful for future discussion of the role of starch in the instability (through the parameter σ), as well as comparison of the local stability analysis with the full stability analysis of the nonuniform steady state, to consider the Hopf bifurcation of the uniform system. This is the case where, at the critical value of the control parameter, the imaginary part of the critical eigenvalue of the linearized operator is nonzero, leading to an oscillatory instability [18]. For reaction parameters such that:

$$(a_{11} - \sigma a_{22})^2 + 4\sigma a_{12}a_{21} < 0 \quad (2.15)$$

there will be a complex conjugate pair of eigenvalues for wavenumbers in the range $0 < k^2 < k_+^{(H)2}$, where $k_+^{(H)2}$ is given in Eq. (A.12). With the above inequality satisfied, a Hopf bifurcation of the uniform system occurs when $(a_{11} + \sigma a_{22}) > 0$. Beyond the Hopf bifurcation point, there will be an unstable complex conjugate pair of eigenvalues for wavenumbers in the range given by Eq. (A.17).

2.3.2 Nonuniform background

In this case, the parameters $\vec{\mu}$, which depend on the concentrations of background chemicals fed through the boundaries, are not constant but rather are functions of the variable z along the direction perpendicular to the feed boundaries. The steady

state solution will now be a function of z , satisfying:

$$f(u_s(z), v_s(z); \vec{\mu}(z)) + \frac{d^2 u_s(z)}{dz^2} = 0 \quad (2.16)$$

$$g(u_s(z), v_s(z); \vec{\mu}(z)) + c \frac{d^2 v_s(z)}{dz^2} = 0, \quad (2.17)$$

with Dirichlet boundary conditions at $z = 0$ and $z = L_z$. The stability of $(u_s(z), v_s(z))$ is given by linearizing about this state:

$$\vec{c}(\vec{r}, t) = \vec{c}_s(z) + \delta \vec{c}(\vec{r}, t), \quad \delta \vec{c}(\vec{r}, t) = \sum_{k_\perp} (\delta u_{k_\perp}(z), \delta v_{k_\perp}(z)) e^{i \vec{k}_\perp \cdot \vec{r}_\perp} e^{\lambda_{k_\perp} t}, \quad (2.18)$$

where $\vec{k}_\perp$ is the wavevector perpendicular to the direction of the gradients. For simplicity of notation, we will drop the subscript “ $\perp$,” taking k to be the transverse wavenumber. The resulting eigenvalue problem is:

$$\begin{pmatrix} (a_{11}(z) + \frac{\partial^2}{\partial z^2} - k^2) / \sigma & a_{12}(z) / \sigma \\ a_{21}(z) & a_{22}(z) + c \frac{\partial^2}{\partial z^2} - ck^2 \end{pmatrix} \begin{pmatrix} \delta u_k(z) \\ \delta v_k(z) \end{pmatrix} = \lambda_k \begin{pmatrix} \delta u_k(z) \\ \delta v_k(z) \end{pmatrix}, \quad (2.19)$$

with $(\delta u_k(z), \delta v_k(z))$ satisfying the same Dirichlet boundary conditions as the steady state. It must be solved numerically, by discretizing the z spatial direction into N_z mesh points and solving the resulting $2N_z \times 2N_z$ matrix eigenvalue problem for each k .

2.3.3 Locally uniform background

Pattern formation in the presence of ramps in control parameters is generally not as well understood as under uniform conditions. The naive assumption is that a structure will form in the region of space where the local value of the control parameter allows it to be stable in the corresponding uniform problem [19]. This “locally uniform” approach amounts to treating each location along the gradients in the z -direction to be an independent and uniform quasi two-dimensional system in the $x-y$ plane. The corresponding locally uniform steady state $(u_s^{local}, v_s^{local})$ which depends

parametrically on z is given by the solution to:

$$f(u, v; \vec{\mu}(z)) = g(u, v; \vec{\mu}(z)) = 0. \quad (2.20)$$

The Turing instability conditions can then be examined at each point in z to determine whether or not they predict the formation of transverse Turing patterns in any interval along z .

Since the resulting eigenvalue problem for the stability of the locally homogenous steady state to a symmetry-breaking instability requires a 2×2 analysis at each z , it is computationally simple. Thus, it has been commonly used to determine the linear stability of the nonuniform stationary states that form for $\vec{\mu} = \vec{\mu}(z)$ along gradients of boundary feeds (Eq. (2.16-2.17)). The validity of this local analysis is assessed in Sec. 5.1.2, by comparing the result with that from the fully nonuniform analysis (Eq. (2.19)) of the steady state along the gradients.

Chapter 3 Review of Experimental Work

The first experimental realization of the steady-state Turing patterns predicted in 1952 was made in 1990 by Castets *et al.* [4], and was subsequently confirmed by others [25, 6]. These sustained patterns have been obtained in only one controlled experimental system to date, the chlorite-iodide-malonic acid (CIMA) chemical reaction-diffusion system.^(a) The study of asymptotic spatiotemporal behavior in chemical systems in a controlled and reproducible fashion was made possible by the relatively recent development of open spatial reactors that have allowed experimentalists to maintain a reaction far from equilibrium through a continuous supply of reactants. Prior to the development of *open* reactors, experiments on pattern formation in chemical reaction-diffusion systems had been limited to *closed* or batch reactors, where only transient phenomena, such as target and spiral patterns in excitable media (including the well-known Belusov-Zhabotinsky reaction), had been extensively studied [21]. In this chapter, we describe the principles of operation of these reactors and the experimental setup used in studies of Turing pattern formation. We review results indicative of the present experimental state of the field, with emphasis on those aspects which are investigated quantitatively in this work.

A detailed description of the chemical model is presented later in Chapter 4, and is not necessary for following the proceeding discussion of experimental results. The key chemical components of the CIMA system are malonic acid ($\text{CH}_2(\text{COOH})_2$, or MA), iodide (I^-) and chlorite (ClO_2^-). Iodide and chlorite are the dynamical species that take part in the pattern formation.

^(a)Experimental evidence for Turing patterns have also been obtained in catalytic CO oxidation on Pt [20]. However, the more extensive body of experimental work has been on the CIMA reaction-diffusion system.

3.1 Open Spatial Reactors

Open spatial reactors were developed by the Bordeaux [4] and Texas [6] groups that pioneered the discovery of Turing patterns. The reactor itself is a gel matrix, which is chemically inert and transparent, and is used primarily to avoid any convective transport. Thus, the only processes at work are the reaction and diffusion of the chemical species. The gels used in these experiments are water-based, acting essentially as water in a loose polymer grid, such that the diffusion of small molecules is not much different from that in pure water. The gel is preloaded with a soluble starch that acts as an indicator by changing color from yellow to purple with changes in triiodide (I_3^-) concentration, which is formed in the CIMA reaction. The large starch molecules are virtually immobilized in the gel matrix and for this reason actually play a role in the pattern formation itself. This will be discussed further in Sec. 4.3.

The gel core of the reactor is in contact with two continuously stirred reservoirs of chemicals. Components of the reaction are distributed in the two reservoirs in such a way that neither is separately reactive. Iodide, chlorite and malonic acid are thus fed into the gel from the reservoirs. The concentrations of these reactants are kept constant and uniform at the boundaries by mixing and continuously flowing fresh reagents. The entire system is maintained at a constant temperature by a water jacket.

The time required for the patterns inside the gel to settle to an asymptotic state varies between several hours to several tens of hours depending on the value of the control parameters (for example, temperature or reservoir chemical concentration). Once the patterns are obtained, they can be sustained indefinitely and show no significant difference after 20–30 h, except for faded color contrast due to slow breakdown of the starch indicator. The patterns are monitored in transmitted light (580 nm, the wavelength of greatest absorption by the starch-triiodide complex [22]) using a CCD camera. The resulting digitized black and white images are then analyzed.

3.2 Typical Experimental Geometries

Two different reactor geometries, allowing experimental observations of different types of patterns, are described below. A schematic diagram of the experimental setup is shown in Fig. 3.1.

3.2.1 Thin-strip reactor

The thin strip reactor is comprised of a thin rectangular gel strip, such that $L \gg w > h$, as in Fig. 3.1(b). Typically, $h < 1$ mm, $L \sim 25$ mm, and $w \sim 3$ mm. Observations are made in the direction perpendicular to the $x - z$ plane (along Oy), which allows viewing of the patterns that develop along the boundary feed gradients (in the z -direction), as well as patterns that form parallel to the boundaries (in the x -direction), breaking the boundary feed symmetry. The symmetry-breaking patterns form in a thickness Δ along z . If the gel is thin enough ($h \sim \lambda$ of the Turing patterns), these patterns are one- or two-dimensional, depending on whether Δ is of the order of one or more wavelengths λ of the structure. The patterns are three-dimensional in nature when h and Δ are both greater than a few wavelengths.

3.2.2 Disc reactor

The disc reactor is made of a disc of gel with thickness w and diameter $L = h$, which is fed from the two circular faces, such as that shown in Fig. 3.1(c). Typically, $L \sim 25$ mm and $w < 1$ mm. Observations are made perpendicular to the feed surfaces (along Oz), thus allowing viewing of symmetry-breaking patterns that form under (locally) uniform parameter values and extend over a large area (in the $x - y$ plane).

3.3 Experimental Results

The existence of an intrinsic wavelength is an important feature of Turing patterns that distinguishes them from other pattern-forming systems such as fluids. In experiments performed on the CIMA system, the wavelength of symmetry-breaking patterns

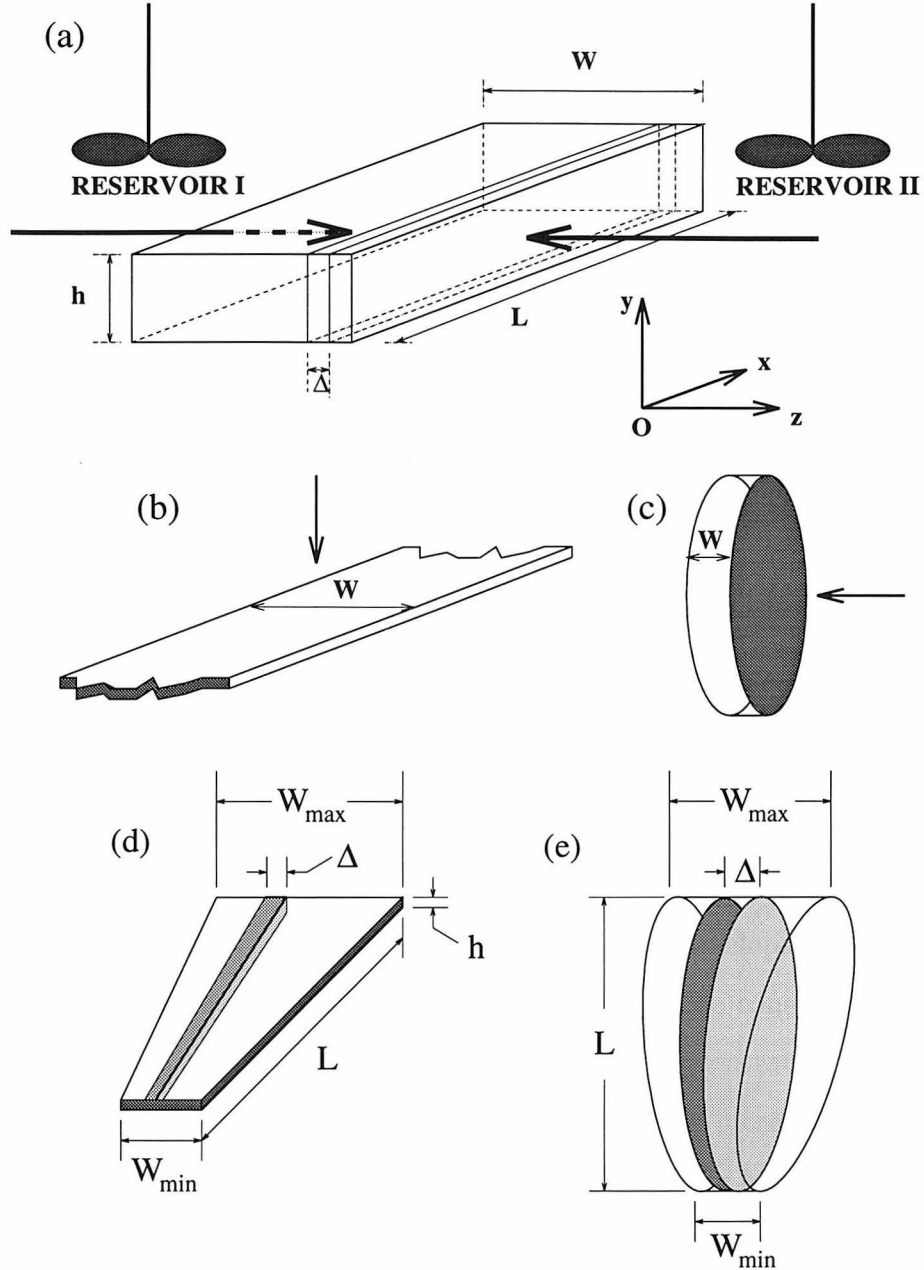


Figure 3.1: Sketch of open reactor geometries, based on illustrations in Refs. [11, 23]: (a) A block of gel, with dimensions $L \gg w > h$ is in contact with two reservoirs I and II. The reservoirs are continuously stirred and fed with fresh supplies of reactants, such that each is separately nonreactive. A gradient in the reservoir species forms perpendicular to the feed boundaries in the z -direction. The symmetry-breaking patterns form transverse to this gradient. The thickness Δ of the finite region along z where they form is equal to at least one wavelength λ of the Turing patterns; (b) Thin-strip and (c) Disc reactors, with arrows indicating the directions of observation; (d) Variable-width thin-strip and (e) Bevelled disc reactors.

is typically of order 0.2 mm. Experiments have verified that this wavelength depends only on the kinetic and diffusion constants and not on any geometric dimensions of the system. In one set of experiments [4], with all other control parameters fixed, the malonic acid feed concentrations for which the pattern was observed ranged from 8×10^{-3} to 13×10^{-3} mole/l. Over this range, the wavelength changed by about 20 %.

3.3.1 Stationary patterns

3.3.1.1 Non-symmetry breaking and symmetry-breaking patterns

In strip reactors: Turing patterns were first observed in the CIMA system in a thick strip reactor ($L = 20$ mm, $h = 1$ mm, and $w = 3$ mm) in the Oy direction [4]. Depending on the control parameter (for example, temperature or reservoir chemical concentrations) the patterns appear as clear and dark bands parallel to the boundary feed surfaces or rows of clear spots in a dark background transverse to the boundary feeds. In Fig. 3.2, reproduced from [19], we show experimental results demonstrating the transition from non-symmetry breaking to symmetry-breaking patterns. The control parameter was taken to be the concentration of one of the reservoir species, $[\text{ClO}_2^-]_{\text{II}}$. At low $[\text{ClO}_2^-]_{\text{II}}$, a single sharp color change develops parallel to the feed surfaces, separating the light colored region of lower iodide concentration along the right reservoir from the dark colored region of higher concentration. As $[\text{ClO}_2^-]_{\text{II}}$ is increased, the number of alternating light and dark bands increases. At even higher $[\text{ClO}_2^-]_{\text{II}}$, a few light bands break up into rows of spots. The number of rows of spots increases with increasing control parameter. At still higher values of the control parameter, the spot pattern disappears, and the stripes are recovered.

A similar experimental investigation has been undertaken by Boissonade *et al.* [24]. They experimentally obtain the phase diagram in the iodide-malonic acid plane, which we have reproduced in Fig. 3.3, showing the different types of patterns that can form as a function of these boundary concentrations. In Fig. 3.4, we have reproduced from Ref. [24] experimental pictures of these patterns, showing *stable* and *unstable* multifront patterns, with the instability occurring in a *single row*, as well as in *multiple*

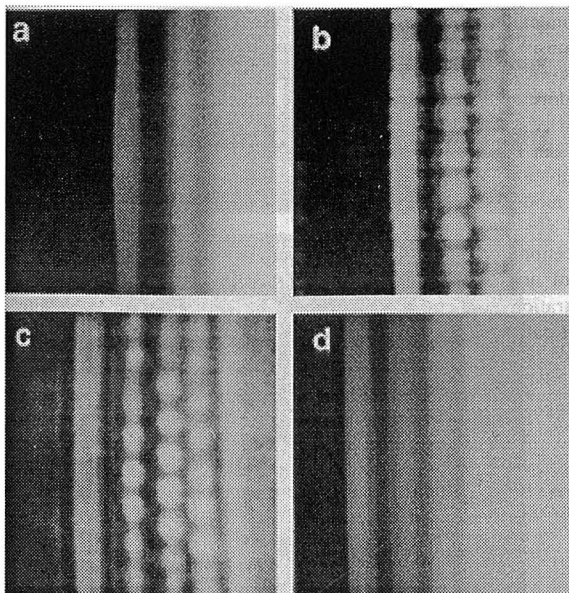


Figure 3.2: Transition from non-symmetry breaking to symmetry-breaking patterns in a thin-strip reactor (reproduced from Perraud *et al.* [19]): The sequence from (a) to (d) is obtained by increasing $[\text{ClO}_2^-]_{II}$ at the right boundary. In (a), the two-band pattern does not break the boundary feed symmetry, while in (b) and (c), symmetry-breaking spots perpendicular to feed gradients are observed in multiple layers as the control parameter is increased. In (d), the spots disappear, and a three-band pattern is recovered.

rows as reported above. In Sec. 5.2, we will investigate quantitatively this sequence of transitions from non-symmetry breaking stripes to symmetry-breaking spots and back to stripes as a function of control parameter in a thin strip reactor geometry.

The pattern of stripes parallel to the feed boundaries are related to Turing patterns. However, this identification is complicated by the presence of the concentration gradients imposed by the reservoir species in the Oz direction [25]. The rows of spots that form transverse to the imposed gradient (Oy viewing), however, break the symmetry of the imposed feed and are genuinely Turing structures. The simple assumption is that a symmetry-breaking pattern develops in the region along z where the local value of the control parameter allows it to be stable in the corresponding uniform problem. We will investigate the validity of such a local approach for determining the stability of the non-symmetry breaking striped patterns to a transverse symmetry-breaking instability in Sec. 5.1.

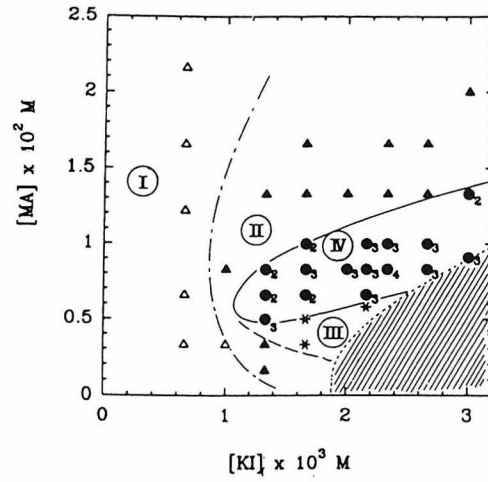


Figure 3.3: Experimental phase diagram of sustained patterns for a section in the iodide-malonic acid plane (reproduced from Ref. [24]): Open triangles denote single front patterns, solid triangles denote triple front patterns, and stars denote multiple front patterns. Solid circles denote spot patterns, with the number next to each symbol indicating the number of unstable rows.

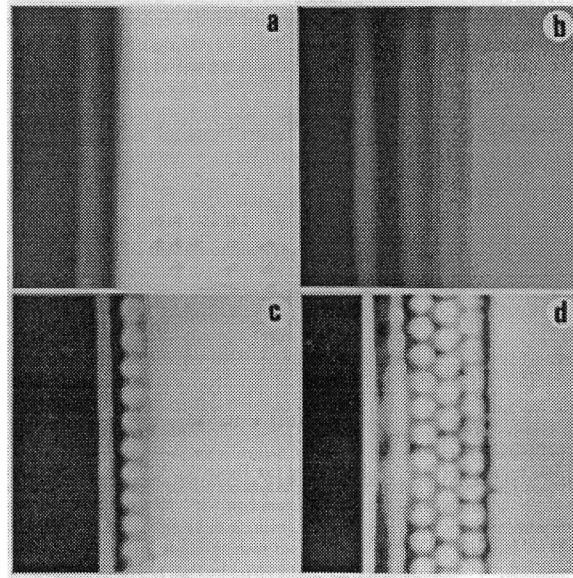


Figure 3.4: Experimental pictures of different patterns obtained in various domains of the phase space in Fig. 3.3 (reproduced from [24]): (a) Triple front pattern; (b) Multiple front pattern; (c) Single row of spots; (d) Three rows of spots.

In disc reactors: In a disc reactor, with Oz viewing, extended two-dimensional symmetry-breaking patterns can be observed. It is desirable to adjust the gel thickness and feed concentrations to achieve a single patterned layer within the gel. The resulting patterns transverse to the boundary feeds can then be observed as two-dimensional structures without having to account for the three-dimensionality of the patterns. However, even under such experimental conditions, chemical gradients are necessarily present, and the transverse patterns are referred to as *quasi-two-dimensional* patterns or *monolayers* to distinguish them from *genuine* two-dimensional structures that form under uniform conditions. A variety of quasi-two-dimensional Turing patterns have been observed and transitions between these states have been studied [22].

In Fig. 3.5, we have reproduced from [2] examples of *hexagonal* and *striped* patterns obtained in the CIMA reaction-diffusion system. The uniform-hexagon-stripe transition as a control parameter is *slowly* varied follows the sequence predicted from the weakly nonlinear theory of pattern selection [1]. *Zig-zag* patterns, arising from a transverse long wavelength instability of the striped patterns, have also been observed [2].

In addition to hexagons and stripes patterns which are ubiquitous to pattern-forming systems, *rhombic* and “*black-eye*” patterns have been observed in the CIMA reaction-diffusion system, which do not appear in other experimental studies of nonequilibrium systems. Rhombic patterns are obtained from the uniform state when a *sudden* jump in control parameter into the regime with patterns is made. These patterns are hexagons, deformed along one symmetry axis such that the characteristic angle between the two wavevectors is different from 60° [26]. The existence and stability of rhombic patterns has been described by a Landau-Ginzburg theory constructed on the basis of symmetries [27]. Predicted and observed bifurcation diagrams for the transition from a uniform state to rhombic patterns have been obtained and are in qualitative agreement [26]. “Black-eye” patterns which appear well beyond the onset of hexagons are less well-studied [2]. They consist of two hexagonal lattices, where it appears that one lattice is a spatial harmonic of the other, and have also been

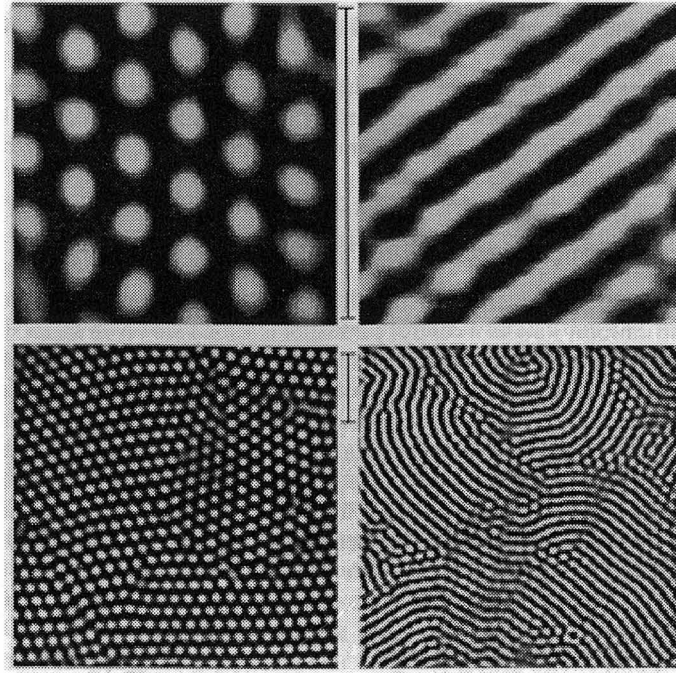


Figure 3.5: Experimentally observed extended symmetry-breaking patterns in a disc reactor (reproduced from [2]): The patterns on the left are hexagons, and those on the right are stripes. The bar inside each picture represents 1 mm.

obtained in numerical simulations of the Brusselator model [28].

3.3.1.2 Patterns in the presence of ramps

Recent experiments by Dulos *et al.* [23] on Turing patterns in ramped systems have aimed at elucidating how quasi-two-dimensional patterns (single unstable layer) evolve into three-dimensional patterns (multiple unstable layers). They use an indirect approach to do so, due to the technical difficulties associated with direct observation of three-dimensional patterns. This involves using a reactor with variable length along the boundary feed direction. A schematic diagram of the experimental set-up and directions of observation are given in Fig. 3.1. By combining observations from Fig. 3.1(d) using a thin strip reactor, and Fig. 3.1(e) using a disc reactor at locations with comparable distances between the feed boundaries, they have indirectly investigated the three-dimensionality of the system, with particular attention to the role of feed gradients on the three-dimensional pattern selection mechanism.

In the bevelled thin strip reactor: The gel strip dimensions in this reactor geometry were $h = 0.2$ mm, $L = 25$ mm, with a variable width w ranging from 1.75 mm to 3.5 mm (see Fig. 3.1(d)). Fig. 3.6, reproduced from [23], shows the unfolding of patterns that form along the boundary feed gradients as the width of the gel is varied. The gel width increases from left to right, and the boundary feeds are the top and bottom faces in each figure. These results can be summarized as follows:

- In the narrowest part of the strip, no symmetry-breaking spot patterns occur (Fig. 3.6(a)).
- As the gel width increases, symmetry-breaking spot patterns emerge and develop over one layer (Fig. 3.6(b)).
- As the gel width continues to increase, the single layer of spots becomes “fuzzy” and seems to disappear, giving way to a uniform band, before two layers of spots form (Fig. 3.6(b) and (c)).
- As the gel thickness increases even further, the two layers of spots also seem to finally vanish (Fig. 3.6(e)). Before disappearing at the end of the gel, however, the amplitude of the spot modulations in one of the two rows decreases or even disappears, but reappears again (Fig. 3.6(d) and (e)).

Dulos *et al.* have focused on the transition between the domains with one and two rows of spots, and the possible influence of the feed gradients on the phase relations between the spots in the two rows. The vanishing amplitude of the spot modulations before this splitting occurs is not well understood. In Sec. 5.2, we present numerical results that aim at addressing the latter question.

In the bevelled disc reactor: In Fig. 3.7, we have reproduced experimental results from [23], showing the sequence of observed patterns in the bevelled disc reactor. The gel width increases from bottom to top and again acts as the control parameter. The following features are apparent:

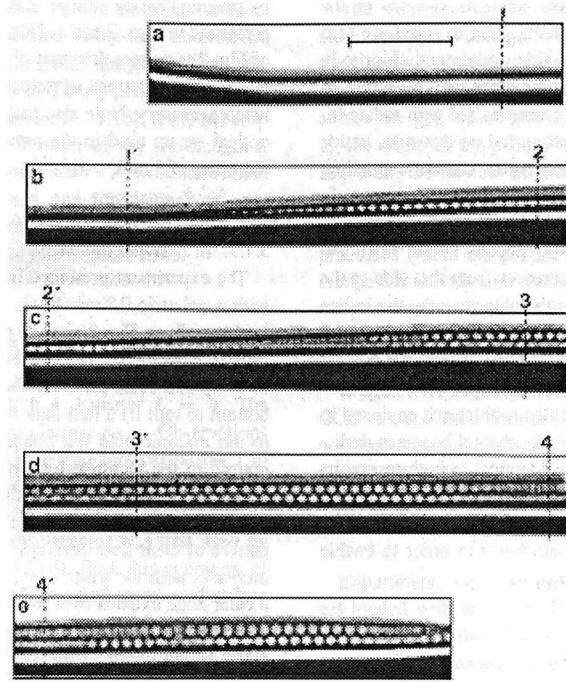


Figure 3.6: Experimentally observed patterns in a variable-width thin-strip reactor (reproduced from [23]): The whole pattern sequence can be reconstructed by placing images (a)-(e) side by side. Pairs of vertical dotted lines (eg., 1 and 1') indicate the same location along the strip. The scale inside (a) corresponds to 1 mm.

- In the narrow part of the gel (region 1), no structures are observed. As the gel width increases, in regions 2 and 3, first hexagon and then stripes appear. The sequence uniform-hexagon-stripe follows the standard stability order predicted from the weakly nonuniform theory of two-dimensional pattern formation. The uniform-hexagon transition is sharp, consistent with the subcritical nature of the bifurcation to hexagons. Also, the sharp transition from hexagons to stripes is consistent with the discontinuous nature of this transition.
- Region 4 shows a mixture of hexagons and stripes. In the standard two-dimensional approach, a mixed mode is unstable. Therefore, it is more likely that this region corresponds to the formation of a second unstable layer in the bevelled strip reactor, where the initial instability is again to hexagons. Region 5 shows stripes of low contrast, which are believed to be a superposition of two layers of stripes. Hence, regions 4 and 5 can be understood in terms of the appearance of a second unstable layer which also undergoes a hexagon-stripe transition.
- Region 6 appears also as a superposition of hexagonal and striped patterns in two layers, and may correspond to the restabilization of hexagons in one of the layers.

Although we do not focus on the bevelled disc experiments in this work, the unfolding of truly three-dimensional patterns in these experiments is a topic of continuing theoretical and experimental investigation. In Sec. 5.4, we discuss issues related to these experiments that would be of further theoretical, numerical and experimental interest.

