MATHEMATICAL MODELLING OF CHEMICALLY REACTING SYSTEMS: ANALYSIS OF ENCILLATOR

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BY

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Certified that the work incorporated in the thesis "**Mathematical Modelling Of Chemically Reacting Systems: Analysis Of Encillator**" submitted by Satish R. Inamdar was carried out by the candidate under my supervision. Such materials as has been obtained from other sources has been duly acknowledged in the thesis.

B.D. Kulkarni

Research Guide

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(Satish R. Inamdar)

CONTENTS

CHAPTER I

INTRODUCTION

1.1 The Encillator Model

The phenomena of multiplicity, instability, etc. in chemical reactors are known to occur in homogeneous as well as heterogeneous systems both under isothermal and nonisothermal conditions. The significant developments in this area have been summarized in several recent papers and reviews (Uppal et. al., 1974; Schmitz, 1975; Slinko and Slinko, 1978; Schmitz, 1978; Noyes, 1980; Gray, 1980; Pismen, 1980; Razon and Schmidt, 1987). Instability in solid catalyzed reactions under isothermal conditions is generally the result of surface dynamic effects (Belyaev et al, 1974; Pikios and Luss, 1977; Dagonnier and Nuyts, 1976). The presence of the solid component offers at least the possibility of explaining the phenomenon in terms of any one of the causes mentioned in th studies cited above. However, in the case of homogeneous reactions which are characterized by the absence of surface effects, these phenomena are difficult to explain. In the absence of any thermal feed back or an additional phase (such as solid catalytic surface), it seems likely that such behavior is caused by intrinsic rates of elementary processes where the products formed from one of these steps interact with those from other steps in the total sequence. The presence of autocatalysis therefore seems a necessary assumption.

The presence of autocatalysis gives rise to a close chain of actions that generates the feedback necessary for nonunique behavior. Two kinds of autocatalytic behavior have been identified by Frank (1978). In one the product acts as a reactant and the case has been analyzed earlier (Lin, 1979; Kawczynski, 1974; Lopushanskya et. al., 1975).

In the second case the product does not influence the rate directly but affects it through its influence on the rate constant. This kind of situation exists in some biological systems as well as in some gas and liquid phase reactions. Froment and Bischoff (1979) also hint that a form different than the conventional one can be considered that can be used to describe the autocatalytic behavior of some of these systems. This case of autocatalysis forms the theme of this thesis.

A similar situation was found to exist in combustion reactions where the instabilities reported are frequently explained by invoking the theory of branching chain reactions with chain interactions (Gray, 1977; Yang, 1974). The mechanism used here is somewhat similar to this. The difficult task, however, is that the system of the above types are of considerable complexity and no reaction mechanism has been clarified completely upto now. It is necessary, therefore, to simplify the situation by presuming that the final product is obtained through a sequence of intermediates and develop a theoretical model that would adequately represent the behavior of the system ranging from a unique stable solution to multiplicity and also the instabilities.

A particular reaction scheme analyzed consists of the sequence ,

$$X \xrightarrow{k_1} Y \xrightarrow{k_2} Z$$

where Y can be regarded as the intermediate. It is clear that for reaction I in CSTR the steady state will be single valued; to generate nonlinearity in the system it is necessary therefore to postulate that the intermediate species Y should have an activating or inhibiting influence on the rate constants. The feedback generated as a result of such autocatalysis/autoinhibition suggests that nonunique behavior may be observed in certain ranges of concentrations (Gilles, 1980; Franck, 1978). The kind of situations envisaged here can arise in some biochemical reactions catalyzed using allosteric enzymes. These enzyme molecules have more than one type of active center and the presence of a bound molecule or substrate on one active center can affect the activity of another center in the molecule. Several examples of instabilities in enzymic and multienzymic systems under homogeneous and heterogeneous conditions are cited by Isao et al (1979). Some of the other examples in the area of homogeneously catalyzed reactions have been noted in the work of Golodov et al (1980), Tikhonova and Zayats (1980), and Tovstokhatko et al (1980). The mechanism of autocatalysis arising due to chain propagation and interaction has been shown to be responsible for the instabilities.

Let us consider the reaction scheme carried out in a CSTR. For brevity, let us assume that the component Y has an activating influence on the rate constant k_1 which is arbitrarily represented as

$$k_1 = k_1' \exp(\alpha y)$$

The parameter α measures an activating influence of intermediate Y on the rate constant for the autocatalytic step. A relationship of the form described above has been chosen primarily for the following reasons: (1) due to its resemblance to the corresponding form in the heterogeneous case where the parameter α is given the physical significance of surface heterogeneity parameter; (2) the equation suggests a fast response of k to variations in the parameter α; this seems especially desirable in view of the fact that different systems with apparently not-too-large variations in parameter values (e.g. Da etc.) indicate varied behavior ranging from unique stable solution to multiple behavior and instabilities; and (3) the resemblance of the form used to that of Semenov law (1935), which postulates exponential autocatalytic acceleration of chemical reactions in branched systems. This law has been followed by diverse chemical reactions (Kondratiev, 1979) and is frequently invoked to explain the characteristic features of branched chain reactions.

The conservation equations for the species assuming Eq. (1), can now be written in dimensionless form as,

$$\frac{dx}{dt} = x_o - x - Da_1 x e^{\alpha y} \tag{2a}$$

$$\frac{dy}{dt} = y_o - y + Da_1 x e^{\alpha y} - Da_2 y \tag{2a}$$

with the initial conditions,

$$x = x_o \,, \qquad y = y_o \,, \qquad \text{at} \qquad t = 0 \tag{2c}$$

where x and y represent dimensionless concentrations of species X and Y, and x_o, y_o are initial dimensionless concentrations, Da_1 and Da_2 are Damkohler numbers respectively for the species. The dimensionless time is defined as, $t = t' F/V$, where t' is real time. Herein after we shall refer to this model as *Encillator*.

The analysis of open chemically reacting systems of the form described above has been an area of interest to chemical engineers for a long time. A chemical reactor in this context is defined as any open macroscopic non-equilibrium system where transformation and transport of some chemically interacting species is taking place. Underlying the recent research into the intrinsic dynamics of open chemically reacting systems are the concepts of *bifurcations* and *attractors*.

The present thesis deals with the bifurcation analysis of reaction-diffusion systems, and extensively analyzes the case of exponential autocatalysis. The emphasis in the present work is on deriving the results analytically and for this reason we regard the reaction-diffusion system as a group of locally identifiable subsystems where only reaction prevails and these subsystems are coupled to each other to incorporate the effects of diffusion. The global dynamic behavior has thus some relation to the local dynamics and at least qualitative behavior seems to be well within reach of prediction. This facility is lost when other nonlinear fields such as due to flow are considered. It is clear that the local subunits of a reaction-diffusion system are in themselves active functional units that can operate far from equilibrium and may exhibit very rich behavior such as bistability, oscillations, plane wave propagation etc.

Of special interest among these behavior is the one concerning the interaction of oscillatory units. It is known that multiple periodic processes with different natural frequencies may synchronize to produce a macroscopic rhythmicity. The phenomenon of chemical wave propagation in such reaction-diffusion systems lead to even more complex type of behavior and is sought to be the cause for the expanding target patterns observed in the Belousov-Zhabotinskii reaction. Theoretical analysis in recent years have lead to the development of a theory of chemical waves from the viewpoint of spatiotemporal synchronization and phase sigularity. The breakdown of the synchronization may lead to turbulence like behavior. The asymptotic regime near the Hopf bifurcation point also possesses interesting properties. Thus, for instance, the oscillatory behavior in the neighborhood of the Hopf bifurcation point is found to be surprisingly similar in most of the systems, although there are great variations in features from system to system otherwise. Close to the point of onset of oscillations only a few relevant variables have distinguishably slow time scales suggesting elimination of the other variables. The system description then of *n* differential equations can be contracted to an universal description which is referred to as Stuart-Landau equation in the case of lumped parameter systems, and Ginzburg-Landau equation for distributed parameter system. The present thesis aims at analyzing several such features and is organized as follows.

1.2 Contents

Chapter one introduces the subject matter of the thesis. The literature on the various topics covered is reviewed in order to justify the work presented here.

Chapter two presents the linear stability analysis of the exponential autocatalytic reaction with diffusion and provides stability criteria in terms of the bounds on the values of system parameters. The analysis reveals the stability behavior of the steady state solutions and the existence of a critical value of concentration of one of the components beyond which the stability properties of the solutions undergoes change. The eigenfunctions for the case of a simple zero eigenvalue are also obtained. The results of the analysis provide a basic framework to obtain additional nonuniform solutions to the system of equations which are presented in the next chapter.

Chapter three is an extension of the work carried out in the earlier chapter, and constructs the non-negative inhomogeneous solutions of the model exponentially autocatalyzed reaction-diffusion scheme. The qualitative properties of the dissipative structures show that the branches of solutions belonging to sub- and super- critical bifurcation exhibit interesting features such as hysterisis, symmetry breaking etc. The presence of initial gradients in the system results in localization of the dissipative structure and the analysis provides its qualitative behavior and an estimate of its size.

In obtaining the results reported in the first two chapters, linearization of the exponential autocatalytic term was performed subject to understanding that the value of exponential autocatalytic parameter α is sufficiently small. This was necessary to cut down the mathematical complications involved. Here in chapter four, however, this nonlinearity in the expressions is retained, and bounds on the parameter values that lead to different types of solutions are derived. These rigorous results also show the existence of a critical concentration beyond which the stability properties undergo a change. Additionally, bifurcating solutions for a simple zero eigenvalue are also obtained.

Chapter five deals with the another multi-time scale theory application where the equations of motion of the homoclinic trajectory are constructed. The conditions to locate the region where the infinite-period finite-amplitude bifurcation occurs have been formulated. The results also throw light on the effects of fluctuations on the exchange of stability for system operating under such conditions.

Chapter six describes the application of the reductive perturbation technique to analyze the reaction-diffusion system under consideration near the Hopf bifurcation point. The Ginzburg-Landau equation as obtained using the reductive perturbation can be useful in understanding other aspects like phase description, rotating waves, development of turbulence etc. in reaction-diffusion systems.

Chapter seven uses the Ginzburg-Landau equation developed in the earlier chapter. Using the constants in the Ginzburg-Landau equation and linear stability analysis it is found that the reaction-diffusion system reveals the existence of multiple regions where instability of uniform oscillations due to diffusion is possible. Also the plot of initial concentrations gives regions where instabilities occur leading to Hopf bifurcation.

Chapter eight presents the multi-time scale analysis of the model reaction-diffusion system and describes the global nonuniform steady patterns and the limit cycle behavior when diffusion plays an important destabilizing role. The stability of the constructed nonlinear structures is also examined.

Chapter nine finally concludes the thesis giving a concise summary of the results obtained and brings out the importance of the work.

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CHAPTER II

BIFURCATION ANALYSIS OF ENCILLATOR : REACTION-DIFFUSION EQUATIONS: LINEAR STABILITY ANALYSIS OF STEADY STATE SOLUTIONS

The linear stability analysis of an exponential autocatalytic reaction with diffusion has been carried out to provide stability criteria in terms of the bounds on the values of system parameters. The analysis reveals the stability behavior of the steady state solutions and the existence of a critical value of concentration of one of the components beyond which the stability properties of the solutions undergo changes. Additionally, bifurcating steady state solutions and thus the eigenfunctions for the case of a simple zero eigenvalue are obtained. The results of the analysis provide a basic framework to obtain additional nonuniform solutions to the system of equations which are presented in the next chapter.

2.1 Introduction

Multiple steady states, oscillations, chaotic behavior etc. in chemical reactions are known to occur in homogeneous as well as heterogeneous systems both under isothermal and non-isothermal conditions. The significant developments in this area have been summarized in several recent papers and reviews (Pismen, 1980; Razon and Schmidt, 1987; Shientuch and Hefer, 1988). Mathematical models constructed to describe these systems are usually in the form of non-linear algebraic, ordinary differential or partial differential equations and include a number of characteristic parameters, the values of which decide the eventual evolution of the system. The theory of algebraic and differential equations has been extensively used in constructing the solutions to these systems. The numerical and semi-analytical methods have led to very valuable information regarding the occurrence of new types of solutions as the parameter varies (Sattinger, 1973; Aris, 1975; Herschkowitz-Kaufman, 1975; Fife, 1979; Kubicel and Marek, 1983; Kuramoto, 1984).

The simple first order differential equation in time representing the chemical reaction rate acquires the form of a partial differential equation when diffusion terms are included. Several reaction-diffusion models of specific interest to chemical engineering practice have been analyzed so far and this area represents one of the topics, closer to the heart of chemical engineers. The realization that the results of such analyses have a wide application has propagated the extent of activities in this area even further. Thus for instance, reaction-diffusion models can serve to explain the propagation of action potential in nerves in the field of biology, or provide explanations for the various ecological patterns observed in nature, or in the evolution of some lower order parameter in some thermodynamic phase transitions. The global applicability of such models to various disciplines (Haken 1983a,b) suggests to regard reaction-diffusion systems as a class of nonlinear field which can be compared and contrasted with other nonlinear fields such as those encountered in fluid dynamical systems or thermodynamic cooperative systems.

The field of reaction-diffusion systems enjoys the advantage of superposition in that a given system may be visualized as consisting of various small subunits where only reaction prevails and that these subsystems are coupled to each other through the diffusion. The global dynamic behavior has thus some relation to the local dynamics and at least the qualitative behavior seems to be well within reach of prediction. It is clear that the local subunits of a reaction-diffusion system are in themselves active functional units that can operate far from equilibrium and may exhibit very rich behavior such as bistability, oscillatory or wave propagation etc.

The existence of oscillatory behavior, formation of dissipative structures, pattern formation, existence of chemical waves and turbulence have been known to occur in chemically reacting systems and B-Z reaction provides a practical example of these types of behavior (Tyson, 1976; Hudson *et al.*, 1979). The semi-analytical treatment in the analysis of this and such reaction schemes invariably involved a form of a model which accounts for the existence of autocatalytic step in the reaction sequence. The analysis has revealed certain features such as the fact that the small amplitude oscillations near the Hopf bifurcation point can be described in terms of simple evolution equations. Also the existence of diffusion gradient within the system provides a coupling of oscillators which can be described in terms of Ginzburg-Landau equation (Haken, 1975). The method of reductive perturbation provides a means to obtain solutions to the system of equations under such conditions. The weakly perturbed or interacting finite amplitude oscillators form a particular class of systems whose dynamics can be described in a simplified form through the method of phase description. The phase description method has in fact a deeper meaning and can be cast into a more general and systematic form, thus widening the scope of the method to encompass those problems that are not necessarily inherent in oscillatory systems. The phase description method has been expounded upon to explain the expanding target patterns in reaction-diffusion systems. The method has however limitations, in the sense that rotating spiral waves cannot be described by this method due to the presence of phase singularity. Reaction-diffusion systems also exhibit turbulencelike behavior under certain conditions. The analysis of rotating spiral waves etc. can also be handled using some of the methodologies that are developed in recent times (Kopell and Howard, 1977; Ortoleva and Ross, 1973, 1974).

The present chapter considers an alternative form of autocatalysis where the product formed affects its own rate through interactions with the rate constant as against the normal autocatalysis where the rate is affected directly by the concentration of the product. As has been stated earlier (Ravi Kumar *et al.*, 1984) this rate form has wide applications in several biochemical systems as also in explaining the phenomena in diverse chemical and combustion type of reactions. The exponential autocatalysis has received wide acceptance (Bar-Eli, 1984a,b,c; Bar-Eli and Reuveni, 1985) and results obtained by using the conventional autocatalysis such as the one used in Brusselator type of models compare well with this model system. The exponential autocatalysis has revealed the existence of multiplicity and oscillatory behavior under homogeneous conditions (Ravi Kumar *et al.*, 1984). The present chapter begins with this reaction scheme to derive bounds on the values of the parameters that lead to the existence of different types of solutions.

More specifically the conditions under which the governing system would have real eigenvalues with positive real part, the conditions when eigenvalues are complex and the conditions when the complex eigenvalues have real positive parts have been derived. The question concerning bifurcation of dissipative structures and their qualitative behavior is analyzed in the next chapter. The numerical results verify the existence of the conditions derived in this chapter and will be presented subsequently.

2.2 The Model

The reaction scheme for the exponentially autocatalyzed is given as :

$$X \rightarrow Y \rightarrow Z \tag{1}$$

Here, the rate constant of the second intermediate step $X \rightarrow Y$ is affected by the product formed. The reaction-diffusion equations for the system are given as :

$$\frac{\partial x}{\partial t} = D_1 \frac{\partial^2 x}{\partial r^2} + x_o - x - Da_1 x \exp(\alpha y)$$

$$\frac{\partial y}{\partial t} = D_2 \frac{\partial^2 y}{\partial r^2} + y_o - y + Da_1 x \exp(\alpha y) - Da_2 y \tag{2}$$

Here, $0 \leq r \leq 1$ and $t \geq 0$. Also x and y are the concentrations of species X and Y, with D_1 and D_2 being the respective diffusivities. It is assumed that Fick's law is obeyed. On the thermodynamic branch we have following solutions,

$$x_{st} = x_s \qquad y_{st} = \theta \tag{3}$$

The steady state relationships by putting all derivatives in equation (2) to zero are given by,

$$\theta = \frac{x_o + y_o - x_s}{1 + Da_2} \qquad \exp(\alpha\theta) = \frac{x_o - x_s}{x_s Da_1} \tag{4}$$

To avoid the spurious boundary layer effects, following boundary conditions are imposed,

$$x(0,t) = x(1,t) = x_s \qquad y(0,t) = y(1,t) = \theta \qquad \text{for } t \geq 0 \tag{5}$$

To make this a well-posed problem, following initial conditions are added,

$$x(r,0) = x_{in}(r) \qquad y(r,0) = y_{in}(r) \tag{6}$$

It is known that, if the initial conditions $x_{in}(r)$ and $y_{in}(r)$ are non-negative, then there is a non-negative pair (x(r,t), y(r,t)) of solutions of system in the region $0 \leq r \leq 1$ and $0 \leq t < \infty$. These solutions are infinitely-differentiable functions of both r and t on (0,1) X (0, ∞). In the following section we shall examine the stability properties of the steady state solutions of equations (2) using linear stability theory. Additionally, the expression for the bifurcating steady state solution and thus eigenfunctions for a simple case of zero eigenvalue is developed.

2.3 Linear Stability Analysis

In this section, the results of linear stability analysis are presented with a view to know the actual stability or instability of solutions.

The steady state equations from equation (2) are written as,

$$D_1 \frac{d^2x}{dr^2} + x_o - x - Da_1 x \exp(\alpha y) = 0$$

$$D_2 \frac{d^2y}{dr^2} + y_o - y + Da_1 x \exp(\alpha y) - Da_2 y = 0 \tag{7}$$

Now the linear stability equations for a solution (x_{st}, y_{st}, y_o) of the steady state equations are obtained by linearizing the equations for,

$$u(r,t) = x(r,t) - x_s \qquad v(r,t) = y(r,t) - \theta \tag{8}$$

about u = v = 0. The resulting equations for sufficiently small values of α give a linear parabolic system and to analyze its asymptotic behavior in time it is sufficient to obtain the eigenvalues λ_m and the eigenfunctions (u_m, v_m) of,

$$D_1 \frac{d^2u}{dr^2} - [1 + Da_1(1 + \alpha\theta)]\, u - (\alpha x_s Da_1) v - z_1 = \lambda u \tag{9a}$$

$$D_2 \frac{d^2v}{dr^2} + Da_1(1 + \alpha\theta) u - (1 + Da_2 - \alpha x_s Da_1) v - z_2 = \lambda v \tag{9b}$$

where,

$$z_1 = x_s + Da_1 x_s (1 + \alpha\theta) - x_o \tag{10a}$$

$$z_2 = (1 + Da_2)\theta - Da_1 x_s (1 + \alpha\theta) - y_o \tag{10b}$$

subject to,

$$u(0) = u(1) = v(0) = v(1) = 0 \tag{11}$$

When all the eigenvalues λ_m of equations (9)-(11) obey $Re \quad \lambda_m < 0 \qquad m = 1, 2, \ldots$ then the steady state solution (x_{st}, y_{st}, y_o) is linearly stable, and if for some m, $Re \quad \lambda_m > 0$, then the solution is linearly unstable.

Defining following terms to simplify the analysis,

$$k_1 = -[1 + Da_1(1 + \alpha\theta)] \tag{12a}$$

$$k_2 = -[\alpha x_s Da_1] \tag{12b}$$

$$k_3 = (\alpha x_s Da_1 - Da_2 - 1) \tag{12c}$$

$$k_4 = Da_1(1 + \alpha\theta) \tag{12d}$$

equation (9) can be rewritten as,

$$D_1 \frac{d^2u}{dr^2} + (k_1 - \lambda)u + k_2 v = z_1$$

$$\tag{13}$$

$$D_2 \frac{d^2v}{dr^2} + (k_3 - \lambda)v + k_4 u = z_2$$

or in an alternative form as,

$$(D^4 + a_1 D^2 + a_2)u = a_3$$

(14)

$$(D^4 + a_1 D^2 + a_2)v = a_4$$

where,

$$a_1 = \frac{D_1(k_3 - \lambda) + D_2(k_1 - \lambda)}{D_1 D_2} \qquad a_2 = \frac{(k_3 - \lambda)(k_1 - \lambda) - k_2 k_4}{D_1 D_2}$$

(15)

$$a_3 = \frac{(k_3 - \lambda)z_1 - k_2 z_2}{D_1 D_2} \qquad a_4 = \frac{z_2(k_1 - \lambda) - k_4 z_1}{D_1 D_2}$$

The particular solutions of equations (14) are given by,

$$c'_1 = \frac{a_3}{a_2} = \frac{(k_3 - \lambda)z_1 - k_2 z_2}{(k_3 - \lambda)(k_1 - \lambda) - k_2 k_4} \tag{16a}$$

$$c'_2 = \frac{a_4}{a_2} = \frac{(k_1 - \lambda)z_2 - k_4 z_1}{(k_3 - \lambda)(k_1 - \lambda) - k_2 k_4} \tag{16b}$$

The solution to eigenvalue problem can then be given as,

$$\begin{pmatrix} u_m(r) \\ v_m(r) \end{pmatrix} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \exp(\nu r)\sin(m\pi r) + \begin{pmatrix} c'_1 \\ c'_2 \end{pmatrix} \tag{17}$$

We have $\nu = 0$, and hence $\exp(\nu r) = 1$.

Combining equations (13) and (17), a linear system of equations is formed,

$$\begin{bmatrix} -m^2\pi^2 D_1 + k_1 - \lambda & k_2 \\ k_4 & -m^2\pi^2 D_2 + k_3 - \lambda \end{bmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = \begin{bmatrix} z_1 & - & m^2\pi^2 D_1 & \dfrac{(k_3-\lambda)z_1 - k_2 z_2}{(k_3-\lambda)(k_1-\lambda) - k_2 k_4} \\ z_2 & - & m^2\pi^2 D_2 & \dfrac{(k_1-\lambda)z_2 - k_4 z_1}{(k_3-\lambda)(k_1-\lambda) - k_2 k_4} \end{bmatrix} \tag{18}$$

which possesses the following characteristic equation,

$$\lambda^2 - (\beta_m + \alpha_m)\lambda + (\alpha_m \beta_m - k_2 k_4) = 0 \tag{19}$$

where,

$$\alpha_m = k_1 - m^2\pi^2 D_1, \qquad \beta_m = k_3 - m^2\pi^2 D_2 \tag{20}$$

The solutions of equation (19) are,

$$\lambda_m^{\pm} = \frac{1}{2}\left\{\alpha_m + \beta_m \pm \sqrt{(\alpha_m - \beta_m)^2 + 4k_2 k_4}\right\} \tag{21}$$

The nature of eigenvalues help us to fix different type of behaviors. The following types can be identified and lead to conditions for the existence of different types of solution behaviors.

(1) $Re\lambda_m^{\pm} \to \infty$ as $m \to \infty$

(2) A real eigenvalue λ_m^{+} has positive real part whenever

$$(k_2 k_4 - \alpha_m \beta_m) > 0$$

This condition results in,

$$k_2 k_4 - k_1 k_3 + m^2\pi^2(k_1 D_2 + k_3 D_1) + (m^2\pi^2)^2 D_1 D_2 > 0 \tag{22}$$

Substituting the values of k_1, k_2, k_3 and k_4, we get,

$$y_o < (1+Da_2)\left\{\frac{\frac{Da_1[\alpha x_s-(1+Da_2)]}{m^2\pi^2 D_2}+\frac{D_1(\alpha x_s Da_1-Da_2-1)}{D_2}-(1+Da_1)+m^2\pi^2 D_1}{\frac{\alpha Da_1(1+Da_2)}{m^2\pi^2 D_2}-\alpha Da_1}\right\}+(x_s-x_o) \tag{23}$$

(3) The eigenvalues $\lambda_m^{\pm}$ are complex whenever in equation (21) the discriminant < 0,

$$(\alpha_m-\beta_m)^2+4k_2k_4<0 \ .$$

Defining,

$$z = Da_1(1+\alpha\theta) \qquad \delta = 1+m^2\pi^2(D_1-D_2) \qquad p = (1+Da_2-\delta) \tag{24}$$

we obtain a quadratic inequality,

$$z^2-(2\alpha x_s Da_1+2p)z+(p-\alpha x_s Da_1)^2<0 \tag{25}$$

Now the condition to have real roots is : $\qquad p > 0.$

This gives,

$$\delta \ < \ (1+Da_2) \tag{26}$$

From equation (25) we obtain the condition :

$$\left\{\frac{(\sqrt{\alpha Da_1 x_s}-\sqrt{1+Da_2-\delta})^2-Da_1}{\alpha Da_1}\right\}(1+Da_2)+(x_s-x_o)<y_o<$$

$$\left\{\frac{(\sqrt{\alpha Da_1 x_s}+\sqrt{1+Da_2-\delta})^2-Da_1}{\alpha Da_1}\right\}(1+Da_2)+(x_s-x_o) \tag{27}$$

Noting the inequality in equation (26), there are no complex eigenvalues, if,

$$(D_2 - D_1) \ < \ \frac{Da_2}{\pi^2} \tag{28}$$

(4) A complex eigenvalue λ_m^+ (or λ_m^-) has real part if the trace given in equation (21) > 0. This implies that,

$$\alpha_m + \beta_m \ > \ 0 \ .$$

This gives following result,

$$y_o > (1 + Da_2)\left\{x_s - \frac{2 + Da_1 + Da_2 - m^2\pi^2(D_1 + D_2)}{\alpha Da_1}\right\} + (x_s - x_o) \tag{29}$$

Combining the inequalities in equations (27) and (29), one sees that there are eigenvalues provided $\delta < 0$, with following condition satisfied :

$$\begin{aligned}(1 + Da_2)\left\{x_s - \frac{2 + Da_1 + Da_2}{\alpha Da_1} - \frac{m^2\pi^2(D_1 + D_2)}{\alpha Da_1}\right\} + (x_s - x_o) < y_o \\ < (1 + Da_2)\left\{x_s + \frac{Da_2 - Da_1 - m^2\pi^2(D_1 - D_2)}{\alpha Da_1} + 2x_s[Da_2 - m^2\pi^2(D_1 - D_2)]^{1/2}\right\} \\ + (x_s - x_o)\end{aligned} \tag{30}$$

Also, from equation (25) substituting the values of p and δ from equation (24) we obtain,

$$\begin{aligned}m^4\pi^4(D_2 - D_1)^2 + 2[Da_2 - \alpha x_s Da_1 - Da_1(1 + \alpha\theta)]\, m^2\pi^2(D_2 - D_1) \\ + \{[Da_1(1 + \alpha\theta)]^2 + (Da_2 - \alpha x_s Da_1)^2 - 2Da_1 Da_2(1 + \alpha\theta)\} < 0\end{aligned} \tag{31}$$

Thus if $D_2 \neq D_1$, only finite number of complex eigenvalues of the system exist.

However, when $D_1 = D_2$, then either all the eigenvalues are complex or else they are all real as the first two terms in equation (31) vanish.

From equation (29) it is seen that the steady state solution becomes linearly unstable through a real eigenvalue if $y_o > y_{oc}$, where,

$$y_{oc} = \min_{\substack{m \geq 1 \\ \text{'misinteger'}}} \left\{ (1+Da_2) \left\{ \frac{\dfrac{Da_1[\alpha x_s - (1+Da_2)]}{m^2\pi^2 D_2} + \dfrac{D_1(\alpha x_s Da_1 - Da_2 - 1)}{D_2} - (1+Da_1) + m^2\pi^2 D_1}{\dfrac{\alpha Da_1(1+Da_2)}{m^2\pi^2 D_2} - \alpha Da_1} \right\} + (x_s - x_o) \right\} \tag{32}$$

The critical value of wave number m is obtained by differentiating equation (23) with respect to m^2 and equating the result to zero. The final result is presented as equation (34) where q is defined as,

$$q = \left\{ \alpha x_s Da_1 \left(1 + Da_2 + \frac{D_2}{D_1} \right) - \frac{D_2}{D_1}(1+Da_2)(1+2Da_1) \right\}^{1/2} \tag{33}$$

$$m_c^2 \pi^2 D_2 \quad = \quad \mu^2 \pi^2 D_2 \quad = \quad (1+Da_2) \pm q \tag{34}$$

Substituting the critical value of m from equation (34) one gets,

$$y_{oc} \geq (1+Da_2)\{ \frac{\frac{D_1}{D_2}(1+Da_2)(2\alpha x_s Da_1 + Da_2 + 1) + 2\alpha x_s Da_1 - (1+Da_2)(3+4Da_1+Da_2)}{\pm \alpha Da_1 q}$$

$$\frac{\pm q\left[\frac{D_1}{D_2}(\alpha x_s Da_1 + Da_2 + 1) - (1+Da_1)\right]}{\pm \alpha Da_1 q} \} + (x_s - x_o) \tag{35}$$

Now for equation (33) we can put condition as $q > 0$. This produces a result,

$$\frac{D_1}{D_2} \quad > \quad \frac{2Da_1 + Da_2(1+Da_1)}{\alpha x_s Da_1} \tag{36}$$

Combining equations (28) and (36) we obtain,

$$\frac{\alpha x_s Da_1 - 2Da_1 - Da_2(1+Da_1)}{2Da_1 + Da_2(1+Da_1)} < \frac{D_2 - D_1}{D_1} < \frac{Da_2}{\pi^2 D_1} \tag{37}$$

The critical wave number m_c is the integer giving rise to y_{oc}. There could be two critical wave numbers, but this is a singular case as small changes in D_1 or D_2 will select one of these numbers.

Depending on D_1 and D_2, it is also possible that the solution (x_s, θ) first becomes unstable through a complex eigenvalue.

Suppose $D_2 - D_1 < Da_2/\pi^2$ and from equation (30) one gets,

$$y_o > (1+Da_2)\left\{x_s - \frac{2+Da_1+Da_2}{\alpha Da_1} - m^2\pi^2\frac{(D_1+D_2)}{\alpha Da_1}\right\} + (x_s - x_o) \tag{38}$$

This gives for $m = 1$,

$$y_{o1} = (1+Da_2)\left\{x_s - \frac{2+Da_1+Da_2}{\alpha Da_1} - \pi^2\frac{(D_1+D_2)}{\alpha Da_1}\right\} + (x_s - x_o) \tag{39}$$

As against this, the rhs in equation (27) specifies the other inequality for y_o. Combining the two inequalities in equations (27) and (38), and putting $m = 1$, the result is,

$$D_2 > \frac{1}{\pi^2} + \frac{1}{\pi^2}\{\alpha Da_1 x_s[Da_2 - \pi^2(D_1 - D_2)]\}^{1/2} \tag{40}$$

Then if $y_{o1} < y_{oc}$, the first unstable eigenvalues are given by the complex conjugate pair $\lambda_1^{\pm}$.

In particular if $D_1 = D_2 = D$ then the first unstable eigenvalue is complex whenever :

$$D > \frac{1}{\pi^2} + \frac{1}{\pi^2}\{\alpha x_s Da_1 Da_2\}^{1/2} \tag{41}$$

2.4 Bifurcation at a simple zero eigenvalue

Now we define our problem to obtain the bifurcating steady state solutions and thus eigenfunctions for a simple zero eigenvalue.

Such an eigenfunction has wave number m provided,

$$\alpha_m \beta_m = k_2 k_4 \tag{42}$$

This gives,

$$m^4\pi^4 D_1 D_2 - m^2\pi^2\{D_1(\alpha x_s Da_1 - Da_2 - 1) - D_2[1 + Da_1(1+\alpha\theta)]\} - Da_1(\alpha x_s - Da_2 - 1) - \alpha Da_1\left[y_{om} + \frac{(x_o - x_s)}{1 + Da_2}\right] = 0 \tag{43}$$

or if Φ is given as,

$$\Phi(m) = (1 + Da_2)\left\{\frac{m^2\pi^2 D_1 - \frac{D_1(\alpha x_s Da_1 - Da_2 - 1)}{D_2} + (1 + Da_1) - \frac{Da_1(\alpha x_s - Da_2 - 1)}{m^2\pi^2 D_2}}{\alpha Da_1\left[\frac{1 + Da_2}{m^2\pi^2 D_2} - 1\right]}\right\} + (x_s - x_o) \tag{44}$$

then,

$$y_{om} = \Phi(m) \tag{45}$$

From equation (45) one notes that :

$$y_{om} \geq \Phi(\mu) \tag{46}$$

This shows that $y_o = 0$ can never be a bifurcation point. This result has been proved elsewhere (Prigogine *et al.*, 1972; Auchmuty and Nicolis, 1975, 1976).

The eigenvalue 0 is a simple eigenvalue of the system provided there are no such positive integers m_1, m_2 so that the equation (43) can be rewritten in a quadratic form as :

$$D_1 D_2 (m^2 - m_1^2)(m^2 - m_2^2) \quad = \quad 0$$

This is equivalent to the condition,

$$\nu = \frac{1}{\pi^2}\left[\frac{(\alpha x_s Da_1 - Da_2 - 1)}{D_2} - \frac{1 + Da_1(1+\alpha\theta)}{D_1}\right] - m_1^2 \tag{47}$$

which is not a square.

For a simple eigenvalue, $\lambda = 0$, the corresponding eigenvector can be given as,

$$\begin{pmatrix} u_m(r) \\ v_m(r) \end{pmatrix} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \sin m\pi r + \begin{pmatrix} c_1' \\ c_2' \end{pmatrix} \tag{48}$$

Since the eigenvector is normalized, we make use of following two identities :

(1) The norm of a vector is given as,

$$\| (u_m, v_m) \|^{1/2} \quad = \quad \sqrt{(u_m^2 + v_m^2)} \quad = \quad 1 \tag{49}$$

(2) The norm of a function is given as,

$$\int_0^1 f(r)\, dr \quad = \quad 1 \tag{50}$$

Substituting for u_m and v_m from equation (48) into equations (49) and (50) we obtain,

For m is even,

$$(c_1^2 + c_2^2) \quad = \quad \frac{1 - (c_1'^2 + c_2'^2)}{2} \tag{51}$$

For m is odd,

$$(c_1+c_2) = (r_2-r_1) \tag{52}$$

where,

$$r_1 = -\frac{8c_1'}{m\pi} \pm \sqrt{\left(\frac{8c_1'}{m\pi}\right)^2 - 4(2c_1'^2-1)} \tag{53a}$$

$$r_2 = -\frac{8c_2'}{m\pi} \pm \sqrt{\left(\frac{8c_2'}{m\pi}\right)^2 - 4(2c_2'^2-1)} \tag{53b}$$

For $\lambda = 0$, from equations (18) and (48), we obtain,

$$\left(\frac{c_2}{c_1}\right)^2 = \frac{k_4(m^2\pi^2D_1-k_1)}{k_2(k_3-m^2\pi^2D_2)} \tag{54}$$

Thus, using equations (51)-(54), the constants c_1 and c_2 can be computed. Similarly, putting the critical value of wave number m_c, and using computed c_1, c_2 we can see that,

$$\frac{c_2}{c_1} > 0 \tag{55}$$

The adjoint $L^*_{y_o}$ of L_{y_o} is given as,

$$L^*_{y_o}\begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} D_1\nabla_r + k_1 & k_4 \\ k_2 & D_2\nabla_r + k_3 \end{pmatrix}\begin{pmatrix} u \\ v \end{pmatrix} \tag{56}$$

with the condition $\quad u = v = 0.$

From equation (56), we end up with equations for u and v as before,

$$(D^4 + a_1 D^2 + a_2)\, u \quad = \quad a_5 \tag{57}$$

$$(D^4 + a_1 D^2 + a_2)\, v \quad = \quad a_6 \tag{58}$$

where a_1, a_2 are defined by equation (49), and, a_5 and a_6 are given as,

$$a_5 \quad = \quad \frac{k_3 z_1 - k_4 z_2}{D_1 D_2} \qquad\qquad a_6 \quad = \quad \frac{k_1 z_2 - k_2 z_1}{D_1 D_2} \tag{59}$$

The particular solutions to equations (57) and (58) are given as,

$$d'_1 \quad = \quad \frac{a_5}{a_2} \quad = \quad \frac{k_3 z_1 + k_4 z_2}{k_3 k_1 - k_2 k_4} \qquad\qquad d'_2 \quad = \quad \frac{a_6}{a_2} \quad = \quad \frac{k_1 z_2 - k_2 z_1}{k_3 k_1 - k_2 k_4} \tag{60}$$

The eigenvalues of the adjoint operator $L^{*}_{y_o}$ are the same as that of L_{y_o}, and the eigenfunction for simple zero eigenvalue is given as,

$$\begin{pmatrix} u_m(r) \\ v_m(r) \end{pmatrix} \quad = \quad \begin{pmatrix} d_1 \\ d_2 \end{pmatrix} \sin m\pi r + \begin{pmatrix} d'_1 \\ d'_2 \end{pmatrix} \tag{61}$$

As before in the case of c_1 and c_2, equations to compute d_1 and d_2 can be derived.

2.5 Conclusions

The chapter presents the analysis of the steady state solutions of the system of non-linear equations which describe an exponential autocatalytic reaction with diffusion. The stability of steady state solutions of the system has been derived using the linear stability analysis. In particular, criteria in terms of the bounds on the values of parameters appearing in the equations are developed, and show different stability properties of solutions. The analysis reveals the existence of the critical value y_{oc} of a component y beyond which the uniform steady state solutions undergo a change in stability properties. It is possible to have additional steady state solutions of the system of equations, which may be stable for the various ranges of y_o. These solutions, however, are inhomogeneous and possess several well-defined maxima or minima. These so called dissipative structures would be the focus of analysis in the next chapter which extensively uses the results derived here.

2.6 Notation

a_1, a_2, a_3, a_4	constants defined in equation (14)
a_5, a_6	constants defined in equation (59)
c_1, c_2	constants defined by equation (17)
c_1', c_2'	constants defined by equation (16)
d_1, d_2	constants defined by equation (61)
d_1', d_2'	constants defined by equation (60)
Da_1, Da_2	Damkohler number for species X and Y
k_1, k_2, k_3, k_4	constants defined by equation (12)
L_{y_o}	Linear matrix differential operator given in equation (18)
$L^*_{y_o}$	Adjoint of the linear operator given in equation (56)
m	wave number
m_c	critical value of wave number defined in equation (34)
p	term defined by equation (24)
q	term defined by equation (33)
r_1, r_2	constants defined by equation (53)
t	dimensionless time
u_m, v_m	eigenfunction defined by equation (17)
x	concentration of species X in CSTR, (gmol/lit)
x_o	initial concentration of species X
x_s	steady state value of x

$x_{in}(r)$	inlet concentration of X
y	concentration of species Y in CSTR, (gmol/lit)
y_o	initial concentration of species Y
y_{oc}	critical value of y_o
$y_{in}(r)$	inlet concentration of Y
z	term defined in equation (24)
z_1, z_2	constants defined by equation (10)

Greek Letters

α	exponential autocatalysis parameter
α_m	defined by equation (20)
β_m	defined by equation (20)
δ	defined by equation (24)
θ	steady state value of y
λ	eigenvalue of linear operator
μ	critical value of wave number
$\varphi(m)$	term defined by equation (44)
$\varphi(\mu)$	term defined by equation (46)

2.7 References

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CHAPTER III

BIFURCATION ANALYSIS OF ENCILLATOR : REACTION-DIFFUSION EQUATIONS: DISSIPATIVE STRUCTURE AND ITS PROPERTIES

The present chapter constructs the non-negative inhomogeneous solutions of a model exponentially autocatalyzed reaction-diffusion system. The qualitative properties of the dissipative structures show that the branches of solutions belonging to sub- and super- critical bifurcation exhibit interesting features such as hysterisis, symmetry breaking etc. The presence of initial gradients in the system results in localization of the dissipative structure and present analysis provides its qualitative behavior and an estimate of its size.

3.1 Introduction

After establishing that there is a critical value y_{∞} of y_o such that for $y > y_{oc}$, the homogeneous solution (x_s, θ) is linearly unstable, we will consider some other steady state non-negative solutions, which are not homogeneous. These solutions arise mathematically as new branches and occur only in open systems operating at far from thermodynamic equilibrium.

The construction of these dissipative structures is carried out using bifurcation theory (Sattinger, 1973; Stakgold and Satttinger, 1973; Auchmuty and Nicolis, 1975), and the results are presented in Section 2. The qualitative properties of these dissipative structures are examined in Section 3, while Section 4 presents the results for the case when one of the species (here initial concentration x_o of X) has a spatial distribution. The properties of localized spatial structures such as its size are also estimated.

3.2 Bifurcation of Dissipative Structures

Writing the evolution equations for steady state equations in linearised form,

$$D_1\nabla_r X - [1+Da_1(1+\alpha\theta)]X - (\alpha x_s Da_1)Y + (x_o - x_s - Da_1 x_s(1+\alpha\theta)) = h(X,Y) \tag{1a}$$

$$D_2\nabla_r Y + Da_1(1+\alpha\theta)X - (1+Da_2-\alpha x_s Da_1)Y + (y_o - (1+Da_2)\theta) + Da_1 x_s(1+\alpha\theta)) = -h(X,Y) \tag{1b}$$

subject to the condition,

$$X(0) = X(1) = Y(0) = Y(1) = 0 \tag{2}$$

Equation (1) may be written as :

$$L_{y_o}\begin{pmatrix} X \\ Y \end{pmatrix} + \begin{pmatrix} (x_o - x_s - Da_1 x_s(1+\alpha\theta)) \\ (y_o - (1+Da_2)\theta + Da_1 x_s(1+\alpha\theta)) \end{pmatrix} = \begin{pmatrix} h(X,Y) \\ -h(X,Y) \end{pmatrix} \tag{3}$$

where L_{y_o} is the linear operator defined as,

$$L_{y_o}\begin{pmatrix} X \\ Y \end{pmatrix} = \begin{pmatrix} D_1\nabla_r - (1+Da_1(1+\alpha\theta)) - (\alpha x_s Da_1) \\ Da_1(1+\alpha\theta))D_2\nabla_r - (1+Da_2-\alpha x_s Da_1) \end{pmatrix} \tag{4}$$

and $h(X,Y)$ is given as $h(X,Y) = \alpha Da_1 XY$.

From a basic theorem in bifurcation, new branches of steady-state solutions can bifurcate from the solution (0, 0) only when $y_o = y_{om}$ for some integer $m \geq 1$. However, this is only a necessary but not a sufficient condition. So, using a similar method described by Sattinger (1973), we will actually construct the bifurcating solutions to find out whether bifurcation really occurs.

In the following we assume that both the solution and the parameter y_o have a power series expansion in a new variable ε. The bifurcating solutions are obtained close to y_{om} (refer to chapter II; equation (45)) and for a simple zero eigenvalue. In particular, we are interested in the critical value of y_o, for which the bifurcating solutions are sought.

For the sake of simplifying the cumbersome mathematical analysis, we notice that the control parameter y_o is grouped into the variable θ, in terms of which the further calculations become easier. So, in the rest of the paper the expressions are written for θ instead of y_o. Also, all the results stated earlier for y_{om} are valid and remain same or can be rearranged for θ_m.