3.3.2 Spatiotemporal patterns

Non-stationary patterns are beyond the scope this investigation. However, for the sake of completeness, we summarize experimental results on such patterns. In Sec. 5.4.3.3, we discuss the prospects for numerical investigations of spatiotemporal phenomena.

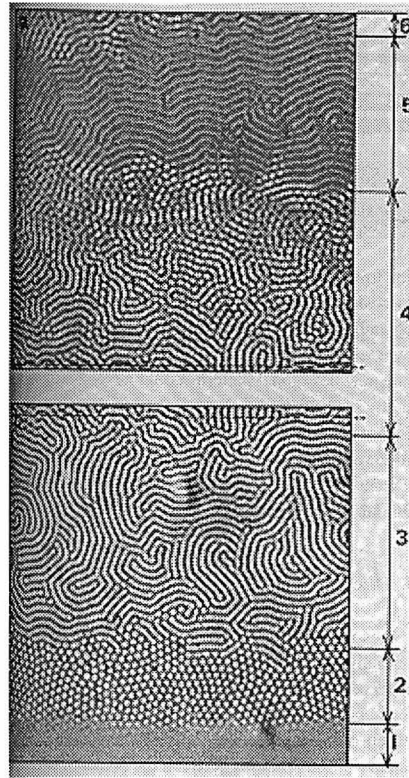


Figure 3.7: Experimentally observed patterns in a variable width disc reactor (reproduced from [23]): The gel width increases from bottom to top. The whole pattern sequence can be reconstructed by juxtaposing the bottom and top frames along the dotted lines. The vertical arrows delimit the successive domains.

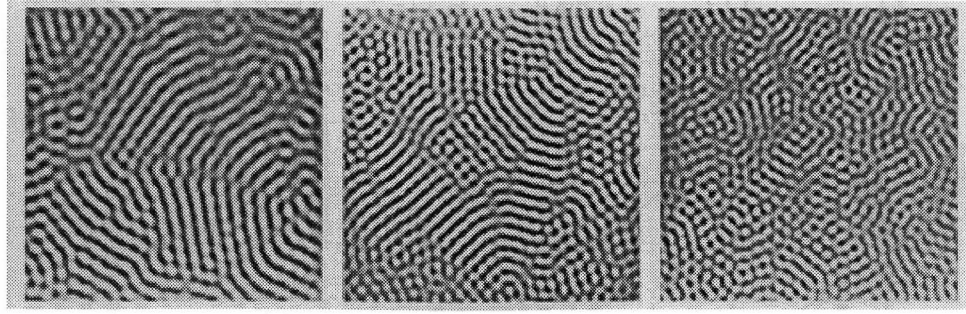


Figure 3.8: Experimentally observed patterns showing the transition to chemical turbulence (reproduced from [22]): The transition from a striped pattern to chemical turbulence occurs as the malonic acid concentration in one of the reservoirs is decreased from left to right.

3.3.2.1 Chemical turbulence

Swinney *et al.* [22] have obtained the first experimental evidence for spatiotemporal chemical patterns in the CIMA system, referred to as *chemical turbulence* due to their lack of long-range spatial and temporal order. This state differs from the stationary hexagonal or striped patterns (see Fig. 3.8), with regard to its large number of defects, small domains of spots (with a short length scale of only 2 to 3 wavelengths), and continuous evolution of the grain boundaries. It has been experimentally verified that the observed state of chemical turbulence is not a transient phenomenon but an asymptotic stable state [22]. The transition to chemical turbulence has been observed from both striped and hexagonal states. The stripe-turbulence transition has been studied in detail in terms of such quantities as the total length of grain boundaries, the average speed of pattern motion, the correlation length of a state, and the wavelength of the pattern [22]. The transition is marked by a rapid variation in of these quantities (a slower variation in the wavelength of pattern is observed). In Fig. 3.9, we have reproduced an experimental phase diagram from [22], showing the chemically turbulent region to lie in parameter space between hexagons and stripes.

The mechanism of chemical turbulence is not well understood at present. In Sec. 5.4, we comment on possibilities for further investigation.

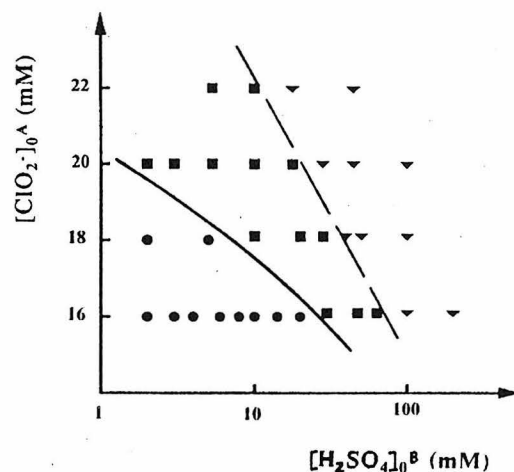


Figure 3.9: Experimentally obtained phase diagram showing hexagons, stripes and chemical turbulence (reproduced from [22]): Stripes (circles), turbulence (squares) and hexagons (triangles), in the plane of two reservoir variables.

3.3.2.2 Chemical waves

In a series of experiments performed in a thin strip reactor [19, 29], quasi-one-dimensional waves in the CIMA system have been observed. These results, reproduced in Fig. 3.10, are obtained for a given low enough starch concentration upon increasing the malonic acid feed concentration. Initially, a single row of spots parallel to the boundary feed is obtained. As the malonic acid concentration is increased, most spots disappear, while a few remaining spots (one to three) act as sources of wave trains. Upon further increasing the malonic acid concentration, all spots disappear, and only waves propagating along the line parallel to the boundary feed remain. However, a few bright spots can persist, acting as sources of wavetrains that propagate away on both sides. The left- and right-going waves are not emitted synchronously, since the bright spot shifts from one side to the other of a narrow invariant region. Hence, this wave source has been dubbed a “*chemical flip-flop*” [24]. It has been verified that these waves are not linked to defects or impurities in the gel [29]. It is believed that they can be understood in terms of the interaction between Turing and Hopf modes [19].

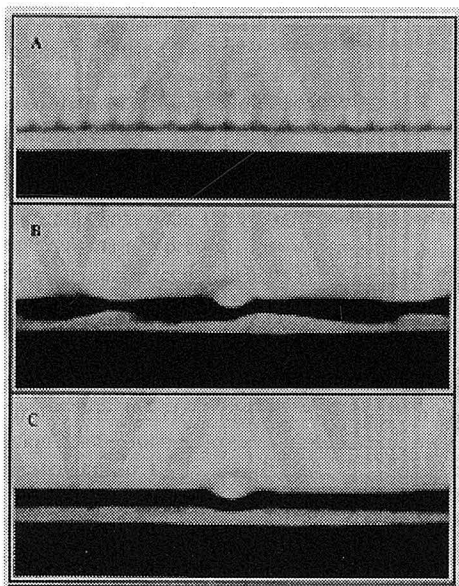


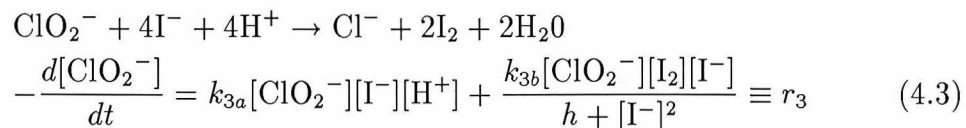
Figure 3.10: Experimentally observed patterns showing the transition to chemical waves (reproduced from [29]): The sequence from (A) to (B) is obtained for decreasing malonic acid reservoir concentration. (A) Turing spots parallel to the feed boundary, (B) Travelling waves, with a single Turing spot acting as a wave source, (C) Pattern obtained by averaging (B) over several periods, indicating that the source corresponds to an elementary Turing spot.

Chapter 4 Chemical Model

4.1 Chemical Model of the CDIMA System

The Turing instability was first observed in the chlorite-iodide-malonic acid (CIMA) reaction, ClO_2^- - I^- -MA, and subsequent experimental work has continued to use this chemical system. Lengyel, Epstein and Rabai (referred to as LRE) have proposed a model for the temporal oscillations in a reaction system which is based on the simpler chlorine dioxide-iodine-malonic acid reaction, ClO_2 - I_2 -MA, referred to as CDIMA [9, 10]. They have shown experimentally that the ClO_2 - I_2 -MA system also exhibits the Turing instability in both closed and open systems [30, 31].

By monitoring the CIMA reaction in a closed system spectrophotometrically, it was determined that after an initial fast consumption of I^- and ClO_2^- during a pre-oscillatory period to produce I_2 and ClO_2 , the reaction of ClO_2 , I_2 and MA accounts for the oscillations. The LRE model consists of three reactions for MA, I_2 , ClO_2 , I^- , ClO_2^- and H^+ [32], with empirically determined rate laws:



where the rate laws are given as above, and the rate constants which are used in the numerical calculations here are given in Table 4.1 from [30], [32], [33], and [34].

Table 4.1: Kinetic constants for the CDIMA system.

Rate or diffusion constant	Dimensions	Value
k_{1a}	(s ⁻¹)	9×10^{-4} ^(a)
k_{1b}	(M)	5×10^{-5} ^(a)
k_2	(M ⁻¹ s ⁻¹)	1×10^3 ^(a)
k_{3a}	(M ⁻² s ⁻¹)	1.2×10^2 ^(a)
k_{3b}	(s ⁻¹)	1.5×10^{-4} ^(a)
h	(M ²)	1.0×10^{-14} ^(a)
k_+	(M ⁻² s ⁻¹)	6.0×10^5 ^(b)
k_-	(s ⁻¹)	1.0 ^(b)
D_{I^-}	(cm ² s ⁻¹)	7.0×10^{-6} ^(c)
$D_{ClO_2^-}$	(cm ² s ⁻¹)	7.0×10^{-6} ^(c)
D_{I_2}	(cm ² s ⁻¹)	6.0×10^{-6} ^(a)
D_{MA}	(cm ² s ⁻¹)	4.0×10^{-6} ^(a)
D_{ClO_2}	(cm ² s ⁻¹)	7.5×10^{-6} ^(a)
D_{H^+}	(cm ² s ⁻¹)	1.0×10^{-5}
$K[S]_o$	(M ⁻¹)	6.25×10^4 ^(d)

^(a)From [33] at 7°C; ^(b)From [32] at 4°C; ^(c)From [30] at 4°C; ^(d)From [34] at 4°C.

Epstein *et al.* [9] have shown that these reactions successfully simulate the temporal behavior of [MA], [I₂], [ClO₂], [I⁻], and [ClO₂⁻] in a batch experimental system. Their numerical results show that while the intermediates [I⁻] and [ClO₂⁻] vary by several orders of magnitude during an oscillation, [MA], [I₂] and [ClO₂] vary more slowly. This suggests a reduction of the five-variable model to a two-variable system by treating the concentrations of the [MA], [I₂] and [ClO₂] reactants as constants, making the model mathematically and numerically more tractable. This procedure illustrates the adiabatic elimination of fast modes in dynamical systems which reduces the full dynamics to only a few degrees of freedom. The resulting two-variable model including diffusion becomes:

$$\frac{\partial u}{\partial t} = k_1' - k_2'u - \frac{4k_{3b}'uv}{h + u^2} + D_u \nabla^2 u \quad (4.4)$$

$$\frac{\partial v}{\partial t} = k_2'u - \frac{k_{3b}'uv}{h + u^2} + D_v \nabla^2 v, \quad (4.5)$$

where $k_1' = k_{1a}[\text{MA}]_o[\text{I}_2]_o/(k_{1b} + [\text{I}_2]_o)$, $k_2' = k_2[\text{ClO}_2]_o$, and $k_{3b}' = k_{3b}[\text{I}_2]_o$. The subscript o refers to the concentration of species which are taken to be constant, and u and v are concentrations of the I^- and ClO_2^- species. The validity of this reduction is addressed in Sec. 5.3. Note that the first term in the reaction rate r_3 (Eq. (4.3)), which is proportional to $[\text{H}^+]$, has been omitted in Eq. (4.5), since it makes negligible contribution to the rate law [9]. We have verified this fact explicitly through numerical integration of the full reaction-diffusion equations with and without the $[\text{H}^+]$ term. Henceforth, it will be neglected in the two-variable reduction of the model. In Sec. 5.3.1, we also determine that elimination of H^+ does not affect the stability of the stationary state.

It is interesting to note that the two-variable LRE model bears a striking resemblance to an unrelated chemical reaction-diffusion model used to describe the respiratory behavior of a bacterial culture [35, 36]. Under certain conditions, this model also leads to the formation of inhomogeneous steady structures in the concentrations of its two reactants (oxygen and fuel).

4.2 The CIMA and CDIMA Reactions

Although the CIMA reaction can be qualitatively understood in terms of the CDIMA reaction, based on similar batch dynamics [34] as well as stationary pattern-forming behavior in open reactors [30], a well-understood quantitative model for it does not exist. In particular, the origin of chlorine dioxide, which is a key intermediate species that is responsible for batch oscillations of the CIMA reaction, has not been worked out [34]. A naive application of the CDIMA model to describe the experimental CIMA system with its associated boundary conditions, iodide and chlorite, results in the unphysical effective elimination of the chlorine dioxide species from the model. This point can be seen from Eq. 4.2 of the CDIMA reaction, where unless chlorine dioxide is introduced as a boundary species, it is not produced in the model.

It has been further pointed out [34], that using iodide and chlorite as reservoir species in the experimental CIMA system could lead to reactive reservoirs. This is an

experimentally undesirable feature, resulting in nonuniform or even oscillatory boundary conditions. On the other hand, since chlorine dioxide does not react with either iodine or malonic acid, employing the CDIMA reaction with these boundary species would make it easy to set up uniform and well-controlled boundary conditions. Since chlorine dioxide, iodine and malonic acid have been identified as the “background” species, and iodide and chlorite as the “dynamical” species, it makes sense to use the former as the set of boundary control parameters.

The first experimental system for studying Turing patterns was the CIMA reaction, and experimentalists have continued their investigations using this reaction, despite the lack of existence of a quantitative model. In the pursuit of aligning experiment and modeling, however, it appears that experiments should move toward using the CDIMA reaction.

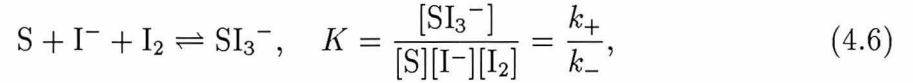
4.3 Role of Starch Indicator in Model

We have seen in Sec. 2.3 that in the absence of a mechanism that slows down the dynamics of the activator species with respect to the inhibitor (*i.e.*, for $\sigma = 1$), a necessary condition for the Turing instability to occur is that $c > 1$. In fact, given the physical values of other parameters, this ratio has to be much greater than one. However, in aqueous media, nearly all simple molecules and ions have diffusion constants on the order of $10^{-5} \text{ cm}^2\text{s}^{-1}$. Lengyel *et al.* [33] originally proposed a qualitative picture to account for the relatively small diffusivity of the activator species. They suggested that the I^- ions move not in a simple gel but in a medium with many traps (gel-bound I_2 and starch) that capture I^- for a period of time before releasing it, thereby causing I^- to diffuse more slowly than in the absence of traps. The effective diffusible concentration of I^- is lower than its stoichiometric concentration, thus the rate of I^- diffusion decreases as if its diffusion coefficient were smaller. They subsequently showed that this qualitative picture can be obtained by the addition of the reaction between the dynamical variable I^- and the starch color indicator to their original two-variable model. The starch-iodide complex thus

formed is effectively immobile due to its large size, and can be modeled as being fully reactive or unreactive. Both assumptions, of fully reactive and fully unreactive immobile complexes, yield models in which the Turing instability can occur. We will briefly review both models, summarize their predictions regarding the role of starch in the dynamics and pattern formation, and compare them with available experimental results.

4.3.1 Unreactive complex

Lengyel *et al.* [17] have modeled the effect of unreactive complex formation on the CDIMA system. The complexing agent is $(S+I_2)$, where S is the starch, and although the formation of starch-triiodide complex (SI_3^-) is a complicated process, it can nevertheless be described as a single reaction:



where K is the equilibrium constant, and the reaction rate is given by:

$$r_4 \equiv k_+[S][I_2][I^-] - k_-[SI_3^-]. \quad (4.7)$$

Using the above, the full 7-variable model for the CDIMA system, with the addition of the reaction with starch, is given by [32]:

$$\frac{\partial[MA]}{\partial t} = -r_1 + D_{MA} \nabla^2[MA] \quad (4.8)$$

$$\frac{\partial[I_2]}{\partial t} = -r_1 + \frac{1}{2}r_2 + 2r_3 - r_4 + D_{I_2} \nabla^2[I_2] \quad (4.9)$$

$$\frac{\partial[ClO_2]}{\partial t} = -r_2 + D_{ClO_2} \nabla^2[ClO_2] \quad (4.10)$$

$$\frac{\partial[I^-]}{\partial t} = r_1 - r_2 - 4r_3 - r_4 + D_{I^-} \nabla^2[I^-] \quad (4.11)$$

$$\frac{\partial[ClO_2^-]}{\partial t} = r_2 - r_3 + D_{ClO_2^-} \nabla^2[ClO_2^-] \quad (4.12)$$

$$\frac{\partial[SI_3^-]}{\partial t} = r_4 \quad (4.13)$$

$$\frac{\partial[\text{H}^+]}{\partial t} = r_1 - 4r_3 + D_{\text{H}^+} \nabla^2[\text{H}^+]. \quad (4.14)$$

It is assumed that there is a large excess of starch uniformly distributed so that its concentration is always very close to its initial value $[\text{S}]_o$, and that the complex formation and dissociation is fast. Then,

$$[\text{SI}_3^-] = K[\text{S}]_o[\text{I}_2]_o \cdot [\text{I}^-] \approx K'[\text{I}^-], \quad K' = K[\text{S}]_o[\text{I}_2]_o. \quad (4.15)$$

Adding Eqs. (4.11) and (4.13), and using Eq. (4.15), the two-component reduction of the above 6-variable system becomes:

$$\sigma \frac{\partial u}{\partial t} = k_1' - k_2' u - \frac{4k_{3b}' uv}{h + u^2} + D_u \nabla^2 u \quad (4.16)$$

$$\frac{\partial v}{\partial t} = k_2' u - \frac{k_{3b}' uv}{h + u^2} + D_v \nabla^2 v, \quad (4.17)$$

where $\sigma = 1 + K' > 1$, and the reaction parameters are the same as those given for Eqs. (4.4) and (4.5). Note that the nonlinear reaction terms f and g retain the same form: the complex formation changes neither the scaling of the concentrations nor the kinetic parameters. Therefore, the steady state of the system is unchanged by this process, but its stability is modified.

4.3.2 Fully reactive complex

Pearson and Bruno [37] have considered the assumption of a fully reactive complex in detail. In this case, the iodide (I^-) species and the complex (SI_3^-) react identically. This means that the reaction kinetic terms in Eqs. (4.8)–(4.13) involving I^- must be replaced with $(\text{I}^- + \text{SI}_3^-)$. In the two-component reduction, the dynamical variable u , corresponding to I^- , is replaced by u^{T} , corresponding to the total concentration of the iodide and complex species, $(\text{I}^- + \text{SI}_3^-)$. The resulting equations for the two-variable model are:

$$\sigma \frac{\partial u^{\text{T}}}{\partial t} = f(u^{\text{T}}, v; \vec{\mu}) + D_u \nabla^2 u \quad (4.18)$$

$$\frac{\partial v}{\partial t} = g(u^T, v; \vec{\mu}) + D_v \nabla^2 v. \quad (4.19)$$

where the functions f and g are the same as in Eqs. (4.16)–(4.17). The difference between the fully nonreactive and fully reactive modeling of complex formation which can be immediately noted from Eqs. (4.16)–(4.17) and Eqs. (4.18)–(4.19) is that: fully nonreactive modeling affects both the reaction and diffusion of the activator u with respect to the inhibitor v , whereas fully reactive modeling affects only the diffusion. Linear stability results for this system can be obtained from those based on the nonreactive complex modeling by the substitution $a_{1j} \rightarrow a_{1j}/\sigma$. For example, from Eq. (2.13) the critical wavenumber in the fully reactive complex modeling is independent of the complexing strength σ , but it is proportional to σ using the above model.

4.3.3 Experimental results on the role of starch indicator

The observation that the color indicator plays a fundamental role in the pattern formation itself motivated an experimental study by Noszticzius *et al.* [38]. Their results can be compared with predictions from the modeling where the starch-triiodide complex is: (i) fully reactive and (ii) fully unreactive.

Reaction dynamics:

- (i) In the case where the bound and free iodide react identically, the resulting model predicts that the net effect of the immobile substrate is to rescale the diffusion coefficient of iodide only, without affecting the dynamics in a batch reactor, since diffusion coefficients do not affect the homogeneous dynamics. This result is in contradiction with experimental findings which show that the complex formation suppresses the chemical oscillations of this system.
- (ii) In the case where the bound iodide is unreactive, the effect of complex formation is to separate the time scales for changes in the activator and inhibitor concentrations. Therefore, the immobile complex rescales the reaction as well as the

diffusion of the iodide species. Increasing σ in this model results in decreasing the real part of the complex conjugate pair of eigenvalues (for which $k = 0$ is the fastest growing mode), thereby suppressing homogeneous oscillations.

Pattern formation:

- (i) Experimental results indicate decrease in the wavelength of patterns with increase in complexing strength, which is accomplished, for example, through increase in starch concentration. starch concentration or. The critical wavenumber with fully reactive modeling is proportional to σ , which is consistent with these results, provided the experimental conditions are not far from criticality.
- (ii) Fully nonreactive modeling predicts the critical wavenumber and parameters to be independent of σ . Similarly, the range of unstable wavenumbers is independent of σ . Beyond onset, however, the most unstable wavenumber in this range will depend on σ (see Eq. 2.14). If the experimental conditions are far from threshold, this modeling is consistent with experimental results.

In general, one does not expect a complex chemical system to reduce to a simple reaction-diffusion activator-inhibitor system. Therefore, it is not surprising that the above experimental results on the role of starch contradict some predictions of both two-variable models. The qualitative picture that emerges is that the complexed iodine species are confined within the three-dimensional structure of the starch molecule and are therefore not exposed to react freely with other reagents [37]. Based on this, the fully nonreactive model is preferred to the fully reactive model, and will be used here.

Chapter 5 Analysis

In this chapter, we use the CDIMA chemical model to investigate several aspects of the experimental CIMA system. The focus is to demonstrate the potential for quantitative analysis of experimental results using a realistic chemical model.

In Sec. 5.1, we investigate numerically the formation of one-dimensional localized structures in the CDIMA reaction-diffusion system along gradients of imposed boundary feeds. The linear stability of these structures to transverse symmetry-breaking perturbations is studied using the two-variable reduction of the LRE model. We show that a local stability analysis based on the simple assumption that a pattern will form in the plane perpendicular to the gradients where the values of the background chemicals predict it to be stable in the corresponding uniform problem is incorrect. We review a proposed modification of this local analysis and show that it does not successfully account for the presence of gradients. We comment on why a local analysis does not correctly describe the stability of patterns along gradients.

In Sec. 5.2, we further explore the structure and linear stability of one-dimensional localized patterns along boundary feeds as a function of two different control parameters: the malonic acid reservoir concentration and gel width. We find that the number of fronts in the stationary, non-symmetry breaking pattern increases with increasing control parameter. Linear stability analysis of the non-symmetry breaking front patterns yields a symmetry-breaking instability as a threshold value of the control parameter is reached. This linear instability vanishes as the the control parameter continues to be increased and the front pattern becomes linearly stable at a higher value of the control parameter. We present results that attempt to quantify this trend. We discuss the qualitative agreement of our results with those obtained by the experiments described in Chap. 3.

The two-variable reduction of the full LRE model of the CDIMA reaction-diffusion system is numerically and mathematically more tractable, and it is utilized in the

preceding parts of this analysis. Hence, in Sec. 5.3, we verify its validity explicitly.

In Sec. 5.4, we present numerical solution of the two-dimensional CDIMA reaction-diffusion system, in a thin-strip geometry for a particular set of reservoir boundary conditions. The nonlinear evolution of the LRE model in two-dimensions verifies the results from the linear stability analysis of the non-symmetry breaking stationary solution for these boundary conditions. The quasi-one-dimensional pattern of spots transverse to the feed gradients forms in a single layer for these boundary conditions and is in qualitative agreement with some reported experiments [24]. These results demonstrate the feasibility of using a realistic chemical model in numerical investigations to allow better comparison with experiments, and we discuss possibilities for further study.

In the proceeding sections, we choose reservoir species consistent with the LRE model of the CDIMA reaction-diffusion system, as well as experiments by the Epstein group [30, 32], in a strip reactor geometry. In the model, malonic acid (MA) is fed into the gel strip from reservoir I on the left, and iodine (I_2) and chlorine dioxide (ClO_2) are fed in from reservoir II on the right. All reaction parameters are given in Table 4.1.

5.1 Analysis of One-Dimensional Patterns Along Gradients

To examine the stability of the stationary patterns that form along the gradients of boundary feeds (z -direction), the simplest approach is to treat each location z as being independent and locally uniform in the transverse plane, thereby neglecting diffusion along the z -direction (longitudinal diffusion). The locally homogenous stationary state in the dynamical species, I^- and ClO_2^- , at each z can be constructed either from the linear (diffusion only) profiles of the reservoir species, MA, I_2 , and ClO_2 , or more correctly, from their reaction+diffusion profiles, obtained by evolving the full model. In either case, using a two-variable activator-inhibitor reduction of the LRE model, the resulting eigenvalue problem for the stability of the locally homogenous steady state to a symmetry-breaking instability requires a simple 2×2 analysis. Hence, it is desirable to use such a local approach if it can be shown that it accurately describes the physical problem. In that case, a transverse instability would occur in a region of width Δ along the gradients which is linearly unstable to a $k \neq 0$ instability. Indeed, even though Turing patterns are obtained under experimental conditions that by necessity lead to nonhomogenous parameter ramps which are functions of the reservoir species, a local linear analysis is most commonly used to predict the formation of a transverse symmetry-breaking instability. In this section, we examine in the context of the two-variable LRE model the validity of a locally uniform approach to determining the stability of the stationary patterns that form along the gradients of boundary feeds. In Sec. 5.3, we return to examine explicitly the two-variable reduction of the full model.

5.1.1 Stationary solution along the z -direction

The full 6-component LRE model equations given in Eqs. (4.8)–(4.13) were evolved forward in time to obtain the steady state solution in one dimension along the gradients. The boundary conditions, $[MA]_I = 1 \times 10^{-2}$ M at the left boundary, and

$[I_2]_{II} = 1 \times 10^{-3}$ M and $[ClO_2]_{II} = 6 \times 10^{-4}$ M at the right boundary, were chosen so as to be consistent with a previous numerical investigation of the LRE model in one dimension by Lengyel *et al.* [33]. Since the boundary conditions giving a transverse instability are *a priori* unknown, we used these values as our starting point. The spatial z -direction was discretized on an irregularly spaced mesh to allow a greater number of mesh points in the regions where there was more structure in the solution, without excessively increasing the overall number of mesh points in the problem. A five-point finite-difference approximation to the diffusion operator was used on the variable mesh. The numerical scheme employed for the time evolution was Crank-Nicholson implicit time-stepping for the linear terms, and Adams-Bashford explicit time-stepping for the nonlinear terms. A banded solver [39] was used at each time step to solve for the solution at the next time step. Further details of the numerical method for determining the stationary state along z are given in Sec. B.1 of Appendix B. The initial concentrations were uniform in the z -direction (and equal to 5×10^{-13} M). The time evolution was continued until there was no appreciable change in the solution.

The results are displayed in Fig. 5.1. The steady state solution for the starch-triiodide complex (SI_3^-) plotted in Fig. 5.1(f) is the experimentally observed profile. As expected, it tracks the iodide (I^-) steady state solution in Fig. 5.1(d). It corresponds to the (non-symmetry breaking) pattern of stripes (in the $x - z$ plane, with x being the uniform direction) parallel to the feed boundaries observed by Perraud *et al.* [19], although the boundary species are different in their experiments on the CIMA reaction from those considered here. Upon increasing the control parameter, they observe a break-up of the stripes to rows of spots parallel to the feed surfaces. This is a symmetry-breaking instability, since the boundary feed symmetry of the system is broken. In the following, we will investigate the linear stability of our numerical steady state along the gradients to such a transverse pattern-forming instability.