To determine the bifurcating solutions, the Poincaré-Lindstédt series is used :

$$\begin{pmatrix} X(r) \\ Y(r) \end{pmatrix} = \varepsilon\begin{pmatrix} X_o(r) \\ Y_o(r) \end{pmatrix} + \varepsilon^2\begin{pmatrix} X_1(r) \\ Y_1(r) \end{pmatrix} + \varepsilon^3\begin{pmatrix} X_3(r) \\ Y_3(r) \end{pmatrix} + \dots \tag{5}$$

and,

$$(\theta - \theta_m) = \varepsilon\gamma_1 + \varepsilon^2\gamma^2 + \ldots. \tag{6}$$

Substituting equation (6) into equation (3) one gets,

$$L_{\theta_m}\begin{pmatrix} X \\ Y \end{pmatrix} - \alpha Da_1\,(\theta - \theta_m)\begin{pmatrix} X \\ -X \end{pmatrix} + \begin{pmatrix} (x_o - x_s - Da_1 x_s(1+\alpha\theta)) \\ (y_o - (1+Da_2)\theta + Da_1 x_s(1+\alpha\theta)) \end{pmatrix}$$
$$= \begin{pmatrix} h(X,Y) \\ -h(X,Y) \end{pmatrix} \tag{7}$$

After collecting terms of equal powers of ε, one gets the following system of equations,

$$L_{\theta_m}\begin{pmatrix} X_k \\ Y_k \end{pmatrix} = \begin{pmatrix} a_k(r) \\ -a_k(r) \end{pmatrix} \qquad 0 \le k < \infty \tag{8}$$

with,

$$X_k(0) = X_k(1) = Y_k(0) = Y_k(1) = 0 \tag{9}$$

The expression $a_k(r)$ involves $\gamma_1, \gamma_2, \ldots, \gamma_k$ and $X_k(r), Y_k(r)$, with $0 \le i \le k-1$. Collecting equal powers of ε one gets,

$$\varepsilon^1 \quad : \qquad a_o(r) = 0 \tag{10a}$$

$$\varepsilon^2 \quad : \qquad a_1(r) = \alpha Da_1(X_o Y_o + \gamma_1 X_o) \tag{10b}$$

$$\varepsilon^3 \quad : \qquad a_2(r) = \alpha Da_1[X_o(Y_1 + \gamma_2) + X_1(Y_o + \gamma_1)] \tag{10c}$$

Now, the first solution of the series is,

$$\begin{pmatrix} X_o(r) \\ Y_o(r) \end{pmatrix} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \sin m\pi r + \begin{pmatrix} c_1' \\ c_2' \end{pmatrix} \tag{11}$$

where the normalised eigenvector is the same as that of $L_{y_{om}}$.

The linear matrix differential operator L_{θ_m} has a simple zero eigenvalue, if and only if the functions $a_k(r)$ obey a solvability condition. This condition is given by the Fredholm alternative and helps us to determine the constants $\gamma_1, \gamma_2, \ldots, \gamma_n$.

The Fredholm alternative is given as,

$$\int_0^1 a_k(r) \sin m\pi r (d_1 - d_2) dr = 0 \tag{12}$$

Since, $d_1 \neq d_2$ is true, equation (12) becomes,

$$\int_0^1 a_k(r) \sin m\pi r = 0 \tag{13}$$

The solutions of the system (8) can show different behavior depending upon whether m is even or odd. Now, we will find out approximations for the first two terms in equation (5) to get a good estimate for $X_k(r)$ and $Y_k(r)$. Towards this end, we need to consider the following two cases of m being even or odd.

3.2.1 m is even

Using the Fredholm alternative in equation (13) and expression for $a_1(r)$ from equation (10b), γ_1 is obtained.

$$\gamma_1 = -\left(\frac{c_1 c'_2 + c'_1 c_2}{c_1}\right) \tag{14}$$

This gives us for k=1 the value of $a_1(r)$ as,

$$a_1(r) = \alpha Da_1\left[X_o Y_o - \left(\frac{c_1 c'_2 + c'_1 c_2}{c_1}\right) X_o\right] \tag{15}$$

Now, to determine $X_1(r)$ and $Y_1(r)$ assume a Fourier series expansion as,

$$\begin{pmatrix} X_1(r) \\ Y_1(r) \end{pmatrix} = \sum_{l=1}^{\infty} \begin{pmatrix} p_l \\ q_l \end{pmatrix} \sin l\pi r \tag{16}$$

Substituting equation (16) in the matrix differential operator for λ=0 with $m \cong \mu$, we obtain,

$$\begin{bmatrix} -l^2\pi^2 D_1 - (1 + Da_1 + Da_1\alpha\theta) - \alpha x_s Da_1 & \\ Da_1(1+\alpha\theta) - lsuper2\pi^2 D_2 - (1 + Da_2 - \alpha x_s Da_1) & \end{bmatrix} \begin{pmatrix} p_l \\ q_l \end{pmatrix} = \begin{pmatrix} b_l \\ -b_l \end{pmatrix} \tag{17a}$$

where,

$$b_l = 2\int_0^1 a_1(r) \sin l\pi r\, dr \qquad 1 \le l < \infty \tag{17b}$$

we obtain $b_l = 0$ if l is even and for l is odd,

$$b_l = 2\alpha Da_1\{(\frac{-4c_1c_2m^2}{\pi(l^2-4m^2)l} + \frac{2}{l\pi}\left[c'_1c'_2 - \frac{c'_1(c_1c'_2+c'_1c_2)}{c_1}\right] \tag{18}$$

Equation (17) forms a system of linear equations, the solution to which, for even values of l is given by,

$$p_l \;=\; q_l \;=0$$

and for odd values of l,

$$\begin{pmatrix} p_l \\ q_l \end{pmatrix} = \frac{b_l}{\Delta_l + \alpha x_s Da_1^2(1+\alpha\theta)} \begin{pmatrix} -l^2\pi^2 D_2 - (1+Da_2) - 2\alpha x_s Da_1 \\ l^2\pi^2 D_1 + 1 \end{pmatrix} \tag{19}$$

where,

$$\begin{aligned} \Delta_l =& l^4\pi^4 D_1 D_2 + \{D_2[1+Da_1(1+\alpha\theta)] + D_1[1+Da_2-\alpha x_s Da_1]\}\, l^2\pi^2 \\ &+ \{(1+Da_1)(1+Da_2) + \alpha Da_1(1+Da_2)\theta + \alpha x_s Da_1[1+Da_1(1+\alpha\theta)]\} \end{aligned} \tag{20}$$

Notice that equation (19) requires the knowledge of θ, which can be obtained by rearranging equation (20) (refer to chapter II for θ_c; equation (35)) with the result,

$$\Delta_l(\theta_c) + \alpha x_s Da_1^2(1+\theta_c) \;=\; (l^4\pi^4 A_1 + l^2\pi^2 A_2 + A_3) + \theta_c(l^2\pi^2 A_4 + A_5) \tag{21}$$

where the various constants A_1, A_2, A_3, A_4 and A_5 are defined as,

$$A_1 = D_1 D_2 \tag{22a}$$

$$A_2 = D_2(1 + Da_1) + D_1(1 + Da_2 - \alpha x_s Da_1) \tag{22b}$$

$$A_3 = (1 + Da_1)(1 + Da_2) + \alpha Da_1[1 + x_s(1 + 2Da_1)] \tag{22c}$$

$$A_4 = \alpha Da_1 D_2 \tag{22d}$$

$$A_5 = \alpha Da_1 D_2 + 2\alpha x_s Da_1 \tag{22e}$$

The various terms in equation (18) can also be grouped together for the sake of brevity using parameters below,

$$B_1 = -8\alpha Da_1 c_1^2 c_2 \mu^2 \tag{23a}$$

$$B_2 = 4\alpha Da_1 (c_1')^2 c_2 \tag{23b}$$

$$C_1 = 2\alpha x_s Da_1 + (1 + Da_2) \tag{23c}$$

to give a simpler form as follows,

$$b_l = \frac{B_1 + lB_2}{\pi c_1 (l^2 - 4\mu^2) l} \tag{24}$$

Equations (16)-(20) together with equations (21)-(24) completely define the solutions $X_1(r)$ and $Y_1(r)$ as,

$$\begin{aligned} X_1 = & -\frac{B_1}{\pi c_1} \sum_{l=1}^{\infty} \frac{(l^2\pi^2 D_2 + C_1)\sin l\pi r}{(l^2 - 4\mu^2) l \,[l^4\pi^4 A_1 + l^2\pi^2(A_2 + \theta_c A_4) + (A_3 + \theta_c A_5)]} \\ & -\frac{B_2}{\pi c_1} \sum_{l=1}^{\infty} \frac{(l^2\pi^2 D_2 + C_1)\sin l\pi r}{l^4\pi^4 A_1 + l^2\pi^2(A_2 + \theta_c A_4) + (A_3 + \theta_c A_5)} \end{aligned} \tag{25}$$

$$Y_1 = \frac{B_1}{\pi c_1} \sum_{l=1}^{\infty} \frac{(l^2\pi^2 D_1 + 1)\sin l\pi r}{(l^2 - 4\mu^2)l\,[l^4\pi^4 A_1 + l^2\pi^2(A_2 + \theta_c A_4) + (A_3 + \theta_c A_5)]}$$

$$+\frac{B_2}{\pi c_1} \sum_{l=1}^{\infty} \frac{(l^2\pi^2 D_1 + 1)\sin l\pi r}{l^4\pi^4 A_1 + l^2\pi^2(A_2 + \theta_c A_4) + (A_3 + \theta_c A_5)} \tag{26}$$

Using the expressions for $X_1(r)$ and $Y_1(r)$ from equations (25) and (26), the constant γ_2 can be obtained with k = 2 in a manner similar to that used for estimating γ_1 using the Fredholm alternative in equation (13).

$$\gamma_2 = \frac{2\psi}{c_1} \tag{27}$$

and ψ is given as,

$$\psi = \xi_3\{\xi_1 + \xi_2\} \tag{28}$$

defining ξ_1, ξ_2 and ξ_3

$$\xi_1 = \{\frac{4B_1c_2}{\pi^2 c_1}\sum_{l_{odd}}^{\infty}\frac{Z_2}{Z_{o1}(l^2-\mu^2)} + \frac{4B_2c_2}{\pi^2 c_1}\sum_{l_{odd}}^{\infty}\frac{Z_2 l}{Z_{o2}(l^2-\mu^2)}$$

$$-\frac{4B_1}{\pi^2}\sum_{l_{odd}}^{\infty}\frac{Z_1}{Z_{o1}(l^2-\mu^2)} - \frac{4B_2}{\pi^2}\sum_{l_{odd}}^{\infty}\frac{Z_1 l}{Z_{o2}(l^2-\mu^2)}\} \tag{29a}$$

$$\xi_2 = \{\frac{2B_1c'_2}{\pi^2 c_1}\sum_{l_{odd}}^{\infty}\frac{Z_1}{l^2 Z_{o1}} + \frac{2B_2c'_2}{\pi^2 c_1}\sum_{l_{odd}}^{\infty}\frac{Z_2}{Z_{o2}l}$$

$$+\frac{(c_1c'_2 + c'_1c_2 - c_1c'_1)}{c_1}\left\{\frac{2B_1}{\pi^2 c_1}\sum_{l_{odd}}^{\infty}\frac{Z_1}{l^2 Z_{o1}} + \frac{2B_2}{\pi^2 c_1}\sum_{l_{odd}}^{\infty}\frac{Z_1}{Z_{o2}l}\right\}\} \tag{29b}$$

$$\xi_3 = \left\{ \frac{1}{2\left(\sum_{l_{odd}}^{\infty} \frac{4l}{\pi(l^2 - 4\mu^2)} + \sum_{l_{odd}}^{\infty} \frac{2c'_1}{l\pi c_1} \right)} \right\} \tag{29c}$$

where

$$Z_{o1} = (l^2 - 4\mu^2)\,[l^4\pi^4 A_1 + l^2\pi^2(A_2 + \theta_c A_4) + (A_3 + \theta_c A_5)] \tag{30a}$$

$$Z_{o2} = [l^4\pi^4 A_1 + l^2\pi^2(A_2 + \theta_c A_4) + (A_3 + \theta_c A_5)] \tag{30b}$$

$$Z_1 = (1 + l^2\pi^2 D_1) \tag{30c}$$

$$Z_2 = (l^2\pi^2 D_2 + C_1) \tag{30d}$$

Now, we will determine ε in terms of the constants γ_1 and γ_2 using the critical value of bifurcation parameter y_o grouped in θ. Truncating the series in equation (6) to first two terms,

$$\theta - \theta_c = \varepsilon\gamma_1 + \varepsilon\gamma_2 \tag{31}$$

For $\gamma_2 > 0$, this gives,

$$\varepsilon = \frac{-\gamma_1 \pm \sqrt{\gamma_1^2 + 4\gamma_2(\theta - \theta_c)}}{2\gamma_2} \qquad \text{for } \theta > \theta_c \tag{32}$$

while for $\gamma_2 < 0$ the result is,

$$\varepsilon = \frac{-\gamma_1 \pm \sqrt{\gamma_1^2 + 4\gamma_2(\theta_c - \theta)}}{2\gamma_2} \qquad \text{for } \theta_c > \theta \tag{33}$$

Substituting the equations for ε (from equation (32)), X_o (from equation (11)) and $X_1(r)$ (equation (5)) we finally obtain,

$$\begin{pmatrix} X(r) \\ Y(r) \end{pmatrix} = \varepsilon \begin{pmatrix} X_o(r) \\ Y_o(r) \end{pmatrix} + \varepsilon^2 \begin{pmatrix} X_1(r) \\ Y_1(r) \end{pmatrix} \tag{34}$$

We note that, when $\gamma_2 > 0$, the bifurcating solutions are stable for $\theta > \theta_c$; however, when $\gamma_2 < 0$ they are not stable. Similar results can be obtained for Y(r). Figs. 1a and b show the qualitative behavior for $\gamma_2 < 0$ and $\gamma_2 > 0$.

3.2.2 *m* is odd

In this case, the solvability condition (13) gives us the required expression for γ_1.

$$\gamma_1 = -\frac{\left(\frac{4c_1c_2}{3m\pi} + \frac{c_1c'_2 + c_2c'_1}{2} + \frac{2c'_1c'_2}{m\pi}\right)}{c_1\left(\frac{1}{2} + \frac{2c'_1}{c_1m\pi}\right)} \tag{35}$$

Then the function $a_1(r)$ may be given using equation (10b) as,

$$a_1(r) = \left\{ X_oY_o - X_o \frac{\left(\frac{4c_1c_2}{3m\pi} + \frac{c_1c'_2 + c_2c'_1}{2} + \frac{2c'_1c'_2}{m\pi}\right)}{c_1\left(\frac{1}{2} + \frac{2c'_1}{c_1m\pi}\right)} \right\} \tag{36}$$

Following the same procedure as given for the case when *m* is even, it is seen in the end that only the constants in the expressions for b_l have changed. Referring to the same form of equation (24) for b_l, the new constants B_1 and B_2 are found to be :

$$B_1 = (-8c_1^2c_2\mu^2) \tag{37a}$$

$$B_2 = 4\left\{ \frac{c'_1c'_2}{2} - \frac{\left(\frac{4c_1c_2}{3m\pi} + \frac{c_1c'_2 + c_2c'_1}{2} + \frac{2c'_1c'_2}{m\pi}\right)}{c_1\left(\frac{1}{2} + \frac{2c'_1}{c_1m\pi}\right)} \right\} \tag{37b}$$

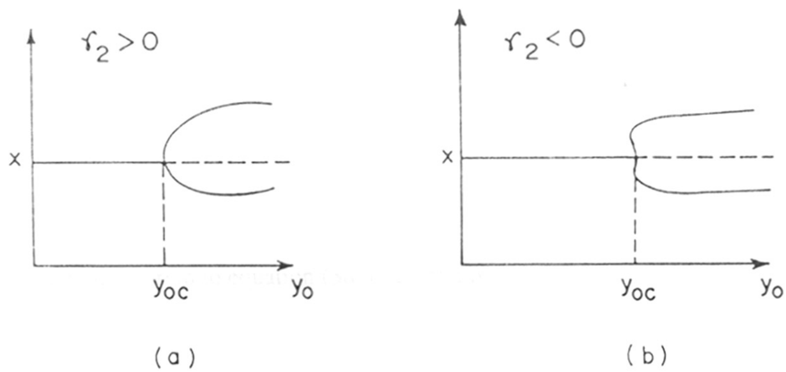

FIG. 1: QUALITATIVE BIFURCATION DIAGRAM FOR THE CASE OF EVEN WAVE NUMBER

With these modified B_1 and B_2, one may easily find that the final expressions for $X_1(r)$ and $Y_1(r)$ remain same as given in equations (25) and (26). Also, the expression for γ_2 as given in equation (27) remains unchanged.

To obtain ε as before we start with equation (31) to get,

$$\varepsilon = \frac{-\gamma_1 \pm \sqrt{\gamma_1^2 + 4\gamma_2(\theta - \theta_c)}}{2\gamma_2} \tag{38}$$

To obtain the least value for θ the discriminant of the quadratic equation (38) is equated to zero. This gives,

$$\hat{\theta} = \theta_c - \frac{\gamma_1^2}{4\gamma_2} \tag{39}$$

Applying binomial theorem to equation (38) one obtains,

$$\varepsilon = -\left(\frac{\gamma_1}{2\gamma_2}\right) \pm \left(\frac{\gamma_1}{2\gamma_2}\right)\left\{1 + \frac{2\gamma_2(\theta - \theta_c)}{g^2} - \frac{2\gamma_2^2(\theta - \theta_c)^2}{g^4} + \ldots\right\} \tag{40}$$

Truncating the series in equation (40) to second order terms and taking positive root of the resulting equation, we obtain :

$$\varepsilon = \frac{(\theta - \theta_c)}{\gamma_1} - \frac{\gamma_2(\theta - \theta_c)^2}{\gamma_1^3} + O[(\theta - \theta_c)^3] \tag{41}$$

Substituting the value of ε in equation (5) results in :

$$\begin{pmatrix} X(r) \\ Y(r) \end{pmatrix} = \left[\frac{\theta - \theta_c}{\gamma_1} - \frac{\gamma_2(\theta - \theta_c)^2}{\gamma_1^3}\right]\begin{pmatrix} (c_1 \sin m_c \pi r + c'_1) \\ (c_2 \sin m_c \pi r + c'_2) \end{pmatrix} + \frac{\gamma_2(\theta - \theta_c)^2}{\gamma_1}\begin{pmatrix} X_1(r) \\ Y_1(r) \end{pmatrix} \tag{42}$$

Likewise if one takes negative root into account, we obtain,

$$\varepsilon \;=\; -\left(\frac{\gamma_1}{\gamma_2}\right) - \frac{(\theta-\theta_c)}{\gamma_1} + O[(\theta-\theta_c)^2] \tag{43}$$

Subsequently, equation (5) becomes,

$$\begin{pmatrix} X(r) \\ Y(r) \end{pmatrix} \;=\; \left[\frac{(\theta-\theta_c)c_1}{2\psi}\right]^{1/2} \begin{pmatrix} (c_1 \sin m_c \pi r + c'_1) \\ (c_2 \sin m_c \pi r + c'_2) \end{pmatrix} + \left[\frac{(\theta-\theta_c)c_1}{2\psi}\right] \begin{pmatrix} X_1(r) \\ Y_1(r) \end{pmatrix} \tag{44}$$

A typical bifurcation diagram for this case is shown in Fig. 2. The various stable and unstable branches are identified on the figure. The figure shows hysterisis like effect for $\theta > \theta_c$ where two stable solutions can be identified. The particular solution approached will of course depend on the initial condition chosen. The branch *d* shown in figure corresponds to solution (.44) obtained using the other root.

3.3 Qualitative Properties of Dissipative Strutures

Here, the qualitative properties of the non-negative bifurcating solutions constructed in the last section are given.

3.3.1 Case : m_c is even

As seen from equations (33) and (34), the critical exponent of non-negative solutions is found to be $\frac{1}{2}$ and the solutions are degenerate. This indicates symmetry breaking transition at the bifurcation point (Prigogine *et al.*, 1972).

The subharmonic solution given by infinite series in equation (34) introduces spatial asymmetry into the solutions due to nonlinear effects.

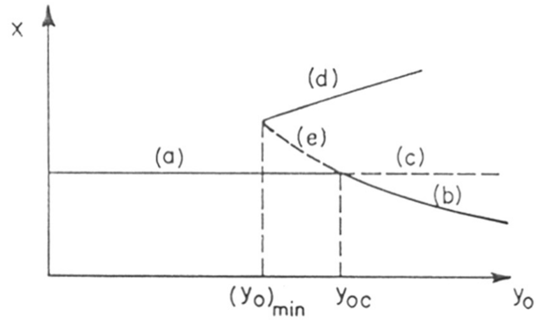

FIG. 2 : QUALITITIVE BIFURCATION DIAGRAM FOR THE CASE OF ODD WAVE NUMBER

For even values of l, $p_l = q_l = 0$, and from this one can state that the new solutions are a superposition of the critical mode i.e. proportional to *sin* $(m_c \pi r)$, where l is an odd integer near the critical value m_c (or μ) or 2μ.

3.3.2 Case : m_c is odd

In the situation $\theta > \theta_c$ one observes that one structure shows symmetry-breaking, while the other on a branch crossing the critical point, shows an effect similar to hysterisis near the bifurcation point. While for $\theta < \theta_c$ there are again two dissipative structures, one of which is unstable and the other requires a transition from uniform solution.

The equation (42) shows that the new solution is a superposition of the critical mode and a distortion which is proportional to $(\theta - \theta_c)^2$. This distortion is the cause for introducing spatial asymmetry to the solutions.

3.3.3 Case : $m \neq m_c$

In this case, bifurcation of new solutions occurs at $\theta = \theta_m$ from a uniform solution for a simple zero eigenvalue. These structures are similar to the ones obtained for $\theta = \theta_c$. For even m the branches degenerate with critical exponent $\frac{1}{2}$, while for odd m they will resemble to that described for the case m_c is odd.

3.4 Localised Spatial Structures

In this section we will consider the case where the initial concentration x_o is not uniformly distributed. This *spatial dispersion* of x_o[4] is responsible for the localization of the dissipative structure within the natural boundaries of the system. This distribution of x_o over the size of the system is assumed to be,

$$x_o(r) = x_o \frac{\cosh\left[2\rho\left(r - \frac{1}{2}\right)\right]}{\cosh \rho} \tag{45}$$

and the concentration y_o is held constant as $y_o(r) = y_o$ for $0 \le r \le 1$.

For steady state equations given as,

$$D_1 x'' - x + x_o - Da_1 x(1+\alpha y) = 0 \tag{46a}$$

$$D_2 y'' - y + y_o + Da_1 x(1+\alpha y) - Da_2 y = 0 \tag{46b}$$

the boundary conditions are given as,

$$x(0) = x(1) = x_s, \qquad y(0) = y(1) = \theta.$$

For a simple zero eigenvalue of the linear stability equations (46a) and (46b), we will determine the form of solutions accounting for spatial dispersion of x_o.