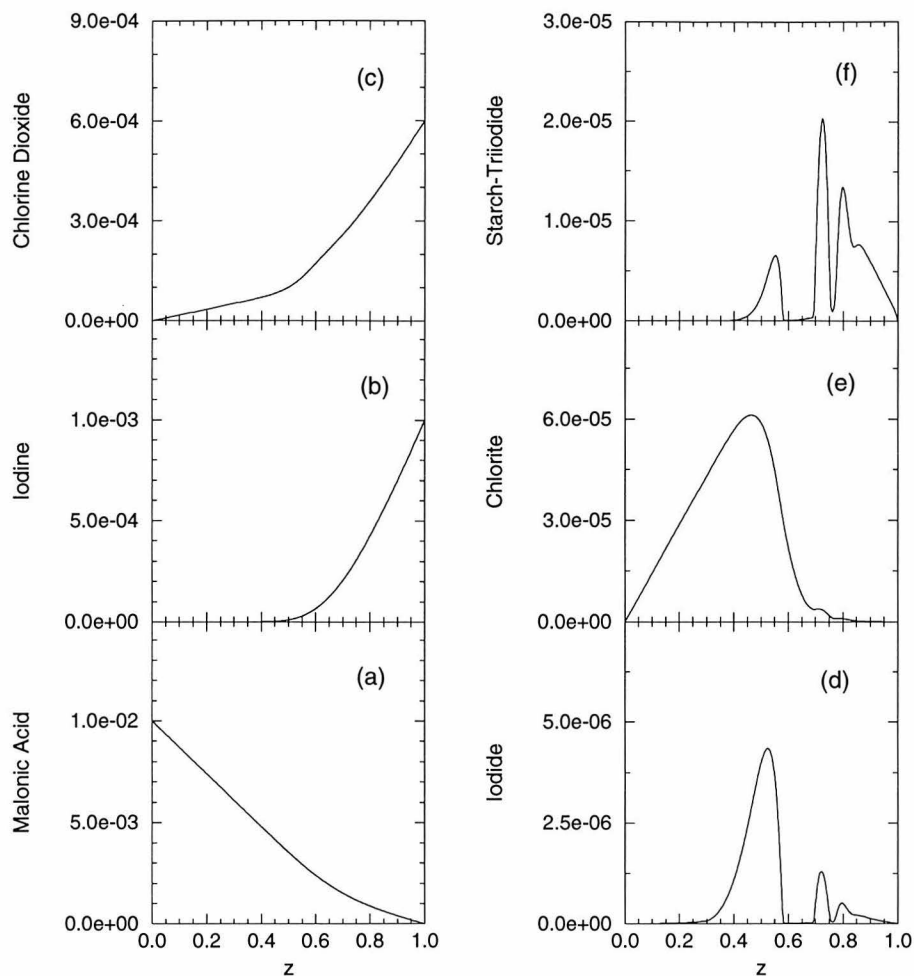


Figure 5.1: One-dimensional steady state solutions: The boundary conditions are $[\text{MA}]_{\text{I}} = 1 \times 10^{-2}$ M at the left boundary, and $[\text{I}_2]_{\text{II}} = 1 \times 10^{-3}$ M and $[\text{ClO}_2]_{\text{II}} = 6 \times 10^{-4}$ M at the right boundary. All other boundary conditions are zero. The z -axis has been normalized with respect to the thickness of the gel in the z -direction, $w = 0.3$ cm. We note that the steady state profiles for the reservoir variables malonic acid (MA), iodine (I_2) and chlorine dioxide (ClO_2) vary considerably from diffusion-only linear profiles. The series of peaks in the starch triiodide (SI_3^-) profile correspond to experimentally observed stripes parallel to the feed boundaries [19].

5.1.2 Linear stability analysis

5.1.2.1 Fully nonuniform analysis

The eigenvalue problem given in Eq. (2.19) was discretized on the same variable mesh as that on which the nonuniform steady state was obtained, and was solved for all eigenvalues and eigenvectors at each value of transverse wavenumber k using EISPACK [40]. Since we have a general real matrix, with no special features such as symmetry, the most general routines were used. Fig. 5.2 shows the real part of successive eigenvalues with largest real parts. This result shows the steady state to be stable to all transverse perturbations. It corresponds to the experimental pattern of stripes parallel to the boundary feeds at a value of the control parameter such that there is no break-up to symmetry-breaking spots. The eigenvector with slowest decaying growth rate at $k = 80 \text{ cm}^{-1}$ is plotted in Fig. 5.3.

Since we are generally interested in the most unstable mode, for this case which is stable, we checked the numerical validity of the gain curve for the slowest decaying eigenvector (top-most continuous curve in Fig. 5.2) against two different numerical methods. First, the linear system for $2N_z$ variables (eigenvector), where N_z is the number of mesh points, was solved as a nonlinear root finding problem in $(2N_z + 1)$ variables, including the eigenvalue. The details of this method are given in Sec. B.3.1. Second, starting with the eigenvalue and eigenvector based on the previous two methods, inverse iteration was used to verify the results. Both checks agree with the results from EISPACK.

The convergence of the slowest decaying gain curve as a function of the variable mesh was also investigated. Starting with a particular distribution of mesh points, the mesh size was successively halved, the corresponding steady state obtained, and the eigenvalues and eigenvectors found. Basically, the number and distribution of mesh points must be sufficient to well resolve both the structure of the steady state and its most unstable eigenvectors for numerical convergence. All numerical calculations were performed on an IBM RS6000 workstation, with the exception of eigenvalue/eigenvector determination using EISPACK with greater than approximately 500

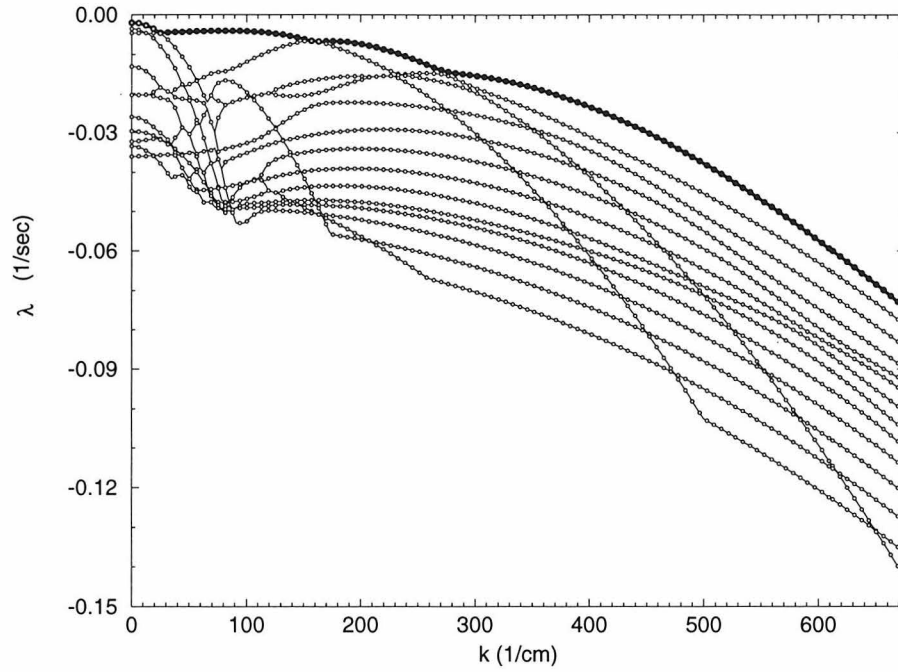


Figure 5.2: Gain curve for the one-dimensional steady state along the gradients: The real parts of the first fourteen eigenvalues with largest real parts have been plotted. The eigenvalues are real, except at points (or along intervals) where two curves intersect. The eigenvalue crossings appear imperfect due to the coarse selection of k values. All eigenvalues are less than zero with the heavy line corresponding to the slowest decaying mode at each k .

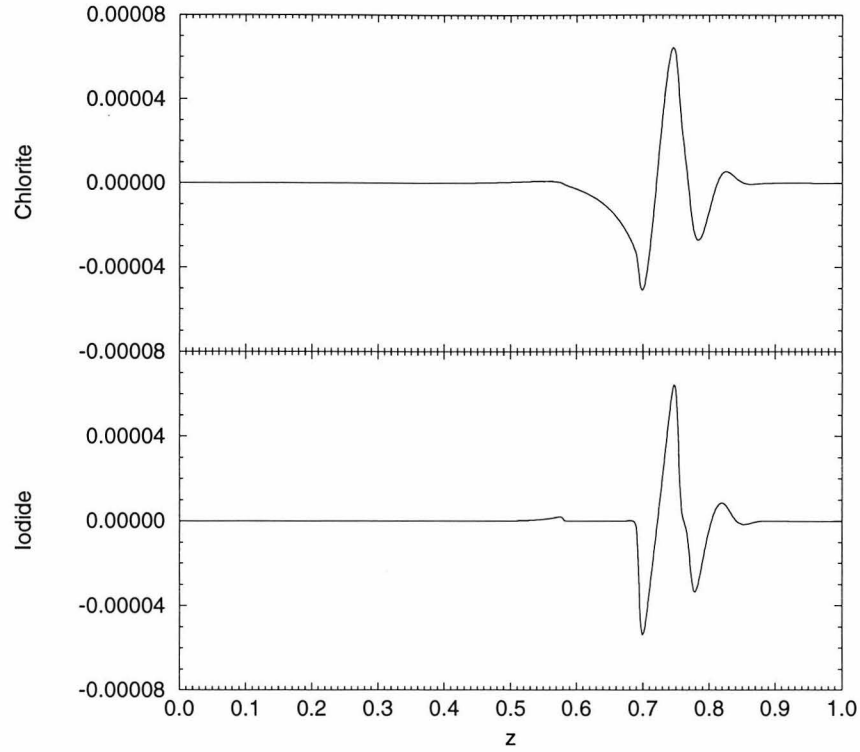


Figure 5.3: Eigenvector corresponding to slowest decaying mode in a fully nonuniform analysis: The eigenvector at $k = 81.6 \text{ cm}^{-1}$ with the largest eigenvalue has been plotted. It is localized roughly in the region along z where the locally uniform stability analysis predicts the corresponding uniform steady state to be unstable to a transverse instability.

mesh points, which was done on a CRAY C90.

5.1.2.2 Locally uniform analysis

Fig. 5.4 shows the calculated steady state solution in the variables I^- and ClO_2^- for the locally uniform system at each point in z along the gradients of the background chemicals. This is obtained according to Eqs. (4.16) and (4.17), neglecting the diffusion terms, and using the numerical reaction+diffusion profiles of Fig. 5.1 for the MA, I_2 and ClO_2 species. The dependence on z in this plot is parametric.

The stability of the local steady state at each z is obtained from Eq. (2.5). Fig. 5.5 is a plot of the Turing instability conditions Eqs. (2.9)–(2.12) for each locally uniform steady state. We have also plotted the boundary which, when less than zero, gives the interval in z where the locally uniform steady state has a complex conjugate pair of eigenvalues for a range in k given in Appendix A. The vertical axis has no labels, since we have plotted quantities which have different dimensions, and only their signs are of interest. The shaded region denotes the interval over which the locally uniform steady state in the $x - y$ plane is linearly stable to homogeneous perturbations and unstable to inhomogeneous perturbations. The width of this region is approximately equal to 0.15 mm, which is within the 0.13–0.33 mm range of experimentally observed Turing wavelengths [22].

Thus, the local stability analysis predicts that for the present control parameters, the experimental pattern of stripes will undergo an instability to symmetry-breaking spots in a finite region along the gradients. This result contradicts that from the numerical stability analysis of the full nonuniform steady state which shows it to be stable.

Fig. 5.6 shows the gain curves for the locally uniform steady states at selected points along the z -axis, consistent with the above linear stability boundaries. Note that Figs. 5.6(d)–(i) illustrate the role of the complexing agent ($S + I_2$) in suppressing the oscillatory instability, since $[I_2]$ (and therefore the complexing strength) sharply increases as the right boundary is approached.

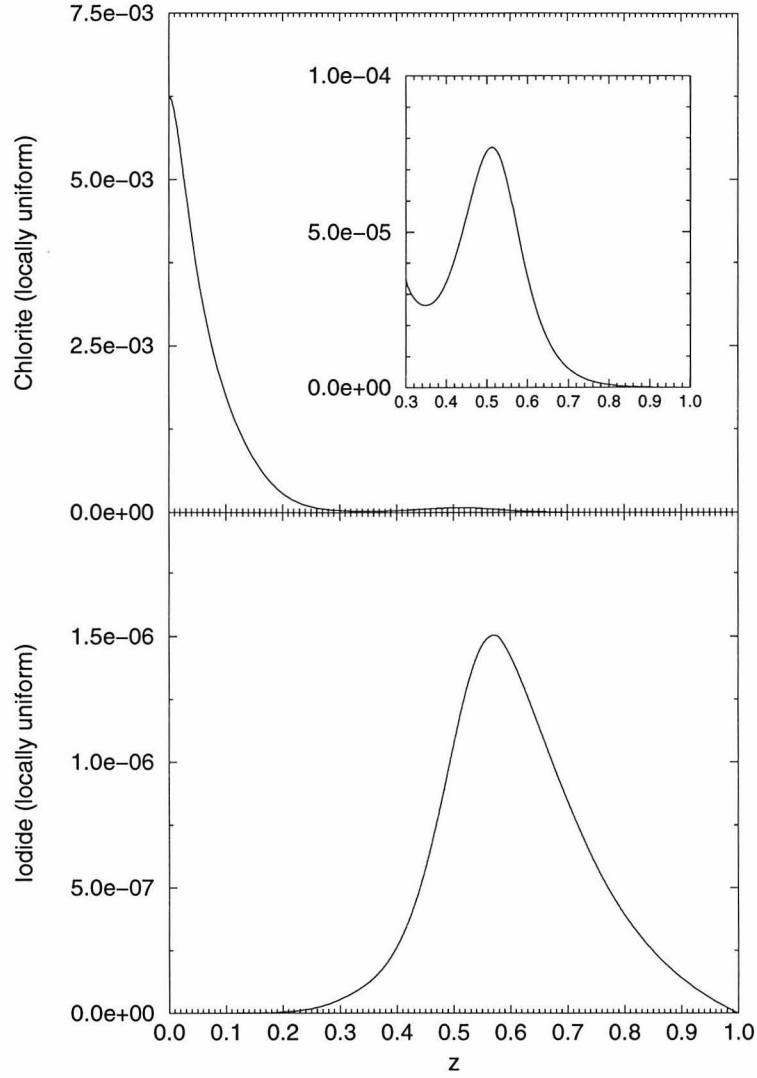


Figure 5.4: The locally uniform (in the $x - y$ plane) steady state solution is plotted at each point z for the two dynamical variables iodide (I^-) and chlorite (ClO_2^-) using the reaction + diffusion profiles of the reservoir variables given in Fig. 5.1.

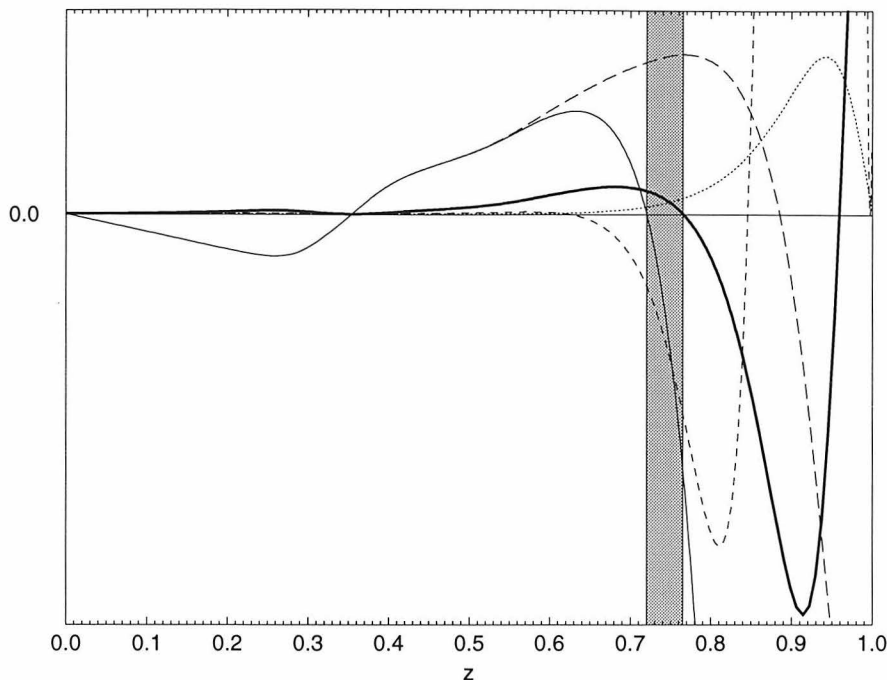


Figure 5.5: Boundaries from locally uniform stability analysis: At each location z , the Turing instability conditions have been plotted for the corresponding uniform steady state. The plotted quantities have different dimensions, and since only the sign of each quantity is of interest, the vertical axis has no scale. When the light solid line corresponding to $(a_{11} + \sigma a_{22})$ is less than zero, the complex conjugate pair of eigenvalues for $k = 0$ has a negative real part. The dotted line is $(a_{11}a_{22} - a_{12}a_{21})$ which is additionally required to be greater than zero for stability of a real $k = 0$ mode. We note that this quantity is everywhere greater than zero. The long-dashed line corresponds to $(ca_{11} + a_{22})$, and the heavy solid line is $(ca_{11} + a_{22})^2 - 4c(a_{11}a_{22} - a_{12}a_{21})$, both of which must be greater than zero in order to have a $k \neq 0$ instability. The dashed line is $((a_{11} - \sigma a_{22})^2 + 4\sigma a_{12}a_{21})$, and where it is less than zero, a complex conjugate pair of eigenvalues exists for a finite range in k . At $z = 0.354$, the light solid $(a_{11} + \sigma a_{22})$ and long-dashed $(ca_{11} + a_{22})$ lines go through zero, while the heavy solid, dotted and dashed lines remain positive. The shaded region indicates where the locally uniform steady state is stable to homogeneous perturbations and unstable to inhomogeneous perturbations.

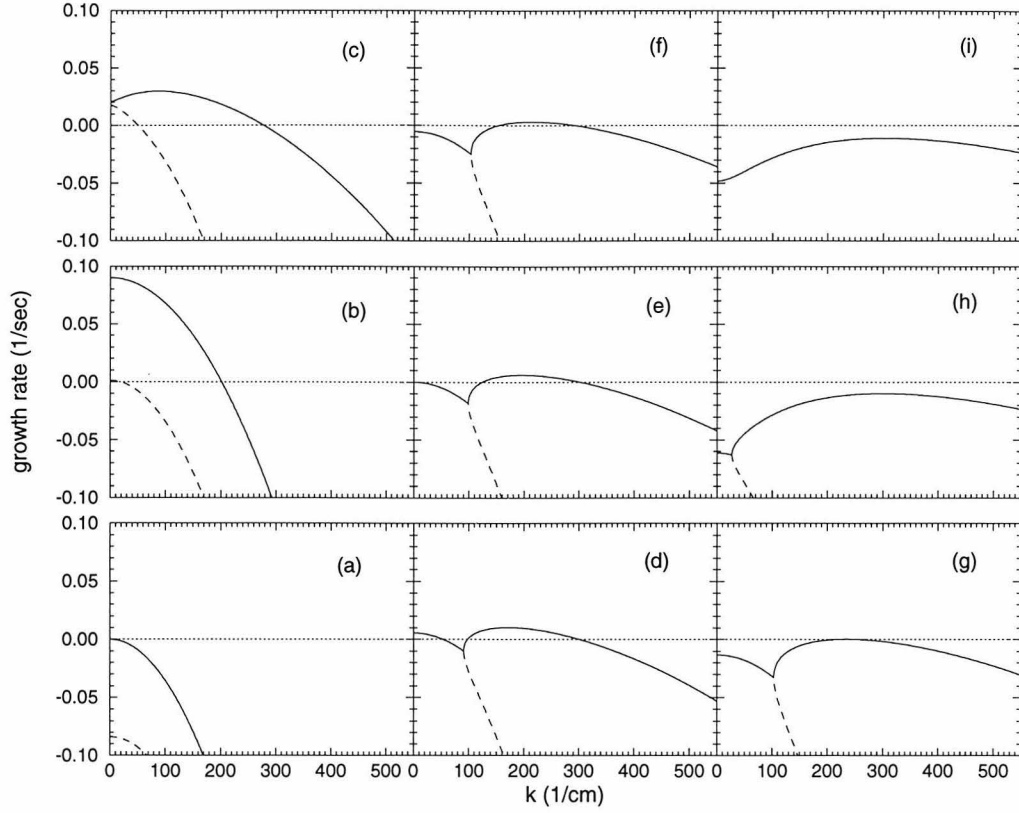


Figure 5.6: Gain curves for locally uniform steady states: The solid line denotes the eigenvalue with the larger real part, λ_+ , and the dashed line denotes the one with the smaller real part, λ_- . At (a) $z = 0.20$, both eigenvalues are real and negative for all k ; (b) $z = 0.50$, both eigenvalues are real and peaked at $k = 0$, with $\lambda_+ > 0$ in the range $0 < k^2 < k_+^2$ and $\lambda_- > 0$ in the range $0 < k^2 < k_-^2$ ($k_{\pm}^2$ given in Appendix A); (c) $z = 0.62$, both eigenvalues are still real, but at $k = 0$, we have a real degenerate pair, giving the boundary of the Hopf bifurcation; (d) $z = 0.70$, complex conjugate pair of eigenvalues with positive real part for $0 < k^2 < (a_{11} + \sigma a_{22})/(\sigma D_v + D_u)$, and $k \neq 0$ instability for $k_-^2 < k^2 < k_+^2$; (e) $z = 0.72$, same as (d), except that the real part of the complex conjugate pair is peaked at zero growth rate; (f) $z = 0.74$, same as (d) with the real part of the complex conjugate pair less than zero at $k = 0$; (g) $z = 0.76$, same as (f), except that the maximum growth rate for $k \neq 0$ is zero, giving the boundary of the symmetry breaking stationary instability; (h) $z = 0.80$, same as (g), except that the maximum growth rate for $k \neq 0$ is negative; (i) $z = 0.85$, both eigenvalues are real and negative.

5.1.2.3 Modified local analysis

The locally uniform analysis neglects diffusion along z which couples the quasi-two-dimensional uniform slices. Lengyel, Kadar and Epstein (LKE) [30] have proposed a modification to account for this diffusion, assuming that diffusion along z is relevant only on a length scale of the order of the Turing wavelength. The basic idea behind the LKE modification is simple. In the presence of gradients in the z -direction, the Turing unstable mode is “split” between its “longitudinal” (along z) and “transverse” dependence:

$$k_c^2 = k_z^2 + k_\perp^2, \quad (5.1)$$

where k_c is the critical wavenumber in the (narrow) Turing unstable region along z , depending only on the local values of reaction and diffusion parameters. A transverse instability can occur provided the width of this region is not smaller than a Turing wavelength (in which case the instability eigenvector along z would also be confined to this region, giving $k_z^2 > k_c^2$).

This modified local analysis is used to better predict the region along the gradients where transverse Turing patterns form, and to obtain more accurately parameter values for investigating (transient) Turing patterns in batch reactors. The mechanics of the modification consists of adding an approximate term to the governing equations for the diffusion of the steady state along z , which does not alter the composition of locally uniform steady state but does affect its stability. A three-point finite difference approximation to the diffusion operator in the z -direction is used:

$$\frac{\partial^2 u}{\partial z^2} \approx \frac{u(z - \frac{\Delta}{2}) - 2u(z) + u(z + \frac{\Delta}{2})}{(\frac{\Delta}{2})^2} \approx \frac{8(\bar{u} - u(z))}{\Delta^2}, \quad (5.2)$$

where $\bar{u}$ is the average value of the locally uniform steady state on the two sides of the region Δ . The validity of this estimate relies on the smallness of the width Δ of this region. The reaction terms f and g are modified:

$$f'(u, v; \vec{\mu}(z)) = f(u, v; \vec{\mu}(z)) + 8D_u((\bar{u} - u(z))/\Delta^2),$$

$$g'(u, v; \vec{\mu}(z)) = g(u, v; \vec{\mu}(z)) + 8D_v((\bar{v} - v(z))/\Delta)^2,$$

and the Jacobian of the reaction terms in the linear stability analysis is modified accordingly. The Turing condition (2.10) is automatically satisfied here, and condition (2.9) can be written as:

$$K' > -a_{11}/a_{22} - 1 \equiv H_1. \quad (5.3)$$

Combining Eqs. (2.11) and (2.12) we get:

$$-a_{11}/a_{22} - 1 > -\frac{a_{11}}{2\sqrt{c(a_{11}a_{22} - a_{12}a_{21}) - ca_{11}}} - 1 \equiv H_2 > \frac{1}{c} - 1 \quad (5.4)$$

where a_{ij} are obtained from the modified reaction terms. The range of the Turing instability is given by the crosspoints of K' and H_1 and of H_1 and H_2 :

$$K'(z) > H_1(z) > H_2(z) \quad (5.5)$$

Since a_{ij} depend on Δ which is a priori unknown, we evaluate H_1 and H_2 iteratively from an initial estimate for Δ until convergence is achieved.

Fig. 5.7 shows that the effect of this modification is to extend the z -range of the transverse instability from approximately one to two Turing wavelengths. These boundaries, given by the functions $K'(z)$, $H_1(z)$ and $H_2(z)$, are combinations of the boundaries given in Fig. 5.5 which resulted straightforwardly from the linear instability conditions. Therefore, although the representation of the boundaries in Fig. 5.5 differs from that in Fig. 5.7, the instability region is the same in the unmodified case.

The proposed modification increases the range of the Turing instability by suppressing the homogeneous oscillatory instability (moving the left boundary to the left), while not affecting the right boundary corresponding to the inhomogeneous instability. Identifying the left boundary of the z -range in which transverse patterns would form with the homogeneous instability is unphysical, since there is no mixing of modes at the linear level. Instead, it seems more appropriate to identify the left

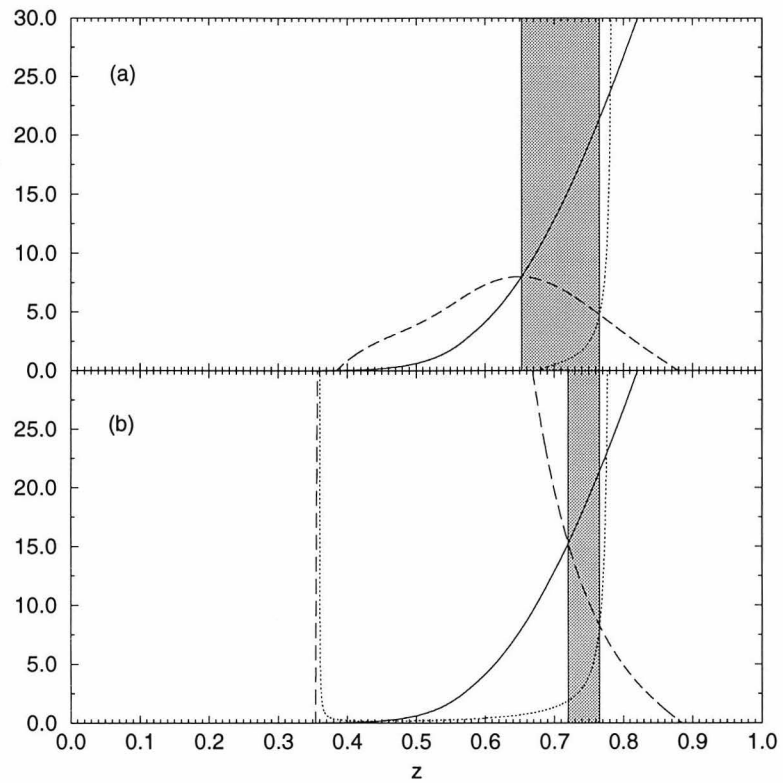


Figure 5.7: Modified local stability analysis: K' , H_1 and H_2 are given by the solid, long-dashed and dotted lines respectively. In (a), these boundaries have been modified to take into account the gradients along z , whereas in (b) they are unchanged. The Turing instability region is indicated by the shading. The shaded region in (b) is identical to that in Fig. 5.5. Note that the right boundary of the Turing region, which denotes $k \neq 0$ criticality, remains unchanged under the modification.

boundary of the Turing region with the z -location where an inhomogeneous instability ceases to exist ($ca_{11} + a_{22} = 0$).

An alternate modification to the local analysis is to carry out the linear stability analysis about the nonuniform steady state along z , such that the diffusion operator in the governing equations acts only on the steady state and not on the instability eigenvector in the z -direction. This “local” analysis incorporates the effect of diffusion along z through the nonuniform steady state, but the instability eigenvectors are “local” and depend only parametrically on z . The resulting eigenvalue problem becomes:

$$\begin{pmatrix} (a_{11}(z) - k^2)/\sigma & a_{12}(z)/\sigma \\ a_{21}(z) & a_{22}(z) - ck^2 \end{pmatrix} \begin{pmatrix} \delta u_k(z) \\ \delta v_k(z) \end{pmatrix} = \lambda_k(z) \begin{pmatrix} \delta u_k(z) \\ \delta v_k(z) \end{pmatrix}, \quad (5.6)$$

where $a_{ij}(z)$ are evaluated at the nonuniform steady state, and $(\delta u_k(z), \delta v_k(z))$ and $\lambda_k(z)$ depend parametrically on z . The stability boundaries are very irregular and not shown in this case. Except at the sharp edges of the nonuniform steady state and over a region roughly equal to the width of the sharp edge (much smaller than a Turing wavelength), this analysis predicts no $k \neq 0$ instability.

5.1.3 Discussion

We conclude that to accurately predict the formation and location of the Turing instability region, at least the one-dimensional steady state along the gradients must be solved for numerically using the full model including longitudinal diffusion. A “local” stability analysis about this steady state does reproduce the result of the fully nonuniform stability analysis which showed the steady state to be stable. However, we have not shown that such a “local” stability analysis based on the steady state which includes diffusion is successful in finding the instability region, since our choice of boundary conditions and reaction parameters has produced a completely stable state. The fact that a local analysis neglecting longitudinal diffusion does not correctly describe the linear stability of stationary localized structures in the presence

of parameter ramps has been recognized [41, 42], yet it is still widely referred to in the literature [30, 31]. As has been suggested [34], two-dimensional numerical integration of the full model with fixed boundary conditions in the direction along the gradients and no-flux (or periodic) boundary conditions in the transverse direction is the definitive method for predicting an instability. This is accomplished in Sec. 5.4.

The locally uniform steady state profiles for the two dynamical variables I^- and ClO_2^- (Fig. 5.4) do not include diffusion along the z direction and are qualitatively different from the numerical solution including diffusion (Figs. 5.1(d), (e)). Hence, it is not surprising that the local stability analysis about this steady state does not agree with the full stability analysis about the steady state which includes diffusion along the gradients. In particular, at the left boundary, the locally uniform ClO_2^- profile is several orders of magnitude greater than the corresponding numerical solution including diffusion. This large discrepancy is accounted for by the diffusion of this species in a region extending over approximately the left half of the gel, which can be seen from the almost linear (diffusive) profile for ClO_2^- over this region (Fig. 5.1(e)). The LKE modification to the locally uniform analysis, which corrects for this diffusion of the steady state along z , assumes that it is relevant only on the length scale of the order of the Turing wavelength. For the parameter values investigated here, this assumption is not valid, and the modified stability analysis does not correctly predict the stability of the structures along the gradients.

The dependence of the locally uniform steady state profiles for the intermediate species on the background concentration gradients is through the reaction terms. The results presented here are for background profiles obtained from reaction and diffusion of all six species. We have checked that these background stationary profiles do not vary considerably from those obtained by setting the intermediate species identically equal to zero. In this way, we rule out the possibility that the diffusion of the intermediate species feeds back into the profiles of the background variables, thereby accounting for the large discrepancy between the locally uniform steady state profiles of the intermediate species and those including diffusion. In particular, the large left boundary value of the locally uniform ClO_2^- species results from the strong suppres-

sion of I_2 relative to ClO_2 at this boundary, which becomes even more pronounced with backgrounds obtained from the intermediate species set identically equal to zero.

Numerical calculations based on the two-variable LRE model with uniform background have shown the transition to a symmetry-breaking instability to be strongly subcritical [43, 44]. In a subcritical (supercritical) transition, the uniform steady state is unstable (stable) for values of the control parameter greater (less) than the critical value, and is stable (unstable) for values of the control parameter less (greater) than the critical value. Although it is not clear how the range of parameters investigated in these works compares with their local values in the actual ramped experimental system or in our numerical example, these results imply that a *linear* stability analysis of the locally homogeneous steady states would not predict the existence of a finite amplitude instability in the subcritical regime. The nature of the transition of the fully nonuniform stationary structures along the ramps to a transverse symmetry-breaking instability has not been determined yet (see Sec. 5.4). Should this transition be supercritical, the fully nonuniform linear stability analysis would accurately predict the formation of quasi-one-dimensional symmetry-breaking spots in the thin-strip experiments.

Dewel *et al.* [45] have used a WKB-like approach to solve for the localized one-dimensional steady states in the presence of slow spatial gradients in the Brusselator model. The structures along the gradients are obtained as marginally stable perturbations to the locally uniform steady state. It is desirable to obtain such a semi-analytic solution here as well. However, in this case, it is difficult to do so. First, there is a large discrepancy at the boundaries between the locally uniform solution and the desired solution including diffusion satisfying Dirichlet boundary conditions. Even if the boundaries are ignored and an approximate solution in the interior of the gel is sought, our numerical results show that the steady state including diffusion is not a weakly nonlinear perturbation to the locally uniform steady state. Therefore, seeking a correction given by marginally unstable modes is not justified.

To summarize, the nonuniformity of background chemicals imposed by the boundary feeds in these experiments has important consequences for pattern formation. We

find that these background concentration profiles seriously affect the stability of the nonuniform steady state. The straightforward assumption implicit in a local analysis is that diffusion along the gradients is unimportant (on length scales longer than the Turing wavelength), and a transverse pattern will form in the region along z where the corresponding uniform problem is unstable to the Turing instability. Our results show this assumption to be invalid. For the parameter values and boundary conditions investigated here, we find diffusion of the dynamical variables along the background gradients to be important over much longer length scales. Hence, a local linear analysis is inappropriate in such cases.

5.2 Parameter Dependence of the Turing Instability in the Ramped CDIMA System

As discussed in the previous section, existing numerical studies of the stability of the stationary patterns along feed gradients have not fully taken into account the reaction+diffusion feed gradients by adopting a locally-uniform approach [34]. Thus, the parameter range for the occurrence of the transverse symmetry-breaking instability in a gradient system within the context of the LRE model is essentially unknown. Hence, we have undertaken a systematic search, using the concentration of one of the reservoir species and the gel width as the control parameters. Variation of either of the control parameters changes the nonlinear reaction+diffusion profile of the background species, however they are not equivalent operations. In the following sections, we present our numerical results and make connection with relevant experimental work.

5.2.1 Variable malonic acid boundary condition

The parameter search for the Turing instability in the CDIMA reaction-diffusion system as a function of the malonic acid concentration at the left boundary was performed for $[\text{MA}]_L$ in the range 0.004 M to 0.035 M. The concentrations of $[\text{I}_2]_R$ and $[\text{ClO}_2]_R$ at the right boundary were held fixed at 0.008 M and 0.006 M, respectively. These values were chosen so as to lie within the range of the initial concentrations of these species used in experiments on this system in batch reactors [32], and therefore should also be experimentally accessible in open reactors.

First, we numerically obtained steady state solutions of the full 7-variable governing equations as a function of $[\text{MA}]_L$, as described in Sec. B.1. The analysis described in Section 5.1.2.1 of the linear stability along the gradients to transverse symmetry-breaking perturbations was repeated for each stationary state. This was performed using the reduction of the full LRE model to the two dynamical variables I^- and ClO_2^- . The eigenvalue and eigenvector corresponding to the fastest growing

(or slowest decaying) mode at each value of the transverse wavenumber k were obtained numerically using inverse iteration, and confirmed for select values of k using EISPACK [40]. In Fig. 5.8, we have plotted the value of the control parameter $[MA]_L$ versus wavenumber, with the solid boundaries denoting marginally stable wavenumbers. The shading indicates the Turing-unstable regions. We note that the unstable regions are disjoint, corresponding to the following scenario: as the control parameter is continuously varied, the stable stationary state along the gradients first becomes unstable to transverse Turing patterns at a critical value of the control parameter, and initially remains unstable as the control parameter continues to increase. It becomes stable again once the control parameter exceeds a second and higher critical value. This is qualitatively consistent with the experimental observations of Perraud *et al.* [19] on the CIMA reaction-diffusion system. Their results (see Fig. 3.2) show that as the concentration of $[ClO_2^-]_R$ at the right boundary is increased from that of Fig. 3.2(a) to that of Fig. 3.2(b), the number of alternating dark and bright bands parallel to the feed boundaries increases, and several layers break up into rows of spots. As $[ClO_2^-]_R$ continues to be increased, the spot patterns develop along more bright bands (Fig. 3.2(c)), until they eventually disappear and the parallel stripes are recovered. In these experimental photos, the dark and light colors correspond to high and low SI_3^- concentrations. Hence, we note that the symmetry-breaking instability to spots is experimentally observed at low SI_3^- concentration.

In Fig. 5.9, we have plotted the stationary solutions for the experimentally observed SI_3^- species from our numerical calculation, at various values of $[MA]_L$. We note that the number of peaks in the steady state solution increases with increasing $[MA]_L$, while the characteristic “wavelength” of the patterns along the gradients remains relatively constant (excluding the large leftmost peak). The transition from one unstable region to another corresponds roughly to the appearance of an additional peak in the stationary solution along the gradient (instability region I corresponds to a steady state with three peaks, region II corresponds to four peaks, and region III corresponds to five peaks). For the instability regions I, II and III, we show density plots of the steady state and the fastest growing (slowest decaying) wavevector in

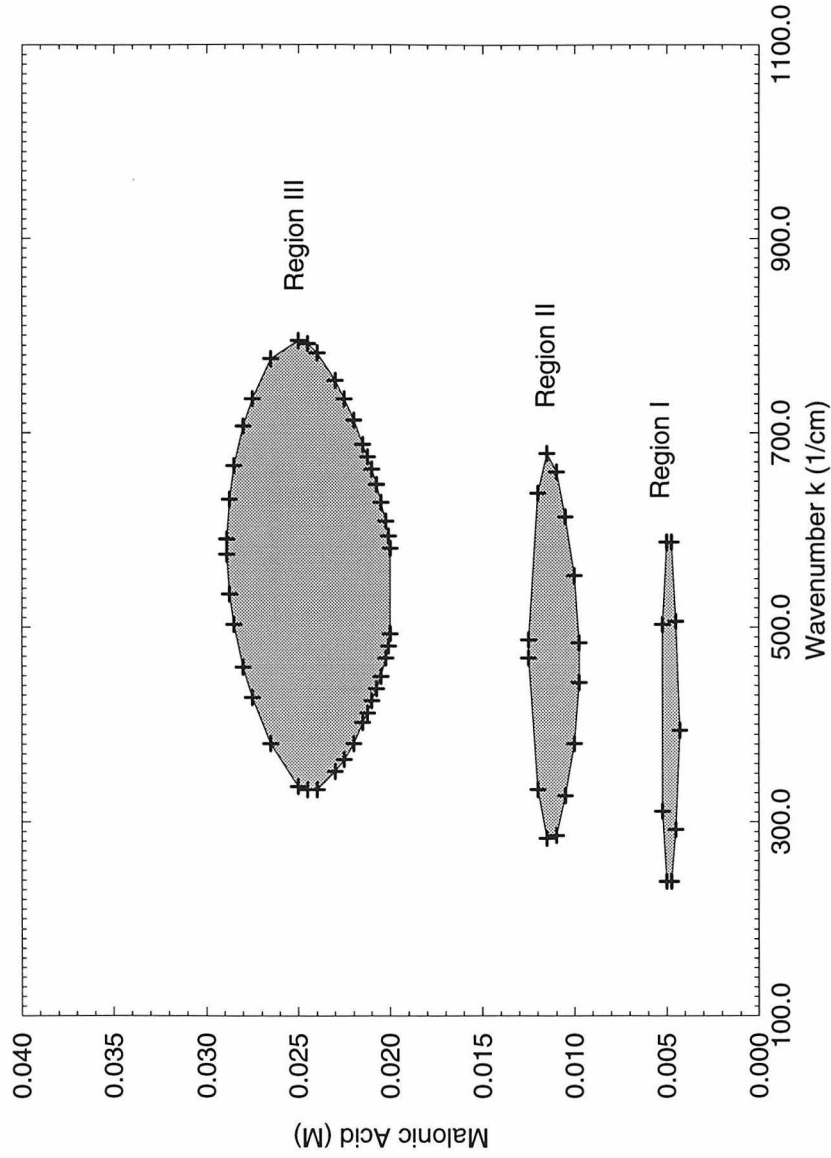


Figure 5.8: Malonic acid concentration (M) at the left boundary versus the wavenumber k of the transverse instability ($1/\text{cm}$): The crosses represent the marginally stable wavenumbers determined from the stability analysis of the one-dimensional steady states corresponding to the given malonic acid feed concentration. A transverse instability occurs for values of malonic acid feed concentration in the shaded regions, with the range of linearly unstable modes delimited by the solid lines for each value of $[\text{MA}]_L$.

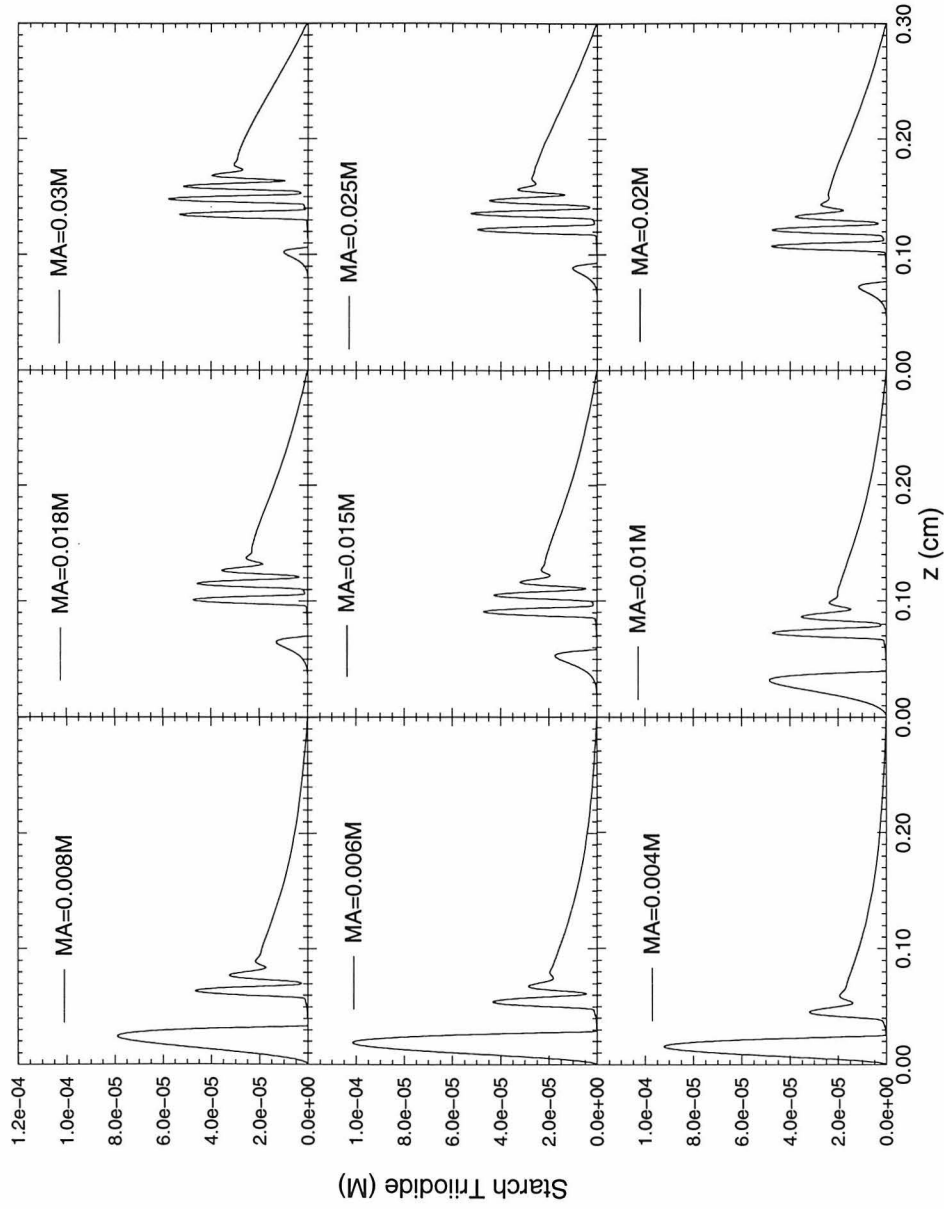


Figure 5.9: Stationary solution for $[SI_3^-]$ along feed gradients for various values of malonic acid feed concentration at the left boundary: This series of plots shows how the stationary state along the gradients changes as $[MA]_L$ is varied. The number of peaks in the solution increases with increasing malonic acid concentration, while the left-most peak becomes smaller. The minima correspond to light bands in the experimental results. Instability region I corresponds to stationary states with three peaks, region II with four peaks and region III with five peaks.

Figs. 5.10, 5.11, and 5.12. In each case, this eigenvector is localized at and roughly tracks one of the minima in the steady state solution. Specifically, the unstable vector appears to be approximately localized at the next-to-last minimum of the SI_3^- solution. The appearance of the symmetry-breaking instability at the minimum of the stationary state is consistent with the experimental observations discussed above.

To better quantify this trend, in Fig. 5.13, we plot the value of all seven chemical species at successive minima of the SI_3^- stationary solution as a function of $[\text{MA}]_L$. In this figure, the circles, triangles, squares and diamonds correspond to the second, third, fourth and fifth minima, respectively. The points corresponding to critical $[\text{MA}]_L$ values are filled (two points for each unstable region). We note that the relevant chemical species for tracking the instability between the disjoint regions in parameter space, are the two dynamical species, I^- and ClO_2^- , plotted in Fig. 5.13(d) and (e). (The SI_3^- concentration depends on the product of the I^- and I_2 concentrations.) The concentration of I^- remains within the range of approximately $(1.0 - 2.2) \times 10^{-7} \text{M}$, and the concentration of ClO_2^- remains approximately constant at 1×10^{-6} in each of the instability regions. (Note that the concentration of SI_3^- does not stay within a more-or-less constant range for each of the instability regions due to the drift in the I_2 concentration.) A simple interpretation of these numerical results is that the instability occurs when the concentrations of the dynamical species I^- and ClO_2^- are within a certain range. As the stationary solution changes with increasing $[\text{MA}]_L$, the instability vanishes when the value of the concentration of the steady state falls outside of this range, and reappears when the concentration at the *next* minimum is within this range again.

The experiments of Perraud *et al.* [19] show that as the control parameter is increased, the stationary pattern of stripes along the gradients first becomes unstable in a single stripe region and then in multiple stripes as the control parameter continues to increase. In our numerical investigations, the most unstable vector remains singly peaked in all cases. To further investigate this point, we have looked at the spatial structure (along z) of the linear instability eigenvectors as a function of k . Fig. 5.14

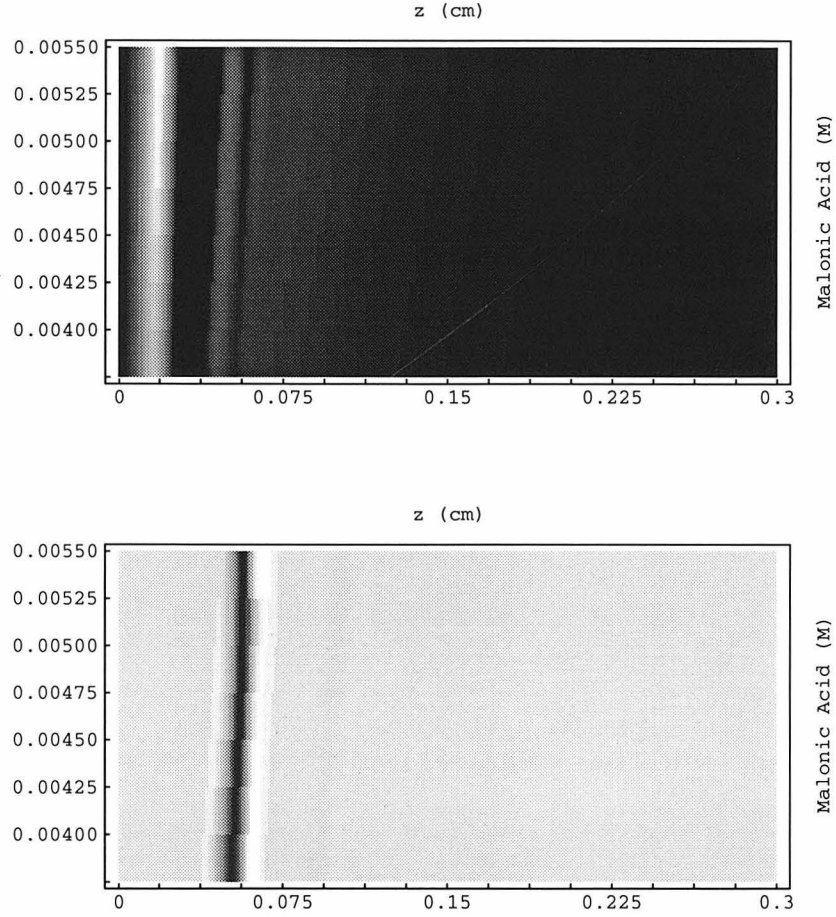


Figure 5.10: Density plots of the stationary solution along the gradients and the fastest-growing instability eigenvector for region I: White and black correspond to large and small values of the solution, respectively. The top plot shows the variation of the stationary state in region I with increasing $[\text{MA}]_L$. The bottom plot shows how the most linearly-unstable eigenvector is singly peaked and tracks the next-to-last minimum in the solution. (It is difficult to discern the *last* minimum in the top plot.) The “staircase” structure is due to the discrete sampling of $[\text{MA}]_L$.

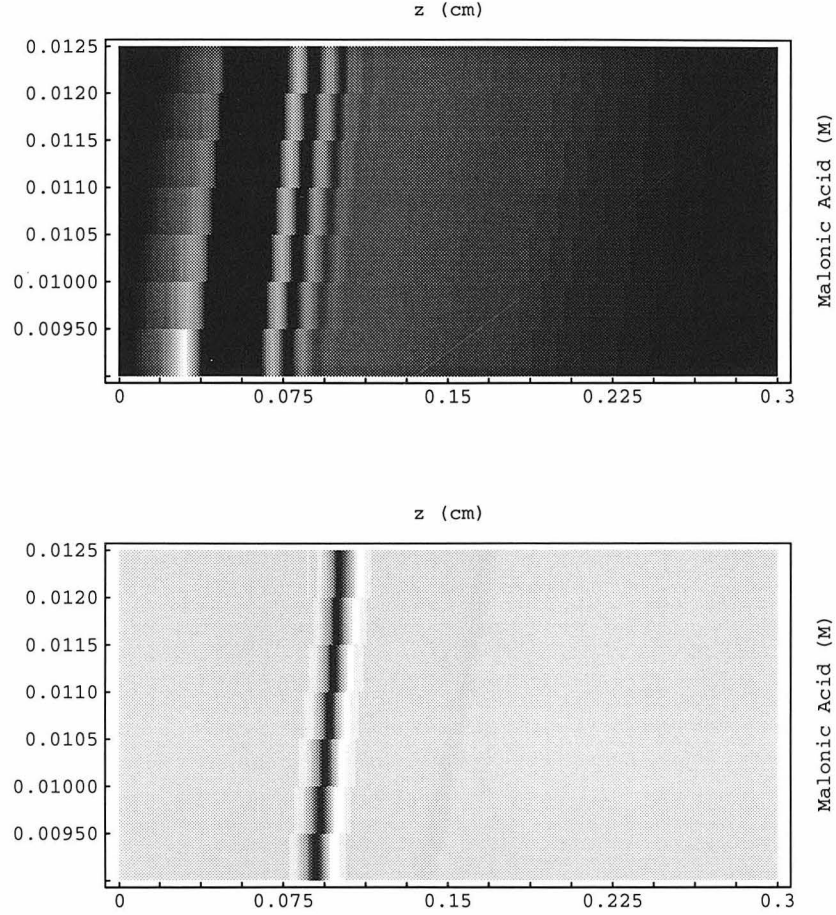


Figure 5.11: Density plots of the stationary solution along the gradients and the fastest-growing instability eigenvector for region II: White and black correspond to large and small values of the solution, respectively. The top plot shows the variation of the stationary state in region II with increasing $[\text{MA}]_L$. The bottom plot shows how the most linearly-unstable eigenvector is singly peaked and tracks the next-to-last minimum in the solution. (It is difficult to discern the *last* minimum in the top plot.) The “staircase” structure is due to the discrete sampling of $[\text{MA}]_L$.

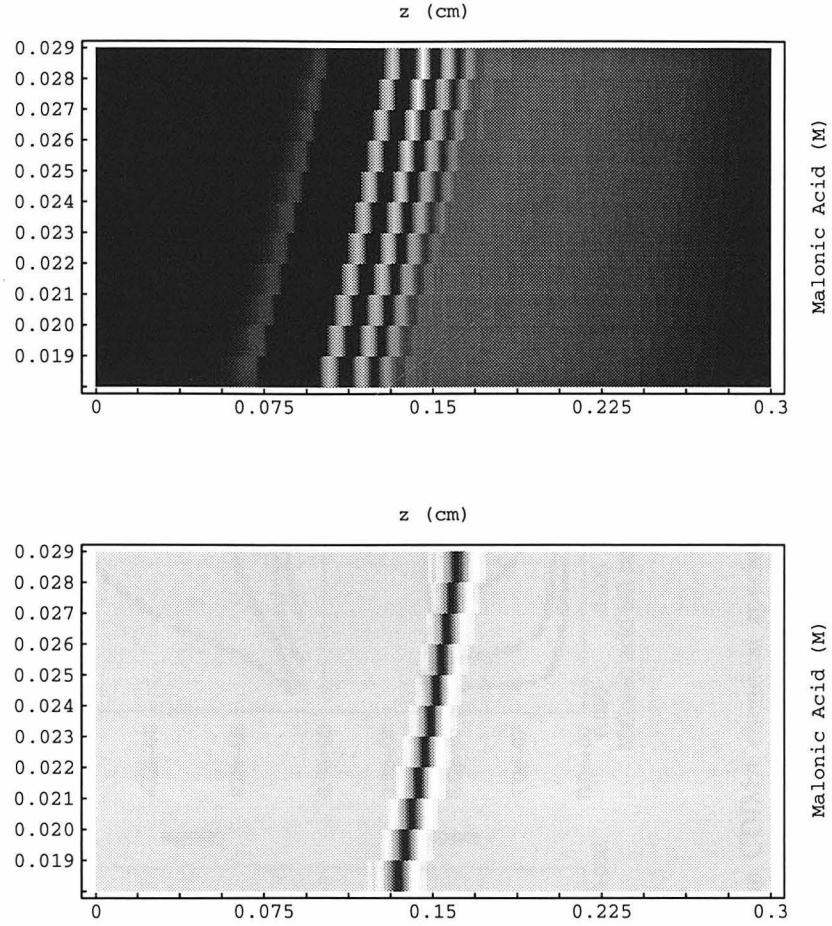


Figure 5.12: Density plots of the stationary solution along the gradients and the fastest-growing instability eigenvector for region III: White and black correspond to large and small values of the solution, respectively. The top plot shows the variation of the stationary state in region III with increasing $[\text{MA}]_L$. The bottom plot shows how the most linearly-unstable eigenvector is singly peaked and tracks the next-to-last minimum in the solution. (It is difficult to discern the *last* minimum in the top plot.) The “staircase” structure is due to the discrete sampling of $[\text{MA}]_L$.

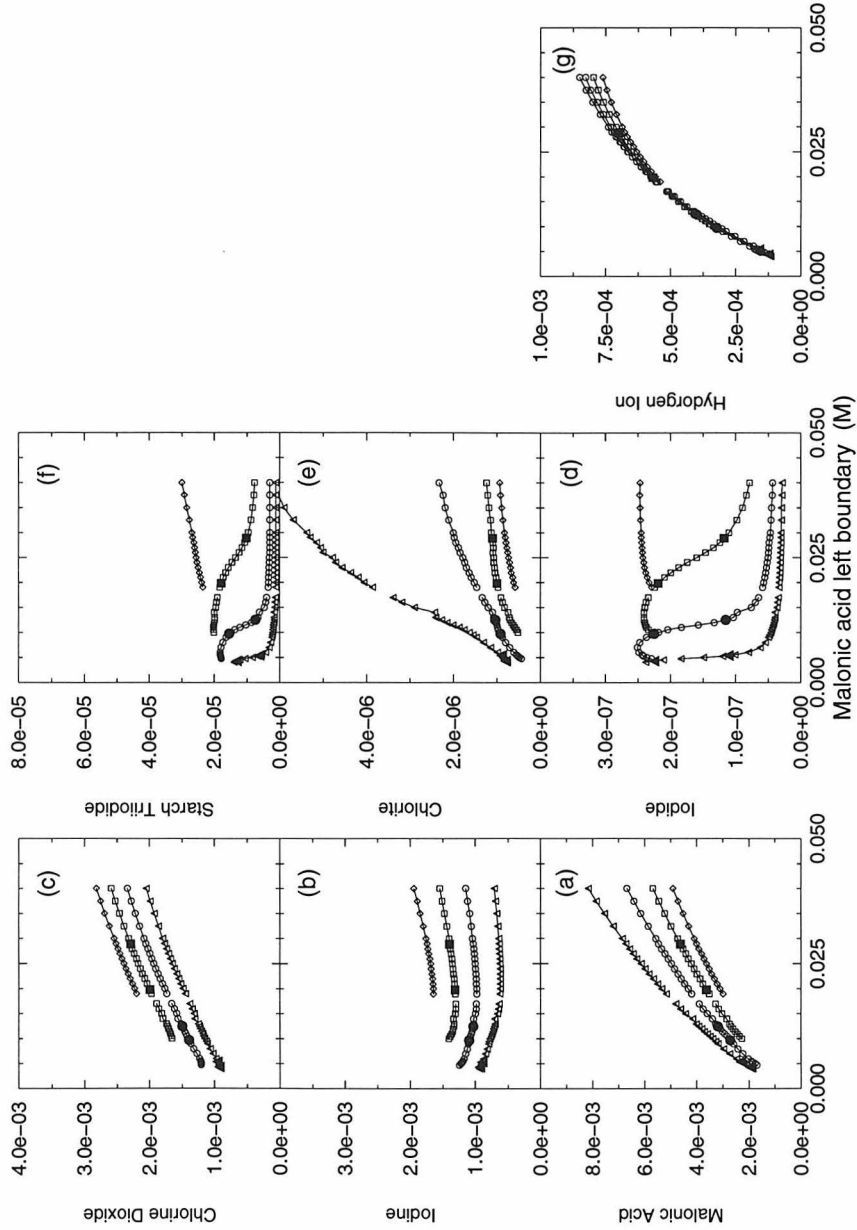


Figure 5.13: Values of stationary profiles of the CDIMA chemical species at successive minima of the stationary $[SI_3^-]$ solution as a function of $[MA]_L$: The open triangles, circles, squares and diamonds represent the second, third, fourth and fifth minima, respectively. The filled symbols correspond to the critical values of $[MA]_L$; the points between the filled symbols correspond to the linearly unstable states. We note that the instability occurs successively along the second, third and fourth minima. Although the values of $[MA]$, $[I_2]$, $[ClO_2]$ and $[H^+]$ in the unstable ranges continue to increase as functions of $[MA]_L$ in going from one instability region to the next, the trend for the dynamical species $[I^-]$ and $[ClO_2^-]$ is different: the value of $[ClO_2^-]$ remains approximately constant, while $[I^-]$ varies within an approximately constant range.