Adding the two equations (46a,b), we obtain,

$$D_1 x'' + D_2 y'' - x - y(1+Da_2) + (x_o + y_o) = 0 \tag{47}$$

We shall associate a new variable $z(r)$ defined as, $z(r) = x(r) + \frac{1}{\gamma} y(r)$, with equation (47) and define γ as (D_1/D_2). It may be noticed that as a consequence of the spatial dispersion of x_o, the system variables $x(r)$ and $z(r)$ and the initial concentration x_o itself may be expressed in terms of parameter ρ defined as $\frac{1}{2} D_1^{-1/2}$,

$$x_o(r) \;=\; x_o \;+\; \rho^2 a(\rho, r) \tag{48}$$

$$x(r) \;=\; x_s \;+\; \rho^2 x(\rho, r) \tag{49}$$

and,

$$z(r) \;=\; x_s \;+\; \frac{\theta}{\gamma} \;+\; \rho^2 z(\rho, r) \tag{50}$$

The term $a(\rho, r)$ in terms of which the following results will be obtained is defined and approximated near ρ equal to zero, as,

$$a(\rho,r) = \frac{x_o}{\rho^2}\left[\frac{\cosh\left[2\rho\left(r-\frac{1}{2}\right)\right]}{\cosh\rho} - 1\right] \tilde{=} \frac{-x_o}{2\cosh\rho}\left[1-4\left(r-\frac{1}{2}\right)^2\right] \tag{51}$$

Then one notes that the boundary conditions for these variables can be written as,

$$X(\rho,0) = X(\rho,1) = Z(\rho,0) = Z(\rho,1) = 0 \tag{52}$$

And at the boundaries $x_o(r)$ becomes $x_o(0)=x_o(1)=x_o$ and near ρ equal to zero $x_o(r)=x_o$.

Using the definitions made, the equations for z and x are,

$$D_1 z'' - \gamma(1+Da_2)z(\rho,r) - [1-\gamma(1+Da_2)x(\rho,r) + a(\rho,r) = 0 \tag{53}$$

and,

$$D_1 x'' - \{(1+Da_1) + \gamma\alpha x_s Da_1 - \alpha Da_1\theta\}x(\rho,r) - \gamma\alpha x_s Da_1 z(\rho,r)$$

$$-a(\rho,r) + \frac{x_o - (1+Da_1)x_s - \alpha x_s Da_1\theta}{\rho^2} - \rho^2\{\gamma\alpha Da_1\{x(\rho,r)[z(\rho,r)-x(\rho,r)]\}\} = 0 \tag{54}$$

Neglecting the derivatives and small values of ρ one obtains from equations (53) and (54),

$$x(\rho,r)(1+Da_1+\alpha Da_1\theta-\gamma\alpha x_s Da_1) = a(\rho,r)\left\{1+\frac{\alpha x_s Da_1}{1+Da_2}\right\}$$

$$+\frac{x_o-(1+Da_1)x_s-\alpha Da_1 x_s\theta}{\rho^2} \tag{55}$$

and,

$$z(\rho,r) = \frac{\gamma(1+Da_2)-1}{\gamma(1+Da_2)}\left\{\frac{a(\rho,R)\left\{1+\frac{\alpha x_s Da_1}{1+Da_2}\right\}+\frac{x_o-(1+Da_1)x_s-\alpha x_s Da_1\theta}{\rho^2}}{(1+Da_1+\alpha Da_1\theta)-\gamma\alpha x_s Da_1}\right\} + \frac{a(\rho,r)}{\gamma(1+Da_2)} \tag{56}$$

The evolution equations (46a,b) may be rewritten using the transformation,

$$Z = D_1[\alpha x_s Da_1 - (1+Da_2)]X + D_2\alpha x_s Da_1 Y \tag{57}$$

in terms of Z as,

$$Z^{iv} + \Omega_3 Z'' + \Omega_4 Z + c_5' = 0 \tag{58}$$

where the constants in the equation are defined as,

$$\Omega_1 = D_1[\alpha x_s Da_1 - (1 + Da_2)] \tag{59a}$$

$$\Omega_2 = \frac{\alpha x_s Da_1^2(1+\alpha\theta)}{\Omega_1} + \frac{\Omega_1}{D_1 D_2} \tag{59b}$$

$$\Omega_3 = \Omega_2 - \frac{\psi}{\Omega_1} \tag{59c}$$

$$\Omega_4 = \frac{\psi}{D_1 D_2} \tag{59d}$$

And other terms are given as,

$$\kappa_1 = x_s - Da_1 x_s(1+\alpha\theta) + x_o \tag{60a}$$

$$\kappa_2 = (1 + Da_2)\theta - x_s Da_1(1+\alpha\theta) + y_o \tag{60b}$$

$$\kappa_3 = [\alpha x_s Da_1 - (1 + Da_2)]\ \kappa_1 + \alpha x_s Da_1 \kappa_2 \tag{60c}$$

$$\kappa_4 = \frac{\kappa_3}{\Omega_1} \tag{60d}$$

$$\kappa_5 = -(\Omega_2\kappa_3 - \psi\kappa_4) \tag{60e}$$

With the assumption that equation (58) has a solution of the form,

$$z_1 = \left(z(r) - \frac{\kappa_5}{\Omega_4}\right) = e^{\phi(r)} \tag{61}$$

Substituting equation (61) into equation (58), and neglecting the terms of higher order in Taylor series expansion, we note that,

$$[\phi'(r)]^4 + \Omega_3[\phi'(r)]^2 + \Omega_4 \;=\; 0 \tag{62}$$

For equation (62), which is quadratic in $\phi'(r)$ at the turning point we observe that, $[\phi'(r)]^2 =$ 0, giving us,

$$\alpha x_s Da_1\left[\frac{1}{1+Da_2}+\gamma\right]-\gamma(1+Da_2)=0 \tag{4.19}$$

Using equations (55), (56) and, equation (63) for turning point the resulting quadratic equation for r is,

$$r^2 \;-\; r \;+\; \beta \;=\; 0 \tag{64}$$

where,

$$\beta \;=\; \frac{\Omega_2}{2\rho^2 x_o \Omega_1} \tag{65}$$

The roots of equation (64) are given by,

$$r\pm \;=\; \frac{1}{2} \;\pm\; \frac{1}{2}\sqrt{1-4\beta} \tag{66}$$

Examining equation (66), we see that for $0 \le \beta \le \frac{1}{4}$ and $0 < r_- < r_+ < 1$, the roots r_- and r_+ are symmetrically situated about $r = 1/2$. So we get the bounds on the solutions. For the cases $0 \le r \le r_-$ and $r_+ \le r \le 1$ the solution Z(r) will be monotonic, whereas, between r_- and r_+, the solution will oscillate.

As β tends to zero, the turning points will be forced towards the boundaries $r = 0$ and $r = 1$, giving rise to a condition,

$$y_o \;<\; y\,|_{\text{boundary}} = \left\{\frac{\gamma[1+\gamma(1+Da_2)]}{\alpha Da_1}+\theta(1+Da_2)-x_o\right\} \tag{67}$$

Hence, the size of dissipative structure can be given as,

$$2\beta = \frac{\Omega_2}{\rho^2 x_o \Omega_1} \tag{68}$$

3.5 Conclusions

In this chapter the nonnegative inhomogeneous bifurcating solutions of dissipative structures of a model exponentially autocatalyzed reaction-diffusion system have been constructed and analyzed. The qualitative properties of dissipative strutures show that the branches of solutions belonging to subcritical or supercritical bifurcation exhibit different features such as symmetry breaking, hysterisis-like effect etc. In presence of spatial dispersion of one of the components the dissipative structures are localized and an estimate of its size is provided.

3.6 Notation

$a_k(r)$	terms defined in equation (8)
$a(\rho, r)$	term defined in equation (51)
b_l	term defined in equation (24)
B_1, B_2	variables given by equations (23) and (37)
c_1, c_2	constants defined by equation (11)
C_1	variable defined by equation (23c)
c_1', c_2'	particular solutions defined by equation (11)
D_1, D_2	diffusivities of species X and Y
Da_1, Da_2	Damkohler number for species X and Y
L_{y_c}	Linear matrix differential operator given in equation (3)
m	wave number
m_c	critical value of wave number defined in equation (34) (refer chapter II)
r	spatial distance
t	dimensionless time
x	concentration of species X in CSTR, (gmol/lit)
$x(r)$	spatial distribution of x defined in equation (49)
$x(\rho, r)$	term defined in equation (49)
x_o	initial concentration of species X
$x_o(r)$	spatial distribution of x_o throughout the system given by equation (45)

x_s	steady state value of x
X	deviation of x from steady state
y	concentration of species Y in CSTR, (gmol/lit)
y_o	initial concentration of species Y
y_{om}	term defined in equation (45) of chapter II
Y	deviation of y from steady state
z	transformed variable $(=x(r)+\frac{1}{\gamma}y(r))$
$z(r)$	defined in equation (50)
$z(\rho, r)$	term defined in equation (50)
Z_{o1}, Z_{o2}, Z_1, Z_2	constants defined in equation (30)

Greek Letters

α	nonsystemic autocatalysis parameter
β	term defined by equation (65)
γ	ratio of diffusivities $[D_1/D_2]$
γ_1, γ_2	constants defined in equation (6)
ε	a small arbitrary parameter in Poincaré-Lindstédt series
θ	steady state value of y
θ_c	critical value of θ in which control parameter y_o is embedded
μ	critical value of wave number
ξ_1, ξ_2, ξ_3	terms defined in equation (29)

ρ a parameter $(=\frac{1}{2}D_1^{-1/2})$

3.7 REFERENCES

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CHAPTER IV

BOUNDS ON STEADY STATES OF REACTION-DIFFUSION SYSTEM OF ENCILLATOR

Bounds on parameter values that lead to different types of solutions for nonsystemically autocatalysed reaction-diffusion system are derived and show the existence of a critical concentration beyond which the stability properties undergo change. Additionally, bifurcating solutions at the zero eigenvalue are obtained.

4.1 Introduction

In the earlier two chapters, the linear stability analysis was carried out to obtain the bounds on the steady states for a situation when the exponential autocatalytic parameter α is sufficiently small (<< 1), so that the linearization of the nonlinear exponential term is posible. However, there can be situations in the biochemical reaction systems, where the value of the parameter α is quite large. The present chapter derives rigorous bounds on the values of the parameters that lead to the existence of different types of solutions in presence of diffusion gradients.

More specifically the conditions under which the governing system would have real eigenvalues with positive real part, the conditions when eigenvalues are complex and the conditions when the complex eigenvalues have real positive parts have been derived. In addition to this, bifurcating solutions for a simple case of zero eigenvalue are obtained. The mathematical aspects of reacting and diffusing systems are well documented (see for example Sattinger, 1973; Auchmuty and Nicolis, 1975,1976; Fife,1979; Kuramoto, 1984), but the present scheme provides an example where the functions involved are transcendental in nature.

4.2 Linear Stability Analysis

The reaction-diffusion system is represented by following coupled nonlinear parabolic partial differential equations.

$$\frac{\partial x}{\partial t} = D_1 \frac{\partial^2 x}{\partial r^2} + x_o - x - Da_1 x \exp(\alpha y)$$

$$\frac{\partial y}{\partial t} = D_2 \frac{\partial^2 y}{\partial r^2} + y_o - y + Da_1 x \exp(\alpha y) - Da_2 y \tag{1}$$

At steady state, the values of x and y, denoted as x_s and θ respectively, are given by

$$\exp(\alpha\theta) = \frac{(x_o - x_s)}{x_s Da_1} \qquad \theta = \frac{x_o + y_o - x_s}{1 + Da_2} \tag{2}$$

Defining deviations from steady state as u and v

$$x = u + x_s \qquad y = v + \theta \tag{3}$$

and linearization of the nonlinear term exp (αv) = ($1+\alpha v$), equation (1) can be rewritten as :

$$\frac{\partial u}{\partial t} = D_1 \frac{\partial^2 u}{\partial r^2} - (1 + Da_1 e^{\alpha\theta})u - (\alpha Da_1 x_s e^{\alpha\theta} v - \alpha Da_1 e^{\alpha\theta} uv \tag{4a}$$

$$\frac{\partial v}{\partial t} = D_2 \frac{\partial^2 v}{\partial r^2} + Da_1 e^{\alpha\theta} u + (\alpha Da_1 x_s e^{\alpha\theta} - (1 + Da_2))v + \alpha Da_1 e^{\alpha\theta} uv \tag{4b}$$

The eigenvalue problem for equations (4a) and (4b) can be fomulated as :

$$D_1 u'' - (1 + Da_1 e^{\alpha\theta})u - \alpha Da_1 x_s e^{\alpha\theta} v = \lambda u \tag{5a}$$

$$D_2 v'' + Da_1 e^{\alpha\theta} u + (\alpha Da_1 x_s e^{\alpha\theta} - (1 + Da_2))v = \lambda v \tag{5b}$$

Using equations (5a) and (5b), and defining constants k_1, k_2, k_3, k_4 for the sake of simplification as,

$$k_1 = -(1 + Da_1 e^{\alpha\theta}) \qquad k_2 = -\alpha Da_1 x_s e^{\alpha\theta} \tag{6}$$

$$k_3 = \alpha x_s Da_1 e^{\alpha\theta} - (1 + Da_2) \qquad k_4 = Da_1 e^{\alpha\theta} \tag{7}$$

the solution to the eigenvalue problem can be given as

$$\begin{pmatrix} u_m(r) \\ v_m(r) \end{pmatrix} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \sin m\pi r \tag{8}$$

From equations (5)-(8) we obtain

$$c_1^2 + c_2^2 = 2 \tag{9}$$

$$\delta_m \;=\; \frac{c_2}{c_1} \;=\; \frac{-m^2\pi^2 D_1 + k_1}{k_2} \qquad (10)$$

giving us c_1 and c_2 as

$$c_1 \;=\; \frac{\sqrt{2}}{\sqrt{1+\delta_m^2}} \qquad\qquad c_2 \;=\; \frac{\sqrt{2}\,\delta_m}{\sqrt{1+\delta_m^2}} \qquad (11)$$

The system of linear equations possesses the following characteristic equation

$$\lambda^2 \;+\; (\beta_m - \alpha_m)\lambda \;+\; \alpha x_s (Da_1 e^{\alpha\theta})^2 \;-\; \alpha_m \beta_m \;=\; 0 \qquad (12)$$

The eigenvalues are the roots of the characteristic equation given by

$$\lambda^{\pm} \;=\; \frac{1}{2}\left\{(\alpha_m - \beta_m) \;\pm\; \left[(\alpha_m + \beta_m)^2 - 4\alpha x_s (Da_1 e^{\alpha\theta})^2\right]^{1/2}\right\} \qquad (13)$$

Analysis of equation (13) helps us to fix the following conditions for different stability behavior of steady state solutions.

(1) λ^+ has positive real part whenever

$$y_o \;>\; (x_s - x_o) \;+\; \frac{(1+Da_2)}{\alpha}\;\ln\left\{\frac{m^4\pi^4 D_1 D_2 + m^2\pi^2[D_1(1+Da_2) + D_2] + (1+Da_2)}{Da_1[m^2\pi^2(\alpha x_s D_1 - D_2) + (\alpha x_s - Da_2 - 1)]}\right\} \qquad (14)$$

(2) The eigenvalues are complex whenever the discriminant in equation (12) obeys the condition, $\Delta < 0$. The resulting inequality is

$$(x_s - x_o) \;+\; \frac{(1+Da_2)}{\alpha}\;\ln\left\{\frac{(\alpha x_s + 1)(1 + Da_2 - \delta) - \psi}{Da_1(\alpha x_s - 1)^2}\right\} \;<\; y_o$$

$$<\; (x_s - x_o) \;+\; \frac{(1+Da_2)}{\alpha}\;\ln\left\{\frac{(\alpha x_s + 1)(1 + Da_2 - \delta) + \psi}{Da_1(\alpha x_s - 1)^2}\right\} \qquad (15)$$

where

$$\psi \;=\; \{4[\alpha x_s(\delta-1)^2 - Da_2(\delta-1)(\alpha^2 x_s^2+1) + \alpha x_s Da_2^2] + (\alpha x_s - 1)^2\}^{1/2} \tag{16}$$

and
$$\delta \;=\; 1 + m^2\pi^2(D_1 - D_2) \tag{17}$$

(3) A complex value will have positive real part provided,

$$y_o \;>\; (x_s - x_o) \;+\; \frac{(1+Da_2)}{\alpha}\;\ln\left\{\frac{\delta' + Da_2 + 1}{Da_1(\alpha x_s - 1)}\right\} \tag{18}$$

where

$$\delta' \;=\; 1 + m^2\pi^2(D_1 + D_2) \tag{19}$$

Combining the two inequalities given by equations (15) and (18), one sees that,

$$\begin{aligned}(x_s - x_o) \;+\; \frac{(1+Da_2)}{\alpha}\;\ln\left\{\frac{\delta' + Da_2 + 1}{Da_1(\alpha x_s - 1)}\right\} \;< y_o \;< \\ (x_s - x_o) \;+\; \frac{(1+Da_2)}{\alpha}\;\ln\left\{\frac{(\alpha x_s + 1)(1 + Da_2 - \delta) - \psi}{Da_1(\alpha x_s - 1)^2}\right\}\end{aligned} \tag{20}$$

The equation (15) and (16) can be rewritten as :

$$\begin{aligned}m^4\pi^4(D_1 - D_2)^2 + 2m^2\pi^2\{(D_1 - D_2)[Da_1 e^{\alpha\theta}(\alpha x_s + 1) - Da_2]\} \\ + \left\{(\alpha x_s - 1)^2 (Da_1 e^{\alpha\theta})^2 - 2Da_2(\alpha x_s + 1) Da_1 e^{\alpha\theta} + Da_2^2 - 1\right\} = 0\end{aligned} \tag{21}$$

Now, to obtain the critical value of the wave number m_c or μ we shall minimise the function in equation (14). If $f = m^2\pi^2$, then we have following quadratic equation :

$$\begin{aligned}f^2\{D_1D_2(\alpha x_s D_1 - D_2)\} + f\{2D_1D_2(\alpha x_s - Da_2 - 1)\} \\ + (\alpha x_s - Da_2 - 1)[(1+Da_2)D_1 + D_2] - (1+Da_2)(\alpha x_s D_1 - D_2) = 0\end{aligned} \tag{22}$$

giving

$$f = \frac{(1 + Da_2 - \alpha x_s) D_1 D_2 \pm q}{D_2 D_2 (\alpha x_s D_1 - D_2)} \tag{23a}$$

where

$$q = \{[D_1 D_2(\alpha x_s - Da_2 - 1)]^2 - (\alpha x_s D_1 - D_2) \left[D_1 D_2 (\alpha x_s - Da_2 - 1)\,[(1 + Da_2) D_1 + D_2] + \frac{(1 + Da_2)}{4} \right] \}^{1/2} \tag{23b}$$

From equations (14), (22) and (23), we obtain the expression for critical value of bifurcating parameter as :

$$y_{\infty} \geq (x_s - x_o) + \frac{(1 + Da_2)}{\alpha} \times \ln\left\{ D_1 D_2 \frac{\left\{ 2(1 + Da_2) - \frac{(\alpha x_s - Da_2 - 1)[(1 + Da_2) D_1 + D_2]}{(\alpha x_s D_1 - D_2)} + \frac{(1 + Da_2 - \alpha x_s) D_1 D_2 \pm q}{(\alpha x_s D_1 - D_2)} \left\{ \frac{2(1 + Da_2 - \alpha x_s)}{(\alpha x_s D_1 - D_2)} + \frac{D_1 (1 + Da_2) + D_2}{D_1 D_2} \right\} \right\}}{\pm q} \right\} \tag{24}$$

From equation (18), one gets

$$y_{o1} = (x_s - x_o) + \frac{(1 + Da_2)}{\alpha} \ln\left\{ \frac{1 + m^2 \pi^2 (D_1 + D_2) + (1 + Da_2)}{(\alpha x_s - 1) Da_1} \right\} \tag{25}$$

Then combining inequalities (20) and (25),

$$D_2 < 2(Da_2 + 2 + \pi^2 D_1) - \{4[\alpha x_s (\delta_o - 1)^2 - Da_2(\delta_o - 1)(\alpha^2 x_s^2 + 1) + \alpha x_s Da_2^2] + (\alpha x_s - 1)^2\}^{1/2} \tag{26}$$

where

$$\delta_o = 1 + \pi^2 (D_1 - D_2) \tag{27}$$

In particular, if $D_1 = D_2 = D$, equation (26) becomes

$$D \quad < \quad \frac{2(Da_2+2)-[4\alpha x_s Da_2^2+(\alpha x_s-1)^2]^{1/2}}{1-2\pi^2} \tag{28}$$

For a simple zero eigenvalue, the eigenfunction has a condition for the wave number as :

$$\alpha_m \beta_m \quad = \quad \alpha x_s (Da_1 e^{\alpha\theta})^2$$

This produces the following quadratic equation :

$$\begin{aligned} m^4 D_1 D_2 \quad + \quad & \frac{m^2}{\pi^2}\{D_1[\alpha x_s Da_1 e^{\alpha\theta}-(1+Da_2)]-D_2(1+Da_1 e^{\alpha\theta})\} \\ & +\frac{1}{\pi^4}\{\alpha x_s Da_1 e^{\alpha\theta}-(1+Da_2)(1+Da_1 e^{\alpha\theta})\} \quad = \quad 0 \end{aligned} \tag{29}$$

or for y_{om} we can rewrite equation (29) using critical value of m as

$$y_{om} \quad \geq \quad (x_s - x_o) \quad + \quad \frac{(1+Da_2)}{\alpha} \quad \mathrm{x}$$

$$\ln\left\{ D_1 D_2 \frac{\left\{ 2(1+Da_2) - \frac{(\alpha x_s - Da_2 - 1)[(1+Da_2)D_1 + D_2]}{(\alpha x_s D_1 - D_2)} + \frac{(1+Da_2-\alpha x_s)D_1 D_2 \pm q}{(\alpha x_s D_1 - D_2)} \left\{ \frac{2(1+Da_2-\alpha x_s)}{(\alpha x_s D_1 - D_2)} + \frac{D_1(1+Da_2)+D_2}{D_1 D_2} \right\} \right\}}{\pm q} \right\} \tag{30}$$

In a similar fashion, we can substitute value of m_c into equation (30), and obtain another relationship, which confirms that $y_o = 0$, can never be a bifurcation point.

Now for the quadratic equation (29) in m^2, there exist two positive integers m_1 and m_2 such that,

$$D_1 D_2 (m^2 - m_1^2)(m^2 - m_2^2) \quad = \quad 0$$

When m_1 is an integer solution, this yields a condition,

$$\nu \quad = \quad \frac{(1+Da_2)-\alpha x_s Da_1 e^{\alpha\theta}}{D_2} \quad + \quad \frac{1+Da_1 e^{\alpha\theta}}{D_1} \quad - \quad m_1^2 \tag{31}$$

which is not a square.