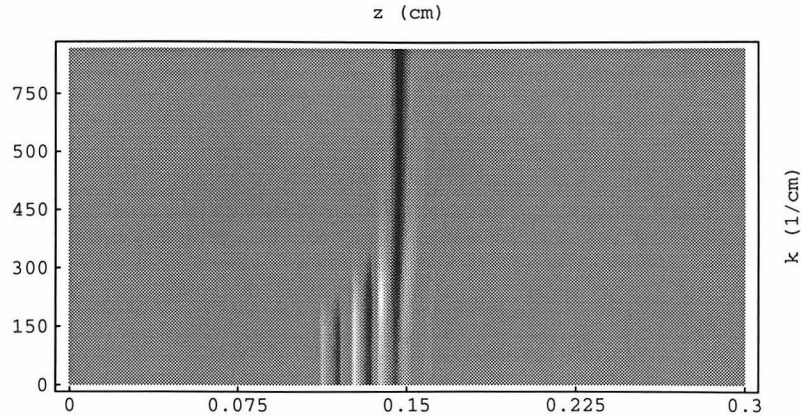


Figure 5.14: Density plot of the iodide eigenvector corresponding to the largest eigenvalue as a function of the transverse wavenumber k and spatial distance along the gradients ($[MA]_L = 0.023$ M): Black and white correspond to low and high values of the eigenfunction, respectively. For small values of k , the eigenvector is multiply peaked while for k larger than approximately 300 cm^{-1} , which includes the unstable range of wavenumbers, it is singly peaked.

shows a density plot of the most unstable (or least stable) eigenvector, corresponding to the I^- species, as a function of transverse wavenumber k for $[MA]_L = 0.023$ M. The horizontal axis represents the spatial coordinate along the gradients, and the vertical axis is the transverse wavenumber, ranging from $k = 0 \text{ cm}^{-1}$ to $k = 900 \text{ cm}^{-1}$. As a different representation, in Fig. 5.15, we have plotted, as a function of z , the eigenvectors corresponding to the two largest growth rates at various values of k : the solid line gives the fastest growing vector, and the dotted line gives the slowest decaying vector. The growth rate corresponding to these two vectors are real for all k .

In Fig. 5.16, we show the first fourteen eigenvalues with largest real parts as a function of k . We note the eigenvalue crossings that define distinct “modes” cutting across the spectrum of eigenvalues. As an interesting aside, we have investigated the eigenvectors corresponding to one such “mode”, denoted by filled triangles in Fig. 5.16. The spatial profile of these eigenvectors changes continuously with increasing k . Hence, their interpretation as a single physical “mode” is not obvious. There does not appear to be a mode crossing between the first and second branches of Fig.

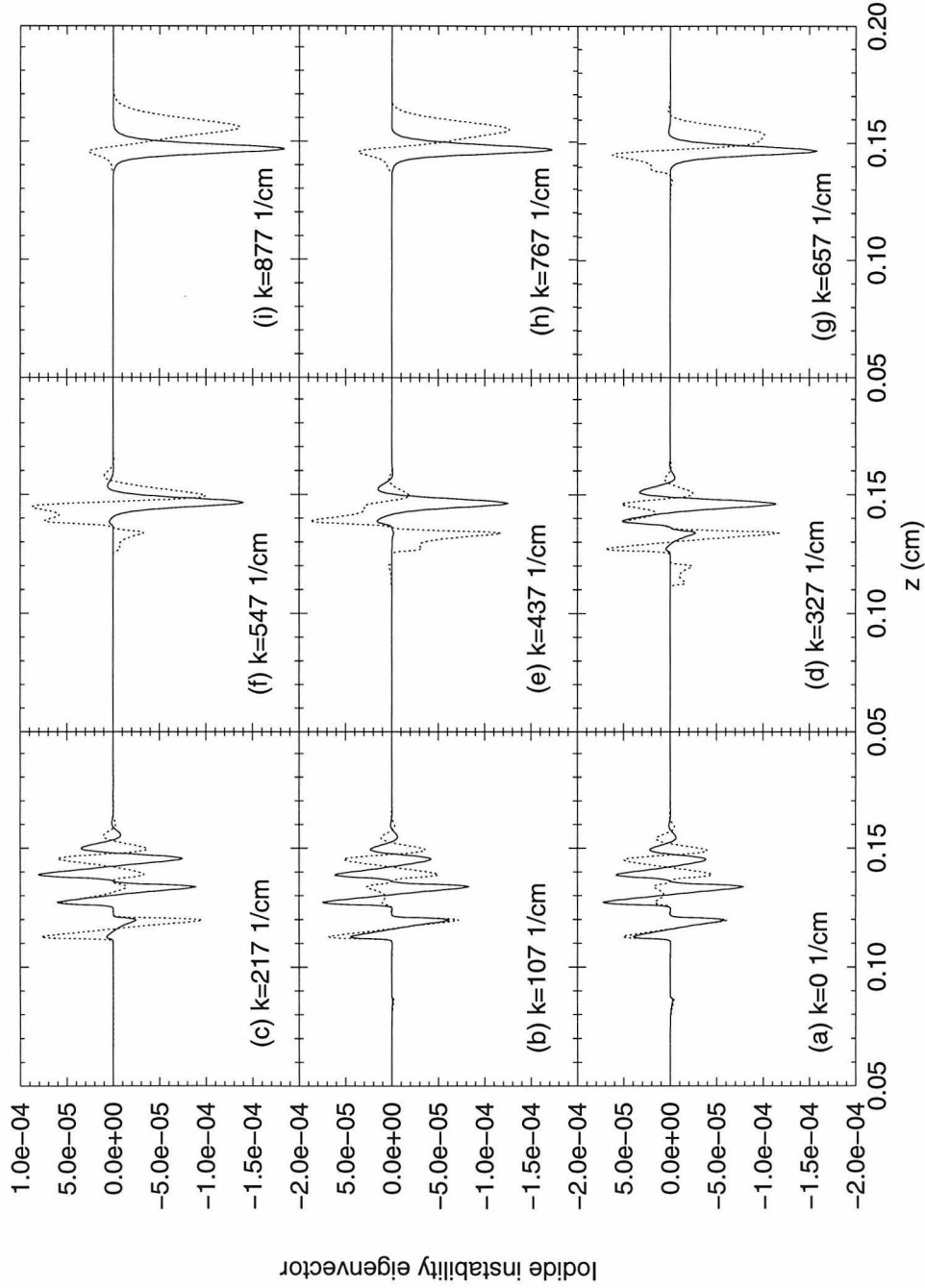


Figure 5.15: Linear stability eigenvectors for the iodide species corresponding to the two largest eigenvalues at various values of k ($[MA]_L = 0.023$ M): The solid line and dotted lines represent the eigenvectors corresponding to the largest and second-largest eigenvalues, respectively. The gel width is 0.3 cm, but the plot range is clipped to emphasize the solution profiles. The fastest growing/slowest decaying eigenvector profiles complement the density plot in Fig. 5.14.

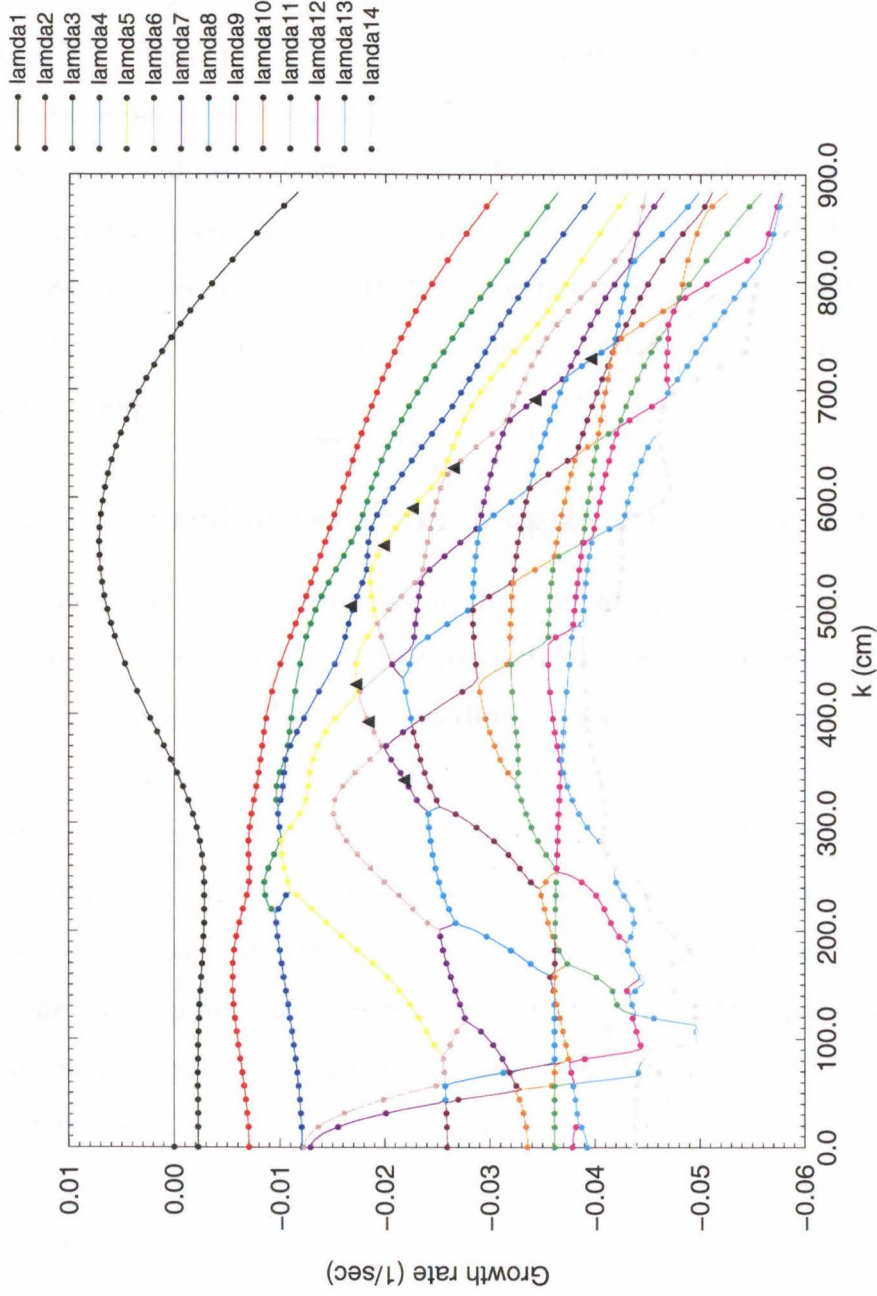


Figure 5.16: Spectrum of eigenvalues for $[MA]_L = 0.023$ M: The real parts of the first fourteen eigenvalues with largest real parts have been plotted. The eigenvalues are real, except along intervals where two curves overlap. Some eigenvalue crossings appear imperfect due to the coarse selection of k values. It appears that the first two eigenspectra do not cross but remain distinct. We note that the eigenvalue crossings define distinct “modes” that cut across the spectrum of eigenvalues. The filled triangles indicate the eigenvalues for one such mode.

5.16, although the structure of the first eigenvector changes considerably from being multi-peaked (and stable) to being singly peaked (and unstable, but subsequently stable again) as k increases. The experiments of Perraud *et al.* could correspond to a case where, as the control parameter is varied, a mode with multiple peaks becomes unstable. This does not occur in our numerical investigation, where the multi-peaked modes remain stable. The appearance of multiple instability layers could also be a nonlinear effect, resulting from linear growth and nonlinear saturation of the singly peaked unstable eigenvector, as well as growth of its side lobes. However, in Sec. 5.4, we will show that in the two-dimensional evolution of the governing equations, the spatial profile of the most linearly unstable mode is in fact preserved in our model.

5.2.2 Variable reservoir length along boundary feeds

Motivated by the experiments of Dulos *et al.* [23] on variable width gel reactors, discussed in Sec. 3.3.1.2, we have undertaken a similar numerical investigation which does not directly address the two-dimensional to three-dimensional transition of the patterns, but rather continues to focus on the localized patterns along the ramps. In particular, we consider the experimental results from the variable-width strip reactor, reproduced in Fig. 3.6. In these experiments, Dulos *et al.* have focused on the transition between the domains with one and two rows of spots, and the possible influence of the feed gradients on the phase relations between the spots in the two rows. The vanishing amplitude of the spot modulations before this splitting occurs is not well understood. Our numerical results address the latter question. We have reproduced the observed qualitative trend of the symmetry-breaking instability occurring and subsequently disappearing in a single layer as the gel width is varied. The boundary conditions are held fixed at $[\text{MA}]_L = 0.023 \text{ M}$, $[\text{I}_2]_R = 0.008 \text{ M}$ and $[\text{ClO}_2]_R = 0.006 \text{ M}$, while the gel width is varied from 0.39 – 0.14 cm. The stationary localized patterns along the gradients as a function of the scaled gel width are shown in Fig. 5.17; Fig. 5.18 gives the linear stability of each solution to a symmetry-breaking instability.

For the parameter values and boundary conditions numerically investigated here, we do not observe the transition from an unstable monolayer to an unstable bilayer as the gel width is increased. In Fig. 5.19, we follow the eigenvector corresponding to the $k \neq 0$ peak of the growth curve as the gel width is varied, and it remains singly peaked. These numerical results are analogous to those presented in Section 5.2.1, where the parameter dependence of the Turing instability in a ramped system was investigated as a function of the malonic acid boundary condition. Here also, we track the concentrations of the chemical species at the location of the minimum of the starch-triiodide complex where the fastest growing/slowest decaying instability eigenvector is localized. The results are given in Fig. 5.20: again, triangles, circles, squares, and diamonds represent the second, third, fourth and fifth minimum, respectively. The solid squares correspond to the critical lengths, below and above which the instability vanishes. We note the following about the concentrations of the chemical species in the unstable interval (at the third minimum of the stationary SI_3^- solution):

- The concentration of ClO_2^- is approximately at 1×10^{-6} M, in agreement with the variable $[\text{MA}]_L$ investigation.
- The concentration of I^- is in the approximate range of $1.8 - 2.2 \times 10^{-7}$ M, again in agreement with the variable $[\text{MA}]_L$ investigation.
- The concentrations of the background species, MA, I_2 and ClO_2 are approximately equal to those in variable $[\text{MA}]_L$ case for region III of Fig. 5.8.

These results confirm the simple interpretation that the concentrations of the dynamical species, the activator I^- and the inhibitor ClO_2^- , are a key factor in the occurrence of a transverse instability. However, this picture may be overly simplified: for values of gel width larger than the upper critical value, the concentration of I^- remains well within the instability interval of the variable $[\text{MA}]_L$ analysis, with the concentration of ClO_2^- remaining approximately the same, while the stationary state remains stable.

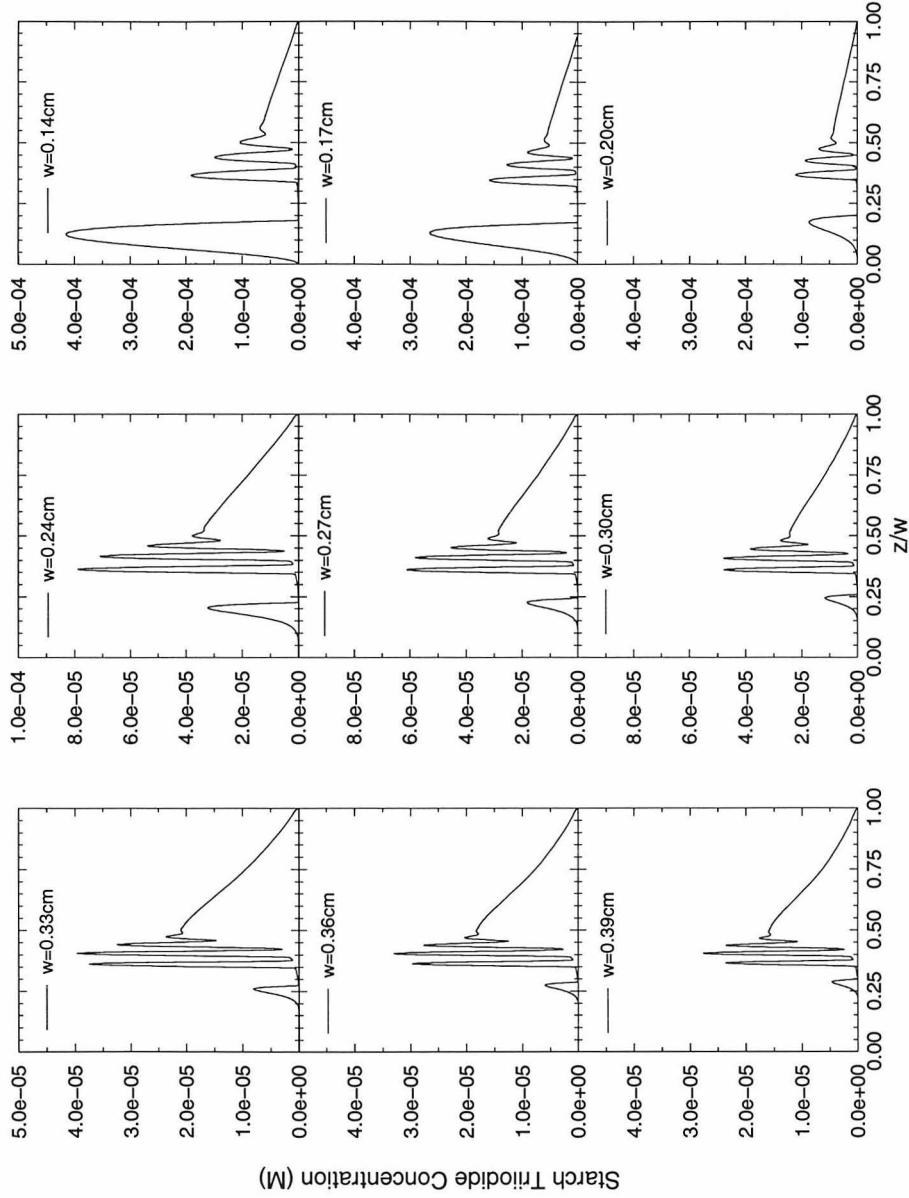


Figure 5.17: Stationary solution for $[Starch\ Triiodide\ Concentration\ (M)]$ along feed gradients for various gel widths: This series of plots shows how the stationary state along the gradients changes as the gel width is varied. The horizontal axis is the scaled length along the gradients. With decreasing gel width, we note: (i) the shifting of the pattern to the right, and (ii) the increase in the concentration scale by approximately an order of magnitude (primarily due to the leftmost peak).

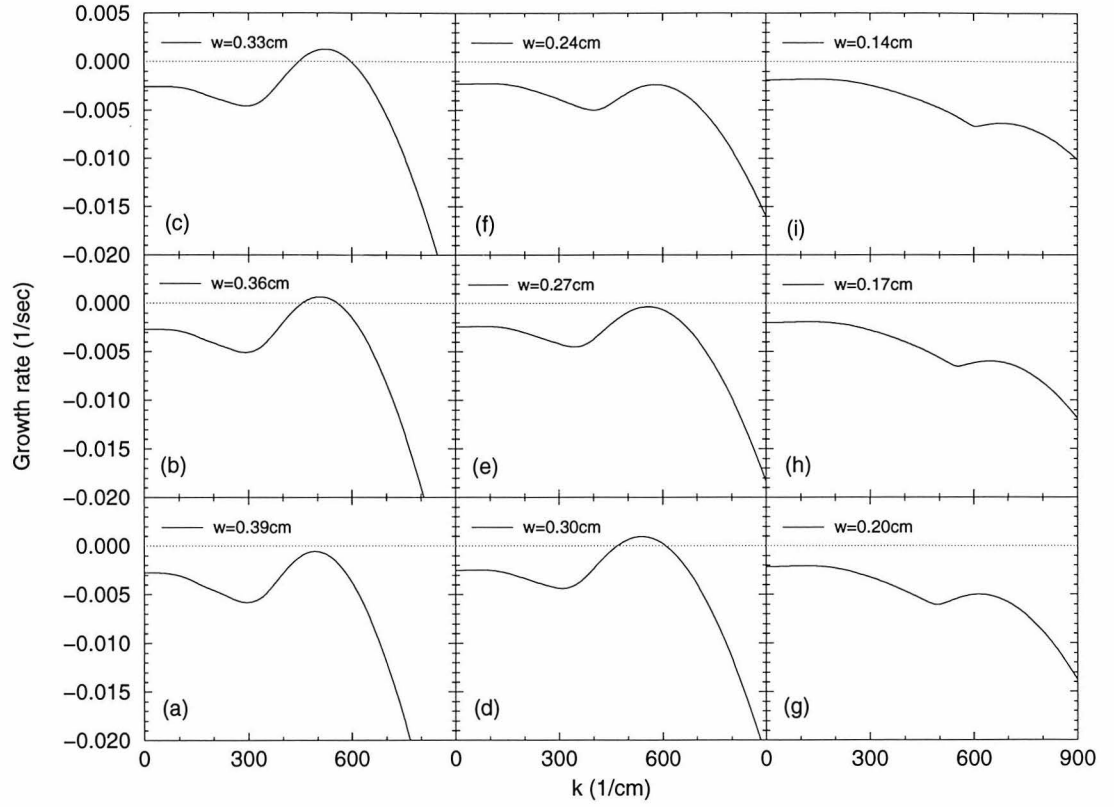


Figure 5.18: Gain curve corresponding to largest eigenvalue for various gel widths: (b)-(d) are unstable; in (g)-(i), the largest eigenvalue now occur at $k = 0$.

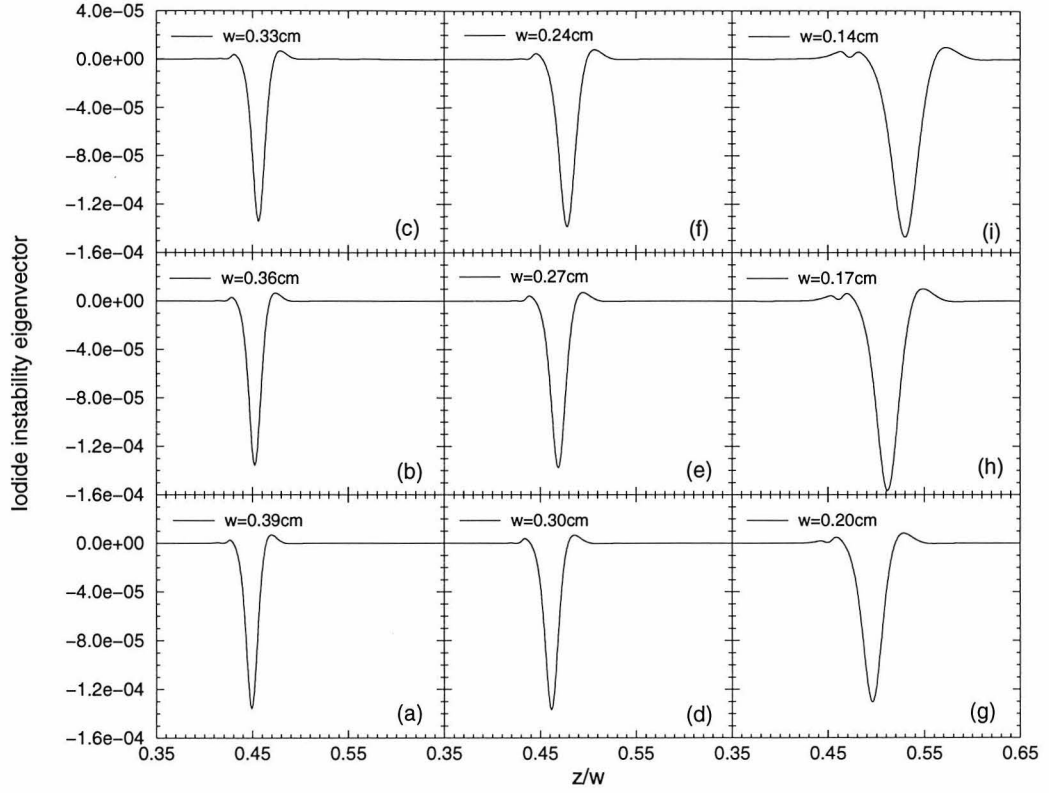


Figure 5.19: Linear stability eigenvector for the iodide species corresponding to the largest ($k \neq 0$) eigenvalue at various gel widths: The horizontal axis is the scaled length, but the plot range is clipped to emphasize the solution profiles. The fastest growing/slowest decaying eigenvector corresponding to $k \neq 0$ remains singly peaked; comparing with Fig. 5.17, it remains localized at the next-to-last minimum of the stationary solution.

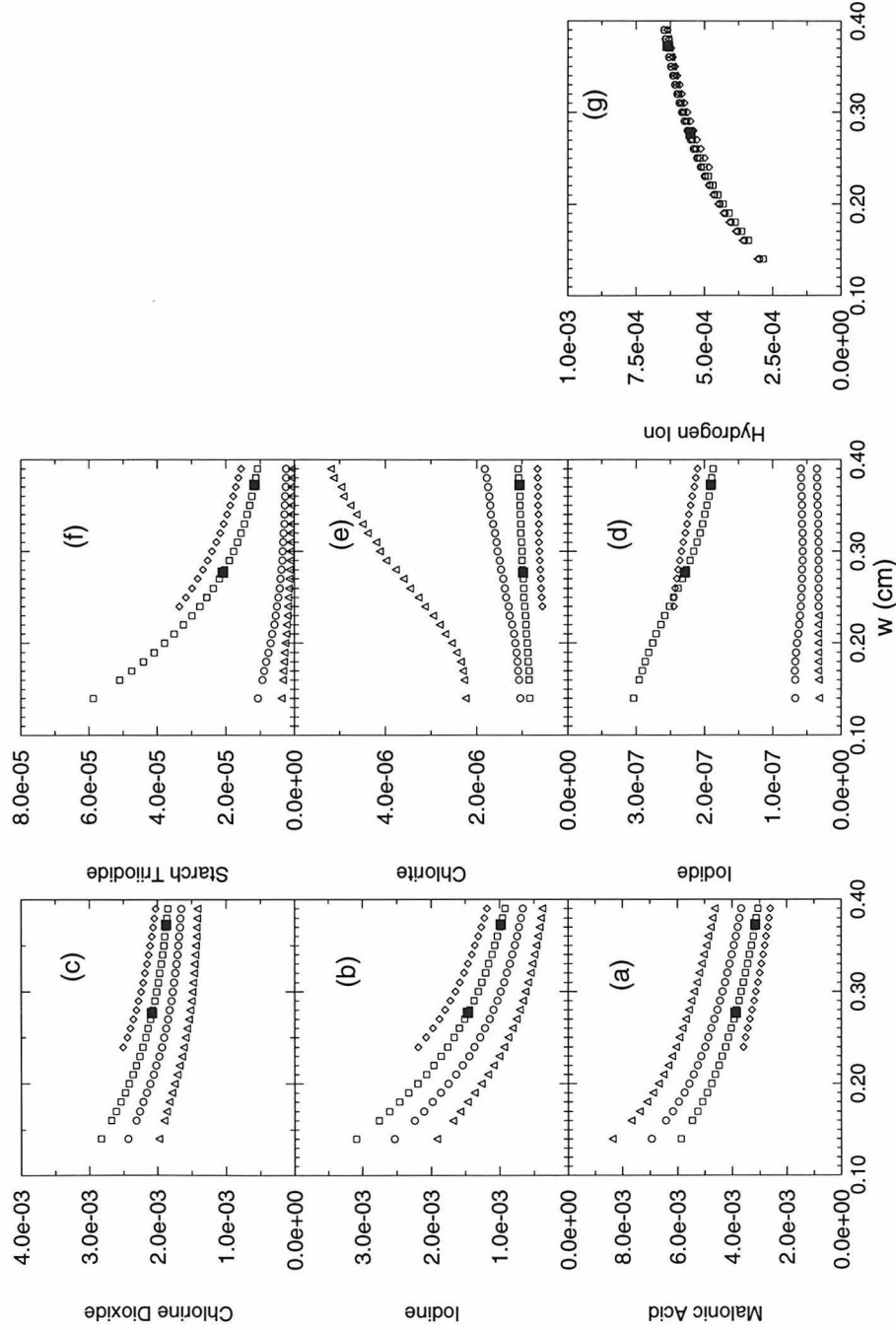


Figure 5.20: Values of stationary profiles of the CDIMA chemical species at successive minima of the stationary $[SI_3^-]$ solution as a function of gel width, w : The open triangles, circles, squares and diamonds represent the second, third, fourth and fifth minima, respectively. The filled symbols correspond to the critical values of gel width; the points between the filled symbols correspond to the linearly unstable states.

5.2.3 Discussion

In the preceding two sections, we have explored the parameter dependence of the Turing instability as a function of malonic acid boundary condition and gel width. Our numerical results, which are based on the LRE model of CDIMA reaction-diffusion system, agree qualitatively with available experiments based on the related CIMA system that adopt a different set of boundary conditions. The agreement between qualitative trends in these experiments and our numerics is encouraging, and will hopefully spark experiments more directly based on the LRE model which could be compared quantitatively with numerical and analytical results.

The choice of the CIMA reaction-diffusion system (as opposed to the CDIMA system) and its and corresponding boundary species (iodide, rather than iodine, and chlorite, rather than chlorine) by the experimenters makes direct comparison of our numerics with their experimental results difficult. However, our numerical simulations display similar features to those present in experimental results as control parameters are varied. These are: (1) the transition to patterns with progressively larger numbers of fronts, and (2) the appearance and subsequent vanishing of the transverse instability. Although the instability is localized near a minimum of the starch triiodide unperturbed solution (as well as that of the iodide) in agreement with experimental results, in our numerical investigations of the CDIMA system, the linear instability eigenvector remains singly peaked, and the observed transition from a single to multiple unstable layers is not obtained. As noted earlier, for the parameters and boundary conditions used in our numerical investigations, the multiply-peaked linear instability eigenvectors remain stable.

5.3 Verification of Two-Variable Reduction of CDIMA Chemical Model

The two-variable reduction of the full LRE model was introduced to render the realistic chemical model for the CDIMA reaction-diffusion system more mathematically tractable, while remaining physically justified [10, 33, 17]. For this reason, the linear stability results presented in Secs. 5.1 and 5.2 are based on the two-variable model. In this section, we examine the assumptions implicit in this reduction. These are:

- adiabatic elimination of the reservoir species, MA, I_2 and ClO_2 , leaving the I^- and ClO_2^- concentrations as the two dynamical variables.
- fast formation/dissociation of starch triiodide complex, such that the concentration of the complex $[SI_3^-]$ is always proportional to that of the iodide $[I^-]$.
- elimination of H^+ , justified by the relatively small magnitude of the reaction terms containing this species.

To investigate the above, we begin with the numerical stationary solution of the full model (including H^+), for the following boundary conditions: $[MA]_L = 0.023M$, $[I_2]_R = 0.008M$, and $[ClO_2]_R = 0.006M$. We study the stability of the full 7-variable system by linearizing about the stationary state and solving the resulting eigenvalue problem for the fastest growing/slowest decaying mode at each transverse wavenumber k using inverse iteration. The results from the stability analysis using inverse iteration are confirmed by time evolution of the linearized equations for select values of k : the largest eigenvalue and corresponding eigenvector are obtained from the average exponential growth of an arbitrary initial vector that is evolved according to the linearized equations and successively renormalized (to prevent overflow/underflow due its exponentially growing/decaying magnitude). The scaled difference, which is better than 2×10^{-9} , is not shown here.

5.3.1 Elimination of the H^+ species

This last point has been addressed earlier in Sec. 4.1, where we noted that including the reaction terms containing H^+ has no significant effect on the stationary state of the full model. Elimination of the H^+ species from the stability analysis of the stationary state is also confirmed by repeating the above analysis, holding $\delta[H^+]$ fixed at zero (6-variable analysis). The eigenvalues are identical to the full 7-variable analysis (the scaled difference is smaller than 1×10^{-8}), and the eigenvectors are identical up to normalization. These results are not shown here.

5.3.2 Role of starch complex

To verify the role of starch in the modeling, we first performed a 3-variable stability analysis in the I^- , ClO_2^- and SI_3^- species using inverse iteration, holding the reservoir species fixed at their reaction+diffusion profiles. We then repeated the above stability analysis but with the starch-triiodide component, $\delta[SI_3^-]$, explicitly set equal to $K'\delta[I^-]$, where $K' = K[I_2]_s$ (see Eq. 4.15), K is a constant (see Eq. 4.6), and $[I_2]_s$ is the stationary iodine solution which is a function of the position along the boundary feeds. (We note that this proportionality of the starch-triiodide concentration to that of the iodide can be directly seen from the complex formation reaction, Eq. 4.6, since the rate of the forward reaction is five orders of magnitude greater than that of the backward reaction). In this 2-variable reduction, the complex formation is accounted for through rescaling of the reaction+diffusion of the iodide species. The agreement between the two- and three-variable stability analyses is better than one-tenth of a percent (except for large values of k , where the agreement is at the one percent level), and is not shown here. This result confirms the modeling of the complex formation, leading to elimination of the complex species and rescaling of the reaction+diffusion of the iodide species.

5.3.3 Comparison of 7-variable and 2-variable stability analyses

In Fig. 5.21, we plot the absolute difference between the largest eigenvalue from the 2-variable stability analysis and the corresponding branch from the 7-variable stability analysis, and we note that the agreement is better than a few percent. The absolute difference for the second-largest eigenvalues has also been examined, and the agreement is better than one-half of a percent, and is not shown here.

In Fig. 5.22, we have plotted eigenvalues corresponding to a few modes in the 7-variable stability analysis. For the full range of $k \in [0, 900] \text{ cm}^{-1}$, we have plotted the two largest eigenvalues. In the inset of Fig. 5.22, we have plotted a few modes corresponding to the largest eigenvalues for $k \in [0, 100] \text{ cm}^{-1}$. All eigenvalues are real. We have verified the largest eigenvalue for $k = 0$ dynamically by time evolution of the linearized equations. Since the stability matrix is too large for direct matrix reduction using EISPACK (for example), these modes have been obtained using inverse iteration. They do not provide a complete picture of the mode crossings, even for the abbreviated range in k and growth rate, since the inverse iteration algorithm relies on a good initial guess for each eigenvalue. Furthermore, the algorithm we use here is not the generalized complex version, and is unable to find complex eigenvalues and eigenvectors. We note that all such modes are stable.

The spectrum for small k in the 7-variable stability analysis, shown in the inset of Fig. 5.22, (also present in the 6-variable analysis) is absent in the 2-variable (as well as the 3-variable) analysis. To understand the weak stability of the 7-variable system relative to the 2-variable system for small k , we have examined the slowest decaying eigenvector for $k = 0$. This eigenvector well approximates the derivative of the stationary solution. Hence, we can associate the weakly stable $k = 0$ mode with a spatial readjustment of the sharp front patterns along z . A 7-variable analysis allows more degrees of freedom for variations in this stationary state, resulting in less strongly bound $k = 0$ modes.

In Fig. 5.23, we have plotted the eigenvectors for the most linearly unstable mode

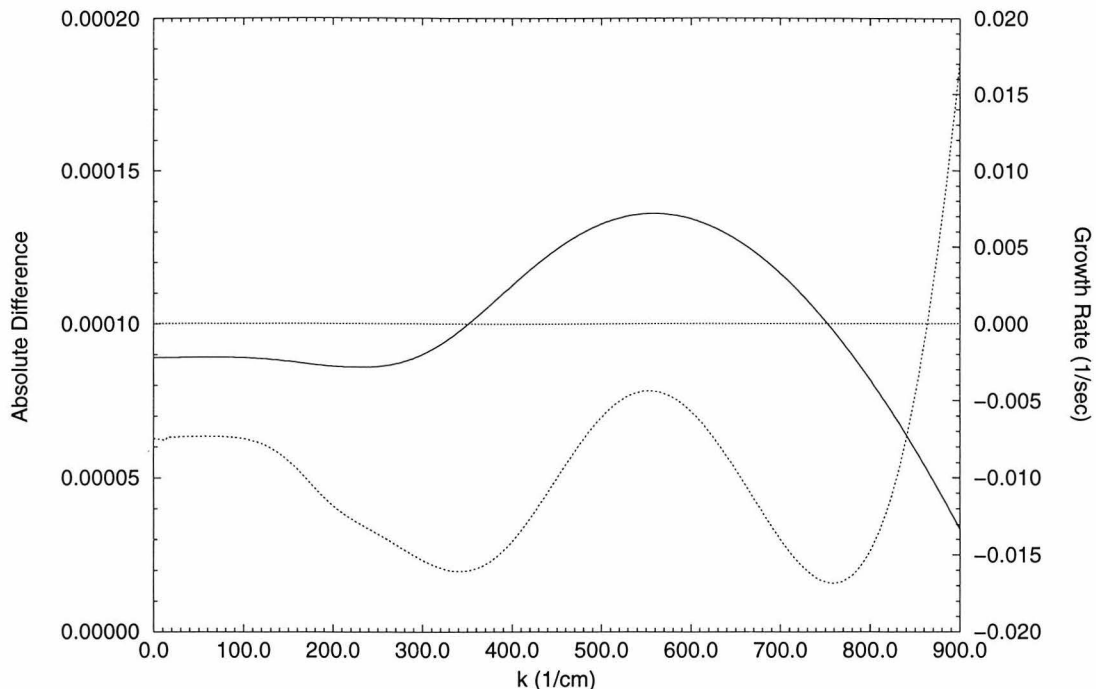


Figure 5.21: Absolute difference between the largest eigenvalue from the 2-variable stability analysis and the corresponding branch from the 7-variable stability analysis: The dotted line represents the absolute difference, and the solid line represents the growth rate. The agreement is better than a few percent.

from the full stability analysis. The overall vertical scale of these plots is irrelevant, although the relative scales among the various species are not. The iodide and chlorite profiles are identical with those obtained from the 2-variable analysis, up to the overall normalization.

In conclusion, we have verified the reduction of the full LRE model to the two-component reaction-diffusion system, comprised of the I^- and ClO_2^- species. We have explicitly shown that the elimination of H^+ and the modeling of the starch complex in the two-variable model are justified. By directly comparing the 7-variable and 2-variable results, we have implicitly verified the assumption that the reservoir species, MA, I_2 and ClO_2^- , do not play a role in determining the pattern-forming instability of the stationary states.

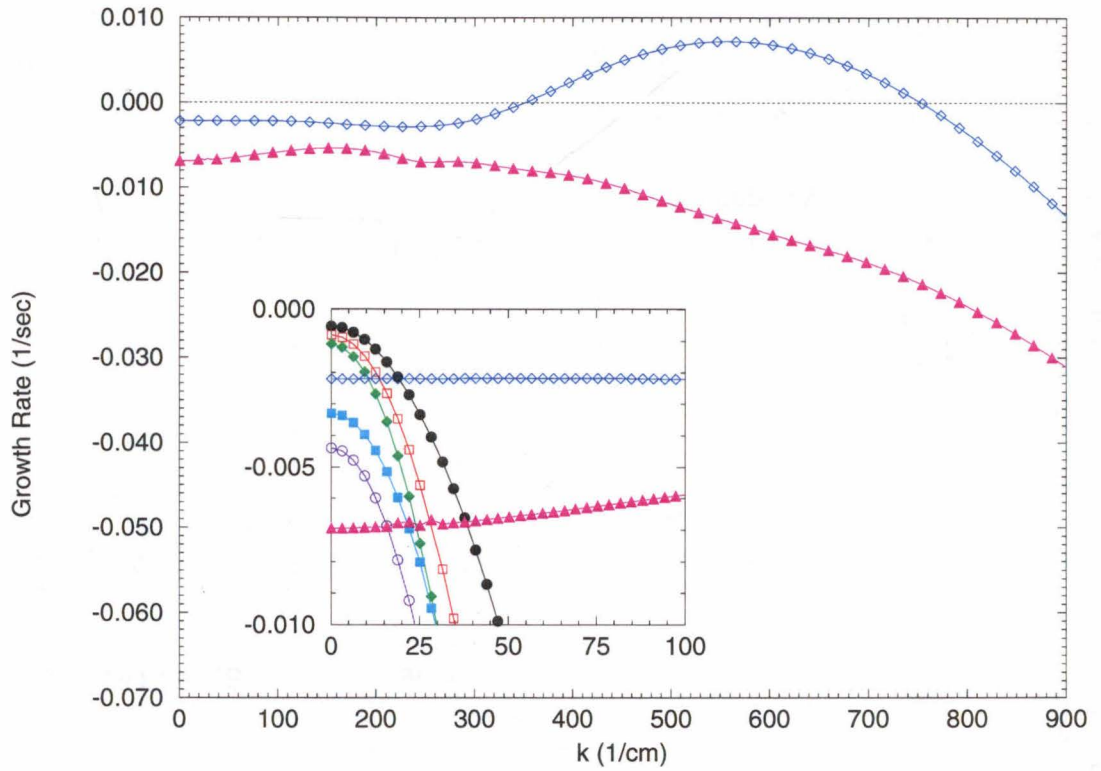


Figure 5.22: Eigenvalues from 7-variable stability analysis: The large plot shows eigenvalues from the 7-variable analysis that correspond to the dominant branches of the 2-variable analysis (see Fig. 5.16). The inset shows some additional real modes which are absent in the 2-variable analysis.

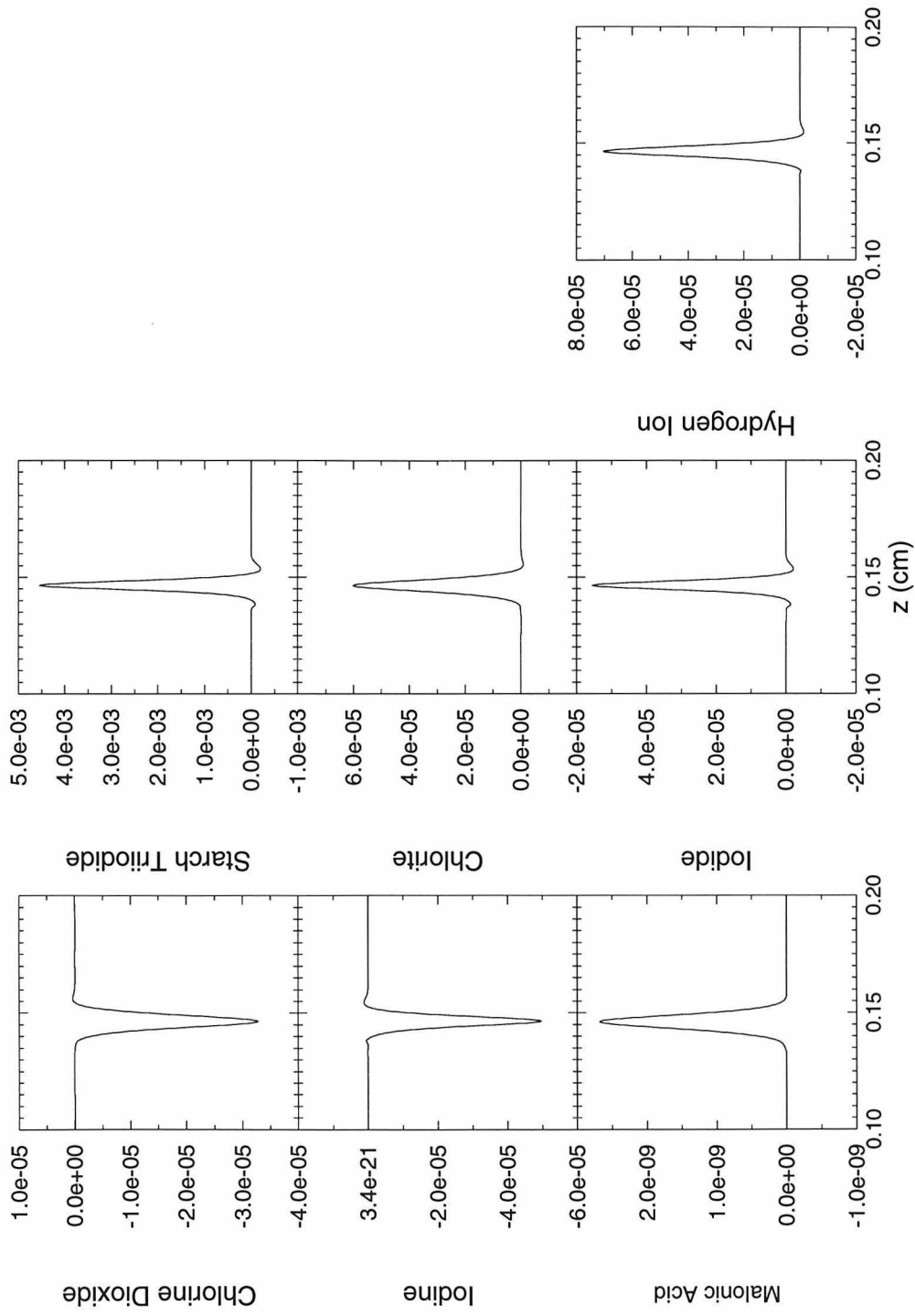


Figure 5.23: Eigenvectors for the most linearly unstable mode from the 7-variable stability analysis: The overall vertical scale is irrelevant, however the relative scales among the different species are not. The gel width is 0.3 cm.

5.4 Analysis of Two-Dimensional Patterns

So far, we have numerically investigated the development of one-dimensional localized structures within the context of the LRE model of the CDIMA reaction-diffusion system. The introduction of a second direction, transverse to the boundary feed gradients, allows the symmetry-breaking to become more explicit. Two-dimensional numerical simulations of Turing patterns in ramped systems have been performed using popular abstract models, such as the Schnakenberg model [46, 47], the Brusselator model [28, 48], as well as the generalized Swift-Hohenberg equation [49]. These models produce patterns which possess similar features to those observed in experimental systems, for example in terms of their qualitative structure and bifurcation sequence. However, as noted in Ref. [32], they do not allow quantitative comparison or prediction of new features at specific parameter values of a real chemical system. Kadar *et al.* [32] have numerically investigated two-dimensional Turing patterns within the LRE model in a closed system where the patterns are transient by nature. In this section, we describe two-dimensional numerical simulations of the LRE model of the ramped CDIMA system, corresponding to sustained patterns in thin-strip open reactors, and discuss the possible implications for further experimental work.

5.4.1 Numerical setup

We used a pseudospectral approach to solve the governing partial differential equation in two dimensions, described in detail in Sec. B.2 of Appendix B. The physical boundary conditions are no-flux in the x -direction transverse to the gradients, and fixed point boundary conditions in the z -direction. The boundary values in the z -direction are the same as those for the one-dimensional structures. For the results given in this section, we set $[\text{MA}]_L = 1.05 \times 10^{-2}$ M. In our numerical implementation, the governing equations are cosine Fourier transformed in the x -direction, and each spectral mode, which is a function of z , is evolved in time using the same numerical scheme and with the same variable mesh as that for the one-dimensional structures. After each time step, the updated solutions are transformed back into real space to

reconstruct the nonlinear terms.

As Table 4.1 indicates, the large order-of-magnitude variations in the real chemical parameters of the LRE model make numerical solution of this model less tractable than the aforementioned abstract models. The stability restriction on the time step of the numerical integration Δt due to the explicit treatment of the nonlinear terms is restrictive, and prohibits solution in two dimensions on a workstation. Hence, we have parallelized the two-dimensional time evolution algorithm, as described in detail in Sec. B.2.2 to run on a 512-node Intel Paragon, which uses the Intel i860 microprocessor (32 Mbytes of memory and 75 Mflops peak performance per processor).

As initial conditions, we used the stationary solution $\vec{u}_s(z)$ along z with a uniform profile in x , to which we added a perturbation given by the most linearly unstable mode, k^* , in the x -direction:

$$\vec{u}(x, z, t = 0) = \vec{u}_s(z) + C \vec{\delta u}_{k^*}(z) \cos(k^* x) \quad (5.7)$$

where $\vec{\delta u}_{k^*}(z)$ is the eigenvector obtained from the linear stability analysis, and C is an overall scale factor to ensure that the perturbation is small and lies in the linear regime. From the linear stability analysis of $\vec{u}_s(z)$, the growth rate for the instability at $k^* = 471.2 \text{ cm}^{-1}$ is $\lambda(k^*) = 0.00465 \text{ s}^{-1}$, giving a characteristic saturation time of $\tau \sim 1/\lambda \sim 215 \text{ s}$. The system size is 0.3 cm in the z -direction and 0.133 cm in the x -direction, corresponding to exactly ten wavelengths in the x -direction. The spatial resolution of the system investigated here was $N_x = 129$, and $N_z = 914$. One-thousand iterations at this resolution required approximately 12 node-hours.

The integration time step was $\Delta t = 0.001 \text{ s}$, chosen to be the same as that for the time evolution in one dimension. In the one-dimensional time evolution, the restriction on the time step due to the explicit treatment of the nonlinear terms was explored empirically, by varying Δt and using a value such that the algorithm was stable. We investigated using a higher order (third order as opposed to second order) Adams-Bashford scheme, to verify that the restriction on Δt was limited by stability as opposed to accuracy. We determined the time step used in the one-dimensional

time evolution to be adequate for the time evolution in two dimensions as follows: By using initial conditions uniform in the x -direction, thereby reducing the two-dimensional time evolution to be effectively in one dimension (and equal to 5×10^{-12} M for all species), we verified that the asymptotic solution was the same as that obtained from the one-dimensional time evolution. Since the steady state solutions in one dimension were not obtained dynamically, but rather using a Newton-Raphson nonlinear root-finding algorithm to polish the dynamically evolved initial conditions, the restriction on the time step was not a computational barrier. However, this is not the case in two dimensions where the asymptotic states are obtained dynamically. It is possible that implementing a numerical algorithm adapted to solving stiff partial differential equations (see Ref. [32] and references therein) or adopting an implicit time-stepping scheme for the nonlinear terms, will improve the total execution time in the two-dimensional evolution.

5.4.2 Results

In Fig. 5.24, we show a density plot of the numerical solution for the starch triiodide species after a total integration time of approximately $T = 1000$ s, as well as that for the initial state, with dark and light shading representing low and high concentrations, respectively. In Fig. 5.25, we have plotted the z -dependence of the k^* mode (solid line) from the saturated two-dimensional solution, as well as the initial instability eigenvector (multiplied by an overall scale factor, equal to the ratio of the peak value of the k^* mode in the starch triiodide, to that of the starch triiodide instability eigenvector). We observe that the structure of the linear instability eigenvector remains robust in the nonlinear evolution in two dimensions. In Fig. 5.26(a), (c), (e) and (g), we show the time evolution of the k^* spectral mode and its higher order harmonics at $z = 0.094$ cm (peak of the linear instability eigenvector) for the starch triiodide species. In Fig. 5.26(b), (d), (f) and (h), we plot the logarithm of the magnitude of these quantities. (These plots are shown for the *non-dimensionalized* quantities: the time conversion factor is 9×10^{-4} s $^{-1}$, and the concentration conversion factor is 5×10^{-5} M.) The

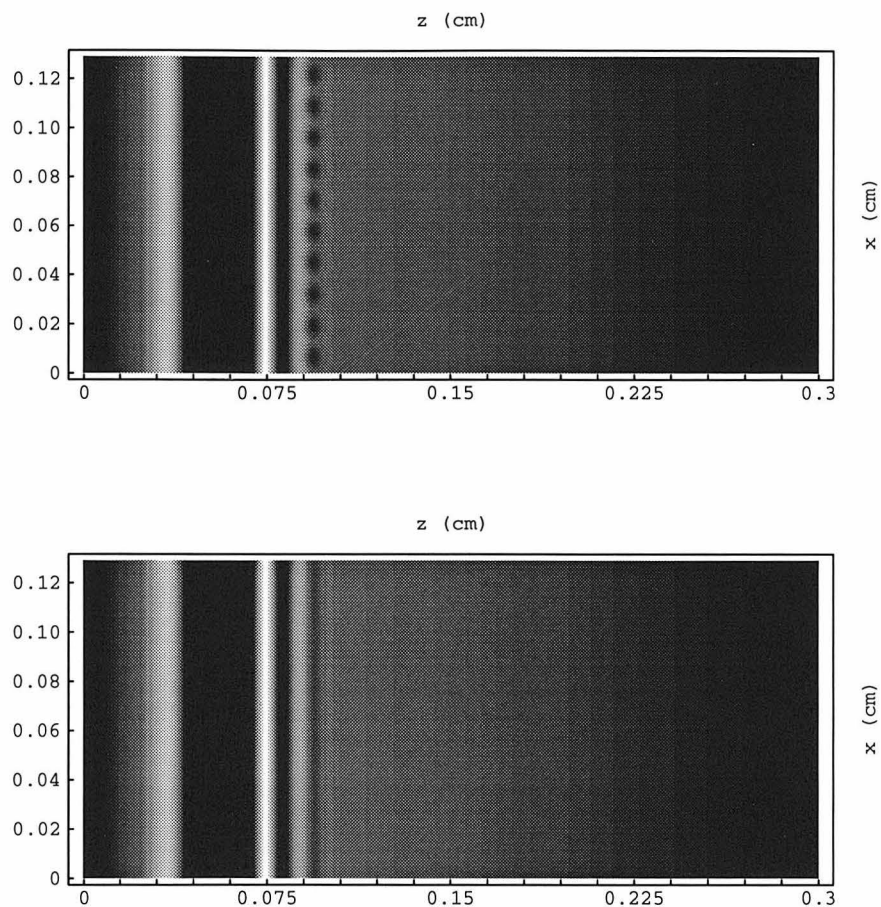


Figure 5.24: Two-dimensional solution for starch triiodide for $[MA]_L = 0.023M$: The top figure shows the numerical solution after $T = 1000$ s of evolution time. The bottom figure shows the initial condition. Dark and light shadings correspond to low and high concentrations, respectively. This figure should be compared with the experimental reproductions in Fig. 3.4c.

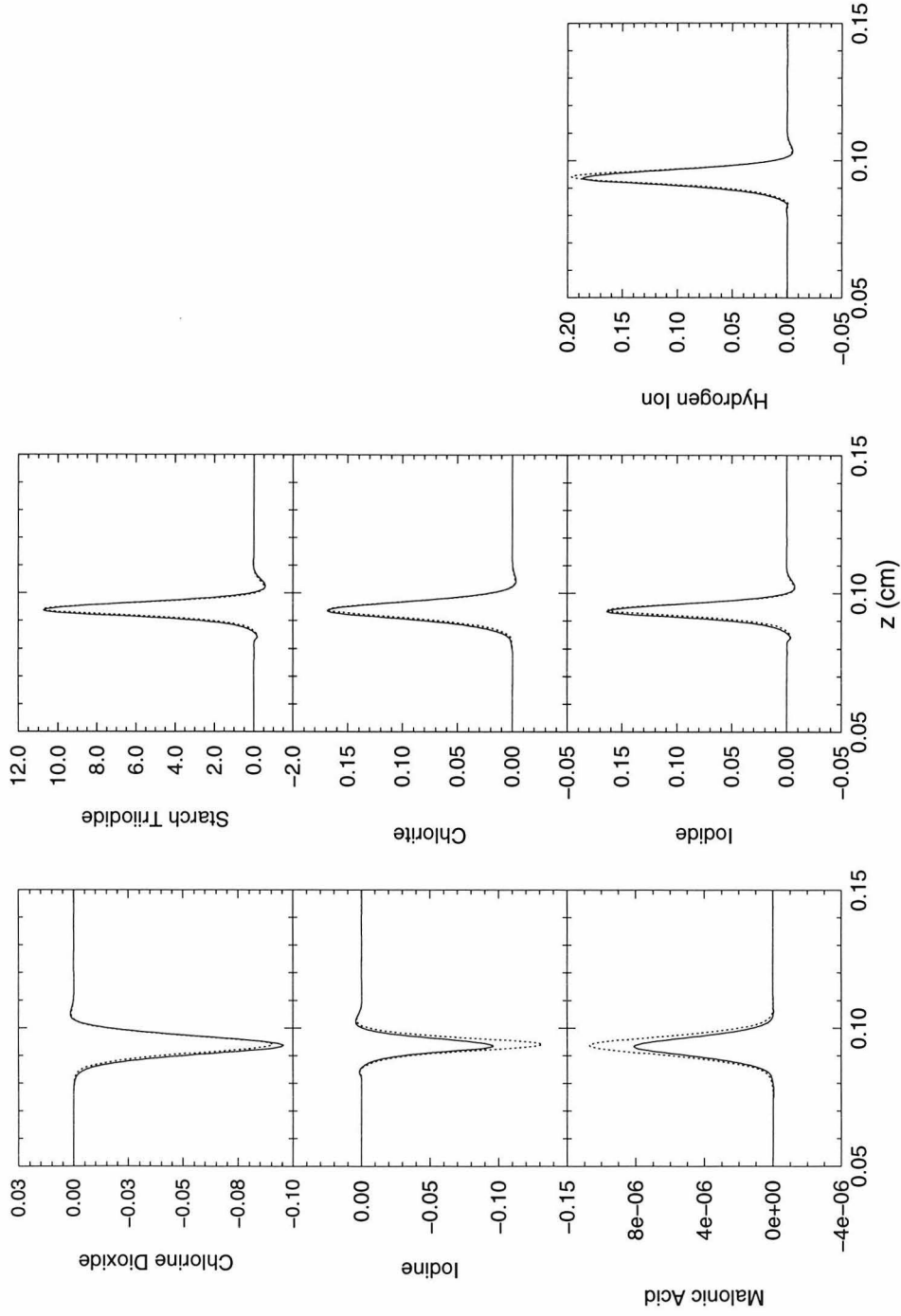


Figure 5.25: Spatial structure in the z -direction of the $\cos(k^*x)$ Fourier coefficient in the two-dimensional solution: The solid line represents the k^* mode from the two-dimensional solution, and the dotted line represents the linear instability eigenvector. The latter has multiplied by an overall scale factor for better comparison. We note that the spatial structure of the instability eigenvector remains robust in the two-dimensional nonlinear evolution.

approach to saturation is apparent. The saturated amplitudes of the higher order harmonics are much smaller than that of k^* . The slope of the linear segment in Fig. 5.26(b), for $t < \tau \sim 0.2$ is 5.129 ± 0.012 (corresponding to 0.004616 ± 0.000011 s) agrees well (to within one percent) with the linear growth rate, and further verifies our linear stability results. To compare the size of the nonlinear perturbations in the x -direction with the unperturbed profile in the z -direction, we have plotted the x - and z -dependence of the two-dimensional solution. In Fig. 5.27(a), we show the x -dependence at the peak of the linear instability eigenvector ($z = 0.094$ cm). We observe that it approximates a pure Fourier mode (verified by its power spectrum). The absence of a strongly nonlinear structure in the x -direction may account for a less severe spatial restriction in two-dimensional simulations of transient patterns in batch using the LRE model [32] allowing those solutions to be obtained with more modest computing resources. In our numerical investigations which take into account the boundary feeds, however, the x - and z -directions are not equivalent, and the z -dependence of the solution is strongly nonlinear. In Fig. 5.27(b), the dashed and dotted lines denote the profiles in the z -direction at $x = 0.067 = 5\lambda$ cm and $x = 0.073 = 5.5\lambda$, respectively. The solid line denotes the profile of the unperturbed one-dimensional stationary state. We note that although the saturated amplitude of the instability is comparable to the variation of the one-dimensional stationary state in the z -direction, indicating the perturbation to be strongly nonlinear, this is not supported by its x -dependence which is given approximately by a pure Fourier mode.