For the normalised eigenvector given in equation (8), using equations (9)-(11), the constants c_1 and c_2 can be computed. Similarly, putting the critical value of wave number m_c, we can see that :

$$\frac{c_2}{c_1} < 0 \tag{32}$$

The adjoint $L_{y_o}^{*}$ of L_{y_o} is given as :

$$L_{y_o}^{*}\begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} D_1\nabla_r + k_1 & k_4 \\ k_2 & D_2\nabla_r + k_3 \end{pmatrix}\begin{pmatrix} u \\ v \end{pmatrix} \tag{33}$$

with the condition $$u = v = 0 \tag{34}$$

The eigenvalues of the adjoint operator $L_{y_o}^{*}$ are the same as that of L_{y_o}, and the eigenfunction

for simple zero eigenvalue is given as :

$$\begin{pmatrix} u_m(r) \\ v_m(r) \end{pmatrix} = \begin{pmatrix} d_1 \\ d_2 \end{pmatrix}\sin m\pi r \tag{35}$$

Using equations (5) and (35) we obtain

$$d_1^2 + d_2^2 = 2 \tag{36}$$

$$\varepsilon_m = \frac{d_1}{d_2} = \frac{-m^2\pi^2 D_2 + k_3}{k_2} \tag{37}$$

which produces expressions for d_1 and d_2 as

$$d_1 = \frac{\sqrt{2}\,\varepsilon_m}{\sqrt{1+\varepsilon_m^2}} \qquad d_2 = \frac{\sqrt{2}}{\sqrt{1+\varepsilon_m^2}} \tag{38}$$

4.3 Results and Conclusion

The chapter presents the analysis of the steady state solutions of the system of non-linear equations which describe an exponentially autocatalyzed reaction with diffusion. The stability of steady state solutions of the system has been derived using the linear stability analysis. In particular, criteria in terms of the bounds on the values of a parameter appearing in the equations are developed. The analysis reveals the existence of the critical value y_{oc} of a component y beyond which the uniform steady state solutions undergo a change in stability properties. It is possible to have additional steady state solutions of the system of equations, which may be stable for the various ranges of y_o. These solutions, however, are inhomogeneous and possess several well-defined maxima or minima. The results here form a basis for obtaining the so called dissipative structures.

4.4 Notation

c_1, c_2	eigenvectors defined in Eq. (8)
d_1, d_2	eigenvectors for the adjoint of linear operator
D_1, D_2	diffusivities for species X and Y respectively
Da_1, Da_2	Damkohler numbers for species X and Y respectively
f	defined in Eq. (23a) $(= m^2\pi^2)$
k_1, k_2, k_3, k_4	constants defined in Eqs. (6) and (7)
L_{y_o}	linear operator
m	wave number
q	defined in Eq. (23b)
r	dimensionless distance
t	dimensionless time
u, v	deviations from steady state for concentrations x and y respectively

$u_m(r)$, $v_m(r)$	eigenfunctions defined in Eq. (8)
x, y	dimensionless concentration of species
x_o, y_o	initial concentrations
x_s	steady state value of x
y_{o1}	critical value of y_o for $m = 1$
y_{oc}	critical value of concentration y_o
y_{om}	defined in Eq. (30)

Greek Letters

α	exponential autocatalysis parameter
α_m, β_m	defined in Eq. (12)
δ_o	defined in Eq. (27)
δ'	defined in Eq. (19)
δ_m	defined in Eq. (10)
ε_m	defined in Eq. (37)
θ	steady state value of y
λ	eigenvalue
ν	defined in Eq. (31)
ψ	defined in Eq. (16)

4.5 References

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CHAPTER V

HOMOCLINIC ORBITS IN ENCILLATOR

The present chapter analytically obtains the results on how to find branches of periodic solutions which terminate with homoclinic orbit. The conditions for infinite-period finite-amplitude bifurcations are derived and the equations describing the trajectory of homoclinic orbit are constructed.

5.1 The linear stability analysis

Equations describing the exponentially autocatalyzed reaction are given as,

$$\frac{dX}{dt} = x_o - X - Da_1 X \exp(\alpha Y) \tag{1a}$$

$$\frac{dY}{dt} = y_o - Y + Da_1 X \exp(\alpha Y) - Da_2 Y \tag{1b}$$

The steady state solutions of Eqs. (1a) and (1b) are given as,

$$x_s = \frac{x_o}{1 + Da_1 e^{\alpha\theta}}\,; \qquad Da_1 = \frac{y_o - \theta\,(1 + Da_2)}{\theta\,(1 + Da_2) - x_o - y_o}\; e^{-\alpha\theta} \tag{2}$$

Now, defining deviations (u, v) from the steady state as,

$$X = x_o + y_o - \theta\,(1 + Da_2) + u \tag{3a}$$

$$Y = \theta + v \tag{3b}$$

the governing equations can be written in terms of deviation variables as,

$$\frac{du}{dt} = [\theta(1 + Da_2) - y_o]\,[1 - e^{\alpha v}] - u - u e^{\alpha v} \frac{\theta(1 + Da_2) - y_o}{x_o + y_o - \theta(1 + Da_2)} \tag{4a}$$

$$\frac{dv}{dt} = [y_o - \theta(1 + Da_2)] - v(1 + Da_2) + [\theta(1 + Da_2) - y_o]\, e^{\alpha v}$$

$$+ u e^{\alpha v} \frac{\theta(1 + Da_2) - y_o}{x_o + y_o - \theta(1 + Da_2)} \tag{4b}$$

For Eqs. (4a) and (4b), $u = v = 0$ is always a steady state solution. The linearization of this autonomous system about the steady state solution results in an equation of type $d\mathbf{x}/dt = \mathbf{A}\,\mathbf{x}$ where the Jacobian matrix can be identified as,

$$A = \begin{bmatrix} \dfrac{-x_o}{x_o+y_o-\theta(1+Da_2)} & -\alpha[-y_o+\theta(1+Da_2)] \\ \dfrac{\theta(1+Da_2)-y_o}{x_o+y_o-\theta(1+Da_2)} & \alpha[\theta(1+Da_2)-y_o]-(1+Da_2) \end{bmatrix} \tag{5}$$

The determinant and trace of the Jacobian in Eq. (5) are given below :

$$\mathrm{Det}(A) \equiv (1+Da_2)\theta^2-(x_o+2y_o)\theta+\frac{y_o(x_o+y_o)}{1+Da_2}+\frac{x_o}{\alpha} \tag{6}$$

$$\begin{aligned}\mathrm{Tr}(A) \equiv\ & \alpha(1+Da_2)\theta^2-[\alpha(x_o+2y_o)+(1+Da_2)]\theta \\ & +\left(x_o+y_o+\frac{x_o+\alpha y_o(x_o+y_o)}{1+Da_2}\right)\end{aligned} \tag{7}$$

The critical values of θ are those for which $Tr(A) = 0$ or $Det(A) = 0$. These conditions given by the quadratic Eqs. (6) and (7) are useful in establishing bounds, where trace and determinant change sign. The upper bounds for trace and determinant never vanishing are given by,

$$[\alpha x_o-(1+Da_2)]^2 \le 4\alpha x_o \tag{8}$$

$$x_o \le \frac{4(1+Da_2)}{\alpha} \tag{9}$$

Referring to Figure 1, one may notice that, the two critical relationships in Eqs. 7 and 8 divide the α-Da_1 plane into a number of regions, which possess different characteristics depending upon the signs of trace and determinant. Following that $Det(A) = 0$ if and only if $dDa_1/d\theta = 0$, the two solutions in θ-Da_1 plane merge at the bifurcation limit point. In region I, the two conditions given by Eqs. 6 and 7 hold, and the solution is unique and linearly stable. In region II, Eq. 6 fails, but Eq. 7 holds. This means that there are two values of θ at which $Det(A)$ changes sign with a change in stability. However, trace does not change sign, with the result, no other changes in stability occur. In region III Hopf bifurcations occur as $Tr(A)$ changes sign twice with $Det(A)$ remaining positive. Finally, in region IV both the conditions (6) and

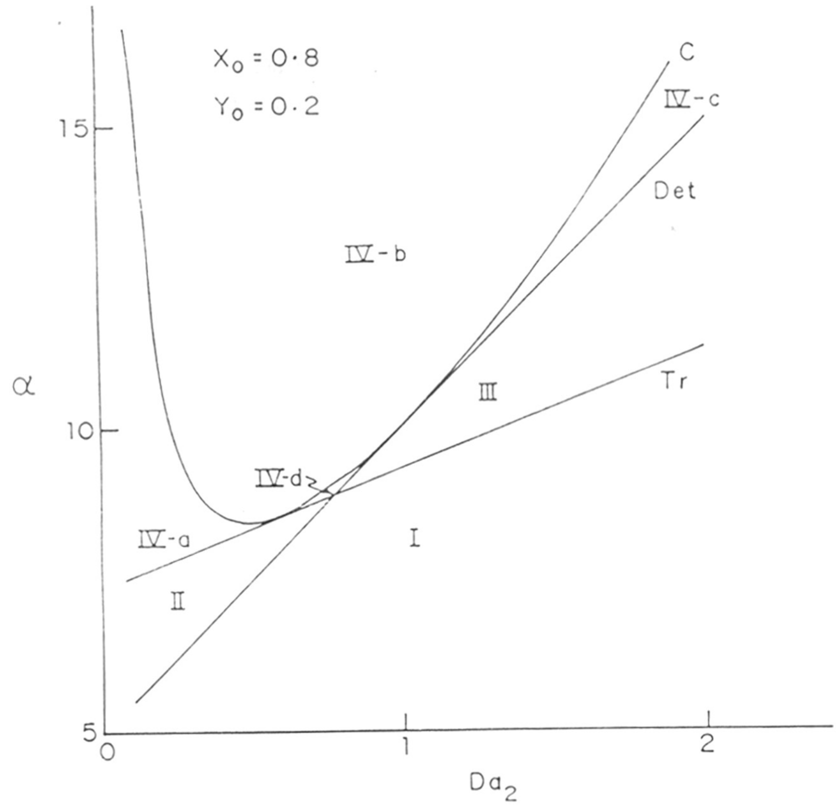

Figure 1: Bifurcation Diagram

(7) fail, and $Tr(A)$ and $Det(A)$ change sign. The homoclinic bifurcation occurs when Eqs. (6) and (7) have a coinciding root. Since, Eqs. 6 and 7 are quadratic in nature, correspondingly we obtain four possible sub-regions for this region IV. The coinciding root can be obtained as,

$$\alpha^{*} = \frac{(1+Da_2)^3}{x_o Da_2}; \qquad \theta^{*} = \left[\frac{x_o}{1+Da_2} + y_o\right]\frac{1}{(1+Da_2)} \tag{10}$$

This curve labeled as C in Figure 1 lies entirely in region IV, and is tangent to the curve D at $Da_2 = 1$, and is tangent to curve T at Da_2^{*}, which is the largest root of $Da_2^2 + Da_2 - 1 = 0$. To examine this condition for infinite period more carefully, we rewrite the system in Eqs. (4a) and (4b) in the neighborhood of the critical parameter curve given by Eq. 10 (Keener, 1982). On this curve, the Jacobian matrix in Eq. (5) becomes,

$$A = \begin{bmatrix} -\dfrac{1+Da_2}{Da_2} & -\dfrac{(1+Da_2)^2}{Da_2} \\ \dfrac{1}{Da_2} & \dfrac{1+Da_2}{Da_2} \end{bmatrix} \tag{11}$$

Since, on this curve trace and determinant are zero, it has a generalized null-space spanned by two eigenvectors, given by $Ae_1 = 0$, and $Ae_2 = e_1$. These eigenvectors are found to be,

$$e_1 = \begin{bmatrix} -1 \\ \dfrac{1}{1+Da_2} \end{bmatrix}; \qquad e_2 = \begin{bmatrix} \dfrac{Da_2}{(1+Da_2)} \\ 0 \end{bmatrix} \tag{12}$$

The vectors e_1 and e_2 provide a natural coordinate system to rewrite Eqs. 4a, 4b. The time variations occur, as clear from structure of A, on a slow time scale suggesting rescaling of time and the variables so that e_1 and e_2 interact on the same order. Further allowing for α and θ to deviate slightly from their critical values, we let,

$$\begin{pmatrix} u \\ v \end{pmatrix} = \varepsilon^2 x \begin{bmatrix} -1 \\ \dfrac{1}{1+Da_2} \end{bmatrix} + \varepsilon^3 y \begin{bmatrix} \dfrac{Da_2}{(1+Da_2)} \\ 0 \end{bmatrix} \tag{13}$$

$$\alpha = \frac{(1+Da_2)^3}{x_o Da_2} + \varepsilon^2\,\delta\alpha \tag{14}$$

$$\theta = \left[\frac{x_o}{1+Da_2} + y_o\right]\frac{1}{(1+Da_2)} + \varepsilon^2\,\delta\theta \tag{15}$$

Noting from Eq. 13 that,

$$\frac{dx}{d\tau} = \frac{(1+Da_2)}{\varepsilon^3}\frac{dv}{dt} \tag{16}$$

and using the Taylor series expansions in Eq. 13, we see that,

$$\begin{aligned} \frac{dx}{d\tau} = \; & y + \varepsilon x\{-\frac{\delta\theta(1+Da_2)^2}{x_o Da_2}[2+(1+Da_2)^2] \\ & -\frac{\delta\alpha}{x_o Da_2^2(1+Da_2)} - \frac{(1+Da_2)^3}{x_o}x\} \end{aligned} \tag{17}$$

$$\begin{aligned} \frac{dy}{d\tau} = \; & x\,\{\frac{\delta\theta(1+Da_2)^5(Da_2-1)}{x_o Da_2^3} + \frac{\delta\theta(1+Da_2)^2}{x_o Da_2} + \frac{x_o\delta\alpha}{Da_2}(1+2Da_2) \\ & -x_o\delta\theta(1+Da_2)^4[2+(1+Da_2)^4] - \frac{(1+Da_2)^4}{x_o Da_2^3}x(1+x_o^2 Da_2^4(1+Da_2))\} \\ & +\varepsilon y\left\{\frac{\delta\theta(1+Da_2)}{x_o} + x\left[\frac{(1+Da_2)^3}{x_o Da_2^2}\right]\right\} \end{aligned} \tag{18}$$

Eqs. 17 and 18 can be rewritten more simply as,

$$\frac{dx}{dt} = y + \varepsilon g_1(x,y,t), \qquad \frac{dy}{dt} = ax^2 + bx + \varepsilon g_2(x,y,t) \tag{19}$$

where $g_1(x,y,\tau)$ and $g_2(x,y,\tau)$ can be identified and the other parameters are,

$$a = -\frac{(1+Da_2)^2}{Da_2} \tag{20}$$

$$b = \frac{x_o\delta\alpha}{1+Da_2} + \frac{(1+Da_2)^4\,\delta\theta}{x_o Da_2} - \frac{\delta\theta(1+Da_2)^3}{x_o Da_2}) \tag{21}$$

For $\varepsilon \to 0$, Eq. 14 reduces to,

$$\frac{dx_o}{d\tau} = y_o, \quad \frac{dy_o}{d\tau} = x_o\,(ax_o + b) \tag{22}$$

We see that for $b < 0$, the origin $x = y = 0$ in Eq. 18 is a center, and $x = -b/a$, $y = 0$ is a saddle point. The solution to Eq. 18 results in the equation for homoclinic trajectory as,

$$x_o(t) = \frac{b}{a}\left(\frac{3}{2}sech^2\frac{\sqrt{-b}\,\tau}{2} - 1\right), \quad y_o(t) = \frac{dx_o}{dt} \tag{23}$$

In obtaining Eq. 23 describing the homoclinic trajectory we have ignored terms of the order of ε in Eqs. 17 and 18. We can make use of the zeroth order solution given by Eq. 23 alongwith the solvability condition or Fredholm alternative which guarantees a nontrivial bounded solution to the corresponding adjoint equation, to include the effects of first order terms in ε. The resultant equality takes the form,

$$0 = \int_{-\infty}^{\infty}\left[-\frac{d^2x_o}{pdt^2}g_1 + \frac{dx_o}{dt}g_2\right]dt \tag{24}$$

where $x_o(t)$ refers to zeroth order solution. Eq. 23 gives the desired result correct to first order terms in ε. For simple functions g_1 and g_2 one can analytically evaluate the integral or obtain its solution numerically when the functions become complex. The only restriction on the resulting solution is that the constant $b < 0$ implying that $Det(A) > 0$.

The $Det(A) = 0$ and $Tr(A) = 0$ equations derived earlier gives us useful information about the way exchange of stability and Hopf bifurcation occurs. The same equations can be written in terms of deviations using the relations,

$$\alpha \;=\; \alpha + \delta\alpha \;, \qquad \theta \;=\; \theta + \delta\theta \tag{25}$$

Eqs. 6 and 7 now become,

$$\begin{aligned}&\delta\theta\{(1+Da_2)\,2\alpha^*\theta^* - \alpha^*(x_o+2y_o)\}\\ &\qquad + \delta\alpha\left\{(1+Da_2)\theta^{*2} - \theta^*(x_o+2y_o) + \frac{(x_o+y_o)y_o}{1+Da_2}\right\} \;=\; 0\end{aligned} \tag{26}$$

$$\begin{aligned}&\delta\theta\{(2\alpha^*\theta^* - 1)(1+Da_2) - \alpha^*(x_o+2y_o)\}\\ &\qquad + \delta\alpha\left\{\theta^{2*}(1+Da_2) - \theta^*(x_o+2y_o) + \frac{y_o(x_o+y_o)}{1+Da_2}\right\} \;=\; 0\end{aligned} \tag{27}$$

where α^* and θ^* are defined in Eq. 10.

Eq. 26 is the curve across which the two steady state solutions of Eq. 17 exchange stability. Similarly, Eq. 27 is the curve across which a Hopf bifurcation occurs from the origin, with $b < 0$. The five critical curves given by $Tr(A) = 0$, $Det(A) = 0$, solution of Eq. 24 and Eqs. 26 and 27 are sketched in the $\delta\theta$-$\delta\alpha$ plane as shown in Figure 2. The positions of these curves change according to the bounds on the parameter Da_2.

The effects of small perturbations in bifurcation control parameters and the steady states upon the exchange of stability that may be possible can be examined. For example, from Figure 3b, we can infer that for $\delta\alpha < 0$, by increasing θ, the steady state solution gains stability at a "knee" in a solution diagram showing bistability and then Hopf bifurcation occurs, followed by a branch of stable periodic solutions which terminate with a homoclinic trajectory.

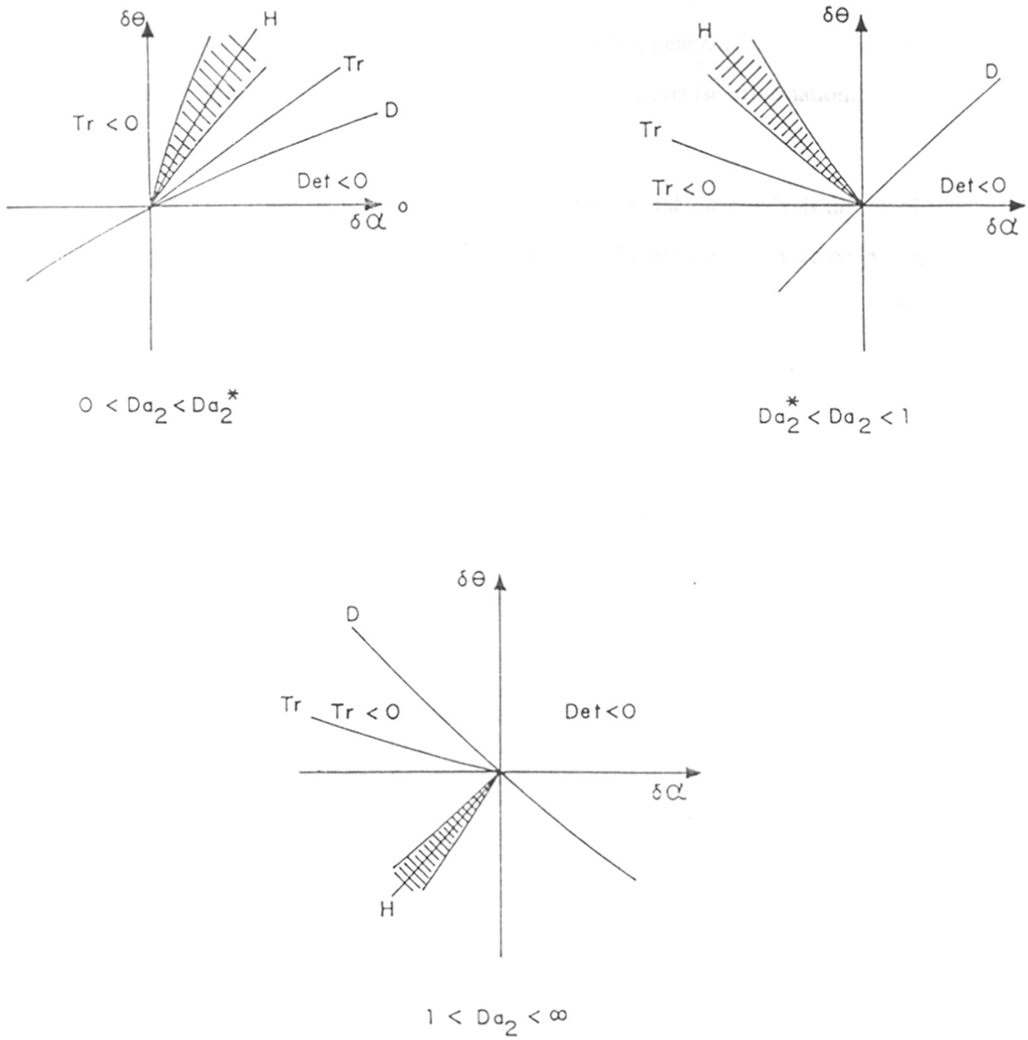

Figure 2: Critical Curves for different values of Da_2

However, these results have a limited range of validity for the following two reasons -- one that the curves $Tr(A) = 0$ and H are nearly tangent for Da_2 near Da_2^*, and second reason being that higher-order corrections are needed to extract more precise information.

5.2 Conclusion

For the two-dimensional autonomous model of exponential autocatalysis the conditions for occurrence of infinite-period finite-amplitude periodic phenomena have been derived and the equations of motion in phase-plane for homoclinic trajectories have been derived using perturbation theory.

5.3 Notation

a	constant defined in Eq. (19)
b	constant defined in Eq. (20)
Da_1, Da_2	Damkohler number for species X and Y
t	dimensionless time
X	concentration of species X in CSTR, (gmol/lit)
x_o	initial concentration of species X
$x_o(t)$	a first order solution for homoclinic trajectory
x_s	steady state value of x
Y	concentration of species Y in CSTR, (gmol/lit)
y_o	initial concentration of species Y
$y_o(t)$	a first order solution for homoclinic trajectory

Greek Letters

α	exponential autocatalysis parameter

θ	steady state value of y
$\delta\alpha$	perturbation added to the parameter α
$\delta\theta$	perturbation added to the steady state value θ

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CHAPTER VI

REDUCTION OF REACTION-DIFFUSION SYSTEM TO SCHRODINGER-LIKE EQUATION

Reation-diffusion equations describing exponential autocatalysis have been reduced to Schrodinger-like equation form using reductive perturbation technique. The later equation has been extensively analysed in physics and establishing its correspondence with the reaction-diffusion systems will help in further enriching the information about them . The methodology leading to such a correspondence is discussed.