The results presented here can be summarized by three points. First, we have demonstrated that a realistic numerical study of two-dimensional pattern formation in the ramped CDIMA reaction-diffusion system can be achieved with the LRE model. This has been made feasible with parallel computing. Second, the observed symmetry-breaking instability is consistent with the expectation from the linear stability analysis, and provides an additional quantitative check of the validity of that analysis. Finally, these patterns agree qualitatively with the structures observed in experiments with a geometry similar to that of our simulations (see Fig. 3.4c). The characteristic wavelength of the symmetry-breaking spots, 0.133 mm for the solution

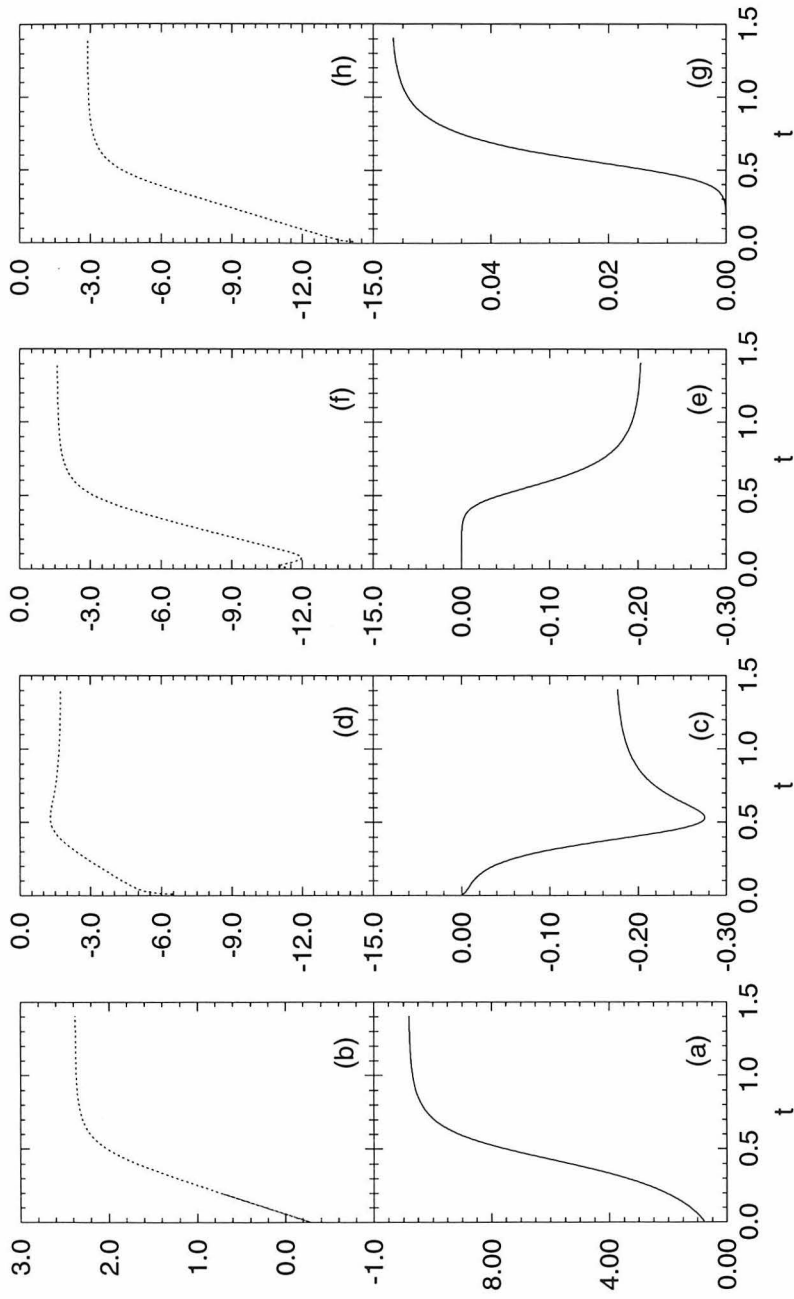


Figure 5.26: Time-evolution of the k^* mode and its higher order harmonics: (a), (c), (e), and (g) show the value of the k^* , $2k^*$, $3k^*$ and $4k^*$ modes for the starch triiodide species at the peak of the linear instability eigenvector ($z = 0.094$ cm), as a function of time. (b), (d), (f) and (h) show the logarithms of magnitudes of these amplitudes. The plots are shown for non-dimensionalized quantities. (The time conversion factor is $9 \times 10^{-4} \text{ s}^{-1}$, and the concentration conversion factor is $5 \times 10^{-5} \text{ M}$.) The slope of the linear segment for $t < 0.2$ is 5.129 ± 0.012 in plot (b), and agrees well with the growth rate $\lambda(k^*) = 5.172$ from the linear stability analysis.

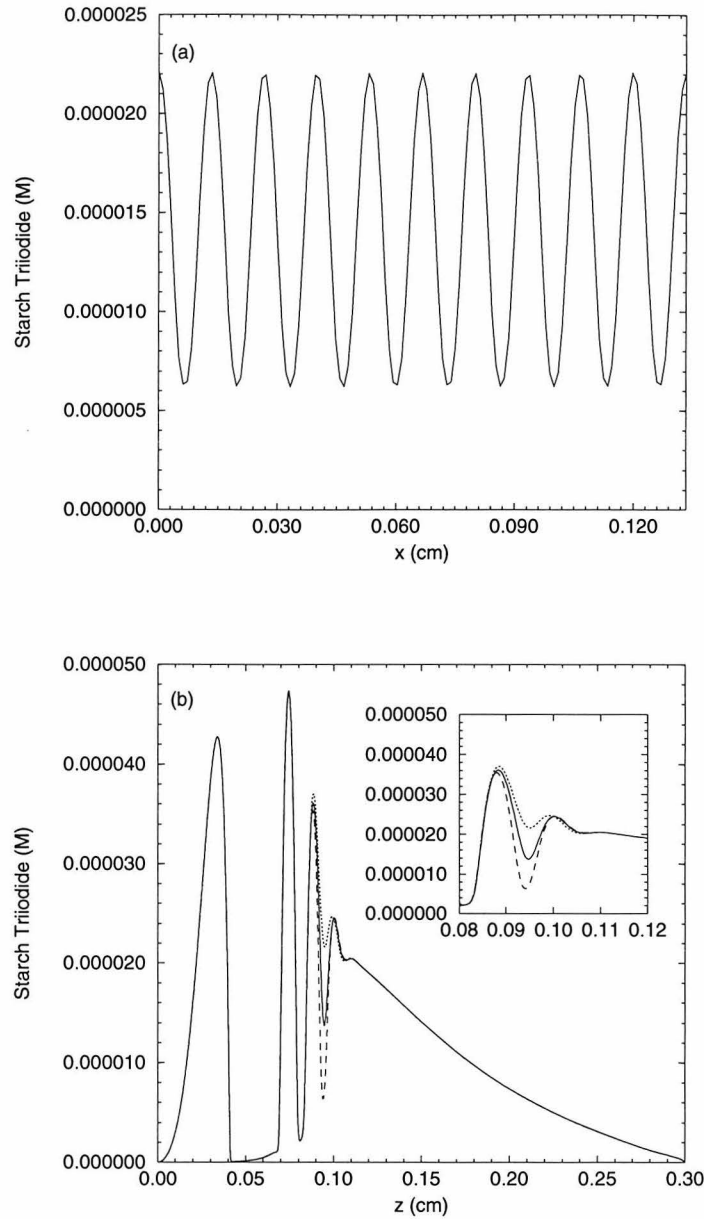


Figure 5.27: Spatial dependence of the two-dimensional solution in the x - and z -directions for SI_3^- : (a) The system size in the x -direction is 0.133 mm, constructed to incorporate exactly ten wavelengths of the most linearly unstable mode k^* . The profile in the x -direction is plotted at $z = 0.094$ cm. We observe that the solution approximates a pure Fourier mode, verified by the relatively small saturated amplitudes of the higher order harmonics of k^* in Fig. 5.26. (b) The dashed and dotted lines denote the profiles in the z -direction at $x = 0.067 = 5\lambda$ cm and $x = 0.073 = 5.5\lambda$, respectively. The solid line denotes the profile of the unperturbed one-dimensional stationary state. We note that saturated amplitude of the instability is comparable to the variation in the profile of the one-dimensional stationary state in the z -direction.

presented here, agrees well with the 0.13 – 0.33 mm range of experimentally observed wavelengths [22]. This gives hope that in the future, quantitative comparisons with experiments will also be made. In the following section, we outline some interesting possibilities for future investigation.

5.4.3 Going further

5.4.3.1 Two dimensions

One interesting question that can be pursued concerns the nature of the transition from the non-symmetry breaking pattern of stripes parallel to the boundary feeds to the one-dimensional symmetry-breaking pattern of spots. Using the malonic acid concentration at the left boundary as the control parameter, for example, the dependence of the saturated amplitude of spots on $[\text{MA}]_L$ in the vicinity of the bifurcation point would determine whether the transition is supercritical or subcritical. Boissonade [50] has explored this problem for the ramped Brusselator model, and found the bifurcation to be supercritical. Numerical investigations by Jensen *et al.* [43, 44, 51] on the two-variable LRE model with *uniform* backgrounds in one dimension have found the bifurcation to be strongly subcritical.

5.4.3.2 Three dimensions

In experimental geometries (disc reactors) where the dimensions of the reactor transverse to the gradients are large (approximately 100 wavelengths), the analog of the one-dimensional row of spots which develops in our numerical simulation (Fig. 5.24) and in experiments using thin-strip reactors (Fig. 3.4c) is a two-dimensional monolayer (Sec. 3.3.1.1). Such experimental patterns, like those shown in Fig. 3.5, are most commonly stripes or hexagons. Dufiet *et al* [52] have pointed out that these monolayers, which are confined by a strong transverse parameter ramp, must be distinguished from *genuine* two-dimensional structures (Sec. 3.3.1.1) with uniform control parameters. In addition, it is not practical to generate sustained genuine two-dimensional structures experimentally. Pattern selection in genuine two- and three-

dimensional systems has been studied analytically and numerically using abstract reaction-diffusion models [53]. However, as noted in [52], the stripe-hexagon competition in monolayers is not identical to that in genuine two-dimensional patterns. In fact, investigating pattern selection in monolayers requires *three-dimensional* numerical simulations. Furthermore, analytical attempts to take into account the presence of ramps in chemical reaction-diffusion systems [45, 54] use a WKB-like approach relying on the slowness of the parameter ramp, and this may not be valid for the actual ramped experimental systems.

The coupling of the basic two-dimensional patterns in successive unstable layers due to the presence of the feed gradients in the third direction distinguishes the three-dimensional pattern selection mechanism from that in a uniform system, and requires further work. In the experiments by Dulos *et al.* using a bevelled disc reactor [23], the sequence of transitions in regions 1, 2 and 3 (see Fig. 3.7), which occurs in a monolayer confined by a transverse gradient of boundary-fed chemical species, resembles that in a uniform background two-dimensional system. However, as shown by Dufiet *et al.* [52], the pattern selection mechanism in monolayers and two-dimensional systems are not identical. In the context of a toy reaction-diffusion model, they have found that genuine two-dimensional systems and monolayers have similar stability properties close to onset. However, far from onset, hexagonal phases with transverse wavevector k in monolayers are restabilized due to their interaction with a longitudinal ($k = 0$) instability. The latter finding is consistent with earlier theoretical predictions [55], as well as experiments in bevelled disc reactors [23].

It would be interesting to numerically investigate the bifurcation diagram for monolayers in the LRE model of the CDIMA system in the range of boundary conditions and reaction parameters accessible to experiments, allowing direct comparison with experimental results. Although we have not fully considered the extension of our parallel numerical scheme to three dimensions, we believe that it should be feasible. We note that the transition from non-symmetry breaking stripes to spots in a thin-strip reactor discussed earlier is one-dimensional in nature since the rotational invariance of a monolayer in the plane transverse to the boundary feeds of a disc

reactor is not present. Hence, although investigating this one-dimensional transition yields the branch of striped patterns in the bifurcation diagram for monolayers, it does not tell us about their stability relative to hexagons.

5.4.3.3 Spatiotemporal behavior

Understanding the mechanism of chemical turbulence is currently an open topic for further experimental and theoretical investigation. It has been pointed out [22] that the appearance of the turbulent state in the region of parameter space where stripes and hexagons are nearly equally stable (see Fig. 3.9) may be understood in terms of the role of defects in roll-hexagon competition on the dynamics of transition between these two symmetries [56]. Although the experiments by Dulos *et al.* [23] in variable-width thin-strip and bevelled disc reactors do not report on time-dependent patterns, a mechanism leading to the coupling of Turing and Hopf instabilities in adjacent unstable layers could lead to similar complex spatiotemporal behaviour. The coupling of Turing-Hopf instabilities is the subject of continuing experimental [57, 23] as well as theoretical [58] work.

Chapter 6 Conclusions

The successful formulation of a realistic model of the chlorine dioxide-iodine-malonic acid reaction-diffusion system has made this system an attractive paradigm for the study of nonequilibrium pattern formation [11], allowing numerical and theoretical work to be compared directly with experiments. We have demonstrated that numerical investigation of the CDIMA model in one and two dimensions is feasible using parallel computing. It is possible that by implementing numerical methods adapted for stiff systems of equations, the computation in two and three dimensions can be further facilitated.

We have focused on investigating the one- and two-dimensional patterns that form in the presence of feed gradients, a necessary feature of the real experimental systems. We have shown that longitudinal diffusion along the boundary feed gradients can be important over length scales longer than the Turing wavelength. Therefore, the frequently invoked locally uniform approach for predicting the linear instability of the stationary patterns along the gradients to a transverse symmetry-breaking instability is inappropriate in such cases. We have explored the dependence of the Turing instability of these stationary patterns on two control parameters. Our results display the following features as the control parameter is varied, in qualitative agreement with similar experiments using the CIMA reaction: (1) the transition to patterns with progressively larger numbers of fronts and (2) the appearance and subsequent vanishing of the transverse instability. We have attempted to quantify the latter trend, by determining that a transverse instability occurs and is localized to that part of the stationary solution along the gradients where the values of the concentrations of the dynamical iodide and chlorite species are within a certain well-defined range. This simple observation does not address the more interesting question of the relationship between the “longitudinal” and “transverse” Turing instabilities, which governs the formation of localized structures along the gradients as well as their transverse sta-

bility. Finally, we have numerically obtained two-dimensional patterns, in qualitative agreement with experiments, that confirm quantitatively our earlier linear stability results.

Building on the work presented here, one can begin to address many interesting questions. For example, determining the nature of the one-dimensional transition from non-symmetry breaking front patterns to symmetry-breaking transverse spots in thin-strip reactors can be pursued using our present numerical methods in two dimensions. Numerical establishment of the bifurcation diagram for two-dimensional monolayers in disc reactors is also a relevant topic for further investigation, and would require extending our numerical computation to three dimensions. These results would be directly comparable with experiments based on the CDIMA reaction.

Although we have focused on stationary patterns in this work, another important direction of development is in understanding spatiotemporal behavior in chemical systems. The state referred to as “chemical turbulence,” described in Sec. 3.3.2.1, is stable in the phase space between stripes and hexagons. This suggests an understanding based on the role of defects in the dynamics of the transition between these two symmetries [22, 56], which can be investigated in the context of a three-dimensional numerical calculation. The varied spatiotemporal behavior arising from the interaction of Turing and Hopf instabilities is also the subject of continuing theoretical [58] and experimental [29] work.

The most relevant feature of this work is that it represents an attempt at bringing theoretical and numerical study of pattern formation in chemical systems closer to experimental studies. Clearly, possibilities for further progress exist for both theoretical and experimental communities. These are made more exciting with the potential for cooperative efforts between the two.

Appendix A Details of the Turing Instability Conditions

A.1 Stability to Homogeneous Perturbations: $k = 0$

The characteristic equation for $k = 0$ is:

$$\sigma \lambda_o^2 - (a_{11} + \sigma a_{22})\lambda_o + (a_{22}a_{11} - a_{12}a_{21}) = 0, \quad (\text{A.1})$$

with,

$$\lambda_o^{(\pm)} = \frac{1}{2\sigma}(a_{11} + \sigma a_{22}) \pm \frac{1}{2\sigma}\sqrt{(a_{11} + \sigma a_{22})^2 - 4\sigma(a_{11}a_{22} - a_{12}a_{21})}. \quad (\text{A.2})$$

We require $\text{Re}(\lambda_o^{(\pm)}) < 0$. Therefore, in the case of $\text{Im}(\lambda_o^{(\pm)}) \neq 0$, we must have:

$$\lambda_o^{(+)} + \lambda_o^{(-)} = a_{11} + \sigma a_{22} < 0, \quad (\text{A.3})$$

and additionally, in the case of $\text{Im}(\lambda_o^{(\pm)}) = 0$:

$$\lambda_o^{(+)}\lambda_o^{(-)} = \sigma [a_{11}a_{22} - a_{12}a_{21}] > 0. \quad (\text{A.4})$$

A.2 Instability to Inhomogeneous Perturbations: $k \neq 0$

We require that at least one of the roots be positive for some $k \neq 0$. Consider the sum of the eigenvalues:

$$\lambda_k^{(+)} + \lambda_k^{(-)} = -(\sigma c + 1)k^2 + (a_{11} + \sigma a_{22}). \quad (\text{A.5})$$

Once stability to $k = 0$ perturbations is imposed according to Eq. (A.3), the above sum will be < 0 , and the real part of one of the roots is necessarily negative. First, we require that the product of the roots be < 0 in order to have a positive real root:

$$\lambda_k^{(+)}\lambda_k^{(-)} = \sigma \left(ck^4 - (a_{22} + ca_{11})k^2 + (a_{11}a_{22} - a_{12}a_{21}) \right) \equiv h(k^2) < 0. \quad (\text{A.6})$$

Since the first and third terms in $h(k^2)$ are > 0 , a necessary condition for $h(k^2) < 0$ is:

$$a_{22} + ca_{11} > 0. \quad (\text{A.7})$$

Furthermore, we know that $h(k^2)$ has a minimum, and from Eq. (A.4) that:

$$h(0) = \sigma(a_{11}a_{22} - a_{12}a_{21}) > 0. \quad (\text{A.8})$$

So, for $h(k^2) < 0$, k^2 must lie between the two roots k_-^2 and k_+^2 :

$$k_{\pm}^2 = \frac{1}{2c} \left[(a_{22} + ca_{11}) \pm \sqrt{(a_{22} + ca_{11})^2 - 4c(a_{11}a_{22} - a_{12}a_{21})} \right]. \quad (\text{A.9})$$

For $k_{\pm}^2$ to be real, we must have:

$$(a_{22} + ca_{11})^2 - 4c(a_{11}a_{22} - a_{12}a_{21}) \geq 0. \quad (\text{A.10})$$

Eq. (A.10) is required for real values $k_{\pm}^2$ of the marginal modes, and Eq. (A.7) is required for $k_{\pm}^2 \geq 0$. Equations (A.3), (A.4), (A.7) and (A.10) constitute the Turing conditions.

A.3 Oscillatory Instability

From Eq. (2.7) there will be a complex conjugate pair of eigenvalues, $\text{Im}(\lambda_k) \neq 0$, for:

$$g(k^2) \equiv (\sigma c - 1)^2 k^4 + 2k^2(\sigma c - 1)(a_{11} - \sigma a_{22}) + (a_{11} - \sigma a_{22})^2 + 4\sigma a_{12}a_{21} \leq 0. \quad (\text{A.11})$$

To determine the behaviour of $g(k^2)$, look at its roots:

$$k_{\pm}^{(\text{H})^2} = -\frac{(a_{11} - \sigma a_{22})}{\sigma c - 1} \pm \frac{\sqrt{-4\sigma a_{12}a_{21}}}{\sigma c - 1}. \quad (\text{A.12})$$

For $\text{Im}(\lambda_k) \neq 0$, require $k_+^{(\text{H})^2} \geq 0$. Under typical experimental conditions, we expect $\sigma c - 1 > 0$. We note that $g(k^2)$ possesses a minimum with:

$$g(0) = (a_{11} - \sigma a_{22})^2 + 4\sigma a_{12}a_{21}. \quad (\text{A.13})$$

Therefore, for $k_+^{(\text{H})^2} \geq 0$, we must have $g(0) < 0$, in which case $\text{Im} \lambda_k \neq 0$ for $0 < k^2 < k_+^{(\text{H})^2}$. The real part of the complex conjugate pair is given by:

$$\text{Re} \lambda_k = -\frac{1}{2} \left[(\sigma c + 1)k^2 - (a_{11} + \sigma a_{22}) \right], \quad (\text{A.14})$$

and behaves as:

$$i) \ a_{11} + \sigma a_{22} < 0 \quad \Rightarrow \quad \text{Re} \lambda_k < 0 \quad (\text{A.15})$$

$$ii) \ a_{11} + \sigma a_{22} > 0 \quad \Rightarrow \quad \text{Re} \lambda_k < 0 \quad \text{for} \quad k_+^{(\text{H})^2} > k^2 > \frac{a_{11} + \sigma a_{22}}{\sigma c + 1} \quad (\text{A.16})$$

$$\text{Re} \lambda_k \geq 0 \quad \text{for} \quad 0 < k^2 \leq \frac{a_{11} + \sigma a_{22}}{\sigma c + 1}. \quad (\text{A.17})$$

Appendix B Numerical Methods

B.1 One-Dimensional Time Evolution of Reaction-Diffusion Equations

In this section, we describe the numerical scheme used to obtain stationary solutions of the governing reaction-diffusion equations in one dimension. The following differential equation must be solved for each chemical species u_i :

$$\frac{\partial u_i}{\partial t} = N_i(u_1, u_2, \dots, u_m) + D_i \frac{\partial^2 u_i}{\partial z^2}, \quad i = 1, \dots, m, \quad (\text{B.1})$$

satisfying the appropriate boundary conditions at the gel boundaries:

$$u_i(0) = u_{iL}, \quad u_i(l_z) = u_{iR}. \quad (\text{B.2})$$

The appropriate initial conditions are that $u_i = 0$ inside the gel, $z \in (0, l_z)$. N_i is the non-linear reaction term, which in general depends on all other chemical species, and D_i is the diffusion constant. Henceforth, we will drop the index i .

B.1.1 Temporal scheme

We use the concept of operator splitting to time-step the above PDE. The linear diffusion term is updated using the implicit Crank-Nicholson (CN) differencing scheme, while the non-linear reaction term is updated using the explicit Adams-Bashforth (AB) scheme:

$$\frac{u^* - u(z, t)}{\Delta t} = \frac{1}{2} [3N(u(z, t)) - N(u(z, t - \Delta t))] \quad \text{“reactive step,”} \quad (\text{B.3})$$

$$\frac{u(z, t + \Delta t) - u^*}{\Delta t} = \frac{1}{2} D \frac{\partial^2}{\partial z^2} [u(z, t + \Delta t) + u(z, t)] \quad \text{“diffusive step,”} \quad (\text{B.4})$$

where u^* is an intermediate solution, $u^n(z) \equiv u(z, t)$ and $u^{n\pm 1}(z) \equiv u(z, t \pm \Delta t)$. Both CN and AB schemes are second-order accurate in time. Combining the two, we obtain:

$$u^{n+1}(z) = u^n(z) + \frac{\Delta t}{2} [\mathcal{L}u^{n+1}(z) + \mathcal{L}u^n(z)] + \frac{\Delta t}{2} [3N(u^n(z)) - N(u^{n-1}(z))], \quad (\text{B.5})$$

where $\mathcal{L}$ is the linear operator $\mathcal{L} = D \partial^2 / \partial z^2$.

B.1.2 Spatial scheme

We use a “five-point,” fourth-order accurate finite-difference approximation to the diffusion operator on a variable mesh of N points. This approximation to the second derivative of a function is obtained using a simple Taylor expansion. For an interior mesh point, for example, we have:

$$\begin{array}{ccccccc} - & - & - & | & | & \times & | & | & - & - & - \\ & & & -\Delta_1 & -\Delta_2 & 0 & \Delta_3 & \Delta_4 & & & \end{array}$$

$$f(\Delta_i) = f(0) + f'(0)\Delta_i + \frac{1}{2!}f''(0)\Delta_i^2 + \frac{1}{3!}f'''(0)\Delta_i^3 + \frac{1}{4!}f^{IV}(0)\Delta_i^4 + \frac{1}{5!}f^V(0)\Delta_i^5. \quad (\text{B.6})$$

Hence,

$$f''(0) = a f(-\Delta_1) + b f(-\Delta_2) + c f(0) + d f(\Delta_3) + e f(\Delta_4). \quad (\text{B.7})$$

Substituting (B.6) into (B.7), we solve the resulting linear system to obtain the coefficients (a, b, c, d, e) . The left and right boundary points must be treated separately. These coefficients are given in Appendix B.4.

Once we have obtained the discrete approximation L_{ij} to $\mathcal{L} = D \partial^2 / \partial z^2$, we substitute it into (B.5):

$$\left(\mathbf{1} - \frac{\Delta t}{2} \mathbf{L} \right) \cdot \vec{u}^{n+1} = \left(\mathbf{1} + \frac{\Delta t}{2} \mathbf{L} \right) \cdot \vec{u}^n + \frac{\Delta t}{2} \left(3 \vec{N}(u^n) - \vec{N}(u^{n-1}) \right), \quad (\text{B.8})$$

where $\vec{u}^{n+1} = (u^{n+1}(z_1), u^{n+1}(z_2), \dots, u^{n+1}(z_{N_z}))$, and similarly for the nonlinear terms. So, the following linear system must be solved in order to update $\vec{u}^n$:

$$\mathbf{A}_+ \cdot \vec{u}^{n+1} = \vec{F}, \quad (\text{B.9})$$

where $\vec{F} = \mathbf{A}_- \cdot \vec{u}^n + \vec{F}_N$, and:

$$\mathbf{A}_\pm = \mathbf{1} \pm \frac{\Delta t}{2} \mathbf{L}, \quad (\text{B.10})$$

$$\vec{F}_N = \frac{\Delta t}{2} \left(3\vec{N}(u^n) - \vec{N}(u^{n-1}) \right). \quad (\text{B.11})$$

There is a restriction on Δt for the overall stability of this semi-implicit scheme due to the explicit treatment of the nonlinear terms. We explored this restriction empirically, by varying Δt and using a value such that the algorithm is stable.

B.1.3 Boundary conditions

The fixed point boundary conditions in this physical problem are imposed in the following way: the boundary points are not evolved, and the problem is reduced from N_z to $N_z - 2$ mesh points. However, since non-zero boundary values affect the two points adjacent to each boundary point through the diffusion term, we must add a correction, $\vec{f}'$, to the right-hand-side in (B.9):

$$\mathbf{A}'_+ \cdot \vec{u}^{n+1} = \mathbf{A}'_- \cdot \vec{u}^n + \vec{F}'_N + \vec{f}' \cdot \Delta t, \quad (\text{B.12})$$

where $f'_1 = L_{21} u_L$, $f'_2 = L_{31} u_L$, $f'_{N_z-3} = L_{N_z-2, N_z} u_R$, $f'_{N_z-2} = L_{N_z-1, N_z} u_R$, and $f'_i = 0$ for all other components. The primed matrices are $(N_z - 2) \times (N_z - 2)$, and the primed vectors are $(N_z - 2)$ -dimensional.

B.1.4 Method of solution

A first explicit Euler time-step for the nonlinear terms is required. Linear algebra routines [39] for banded linear systems were used to solve (B.12). The matrix $\mathbf{A}'_+$ is

LU-decomposed once; the solution is successively updated by backsubstitution. Once the initial conditions were evolved for some length of time, this intermediate result was used as the initial input to a globally convergent Newton-Raphson nonlinear root-finding routine [39], to solve directly for the stationary solution of the spatially discretized Eq. B.1:

$$\vec{F}(\vec{x}) = 0, \quad (\text{B.13})$$

$$\vec{x}_{\text{new}} = \vec{x}_{\text{old}} + \vec{\delta x}, \quad (\text{B.14})$$

$$\vec{\delta x} = -\mathbf{J}^{-1} \cdot \vec{F}, \quad (\text{B.15})$$

where

$$\vec{x}_{\text{new}} = (\vec{u}(z_1), \vec{u}(z_2), \dots, \vec{u}(z_{N_z})) , \quad (\text{B.16})$$

$$\vec{u}(z) = (u_1(z), u_2(z), \dots, u_m(z)) , \quad (\text{B.17})$$

$$F_{(i-1)*m+j}(\vec{x}) = N_j(\vec{u}(z_i)) + D_j \frac{\partial^2 u_j}{\partial z^2}, \quad i=1, \dots, N_z; \quad j=1, \dots, m, \quad (\text{B.18})$$

$$J_{rs} = \frac{\partial F_r}{\partial x_s}, \quad r, s = 1, \dots, N_z \cdot m. \quad (\text{B.19})$$

Since this is an $(N_z \times m)$ -dimensional nonlinear root-finding problem, we have modified the Newton-Raphson routine to use a banded linear solver in Eq. B.15 by ordering $\vec{x}$ as in Eq. B.16. We enforced iterative improvement of the solution at each step.