6.1 Introduction

The set of first order differential equations in time describing the evolution of chemical reactions or the partial differential form when diffusion gradients are included, has been extensively investigated to seek the dynamic behavior of chemical reactions (Haken, 1975,1983). The system of equations admits steady state solutions, the stability of which is determined by the set of control parameters μ. The steady state turns unstable for some critical value of μ and starts performing periodic motion beyond the critical value,μ_c. This phenomenon of branching of time periodic motion from a stationary branch of solutions is called Hopf bifurcation (Kuramoto, 1984). Closer to the point of onset of oscillations, all systems, despite the variations in their grossly manifested behavior in orbital form or pattern, exhibit similar manner. This primarily arises due to great variations in the time scales of the associated variables; in other words the system near the critical point possesses a few variables that vary on slow time scales while the others varying on fast time scales get eliminated in a projected description. Small amplitude oscillations near the Hopf bifurcation point can thus be described in terms of simple evolution equation which acquires an universal form.

The aim is to deduce this universal form and show that it is a special case of the more general Schrodinger's equation. The later equation has been extensively studied in the general area of physics and establishing its correspondence with reaction-diffusion system will help in enriching the information about them. The universal form as derived here is not new and in fact in the contemporary areas of physical and applied mathematical sciences it is known as Ginzburg-Landau equation. The central principle in the derivation of this universal form is the use of multiple scales in space and time with a view to stretch the coordinates such that some generalized form of reduced equation becomes possible. These techniques are generally referred to as reductive perturbation method (Tanuiti, 1968; Newell and Whitehead, 1969; Kuramoto, 1984). There is adequate information in mathematical and physics literature on this subject, but little of it has permeated the chemical engineering literature at large. We shall therefore deal with the reductive perturbation technique in some detail here and show its application by considering the case of exponential autocatalysis model. This model first published in this journal (Ravi Kumar et. al., 1983) has found general acceptance in contemporary areas of physical sciences (Bar-Eli, 1984a,b,c, 1985) and has been extensively investigated from the view point of establishing bounds on steady states in presence of diffusion (Inamdar and Kulkarni, 1990a), existence of dissipative structures.

6.2 General Reductive Perturbation Technique

For a general homogeneous equation such as,

$$\frac{dX}{dt} = F(X, \mu) \tag{1}$$

where X is a vector representing concentration of chemical species and μ is some control paramter, we shall begin by expressing Eq. 1 in a deviational form ($\mathbf{u} = \mathbf{X} - \mathbf{X_s}$) and expanding it in a Taylor series as,

$$\frac{d\mathrm{u}}{dt} = \mathrm{Lu} + \mathrm{Muu} + \mathrm{Nuuu} + \ldots . \tag{2}$$

where,

$$L_{ij} = \frac{\partial F_i(X_o)}{\partial X_{o_j}} \tag{3a}$$

$$\mathrm{Muu} = \sum_{j,k} \frac{1}{2!} \frac{\partial^2 F_i(X_o)}{\partial X_{o_j} \partial X_{o_k}} u_j u_k \tag{3b}$$

$$\mathrm{Nuuu} = \sum_{j,k,l} \frac{1}{3!} \frac{\partial^3 F_i(X_o)}{\partial X_{o_j} \partial X_{o_k} \partial X_{o_l}} u_j u_k u_l \tag{3c}$$

The parameter μ can be varied about μ_c, and one can notice that the solution X_o can remain stable for sufficiently small perturbations. However, the solution loses its stability for $\mu > \mu_c$. The stability of solution X_o is related to the distribution of the eigenvalues in the complex plane. If the real parts of all eigenvalues is negative the system is considered to be stable. At criticality condition, when a pair of eigenvalue crosses the imaginary axis, Hopf bifurcation occurs.

Referring to Eq. 2, near criticality, the operators and variables involved can be expanded using the Poincáre-Linstédt series, in powers of μ where μ is defined as $(\mu - \mu_c/\mu_c)$. However it is more convenient to define a small parameter ε as $\varepsilon^2\chi = \mu$, whereχ= sgn μ.

$$L = L_o + \chi\varepsilon^2 L_1 + \varepsilon^4 L_2 + \dots \tag{4a}$$

$$\lambda = \lambda_o + \chi\varepsilon^2\lambda_1 + \varepsilon^4\lambda_2 + \dots \tag{4b}$$

$$u = \varepsilon u_1 + \varepsilon^2 u_2 + \dots \tag{4c}$$

$$M = M_o + \chi\varepsilon^2 M_1 + \varepsilon^4 M_2 + \dots \tag{4d}$$

$$N = N_o + \chi\varepsilon^2 N_1 + \varepsilon^4 N_2 + \dots \tag{4e}$$

Notice that the eigenvalues are also expanded in power series and the λ_v in general are complex, and can be represented as, $\lambda_v = \sigma_v + \omega_v$.

We shall now define the left and right eigenvectors of L_o corresponding to the eigenvalue λ_o,

Right eigenvector $L_o \; U = \lambda_o \; U$ Left eigenvector $U^* \; L_o = \lambda_o \; U^*$ (5a)

$L_o \; \overline{U} = \lambda_o \; \overline{U}$ $\overline{U}^* \; L_o = \lambda_o \; \overline{U}^*$ (5b)

The right and left eigenvectors U and U^* satisfy a relation, $U^*\overline{U} = \overline{U}^* U = 0$,

and are normalized as, $U^* U = \overline{U}^*\overline{U} = 1$.

Note that the eigenvalues λ_o, λ_1 are given as, $\lambda_o = i\omega_o = U^* L_o U, \lambda_1 = \sigma_1 + i\omega_1 = U^* L_1 U$.

Introducing scaling for the time via,

$$\tau = \varepsilon^2 t, \tag{6a}$$

$$\frac{d}{dt} \rightarrow \frac{\partial}{\partial t} + \varepsilon^2 \frac{\partial}{\partial \tau} \tag{6b}$$

and substituting Eq. 6b into Eq. 2 gives,

$$\left(\frac{\partial}{\partial t} + \varepsilon^2 \frac{\partial}{\partial \tau} - \mathbf{L}_o - \varepsilon^2 \chi \mathbf{L}_1 - \ldots\right) \quad (\varepsilon \mathbf{u}_1 + \varepsilon^2 \mathbf{u}_2 + \ldots)$$

$$= \varepsilon^2 \mathbf{M}_o \mathbf{u}_1 \mathbf{u}_1 + \varepsilon^3 (2\mathbf{M}_o \mathbf{u}_1 \mathbf{u}_2 + \mathbf{N}_o \mathbf{u}_1 \mathbf{u}_1 \mathbf{u}_1) + O(\varepsilon^4) \tag{7}$$

Equating coefficients of equal powers of ε in Eq. 7, we obtain,

$$\left(\frac{\partial}{\partial t} - \mathbf{L}_o\right) \mathbf{u}_\nu = \mathbf{B}_\nu, \qquad \nu = 1, 2, \ldots \tag{8}$$

The first few **B** are,

$$\mathbf{B}_1 = 0, \tag{9a}$$

$$\mathbf{B}_2 = \mathbf{M}_o \mathbf{u}_1 \mathbf{u}_1, \tag{9b}$$

$$\mathbf{B}_3 = -\left(\frac{\partial}{\partial \tau} - \chi \mathbf{L}_1\right) \mathbf{u}_1 + 2\mathbf{M}_o \mathbf{u}_1 \mathbf{u}_2 + \mathbf{N}_o \mathbf{u}_1 \mathbf{u}_1 \mathbf{u}_1 \tag{9c}$$

For the system of linear homogeneous Eqs. 8 we can write a solvability condition,

$$\int_0^{2\pi/\omega_o} \mathbf{U}^{*}.\mathbf{B}_\nu e^{-i\omega_o t} dt = 0 \tag{10}$$

Since, $\mathbf{u}_\nu$ are 2π-periodic functions of $\omega_o t$, the solvability condition in Eq. 10 finally reduces to,

$$\mathbf{U}^{*} . \mathbf{B}_\nu^{(1)}(\tau) = 0 \tag{11}$$

Then, for ν=1, we have a neutral solution as,

$$\mathrm{u}_1(t,\tau) \;=\; \mathrm{W}(\tau)\mathrm{U}e^{i\omega_o t} \;+\; \mathrm{c.c.} \tag{12}$$

where c.c. stands for complex conjugate and $W(\tau)$ is some complex amplitude yet to be specified.

Using the solvability condition and neutral solution, for ν=2, we obtain an expression for u_2,

$$\mathrm{u}_2 \;=\; \mathrm{V}_+\mathrm{W}^2e^{2i\omega_o t} + \mathrm{V}_-\overline{\mathrm{W}}^2e^{-2i\omega_o t} + \mathrm{V}_o\,|\,\mathrm{W}\,|^2 + \mathrm{v}_o\mathrm{u}_1 \tag{13}$$

where,

$$\mathrm{V}_+ \;=\; \overline{\mathrm{V}}_- \;=\; -(\mathrm{L}_o - 2i\omega_o)^{-1}\,\mathrm{M}_o\mathrm{UU} \tag{14a}$$

$$\mathrm{V}_o \;=\; -2\mathrm{L}_o^{-1}\mathrm{M}_o\mathrm{U}\overline{\mathrm{U}} \tag{14b}$$

The constant v_o cannot be determined at this stage, but is not required in the present analysis. Now writing the solvability condition for ν=3, and knowing u_2, we obtain following form,

$$\frac{\partial \mathrm{W}}{\partial \tau} \;=\; \chi\lambda_1\mathrm{W} - g\,|\,\mathrm{W}\,|^2\,\mathrm{W} \tag{15}$$

where the complex variable g is given as,

$$g \;=\; g' + ig'' \;=\; -2\mathrm{U}^*\mathrm{M}_o\mathrm{U}\mathrm{V}_o - 2\mathrm{U}^*\mathrm{M}_o\overline{\mathrm{U}}\mathrm{V}_+ - 3\mathrm{U}^*\mathrm{N}_o\mathrm{U}\mathrm{U}\overline{\mathrm{U}} \tag{16}$$

Defining the amplitude R and the phase Θ via W = R exp (i Θ), we obtain a non-trivial solution,

$$R \;=\; R_s, \qquad \Theta \;=\; \tilde{\omega}t + \mathrm{const.} \tag{17a}$$

$$R_s \;=\; \sqrt{\sigma_1/\,|\,g'\,|}, \qquad \tilde{\omega} \;=\; \chi(\omega_1 - g''R_s^2) \tag{17b}$$

which appears only in the supercritical region (*soft excitation*) ($\chi>0$) for positive g' and the subcritical region (*hard excitation*) for negative g'. The bifurcating solution shows a perfectly smooth circular motion in the complex W plane. Hence, in the end, one can write an expression for the original vector X approximately as,

$$\mathrm{X} \;\bar{=}\; \mathrm{X}_o + \varepsilon \mathrm{u}_1 \;=\; \mathrm{X}_o + \varepsilon\left\{\mathrm{UR}_s \exp\left[i\left(\omega_o + \varepsilon^2 \tilde{\omega}\right)t\right] + \mathrm{c.c.}\right\} \tag{18}$$

which describes a finite amplitude elliptic orbital motion in the critical eigenplane.

Now extending the above analysis for the reaction-diffusion system, we have an additional term accounting for the diffusion as,

$$\frac{\partial \mathrm{u}}{\partial t} = (\mathrm{L} + D\nabla^2)\mathrm{u} + \mathrm{Muu} + \mathrm{Nuuu} + \ldots. \tag{19}$$

Allowing for slowly varying space coordinate apart from two time scales t and τ characterized by the slowness parameter $\varepsilon(=|\mu|^{1/2})$, the extra space dependence of ε is embedded in a scaled coordinate defined by, $s = \varepsilon r$. Also, transforming the Laplacian as, $\nabla \rightarrow \varepsilon\nabla_s$, we have,

$$\left(\frac{\partial}{\partial t} + \varepsilon^2\frac{\partial}{\partial \tau} - \varepsilon^2 D\nabla_s^2 - \mathrm{L}_o - \varepsilon^2\chi \mathrm{L}_1 - \ldots\right) \quad (\varepsilon \mathrm{u}_1 + \varepsilon^2 \mathrm{u}_2 + \ldots)$$
$$= \varepsilon^2 \mathrm{M}_o \mathrm{u}_1\mathrm{u}_1 + \varepsilon^3(2\mathrm{M}_o\mathrm{u}_1\mathrm{u}_2 + \mathrm{N}_o\mathrm{u}_1\mathrm{u}_1\mathrm{u}_1) + O(\varepsilon^4) \tag{20}$$

With the additional term for the transformed Laplacian and s dependence, the remaining conditions can be rewritten, and we finally obtain the reduced equation as,

$$\frac{\partial \mathrm{W}}{\partial \tau} = \chi\lambda_1 \mathrm{W} + d\nabla_s^2 \mathrm{W} - g\,|\,\mathrm{W}\,|^2\,\mathrm{W} \tag{21}$$

where d is generally a complex number defined as,

$$d = d' + i\,d'' = \mathrm{U}^* D\,\mathrm{U} \tag{22}$$

Further using the transformation,

$$(\tau, s, \mathbf{W}) \quad \rightarrow \quad (\sigma^{-1}\tau, \sqrt{d'/\sigma_1}\, s, \sqrt{\sigma_1/\,|\,g'\,|}\,\mathbf{W}) \tag{23}$$

and rewriting s and τ as r and t, Eq. 21 reduces to a more convenient form,

$$\frac{\partial \mathrm{W}}{\partial t} \;=\; (1 + ic_o)\mathrm{W} + (1 + ic_1)\nabla^2\mathrm{W} - (1 + ic_2)\,|\,\mathrm{W}\,|^2\,\mathrm{W} \tag{24}$$

where,

$$c_o \;=\; \omega_1/\sigma_1, \qquad c_1 \;=\; d''/d', \qquad c_2 \;=\; g''/g' \tag{25}$$

and the bifurcation has been assumed to be supercritical. Subsequently, the transformation W -> W exp (ic$_o$t) eliminates c$_o$ and reduces Eq. 24 to the form,

$$\frac{\partial \mathrm{W}}{\partial t} \;=\; \mathrm{W} + (1 + ic_1)\nabla_x^2\mathrm{W} - (1 + ic_2)\,|\,\mathrm{W}\,|^2\,\mathrm{W} \tag{26}$$

This form can be identified as a special case of the more general Schrodinger's equation. In the next section we shall apply this technique to the case of reaction-diffusion scheme representing exponential autocatalysis.

6.3 Reaction-Diffusion Model involving Exponential Autocatalysis

The reaction-diffusion equations to exponentially autocatalyzed scheme are given as,

$$\frac{\partial x}{\partial t} \;=\; D_1\frac{\partial^2 x}{\partial r^2} + x_o - x - Da_1 x \exp(\alpha y) \tag{27a}$$

$$\frac{\partial y}{\partial t} \;=\; D_2\frac{\partial^2 y}{\partial r^2} + y_o - y + Da_1 x \exp(\alpha y) - Da_2 y \tag{27b}$$

Under steady state conditions, the stationary solutions come out as,

$$\exp(\alpha\theta) \;=\; \frac{x_o - x_s}{x_s Da_1} \qquad \theta \;=\; \frac{x_o + y_o - x_s}{(1 + Da_2)} \tag{28}$$

Defining the deviations as,

$$x = u + x_s \qquad y = v + \theta \tag{29}$$

the system of Eqs. 27a and 27b reduces to following equations after linearization of the nonlinear term exp $(\alpha v) = (1+\alpha v)$,

$$\frac{\partial u}{\partial t} = D_1 \frac{\partial^2 u}{\partial r^2} - (1 + Da_1 e^{\alpha\theta})u - (\alpha Da_1 x_s e^{\alpha\theta})v - \alpha Da_1 e^{\alpha\theta} uv \tag{30a}$$

$$\frac{\partial v}{\partial t} = D_2 \frac{\partial^2 v}{\partial r^2} + Da_1 e^{\alpha\theta} u + (\alpha Da_1 x_s e^{\alpha\theta} - (1 + Da_2))v + \alpha Da_1 e^{\alpha\theta} uv \tag{30b}$$

Following the general procedure outlined in section 1, we obtain the following specific results for a case of exponential autocatalysis. Beginning with Eqs. 3 and 4 the operators L_o and L_1 can be identified as,

$$\mathrm{L}_o = \frac{1}{(\alpha x_s - 1)} \begin{bmatrix} -(\alpha x_s + Da_2 + 1) & -\alpha x_s(Da_2+2) \\ Da_2+2 & \alpha x_s + Da_2 + 1 \end{bmatrix} \tag{31a}$$

$$\mathrm{L}_1 = \frac{Da_2+2}{\alpha x_s - 1} \begin{bmatrix} -1 & -\alpha x_s \\ 1 & \alpha x_s \end{bmatrix} \tag{31b}$$

Further defining A and B as,

$$A = \frac{-(\alpha x_s + Da_2 + 1)}{\alpha x_s(Da_2+2)}, \qquad B = \frac{\alpha x_s - (1+Da_2)^2}{\omega_o \alpha x_s(Da_2+2)} \tag{32}$$

we obtain the eigenvectors as solutions to Eqs. 5a and 5b,

$$\mathrm{U} = \begin{pmatrix} 1 \\ (A + iB) \end{pmatrix} \qquad \overline{\mathrm{U}} = \begin{pmatrix} 1 \\ (A - iB) \end{pmatrix} \tag{33a}$$

$$\mathrm{U}^* = \frac{1}{2B} \,(B + iA, \; -i) \qquad \overline{\mathrm{U}}^* = \frac{1}{2B} \,(B + iA, \; i) \tag{33b}$$

The eigenvalue λ_1 defined as, $\lambda_1 = \sigma_1 + i\omega_1$, gives us,

$$\sigma_1 = \frac{-(Da_2+2)}{2B(\alpha x_s-1)} \quad [B(1-\alpha x_s)] \tag{34a}$$

$$\omega_1 = \frac{-(Da_2+2)}{2B(\alpha x_s-1)} \quad [\alpha x_s(B^2+A^2)+A(\alpha x_s+1)+1] \tag{34b}$$

Also, the parameter d generally defined as a complex variable $d = d' + i d''$,,is given by,

$$d' = \frac{1}{2}\ (D_1+D_2) \qquad d'' = \frac{A}{2B}\ (D_1-D_2) \tag{35}$$

The vectors $\boldsymbol{M}$ and N are given as :

$$\mathbf{M}_o = \frac{\alpha(Da_2+2)}{2(\alpha x_s-1)} \begin{pmatrix} 0 & -1 & -1 & 0 \\ 0 & 1 & 1 & 0 \end{pmatrix} \tag{36}$$

and $N = 0$,

while the vectors $\mathbf{V}_+$ and $\overline{\mathbf{V}}_-$, given by Eq. 14a, are,

$$\mathbf{V}_+ = \overline{\mathbf{V}}_- = \frac{\alpha(Da_2+2) \quad (A+iB)}{\eta} \begin{pmatrix} (\alpha x_s+Da_2+1)-2i\omega_o-\alpha x_s(Da_2+2) \\ -(Da_2+2)+(\alpha x_s+Da_2+1)+2i\omega_o \end{pmatrix} \tag{37a}$$

where

$$\eta = \{\alpha x_s(Da_2+2)^2-[(\alpha x_s+Da_2+1)^2+4\omega_o^2]\} \tag{37b}$$

The vector $\boldsymbol{V_o}$ given in Eq. 14b becomes,

$$\mathbf{V}_o = \frac{2A\alpha(Da_2)}{\{(\alpha x_s-1)[(1+Da_2)^2-\alpha x_s]\}} \begin{pmatrix} (\alpha x_s+Da_2+1)-\alpha x_s(Da_2+2) \\ -(Da_2+2)+(\alpha x_s+Da_2+1) \end{pmatrix} \tag{38}$$

The term g in Eq. 16, can now be written as,

$$g' = \frac{[\alpha(Da_2+2)]^2}{2B(\alpha x_s-1)(\Omega_1^2-4\Omega_1\omega_o^2)}(B\Omega_2-\Omega_3(A+1)) \tag{39a}$$

$$g'' = \frac{[\alpha(Da_2+2)]^2}{2B(\alpha x_s-1)(\Omega_1^2-4\Omega_1\omega_o^2)}(\Omega_2(A+1)-B\Omega_3) \tag{39b}$$

where,

$$\Omega_1 = (\alpha x_s-1)[(1+Da_2)^2-\alpha x_s] \tag{40a}$$

$$\begin{aligned}\Omega_2 = {} & (\Omega_1-4\omega_o^2)(2A(\alpha x_s-1)-2A^2(\alpha x_s-1)(1+Da_2)) \\ & +\Omega_1[A((\alpha x_s-1)-A(\alpha x_s-1)(1+Da_2)-2B\omega_o)+B(2\omega_o \\ & +B(\alpha x_s-1)(1+Da_2)-2A\omega_o)]\end{aligned} \tag{40b}$$

$$\begin{aligned}\Omega_3 = {} & (\Omega_1-4\omega_o^2)(2AB(1-\alpha x_s)(1+Da_2)) \\ & +\Omega_1[B((\alpha x_s-1)-A(\alpha x_s-1)(1+Da_2)-2B\omega_o) \\ & +A(2\omega_o+B(\alpha x_s-1)(1+Da_2)-2A\omega_o)]\end{aligned} \tag{40c}$$

So the constants in Ginzburg-Landau equation, c_o, c_1 and c_2 are found to be,

$$c_o = \frac{\alpha x_s(B^2+A^2)+A(\alpha x_s+1)+1}{B(1-\alpha x_s)} \tag{41a}$$

$$c_1 = \frac{B(\gamma^2+1)}{A(\gamma^2-1)} \tag{41b}$$

$$c_2 = \frac{\Omega_2(A+1)-B\,\Omega_3}{B\,\Omega_2-\Omega_3(A+1)} \tag{41c}$$

where,

$$\gamma = \sqrt{D_1/D_2} \tag{42}$$

The constants c_o, c_1 and c_2 as obtained above define the Ginzburg-Landau Eq. 24 for the exponentially autocatalysed reaction-diffusion system.

6.4 Results and Conclusions

Evaluation of these constants and therefore that of the Ginzburg-Landau equation is central to the any further development such as obtaining the plane waves, rotating waves, turbulence and entrainment phenomena in discrete oscillators. The quantity $\beta(=1+c_1c_2)$ defined in terms of the constants appearing in Ginzburg-Landau equation is an important parameter for the stability of the uniform oscillations, such that if $\beta > 0$ implies stability and vice-versa. However, the stability of uniform limit cycle oscillations is not guaranteed for infinitely large system size.Also negative values of β signal the occurence of chemical turbulence in the reaction-diffusion systems.

The Ginzburg-Landau equation has been studied by many authors from different viewpoints in the applied mathematics and physics literature. Thus the equation is studied in presence of periodic boundary conditions to provide estimates of the dimension of chaotic attractor (Doering et. al., 1988; Ghidaglia and Heron, 1987), while Stuart and Deprima (1978) reported the stability of periodic wave solutions. Other types of solutions such as bursting solutions, quasiperiodic solutions, homoclinic solutions and heteroclinic orbits connecting counter-rotating patterns are also discussed (Hocking and Stewartson, 1972; Kramer and Zimmerman, 1985; Holmes, 1986; Landman, 1987; Doelman 1989). In each of the these studies one realizes the importance of the parameters c_o, c_1 and c_2, the relative measures of which fix the type of behavior that is possible. While the conditions for the occurrence of these various types of solutions can now be easily derived for the case of exponential autocatalysis,we shall not elaborate on this aspect here. The various results for the exponential autocatalysis can follow in a routine way. The central point of importance is the derivation of the Ginzburg-Landau equation and the evaluation of the constants c_o, c_1 and c_2. The present work provides this link and establishes the connection with chemical engineering systems.

6.5 Notation

c_o, c_1, c_2	constants in Ginzburg-Landau equation
D	Diffusivities of the first and second species
Da	Damkohler number
L	Linear operator
$M, N...$	vectors denoting the nonlinearities of second order, third order and so on
U	eigenvector
X	vector denoting the system variable(s)

Greek letters

α	exponential autocatalysis parameter
β	$(1 + c_1 c_2)$
γ	defined in eqn.42
ε	a small positive quantity
λ	eigenvalue
μ	system parameter
τ	scaled time

Subscripts

1,2	first and second components of **X** respectively

Superscripts

$*$	complex conjugation

– left eigenvector

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CHAPTER VII

DIFFUSIVE INSTABILITY NEAR HOPF BIFURCATION FOR EXPONENTIALLY AUTOCATALYZED REACTION-DIFFUSION SYSTEM

The previous chapter presents the analysis of an exponentially autocatalyzed reaction-diffusion system near the Hopf bifurcation point using reductive perturbation approach. to obtain description in terms of Ginzburg-Landau equation. The conditions for the occurrence of instability, in presence and absence of diffusion, leading to Hopf bifurcation are derived here. The nature of governing equations leads to multi-valued instability conditions and eventually results in more than one regions in parameter space where instability of uniform oscillations due to diffusion is possible.

7.1 Analysis of Diffusive Instabilities

The reaction-diffusion equations to exponentially autocatalyzed scheme are given as :

$$\frac{\partial x}{\partial t} = D_1\frac{\partial^2 x}{\partial r^2}+x_o-x-Da_1 x\exp(\alpha y) \qquad (1\ )$$

$$\frac{\partial y}{\partial t} = D_2\frac{\partial^2 y}{\partial r^2}+y_o-y+Da_1 x\exp(\alpha y)-Da_2 y \qquad (2)$$

The homogeneous solutions to Eqs. (1a) and (1b) come out as,

$$\exp(\alpha\theta) = \frac{x_o-x_s}{x_s Da_1} \qquad \theta = \frac{x_o+y_o-x_s}{(1+Da_2)} \qquad (3)$$

Defining the deviations as $x = u + x_s$, and $y = v + \theta$, the system of Eqs. (1) and (2) reduces to following equations after linearization of the nonlinear term exp (αv) = ($1+\alpha v$),

$$\frac{\partial u}{\partial t}=D_1\frac{\partial^2 u}{\partial r^2}-(1+Da_1e^{\alpha\theta})u-(\alpha Da_1x_se^{\alpha\theta}v-\alpha Da_1e^{\alpha\theta}uv \qquad (4a)$$

$$\frac{\partial v}{\partial t}=D_2\frac{\partial^2 v}{\partial r^2}+Da_1e^{\alpha\theta}u+(\alpha Da_1x_se^{\alpha\theta}-(1+Da_2))v+\alpha Da_1e^{\alpha\theta}uv \qquad (4b)$$

Assuming that the deviations u and v follow a relation,

$$u,\ v \propto \exp(i\bar{q}r + \lambda t) \qquad (5)$$

Eqs. (4a) and (4b) can be rewritten in terms of linear matrix differential operator as,

$$\frac{\partial}{\partial t}\begin{pmatrix}u\\ v\end{pmatrix} = \begin{pmatrix}-D_1q^2-(1+Da_1e^{\alpha\theta}) & -\alpha Da_1x_se^{\alpha\theta}\\ Da_1e^{\alpha\theta} & -D_2q^2+\alpha x_sDa_1e^{\alpha\theta}-(1+Da_2)\end{pmatrix} + \begin{pmatrix}-\alpha Da_1e^{\alpha\theta}uv\\ \alpha Da_1e^{\alpha\theta}uv\end{pmatrix} \qquad (6)$$

The characteristic polynomial can then be obtained as,

$$\lambda^2 \;+\; \kappa(q)\lambda \;+\; \beta(q) \;=\; 0 \tag{7}$$

where,

$$\kappa(q) \;=\; q^2(D_1+D_2)+(Da_2+2)+Da_1e^{\alpha\theta}(1-\alpha x_s) \tag{8a}$$

$$\begin{aligned}\beta(q) \;=\; & D_1D_2q^4-q^2\{D_1[\alpha x_s Da_1e^{\alpha\theta}-(1+Da_2)]-D_2(1+Da_1e^{\alpha\theta})\} \\ & +(1+Da_2)-\alpha x_s Da_1e^{\alpha\theta}+(1+Da_2)Da_1e^{\alpha\theta}\end{aligned} \tag{8b}$$

The condition that $\kappa(q)$ and $\beta(q)$ are non-negative for all q assures the stability of the steady state (x_s, θ). This stability condition can be violated in two different ways.

(i) Both $\kappa(q)$ and $\beta(q)$ remain positive for all q except for some where $\kappa(q) = 0$. This is referred to as type I instability and implies that,

$$\kappa(q) \;=\; 0 \qquad \text{with} \qquad q \;=\; 0 \tag{9}$$

This results in an equation for a critical value for the bifurcating parameter y_{oc} as,

$$y_{oc} \;=\; (x_s-x_o) \;+\; \frac{(1+Da_2)}{\alpha}\;\ln\left[\frac{Da_2+2}{Da_1(\alpha x_s-1)}\right] \tag{10}$$

The logarithmic term in Eq. (10) above is subject to a constraint,

$$x_s \;>\; \frac{1}{\alpha} \tag{11}$$

(ii) It is also possible that both $\kappa(q)$ and $\beta(q)$ remain positive for all q except for some q where $\beta(q)$ vanishes. This type referred to as type II instability can be expressed as,

$$\beta(q_c) \;=\; 0 \qquad \text{and} \qquad \frac{\partial\beta(q_c)}{\partial(q_c)} \;=\; 0 \tag{12}$$

and give the following expressions for critical wave number q_c and y_{oc}'.

The critical wave number q_c is given as,

$$q_c^2 = \frac{D_1[\alpha x_s Da_1 e^{\alpha\theta} - (1+Da_2)] - D_2(1+Da_1 e^{\alpha\theta})}{2D_1 D_2}$$

$$\pm \frac{1}{2D_1 D_2} \quad \{[D_1[\alpha x_s Da_1 e^{\alpha\theta} - (1+Da_2)] - D_2(1+Da_1 e^{\alpha\theta})]^2$$

$$-4D_1 D_2[(1+Da_2)(1+Da_1 e^{\alpha\theta}) - \alpha x_s Da_1 e^{\alpha\theta}]\}^{1/2} \qquad (13)$$

and the critical value y_{oc}' is given as,

$$y_{oc}' = (x_s - x_o) + \frac{(1+Da_2)}{\alpha} \ln\left(\frac{z}{Da_1}\right) \qquad (14)$$

where z is given as

$$z = Da_1 e^{\alpha\theta}$$

$$= \frac{-b' \pm \sqrt{b'^2 - 4a'c'}}{2a'} \qquad (15)$$

and the various constants are identified as,

$$a' = \frac{D_1}{D_2}(\alpha x_s)^2 + \frac{D_2}{D_1} - 2\alpha x_s \qquad (16a)$$

$$b' = 2\left\{\frac{D_2}{D_1} - \frac{D_1}{D_2}\alpha x_s(1+Da_2) + (\alpha x_s - Da_2 - 1)\right\} \qquad (16b)$$

$$c' = \frac{D_1}{D_2}(1+Da_2)^2 + \frac{D_2}{D_1} - 2(1+Da_2) \qquad (16c)$$

We have thus obtained the conditions [Eqs. (10) and (14)] for the occurrence of type I and type II instability. Eqs. (10) and (14) are plotted in Fig. 1 where parametric maps of x_o versus y_o are presented for a defined set of other parameters. The cases for $D_1 = D_2$ and $D_1 > D_2$ are shown separately. It is interesting to note that the transcendental nature of the governing equations give rise to a set of two values for the critical concentration y_{oc}. Clearly the requirement of $\kappa(q)$ to be positive for all q for the stability of system requires that $y_o > y_{oc}$.

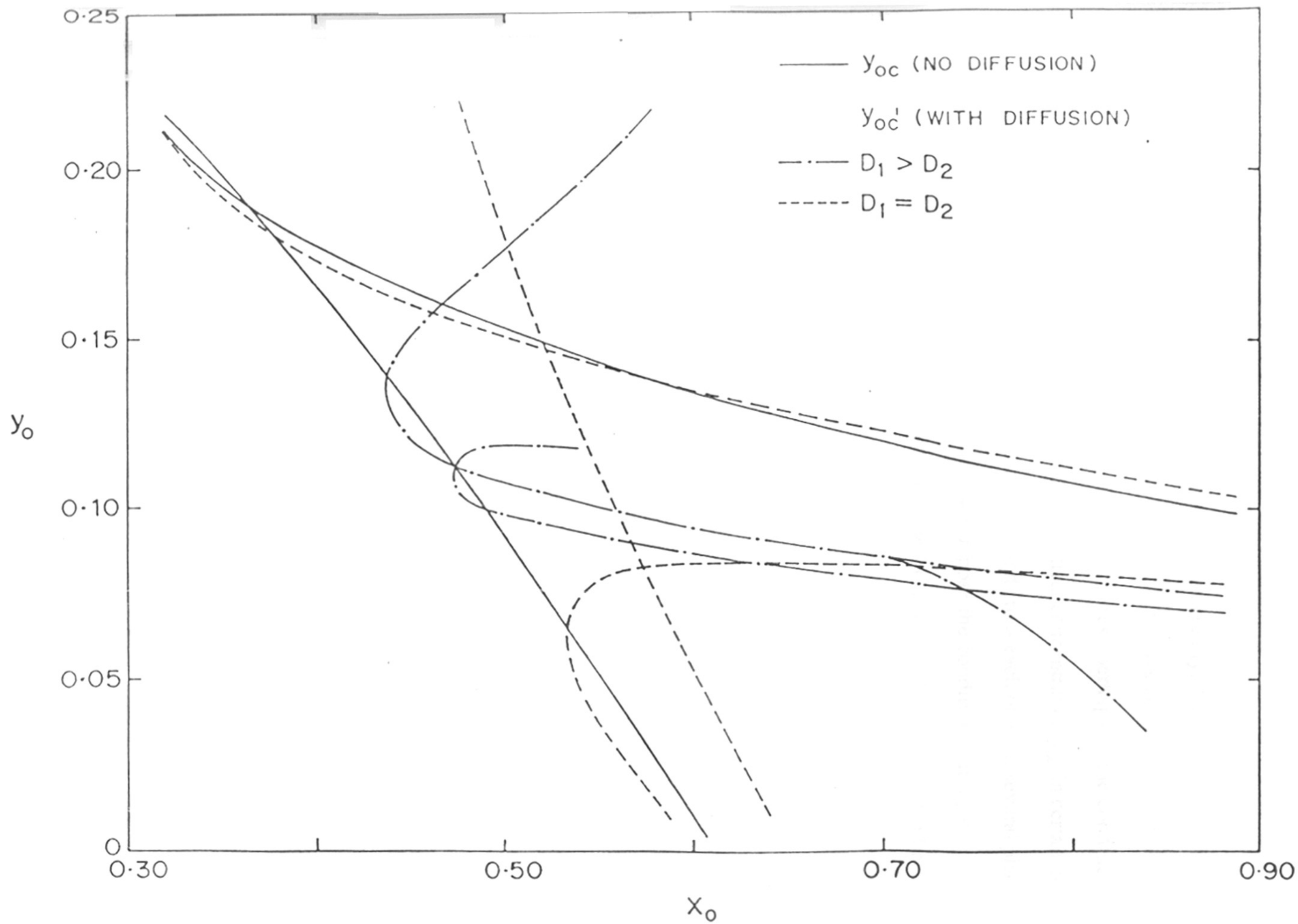


FIG. 1. INSTABILITY CRITERIA IN PRESENCE AND ABSENCE OF DIFFUSION

The region below the line $y_{\propto}$ therefore signals type I instability. The particular curve to be chosen is decided by the steady state x_s and θ to which the system evolves which in turn depends on the initial conditions specified. Of more interest, perhaps, is the condition (14) which shows a set of four possible values for the critical concentration $y_{\propto}'$ in certain region. As seen from the figure the two critical curves cut and cross each other at several places. In order that diffusion plays an important role we impose the condition that $y_{\propto} < y_{\propto}'$ so that type II instability does not occur earlier than type I instability. The multi-valued nature of these criteria gives rise to interesting possibilities to satisfy this condition in many different ways.

Following the general procedure outlined in Kuramoto (1983), we shall now reduce the reaction-diffusion equation using reductive perturbation technique to the following specific form of the Ginzburg-Landau equation.

$$\frac{\partial \mathrm{W}}{\partial t} = (1+ic_o)\mathrm{W} + (1+ic_1)\nabla_x^2\mathrm{W} - (1+ic_2)\,|\,\mathrm{W}\,|^2\,\mathrm{W} \tag{17}$$

where,

$$c_o = \frac{\alpha x_s(B^2 + A^2) + A(\alpha x_s + 1) + 1}{B(1-\alpha x_s)} \tag{18a}$$

$$c_1 = \frac{B(\gamma^2+1)}{A(\gamma^2-1)} \tag{18b}$$

$$c_2 = \frac{\Omega_2(A+1) - B\,\Omega_3}{B\,\Omega_2 - \Omega_3(A+1)} \tag{18c}$$

and the other quantities are defined as,

$$A = \frac{-(\alpha x_s + Da_2 + 1)}{\alpha x_s (Da_2 + 2)}, \qquad B = \frac{\alpha x_s - (1 + Da_2)^2}{\omega_o \alpha x_s (Da_2 + 2)} \tag{19}$$

$$\Omega_1 = (\alpha x_s - 1)[(1 + Da_2)^2 - \alpha x_s] \tag{20a}$$

$$\begin{aligned} \Omega_2 = {} & (\Omega_1 - 4\omega_o^2)(2A(\alpha x_s - 1) - 2A^2(\alpha x_s - 1)(1 + Da_2)) \\ & + \Omega_1[A((\alpha x_s - 1) - A(\alpha x_s - 1)(1 + Da_2) - 2B\omega_o) + B(2\omega_o \\ & + B(\alpha x_s - 1)(1 + Da_2) - 2A\omega_o)] \end{aligned} \tag{20b}$$

$$\begin{aligned} \Omega_3 = {} & (\Omega_1 - 4\omega_o^2)(2AB(1 - \alpha x_s)(1 + Da_2)) \\ & + \Omega_1[B((\alpha x_s - 1) - A(\alpha x_s - 1)(1 + Da_2) - 2B\omega_o) \\ & + A(2\omega_o + B(\alpha x_s - 1)(1 + Da_2) - 2A\omega_o)] \end{aligned} \tag{20c}$$

The constants c_o, c_1 and c_2 as obtained above define the Ginzburg-Landau equation for the exponentially autocatalysed reaction-diffusion system. Evaluation of these constants and therefore that of the Ginzburg-Landau equation is central to the subsequent development such as obtaining the plane waves, rotating waves, turbulence and entrainment phenomena in discrete oscillators. The quantity β (=$1+c_1 c_2$) defined in terms of the constants appearing in Ginzburg-Landau equation is an important parameter for the stability of the uniform oscillation, such that if $\beta > 0$ implies stability and vice-versa. However, the stability of uniform limit cycle oscillation is not guaranteed for infinitely large system size.

7.2 Conditions for Instabilities in Reaction-Diffusion System

In order to ensure that type II instability does not occur earlier than type I instability as the value of y_o increases, we impose the condition $y_{oc} < y_{oc}'$ or equivalently in terms of γ [= $(D_1/D_2)^{1/2}$] as

$$F(\gamma) \equiv (A\gamma^4) + (B\gamma^2) + C = 0 \tag{21}$$

where

$$A = \left\{\frac{(\alpha x_s - Da_2 - 1)\quad (Da_2+2)}{(\alpha x_s - 1)} - (1+Da_2)\right\}^2 \tag{22a}$$

$$B = 2\left\{\frac{(\alpha x_s - Da_2 - 1)\quad (Da_2+2)}{\alpha x_s - 1} - \frac{\alpha x_s (Da_2+2)^2}{(\alpha x_s - 1)^2} - (1+Da_2)\right\} \tag{22b}$$

$$C = \left\{\frac{Da_2+2}{\alpha x_s - 1} + 1\right\}^2 \tag{22c}$$

In the present instance the parameter β defining the stability of the plane waves is used alongwith the condition describing the occurrence of type I instability prior to type II instability $y_{oc} < y_{oc}'$ and the results are plotted in the form of γ versus x_o in Figs. (2a and 2b). The condition that $\beta < 0$ or $\beta > 0$ and $F(\gamma) > 0$ and $F(\gamma) < 0$ are marked along the curves.

We notice that for a given set of parameter values such as (Da_1, Da_2, D_1, D_2 and α etc.), Eqs. (10) and (14) give rise to multiple values for y_{oc} and y_{oc}' and therefore various different possibilities of satisfying the requirement of $y_o < y_{oc}'$. Two such possibilities are presented as Figs. (2a and 2b). In either situation we notice that the conditions $\beta < 0$ for stability and $F(\gamma) > 0$ can be realized. The region $F(\gamma) > 0$ suggests that the onset of spatially uniform oscillations precede the spatially non-uniform ones. Further if $\beta < 0$ then these oscillations are unstable. The exponentially autocatalysed reaction-diffusion system thus shows the multiple existence of an instability condition of uniform oscillations due to diffusion.

7.3 Conclusions

To sum up, the present chapter employs the Ginzburg-Landau equation for the exponentially autocatalysed reaction-diffusion system, and analytically describes the behavior of system near the Hopf bifurcation. The conditions derived in general explain the manner in which transitions in a reaction-diffusion system can occur.

7.4 Notation

A, B	terms defined in Eq. (19)

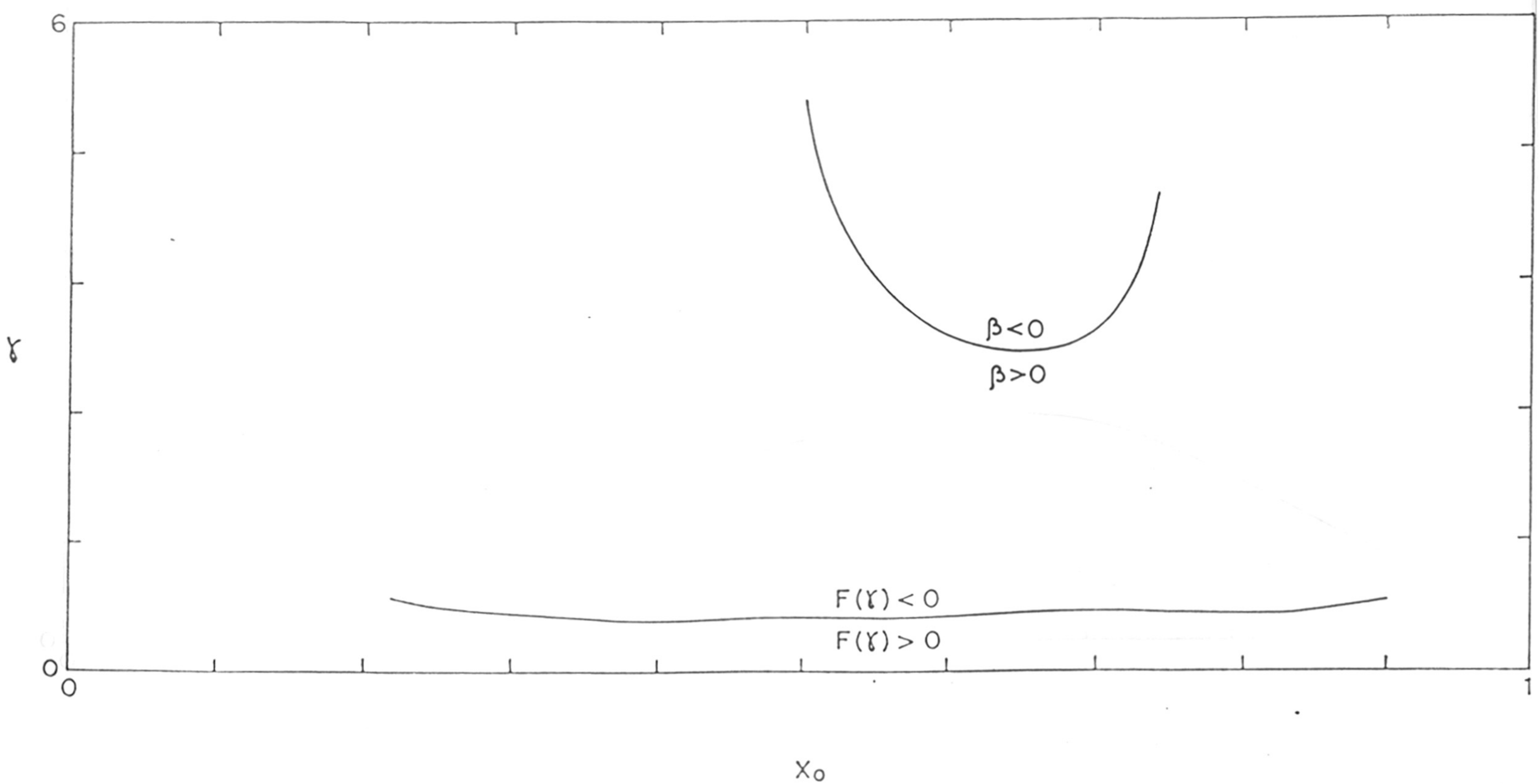
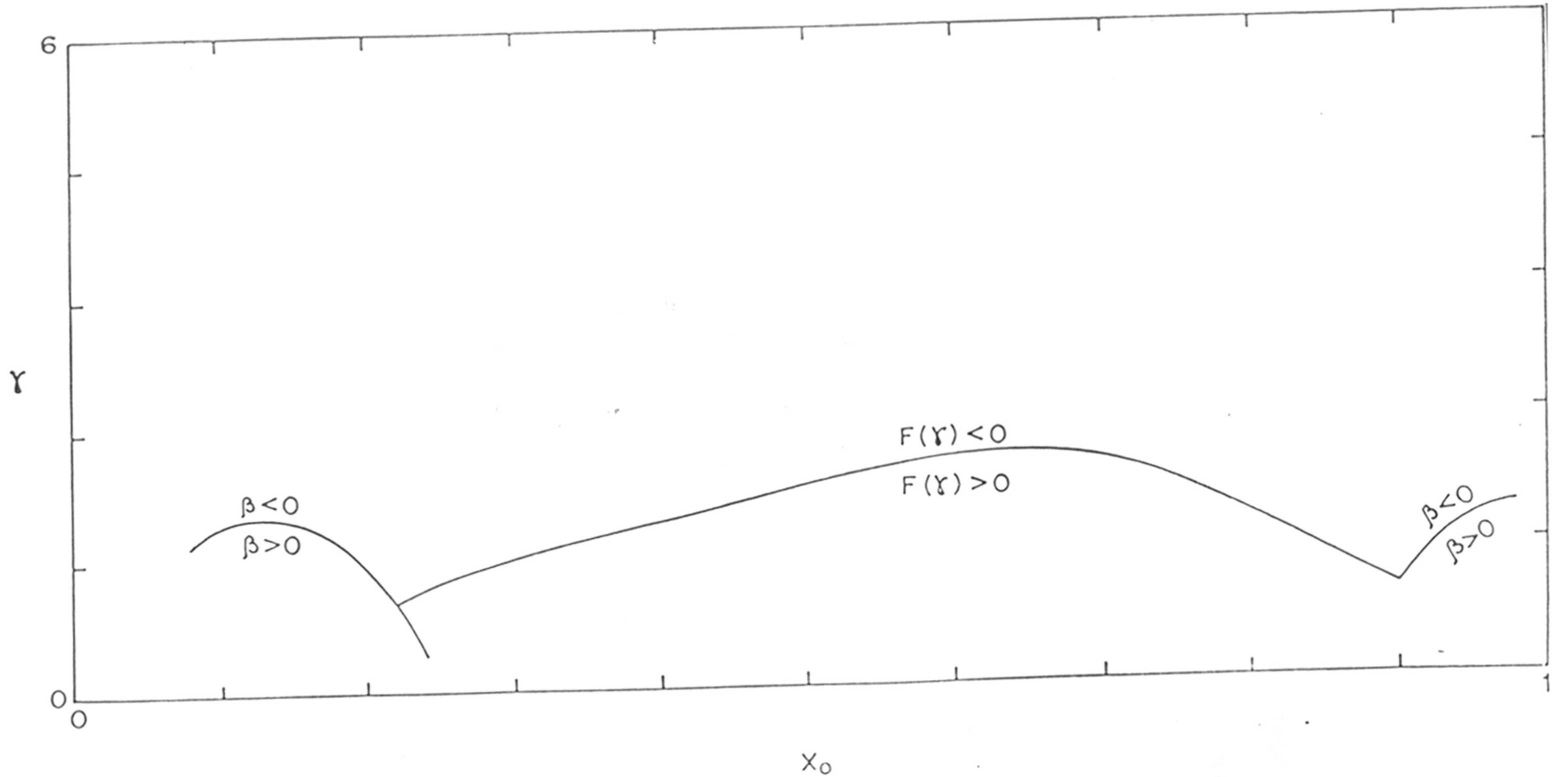