B.2 Two-Dimensional Time Evolution of Reaction-Diffusion Equations

B.2.1 Reduction to one-dimensional time evolution

To investigate the formulation of two-dimensional structures in the gradient CDIMA system, we numerically solved:

$$\frac{\partial u_i}{\partial t} = N_i(u_1, u_2, \dots, u_m) + D_i \frac{\partial^2 u_i}{\partial z^2} + D_i \frac{\partial^2 u_i}{\partial x^2}, \quad i = 1, \dots, m. \quad (\text{B.20})$$

The z and x -directions are along and transverse to the gradients, respectively. The boundary conditions are fixed in the z -direction, and no-flux in the x -direction. Given the no-flux boundary conditions in the x -direction, it is natural to use the discrete cosine Fourier transform^(a) in that direction:

$$\begin{aligned}\tilde{u}_k(z, t) = & \frac{1}{2} \left[u(x_0=0, z, t) + (-1)^k u(x_{N_x}=l_x, z, t) \right] \\ & + \sum_{j=1}^{N_x-1} u(x_j, z, t) \cos\left(\frac{\pi j k}{N_x}\right), \quad k = 0, \dots, N_x, \quad (\text{B.21})\end{aligned}$$

where $x_j = j l_x / N_x$, ($j = 0, 1, \dots, N_x$). We have again dropped the index over chemical species. The wavenumber in the x -direction, q_k , is given by:

$$q_k = \frac{\pi k}{l_x}, \quad k = 0, \dots, N_x. \quad (\text{B.22})$$

The evolution equation for the wavenumber q_k is:

$$\frac{\partial \tilde{u}_k}{\partial t} = \tilde{N}_k + D \frac{\partial^2 \tilde{u}_k}{\partial z^2} - D \left(\frac{\pi k}{l_x} \right)^2 \tilde{u}_k, \quad (\text{B.23})$$

where $\tilde{N}_k$ is the cosine Fourier transform of the nonlinear term in the x -direction. This is now equivalent to the one-dimensional time evolution of Sec. B.1. Again, we use a finite-difference approximation to the diffusion term on a variable mesh in the z -direction, with CN time-stepping for the linear terms and AB time-stepping for the nonlinear terms, giving:

$$\left(\mathbf{1} - \frac{\Delta t}{2} \mathbf{L}_k \right) \cdot \vec{\tilde{u}}_k^{n+1} = \left(\mathbf{1} + \frac{\Delta t}{2} \mathbf{L}_k \right) \cdot \vec{\tilde{u}}_k^n + \frac{\Delta t}{2} \left(3 \vec{\tilde{N}}_k^n - \vec{\tilde{N}}_k^{n-1} \right), \quad (\text{B.24})$$

where $\vec{\tilde{u}}_k^n = (\tilde{u}_k^n(z_1), \tilde{u}_k^n(z_2), \dots, \tilde{u}_k^n(z_{N_z}))$, and

$$\mathbf{L}_k = D \left(\mathbf{L} - \frac{k^2 \pi^2}{l_x^2} \mathbf{1} \right). \quad (\text{B.25})$$

^(a)The form of the cosine transform implemented here uses $N_x + 1$ data points, where N_x is a power of 2. The boundaries are at $j = 0$ and $j = N_x + 1$.

To update $\vec{\tilde{u}}_k^n$, the following linear system must be solved:

$$\mathbf{A}_+^k \cdot \vec{u}_k^{n+1} = \vec{F}^k, \quad (\text{B.26})$$

where $\vec{F}^k = \mathbf{A}_-^k \cdot \vec{u}_k^n + \vec{F}_N^k$, and:

$$\mathbf{A}_\pm^k = \mathbf{1} \pm \frac{\Delta t}{2} \mathbf{L}_k, \quad (\text{B.27})$$

$$\vec{F}_N^k = \frac{\Delta t}{2} \left(3\vec{\tilde{N}}_k^n - \vec{\tilde{N}}_k^{n-1} \right). \quad (\text{B.28})$$

As in the one-dimensional case, there is a restriction on Δt due to the explicit treatment of the nonlinear terms. We used the same Δt in the one- and two-dimensional time evolutions.

The fixed point boundary conditions are imposed similar to those in the one-dimensional case, where now:

$$\mathbf{A}'_+^k \cdot \vec{\tilde{u}}_k^{n+1} = \mathbf{A}'_-^k \cdot \vec{\tilde{u}}_k^n + \vec{F}'_N^k + \vec{f}'^k \cdot \Delta t, \quad (\text{B.29})$$

with $\vec{f}'^k$ given by:

$$\vec{f}'^k = N_x \delta_{k0} \vec{f}'. \quad (\text{B.30})$$

Once $\vec{\tilde{u}}_k^n$ is updated, the full matrix is assembled in Fourier space, $\tilde{u}^{n+1}(q_k, z_j)$, and transformed back into real space, $u^{n+1}(x_i, z_j)$, in order to reconstruct the nonlinear terms for the next time step.

B.2.2 Parallelization scheme

The time evolution in two dimensions is most naturally parallelizable in the x -direction over the spectral index k , as $N_x + 1$ one-dimensional time evolutions. However, this is not the scheme of choice. To reconstruct the nonlinear terms using the updated solutions in real space requires $\mathcal{O}(N_x \cdot N_z)$ matrix elements to be shared between nodes at each time step. Consequently, the overhead in message-passing

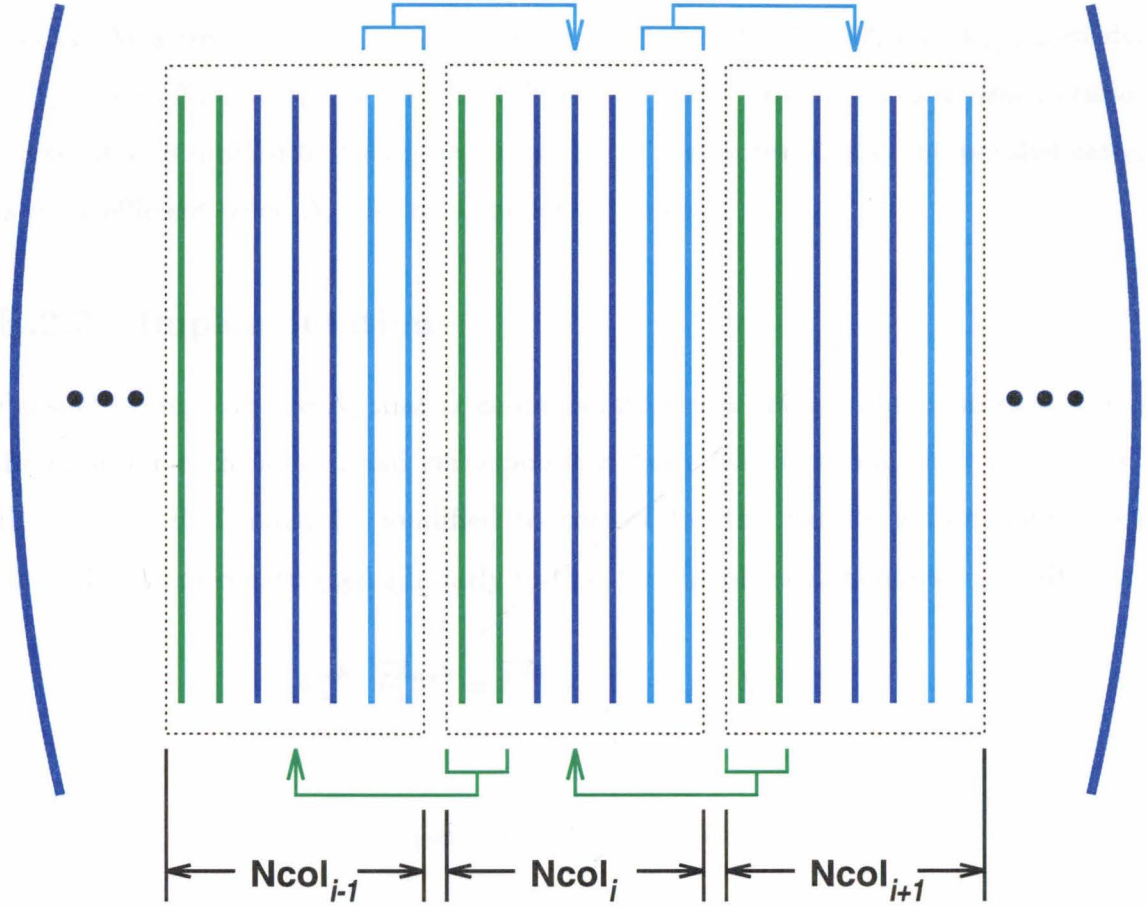


Figure B.1: Schematic representation of parallelization of matrix $\mathbf{u}$ in the two-dimensional analysis: The horizontal and vertical directions represent z and x respectively. The dotted lines enclose blocks of columns that are assigned to separate nodes. The two columns at each end of each block must be passed to the node operating on the adjacent block at each time step.

between nodes outweighs the gain in parallelizing over the spectral index.

A preferred scheme involves parallelization in the z -direction, where the N_z matrix columns are distributed among M nodes. This is illustrated in Figure B.1, where three adjacent blocks of the matrix (handled by nodes $i-1$, i and $i+1$) are shown schematically. Since the fourth-order finite-differencing scheme in the z -direction requires the value of the field at five mesh points, node i requires the two rightmost columns of node $i-1$ and the two leftmost columns of node $i+1$ to construct the diffusion term in z for its first and last columns, respectively. Hence, the message-passing between nodes is reduced to $\mathcal{O}(N_x)$.

The number of columns N_{col} comprising a block need not be the same for all blocks. As a result, this scheme works for any values for N_z , M and N_{col_i} , provided $\sum_{i=1}^M N_{\text{col}_i} = N_z$ and $N_{\text{col}_i} > 4$ for all i . Since the speed with which each time iteration is executed is limited by the node operating on the largest block, the parallelization is most efficient when N_{col} is the same for all nodes.

B.2.3 Implementation

Parallelization over the N_z matrix columns introduces artificial boundaries in the z -direction for each node i , and corresponding “parallelization boundary conditions.” Hence, Eq. B.29 must be modified to correct for the parallelization boundaries, through a term constructed similarly to that for the physical boundary conditions:

$$\mathbf{A}_+''^k \cdot \vec{u}_k^{n+1} = \vec{F}''^k + \vec{f}''^k \cdot \Delta t + \vec{h}''^k \cdot \Delta t, \quad (\text{B.31})$$

where

$$\vec{F}''^k = \mathbf{A}_-''^k \cdot \vec{u}_k^n + \vec{F}_N''^k. \quad (\text{B.32})$$

The double-primed quantities denote $(N_{\text{col}_i} \times N_{\text{col}_i})$ -dimensional matrices and N_{col_i} -dimensional vectors. The matrices $\mathbf{A}_\pm''^k$ are constructed from the $N_{\text{col}_i} \times N_{\text{col}_i}$ restriction to each node i of the $N_z \times N_z$ finite-difference matrix $\mathbf{L}$ for the full mesh.

The implementation of the parallelized two-dimensional analysis is illustrated by the flow diagram shown in Fig. B.2. The operations shown in the flow diagram are executed by all nodes i for their respective $N_x \times N_{\text{col}_i}$ block of the matrix. The notation is consistent with that used in the discussion of the numerical algorithm. The $N_x \times N_{\text{col}_i}$ matrices $\mathbf{N}$ and $\mathbf{U}$ contain the values in real space of the nonlinear term and the solution for each chemical species, respectively, on the x - z block of the mesh. The flow diagram can be summarized as follows:

- (i) The *Main Loop* is over the time iteration index n .
- (ii) At each time iteration, once the nonlinear term $\mathbf{N}$ for each species is constructed in real space, $\mathbf{N}$ and $\mathbf{U}$ are cosine Fourier-transformed in the x -direction.

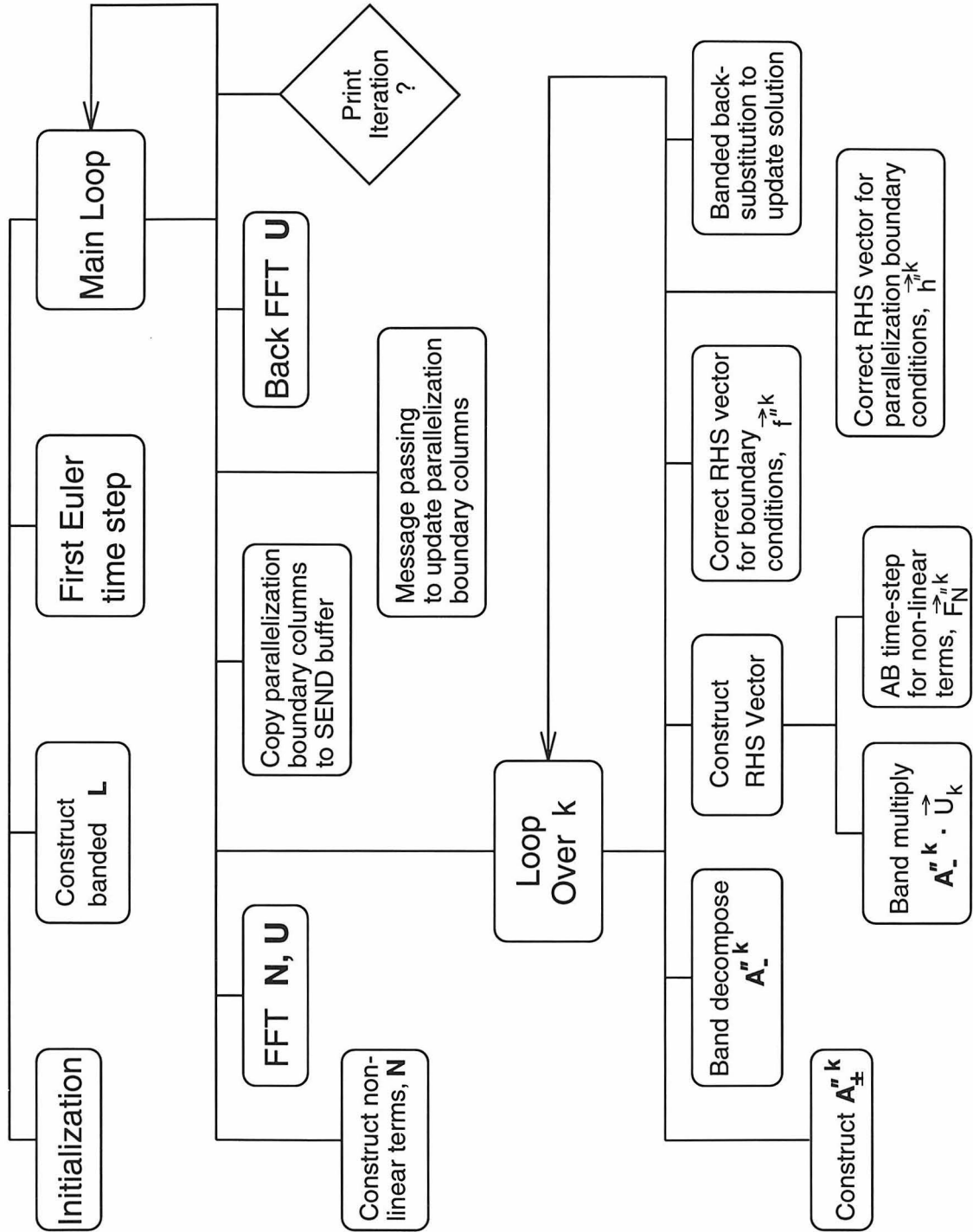


Figure B.2: Flow diagram of parallelized two-dimensional time evolution scheme.

- (iii) The time evolution algorithm is applied for each k (*Loop over k*), where in Eq. B.31 banded matrices and linear algebra routines are used.
- (iv) Once the solution is updated by each node, all nodes send and receive updated parallelization boundary values, as depicted in Fig. B.1, for the next time iteration.
- (v) The solution is back-cosine-Fourier-transformed so that the nonlinear term in real space can be constructed during the next time iteration.
- (vi) To print the full updated solution, all nodes send their block to a single designated node.

B.3 Linear Stability Analysis

B.3.1 Application of Newton-Raphson root-finding method to solving eigensystems

In this section, we describe our implementation of the Newton-Raphson root-finding method to solve the eigenvalue problem given by Eq. 2.19 for the two-component reaction-diffusion equation of Eqs. 2.16 and 2.17. The basic idea is to treat the eigensystem as a nonlinear root-finding problem for $(2N + 1)$ variables, where $2N$ variables account for the eigenvector $(\delta u_k(z), \delta v_k(z))$ with N mesh points in the z -direction, and the last variable is the eigenvalue. The discretized linear system of $2N$ equations is supplemented by an additional equation, imposing normalization of the eigenvector:

$$\begin{aligned} \sigma(z)\lambda_k \delta u_k(z) - \left(a_{11}(z) - D_u k^2\right) \delta u_k(z) + a_{12}(z) \delta v_k(z) \\ - D_u \frac{\partial^2 \delta u_k}{\partial z^2} = 0, \end{aligned} \quad (\text{B.33})$$

$$\begin{aligned} \lambda_k \delta v_k(z) - a_{21}(z) \delta u_k(z) - \left(a_{22}(z) - D_v k^2\right) \delta v_k(z) \\ - D_v \frac{\partial^2 \delta v_k}{\partial z^2} = 0, \end{aligned} \quad (\text{B.34})$$

$$\int_0^L (\delta u_k(z) \delta u_k(z) + \delta v_k(z) \delta v_k(z)) dz - 1 = 0. \quad (\text{B.35})$$

Ordering the solution as:

$$\vec{x}_k = (\delta u_k(z_1), \delta v_k(z_2), \delta u_k(z_2), \dots, \delta u_k(z_{N_z}), \delta v_k(z_{N_z}), \lambda_k) \quad (\text{B.36})$$

and using a fourth order, five-point finite difference approximation to the diffusion term, we obtain the following set of coupled nonlinear equations:

$$F_i(\vec{x}_k) = 0, \quad i = 1, \dots, 2N_z + 1. \quad (\text{B.37})$$

Starting with an initial guess $\vec{x}_{\text{old}}$ for the eigenvalue and eigenvector, the solution is updated according to Eq. B.15, where $\tilde{J}_{ij} = \partial F_i / \partial x_{k_j}$ is given by:

$$\tilde{\mathbf{J}} = \left(\begin{array}{c|c} \mathbf{J} & \vec{v}_1 \\ \hline \vec{v}_2 & 0 \end{array} \right) = \mathbf{A} + \mathbf{a} \otimes \mathbf{b} + \mathbf{c} \otimes \mathbf{d}, \quad (\text{B.38})$$

where,

$$\begin{aligned} a_i &= \begin{cases} v_{1i}, & i \leq 2N \\ -1/2, & i = 2N + 1 \end{cases} & c_i &= \begin{cases} 0, & i \leq 2N \\ 1, & i = 2N + 1 \end{cases} \\ b_j &= \begin{cases} 0, & j \leq 2N \\ 1, & j = 2N + 1 \end{cases} & d_j &= \begin{cases} v_{2j}, & j \leq 2N \\ -1/2, & j = 2N + 1 \end{cases} \end{aligned} \quad (\text{B.39})$$

With $\vec{x}_k$ ordered as in Eq. B.36, the matrix $\mathbf{J}$ (and therefore $\mathbf{A}$) is banded with $m_2 = 9$ upper diagonal elements and $m_1 = 9$ lower diagonal elements. This has the advantage of reduced storage, with $2N \times 2N$ elements going down to $2N \times (m_1 + m_2 + 1)$ elements, as well as allowing efficient solution of linear systems using banded LU decomposition and backsubstitution [39]. The matrix $\tilde{\mathbf{J}}$ is also sparse and different from $\mathbf{A}$ in a single

row and column. To take advantage of the bandedness of $\mathbf{A}$ in solving Eq. B.15 at each Newton time step, we used the Woodbury formula, as described in [39]. This formula allows solution of Eq. B.15, through a series of auxiliary banded solves using the matrix $\mathbf{A}$. We used iterative improvement of the solution obtained in this way at each Newton step. An extension of the present algorithm to compute complex eigenvalues and eigenvectors is possible, but has not been pursued here.

B.4 Fourth-Order Finite-Difference Coefficients on a Variable Mesh

We show here the coefficients for the finite-difference approximation to the diffusion operator, introduced in Section B.1.2.

B.4.1 Interior points

$$\begin{array}{ccccccc} - & - & - & | & | & \times & | & | & - & - & - \\ & & & -\Delta_1 & -\Delta_2 & 0 & \Delta_3 & \Delta_4 & & & \end{array}$$

$$f''(0) = a f(-\Delta_1) + b f(-\Delta_2) + c f(0) + d f(\Delta_3) + e f(\Delta_4) \quad (\text{B.40})$$

$$\begin{aligned} a &= \frac{2(\Delta_2\Delta_3 + \Delta_2\Delta_4 - \Delta_3\Delta_4)}{\Delta_1(-\Delta_1 + \Delta_2)(\Delta_1 + \Delta_3)(\Delta_1 + \Delta_4)} \\ b &= \frac{2(\Delta_1\Delta_3 + \Delta_1\Delta_4 - \Delta_3\Delta_4)}{\Delta_2(\Delta_1 - \Delta_2)(\Delta_2 + \Delta_3)(\Delta_2 + \Delta_4)} \\ c &= \frac{2(\Delta_1\Delta_2 - \Delta_1\Delta_3 - \Delta_2\Delta_3 - \Delta_1\Delta_4 - \Delta_2\Delta_4 + \Delta_3\Delta_4)}{\Delta_1\Delta_2\Delta_3\Delta_4} \\ d &= \frac{2(-\Delta_1\Delta_2 + \Delta_1\Delta_4 + \Delta_2\Delta_4)}{\Delta_3(\Delta_1 + \Delta_3)(\Delta_2 + \Delta_3)(-\Delta_3 + \Delta_4)} \\ e &= \frac{2(\Delta_1\Delta_2 - \Delta_1\Delta_3 - \Delta_2\Delta_3)}{\Delta_4(\Delta_1 + \Delta_4)(\Delta_2 + \Delta_4)(-\Delta_3 + \Delta_4)} \end{aligned} \quad (\text{B.41})$$

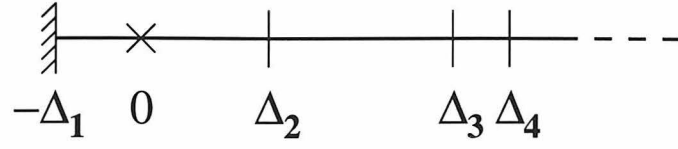
B.4.2 Left boundary point



$$f''(0) = a f(0) + b f(\Delta_1) + c f(\Delta_2) + d f(\Delta_3) + e f(\Delta_4) \quad (\text{B.42})$$

$$\begin{aligned}
 a &= \frac{2(\Delta_1\Delta_2 + \Delta_1\Delta_3 + \Delta_2\Delta_3 + \Delta_1\Delta_4 + \Delta_2\Delta_4 + \Delta_3\Delta_4)}{\Delta_1\Delta_2\Delta_3\Delta_4} \\
 b &= \frac{2(\Delta_2\Delta_3 + \Delta_2\Delta_4 + \Delta_3\Delta_4)}{\Delta_1(-\Delta_1 + \Delta_2)(-\Delta_1 + \Delta_3)(\Delta_1 - \Delta_4)} \\
 c &= \frac{2(\Delta_1\Delta_3 + \Delta_1\Delta_4 + \Delta_3\Delta_4)}{(\Delta_1 - \Delta_2)\Delta_2(-\Delta_2 + \Delta_3)(\Delta_2 - \Delta_4)} \\
 d &= \frac{2(\Delta_1\Delta_2 + \Delta_1\Delta_4 + \Delta_2\Delta_4)}{(\Delta_2 - \Delta_3)\Delta_3(-\Delta_1 + \Delta_3)(-\Delta_3 + \Delta_4)} \\
 e &= \frac{2(\Delta_1\Delta_2 + \Delta_1\Delta_3 + \Delta_2\Delta_3)}{(\Delta_1 - \Delta_4)(\Delta_2 - \Delta_4)\Delta_4(-\Delta_3 + \Delta_4)}
 \end{aligned} \quad (\text{B.43})$$

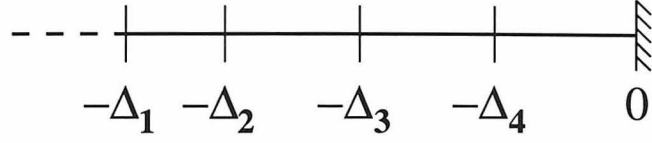
B.4.3 Left interior boundary point



$$f''(0) = a f(-\Delta_1) + b f(0) + c f(\Delta_2) + d f(\Delta_3) + e f(\Delta_4) \quad (\text{B.44})$$

$$\begin{aligned} a &= \frac{2(\Delta_2\Delta_3 + \Delta_2\Delta_4 + \Delta_3\Delta_4)}{\Delta_1(\Delta_1 + \Delta_2)(\Delta_1 + \Delta_3)(\Delta_1 + \Delta_4)} \\ b &= \frac{2(\Delta_1\Delta_2 + \Delta_1\Delta_3 - \Delta_2\Delta_3 + \Delta_1\Delta_4 - \Delta_2\Delta_4 - \Delta_3\Delta_4)}{\Delta_1\Delta_2\Delta_3\Delta_4} \\ c &= \frac{2(-\Delta_1\Delta_3 - \Delta_1\Delta_4 + \Delta_3\Delta_4)}{\Delta_2(\Delta_1 + \Delta_2)(-\Delta_2 + \Delta_3)(-\Delta_2 + \Delta_4)} \\ d &= \frac{2(\Delta_1\Delta_2 + \Delta_1\Delta_4 - \Delta_2\Delta_4)}{\Delta_3(\Delta_1 + \Delta_3)(-\Delta_2 + \Delta_3)(-\Delta_3 + \Delta_4)} \\ e &= \frac{2(-\Delta_1\Delta_2 - \Delta_1\Delta_3 + \Delta_2\Delta_3)}{\Delta_4(\Delta_1 + \Delta_4)(-\Delta_2 + \Delta_4)(-\Delta_3 + \Delta_4)} \end{aligned} \quad (\text{B.45})$$

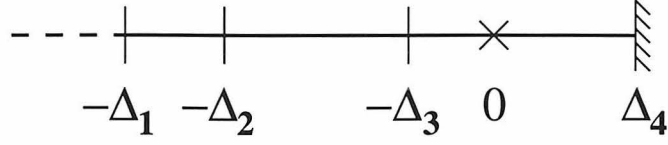
B.4.4 Right boundary point



$$f''(0) = a f(-\Delta_1) + b f(-\Delta_2) + c f(-\Delta_3) + d f(-\Delta_4) + e f(0) \quad (\text{B.46})$$

$$\begin{aligned}
 a &= \frac{2(\Delta_2\Delta_3 + \Delta_2\Delta_4 + \Delta_3\Delta_4)}{\Delta_1(-\Delta_1 + \Delta_2)(-\Delta_1 + \Delta_3)(\Delta_1 - \Delta_4)} \\
 b &= \frac{2(\Delta_1\Delta_3 + \Delta_1\Delta_4 + \Delta_3\Delta_4)}{\Delta_2(\Delta_1 - \Delta_2)(-\Delta_2 + \Delta_3)(\Delta_2 - \Delta_4)} \\
 c &= \frac{2(\Delta_1\Delta_2 + \Delta_1\Delta_4 + \Delta_2\Delta_4)}{\Delta_3(\Delta_1 - \Delta_3)(-\Delta_2 + \Delta_3)(-\Delta_3 + \Delta_4)} \\
 d &= \frac{2(\Delta_1\Delta_2 + \Delta_1\Delta_3 + \Delta_2\Delta_3)}{\Delta_4(-\Delta_1 + \Delta_4)(-\Delta_2 + \Delta_4)(-\Delta_3 + \Delta_4)} \\
 e &= \frac{2(\Delta_1\Delta_2 + \Delta_1\Delta_3 + \Delta_2\Delta_3 + \Delta_1\Delta_4 + \Delta_2\Delta_4 + \Delta_3\Delta_4)}{\Delta_1\Delta_2\Delta_3\Delta_4}
 \end{aligned} \quad (\text{B.47})$$

B.4.5 Right interior boundary point



$$f''(0) = a f(-\Delta_1) + b f(-\Delta_2) + c f(-\Delta_3) + d f(0) + e f(\Delta_4) \quad (\text{B.48})$$

$$\begin{aligned}
 a &= \frac{2(-\Delta_2\Delta_3 + \Delta_2\Delta_4 + \Delta_3\Delta_4)}{\Delta_1(-\Delta_1 + \Delta_2)(\Delta_1 - \Delta_3)(\Delta_1 + \Delta_4)} \\
 b &= \frac{2(\Delta_1\Delta_3 - \Delta_1\Delta_4 - \Delta_3\Delta_4)}{\Delta_2(\Delta_1 - \Delta_2)(-\Delta_2 + \Delta_3)(\Delta_2 + \Delta_4)} \\
 c &= \frac{2(-\Delta_1\Delta_2 - \Delta_1\Delta_4 - \Delta_2\Delta_4)}{\Delta_3(\Delta_1 - \Delta_3)(\Delta_2 - \Delta_3)(\Delta_3 + \Delta_4)} \\
 d &= \frac{2(-\Delta_1\Delta_2 - \Delta_1\Delta_3 - \Delta_2\Delta_3 + \Delta_1\Delta_4 + \Delta_2\Delta_4 + \Delta_3\Delta_4)}{\Delta_1\Delta_2\Delta_3\Delta_4} \\
 e &= \frac{2(\Delta_1\Delta_2 + \Delta_1\Delta_3 + \Delta_2\Delta_3)}{\Delta_4(\Delta_1 + \Delta_4)(\Delta_2 + \Delta_4)(\Delta_3 + \Delta_4)}
 \end{aligned} \quad (\text{B.49})$$

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