FIGURE 2a : REGION IN PARAMETER SPACE FOR UNIFORM OSCILLATIONS TO BECOME UNSTABLE DUE TO DIFFUSION

99a



FIGURER 2b: REGION IN PARAMETER SPACE FOR UNIFORM OSCILLATIONS TO BECOME UNSTABLE DUE TO DIFFUSION

a', b', c'	terms defined in Eqs. (16a), (16b) and (16c) respectively
A', B', C'	terms defined in Eqs. (22a), (22b) and (22c) respectively
c_o, c_1, c_2	constants defined in Eqs. (17a), (17b) and (17c) respectively
D_1, D_2	diffusivities of the species X and Y respectively
Da_1, Da_2	Damkohler numbers for speices X and Y respectively
$F(\gamma)$	function defined in Eq. (21)
q	wave number
q_c	critical wave number
r	dimensionless space variable
t	dimensionless time
u, v	deviations from steady state
W	complex field defined in Eq. (17)
x,y	dimensionless concentration of species X and Y
x_o, y_o	dimensionless initial concenttrations
x_s	steady state value of x
y_{oc}	critical initial concentration with effect of diffusion not accounted
y_{oc}'	critical initial concentration with diffusion effects accounted
z	variable defined in Eq. (15)

Greek Letters

α	exponential autocatalytic parameter
β	stability parameter for plane waves ($= 1 + c_1c_2$)

$\beta(q)$	determinant defined in Eq. (8b)
γ	ratios of diffusivities = $(D_1/D_2)^{1/2}$
$\kappa(q)$	trace defined in Eq. (8a)
λ	eigenvalue
θ	steady state value of y
Ω_1, Ω_2, Ω_3	terms defined in Eqs. (20a), (20b) and (20c) respectively
ω_o	frequency of oscillation near Hopf bifurcation point

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CHAPTER VIII

MULTI-TIME SCALE APPROACH TO ANALYSIS OF ENCILLATOR : LIMIT CYCLE AND GLOBAL NON-UNIFORM STEADY PATTERNS

Limit cycle and non-uniform global steady patterns that appear in an exponentially autocatalyzed reaction-diffusion system (Encillator) have been constructed using a two-time scale approach. The stability of these nonlinear structures is also examined.

8.1 The Encillator

The reaction-diffusion system is represented by the following coupled nonlinear partial differential equations.

$$\frac{\partial X}{\partial t} = D_1 \Delta X + x_o - X - Da_1 X \exp(\alpha Y) \tag{1a}$$

$$\frac{\partial Y}{\partial t} = D_2 \Delta Y + y_o - Y + Da_1 X \exp(\alpha Y) - Da_2 Y \tag{1b}$$

where the operator $\Delta = \partial^2/\partial r^2$. Here, X and Y are the concentrations of species, and D_1, D_2 are the diffusivities. It is assumed that Fick's law holds. The initial reactant concentrations are given by x_o and y_o.

The steady state homogeneous solution to system in Eq. (1) is given as,

$$\exp(\alpha\theta) = \frac{(x_o - x_s)}{x_s Da_1}, \qquad \theta = \frac{x_o + y_o - x_s}{1 + Da_2} \tag{2}$$

where x_s and θ are the steady state values of X, Y respectively.

The existence of this solution in Eq. (2) depends upon the boundary conditions. In the present case, we assume the concentrations to be fixed at the boundaries i.e. Dirichlet condition. This boundary condition is given as,

$$\begin{aligned} X(0,t) &= X(1,t) = x_s \\ Y(0,t) &= Y(1,t) = \theta, \qquad \text{for} \quad t > 0 \end{aligned} \tag{3}$$

To make this a well-posed problem, we add the following initial conditions,

$$X(r,0) = X(r,1) = X_{in}(r) = x_o, \tag{4a}$$

$$Y(r,0) = Y(r,1) = Y_{in}(r) = y_o \tag{4b}$$

Assuming the initial conditions x_o and y_o to be non-negative, there exists a non-negative pair $(X(r,t), Y(r,t))$ of solutions of the system defined for $0 \leq r \leq 1$ and $0 \leq t < \infty$. These solutions are infinitely differentiable functions of both r and t on $(0,1) \, \mathrm{X} \, (0,\infty)$.

Defining deviations from steady state as $u = \begin{pmatrix} x \\ y \end{pmatrix}$,

$$X = x + x_s, \qquad Y = y + \theta,$$

which obey homogeneous boundary conditions, and linearization of the exponential term

$$\exp(\alpha\, y) = 1 + \alpha\, y,$$

results in following evolution equations,

$$\frac{\partial x}{\partial t} = D_1 \Delta x - (1 + Da_1 e^{\alpha\theta})x - (\alpha Da_1 x_s e^{\alpha\theta})y - \alpha Da_1 e^{\alpha\theta} xy \tag{5a}$$

$$\frac{\partial y}{\partial t} = D_2 \Delta y + Da_1 e^{\alpha\theta} x + (\alpha x_s Da_1 e^{\alpha\theta} - Da_2 - 1)y + \alpha Da_1 e^{\alpha\theta} xy \tag{5b}$$

The boundary and initial conditions, in terms of the deviation variables, are,

$$x(0,t) = x(1,t) = y(0,t) = y(1,t) = 0, \qquad t \geq 0 \tag{6}$$

and,

$$x(r,0) = X_{in}(r) - x_s, \tag{7}$$

$$y(r,0) = Y_{in}(r) - \theta, \qquad 0 \leq r \leq 1 \tag{8}$$

Introducing $\eta = D_1/D_2$, and $D = D_2$, for any parameter $\gamma = (\alpha, x_o, y_o, Da_1, Da_2, D, \eta)$, the linear differential operator can be written as,

$$L(\gamma) = \begin{pmatrix} \eta D \Delta - (1 + Da_1 e^{\alpha\theta}) & -\alpha x_s Da_1 e^{\alpha\theta} \\ Da_1 e^{\alpha\theta} & D\Delta + \alpha x_s Da_1 e^{\alpha\theta} - (1 + Da_2) \end{pmatrix} \tag{9}$$

The nonlinear operator is,

$$N(\gamma, u) = \begin{pmatrix} -\alpha Da_1 e^{\alpha\theta} xy \\ \alpha Da_1 e^{\alpha\theta} xy \end{pmatrix} \tag{10}$$

So, the original Eq. (5) becomes,

$$u_t = L(\gamma) + N(\gamma, u) \tag{11}$$

We are now interested in finding out the asymptotic solutions of Eq. (11) for $t \to \infty$ which are nontrivial solutions $u \neq 0$ with a boundary condition described in Eq. (6).

The sufficient condition for instability with respect to boundary condition (6) is that the solution $u = 0$ be unstable to small disturbances. Hence, the linearized form of Eq. (11),

$$\left[\frac{\partial}{\partial t} - L(\gamma)\right] u = 0, \tag{12}$$

would have a nontrivial solution for the specified boundary condition.

The solution to Eq. (12) can be given as,

$$u(r, t) = \Xi(r) e^{\lambda t} \tag{13}$$

where $\Xi(r) = (\xi(r), \kappa(r))^T$ corresponds to a solution to r - dependent part, and λ is the eigenvalue for the time-dependent part. Then the eigenvalue problem to steady state version of Eq. (11) can be written as,

$$[L(\gamma) - \lambda I] \ \Xi(r) = 0 \tag{14}$$

The solution to Eq. (12) then becomes,

$$u(r, t) = \sum_{n=1}^{\infty} c_n e^{\lambda_n t} \Xi_n(r) \tag{15}$$

The eigenfunctions for any wavenumber n, can be written for the Dirichlet problem as,

$$\Xi(r) \;=\; \begin{pmatrix} \xi_n(r) \\ \kappa_n(r) \end{pmatrix}, \text{ where,}$$

$$\xi_n(r) \;=\; \sin n\pi r\,, \qquad \kappa_n(r) \;=\; M_n \sin n\pi r \tag{16}$$

Using Eqs. (9) and (14), we can write the characteristic equation in terms of trace $Tr(\gamma, \mathrm{n})$ and determinant $Det(\gamma, \mathrm{n})$ as,

$$\lambda_n^2 \;-\; \mathrm{Tr}(\gamma, n)\,\lambda_n \;+\; \mathrm{Det}(\gamma, n) \;=\; 0\,, \tag{17}$$

The trace and determinant expressions are given as,

$$\mathrm{Tr}(\gamma, n) \;=\; (\alpha x_s Da_1 e^{\alpha\theta} - Da_2 - 1) - (1 + Da_1 e^{\alpha\theta}) - n^2\pi^2 D\,(1+\eta) \tag{18}$$

$$\begin{aligned}\mathrm{Det}(\gamma, n) \;=\;& (n^2\pi^2 D)^2\eta - n^2\pi^2 D\,[\eta(\alpha x_s Da_1 e^{\alpha\theta} - Da_2 - 1) - (1 + Da_1 e^{\alpha\theta})] \\ & - [\alpha x_s Da_1 e^{\alpha\theta} - Da_2 - 1]\,(1 + Da_1 e^{\alpha\theta}) + \alpha x_s (Da_1 e^{\alpha\theta})^2 \end{aligned} \tag{19}$$

The eigenvalues are then obtained as,

$$\begin{aligned} 2\lambda_n^{\pm} \;=\;& [[Da_1 e^{\alpha\theta}(\alpha x_s - 1) - (Da_2 + 2)] - n^2\pi^2 D\,(1+\eta)] \;\pm\; \{(n^2\pi^2 D)^2\,(1-\eta)^2 \\ & + 2(1-\eta) n^2\pi^2 D\,[Da_2 - Da_1 e^{\alpha\theta}(\alpha x_s + 1)] + Da_2^2 \\ & + Da_1 e^{\alpha\theta}[(\alpha x_s - 1)^2 Da_1 e^{\alpha\theta} - 2Da_2(\alpha x_s + 1)]\}^{1/2} \end{aligned} \tag{20}$$

and, the eigenfunctions can be obtained in terms of the eigenvalues as,

$$\lambda_n^{\pm} + (1 + Da_1 e^{\alpha\theta}) + n^2\pi^2\eta D + \alpha x_s Da_1 e^{\alpha\theta} M_n^{\pm} \;=\; 0 \tag{21}$$

Note that, the eigenvalues have negative real part if and only if $Tr(L(\gamma) < 0$ and $Det(L(\gamma)) > 0$, in which case the solution is linearly stable. If either $Tr(L(\gamma)) > 0$ or $Det(L(\gamma)) < 0$, then the solution is linearly unstable. If $Det(L(\gamma))$ changes sign, an exchange of stability takes place as one eigenvalue of $L(\gamma)$ changes sign. This results in bifurcation of steady state solution branches. If $Det(L(\gamma)) > 0$ and $Tr(L(\gamma))$ changes sign, exchange of stability occurs as the real part of the eigenpair of $L(\gamma)$ changes sign. This corresponds to Hopf bifurcation, which generates a nontrivial branch of periodic solutions. However, if $Det(L(\gamma)) < 0$ when $Tr(L(\gamma))$ changes sign, no bifurcation occurs, and hence there is no exchange of stability. This is depicted in Fig. (1).

In this present study, we are interested in analyzing the possible modes through which instability sets in ending up with Hopf bifurcation. This can happen in two ways.

(i) At some $\gamma=\gamma_c$, an eigenvalue $\lambda^{\pm}_{n_c}$ crosses the imaginary axis with nonvanishing imaginary part. This case is in accordance with the conditions, that for critical value of parameter γ_c, and for any wave number n if trace is negative and determinant is nonnegative, the solution is stable. For the critical value of wave number n, we may have a vanishing trace condition, leading to Hopf bifurcation which is the onset of instability. To find the critical value n_c we then put the trace derivative $\frac{d\,\mathrm{Tr}(\gamma,n)}{dn}\big|_{n=n_c}$ to zero. This yields the result $n_c = 1$. Substituting for the critical value of n we obtain the locus of points corresponding to neutral stability ($\mathrm{Re}\,\lambda^{\pm}_{n_c} = 0$ in the plane (Da_1, Da_2) as,

$$Da_1 e^{\alpha\theta}(\alpha x_s - 1) - (Da_2 + 2) \quad = \quad \pi^2 D(1+\eta) \tag{22}$$

(ii) At $\gamma=\gamma_c$, the only value of n_c that crosses the imaginary axis from negative to positive has vanishing imaginary part. This means that at critical value of wave number n_c trace is negative and determinant is zero, while for other values of n the solution is stable as trace is again negative and determinant is non-negative. Then the critical value of wave number is obtained by putting determinant derivative $\frac{d\,\mathrm{Det}(\gamma,n)}{dn}\big|_{n=n_c}$ to zero. This gives,

$$n_c \quad = \quad \| \pi^{-1} D^{-1/2} \eta^{-1/4} \{(1+Da_2) + Da_1 e^{\alpha\theta}[(1+Da_2) - \alpha x_s]\}^{1/4} \| \tag{23}$$

$$
\begin{tikzcd}
\left\{\begin{array}{l} \mathrm{Det}\left[L(\gamma)\right] > 0 \\ \mathrm{Tr}\left[L(\gamma)\right] < 0 \end{array}\right\} \arrow[r, "\text{Hopf}"] \arrow[d, "\text{SS}"] & \left\{\begin{array}{l} \mathrm{Det}\left[L(\gamma)\right] > 0 \\ \mathrm{Tr}\left[L(\gamma)\right] > 0 \end{array}\right\} \arrow[d, "\text{SS}"'] \\
\left\{\begin{array}{l} \mathrm{Det}\left[L(\gamma)\right] < 0 \\ \mathrm{Tr}\left[L(\gamma)\right] < 0 \end{array}\right\} \arrow[r, dashed] & \left\{\begin{array}{l} \mathrm{Det}\left[L(\gamma)\right] < 0 \\ \mathrm{Tr}\left[L(\gamma)\right] > 0 \end{array}\right\}
\end{tikzcd}
$$

FIGURE.1. STABILITY EXCHANGE DIAGRAM

Also, the locus of neutrally stable states is given by following equation,

$$\{\eta[(1+Da_2)+Da_1 e^{\alpha\theta}[(1+Da_2)-\alpha x_s]]\}^{1/2}$$
$$= \frac{\eta[\alpha x_s Da_1 e^{\alpha\theta}-(1+Da_2)]-(1+Da_1 e^{\alpha\theta})}{2} \tag{24}$$

Inserting Eq. (24) into the condition $Tr(L(\gamma_c, n_c) < 0$, we obtain an inequality as,

$$(1-\eta)\quad [\eta[\alpha x_s Da_1 e^{\alpha\theta}-(1+Da_2)]+(1+Da_1 e^{\alpha\theta})] \quad < \quad 0 \tag{25}$$

and from the sufficiency condition of minimum $Det(\gamma, n)$ one obtains,

$$1 \; < \; \eta, \qquad \text{or} \qquad D_1 \; > \; D_2 \tag{26}$$

Fig. (2) depicts for some specific values of Da_l the linear stability diagram in the neighborhood of $u = 0$. It should be noted that in this work the diffusion plays the destabilizing role where the mixing in an stirred vessel is very poor.

8.2 Multiple time scale analysis

In this section, we would apply the technique of multiple time scale to obtain the global nonuniform steady patterns. The multiple time scale analysis takes advantage of the existence of slow and fast time scales, inherent in the system to construct an asymptotic solution. The method has been extensively employed and illustrated in the literature (Newell and Whitehead, 1969; Nayfeh, 1973; Ortoleva and Ross; 1974; Bender and Orszag, 1978; Bonilla and Velarde, 1979; Keener, 1982; Ramakrishna and Amundson, 1985).

To construct the nonuniform steady solution that branches at $Da_l = Da_{lc}$, in region III-b of Fig. (2), we see that in terms of a small expansion parameter ε the perturbations upon the trivial fixed point $x=y=0$ can be arbitrarily written as,

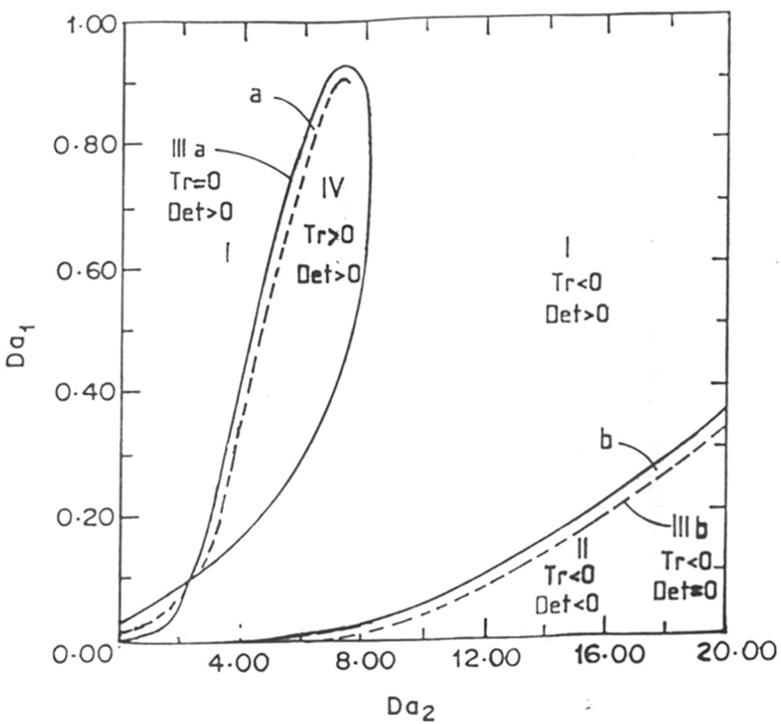

Figure 2 : Stability diagram of Encillator in the neighbourhood of the homogeneous steady state (2). Region I is of stability. Region III-a [Equation (22)] and III-b [Equation (24)] contains the unstable zone between the solid line and dotted line. In region III-a along *a* there is bifurcation to limit cycle behavior. In region III-b, along *b* spatial dissipative structures can occur. In region IV limit cycle behavior is expected.

$$x(r,0) \;=\; h(r,\varepsilon); \qquad h_\varepsilon(r,0) = \left(\frac{\partial h(r,\varepsilon)}{\partial \varepsilon}\right)_{\varepsilon=0}, \tag{27a}$$

$$y(r,0) \;=\; g(r,\varepsilon); \qquad g_\varepsilon(r,0) \;=\; \left(\frac{\partial g}{\partial \varepsilon}\right)_{\varepsilon=0}, \tag{27b}$$

$$h(r,0) \;=\; g(r,0) \;=\; 0 \tag{27c}$$

The two time scales used in the asymptotic analysis are defined as, a fast time scale $\tilde{t} = t$, and a slow scale $\tau = [Da_1(\varepsilon) - Da_{1c}]\, t$. Now we define following expansions for the variables x and y,

$$x(r,t,\tau) \cong \sum_{i=1}^{\infty} \varepsilon^i x_i(r,t,\tau), \qquad y(r,t,\tau) \cong \sum_{i=1}^{\infty} \varepsilon^i y_i(r,t,\tau) \tag{28}$$

and the corresponding expansions for initial and boundary conditions as,

initial condition :

$$x_j(r,0,0) \;=\; \frac{1}{j!}\frac{\partial^j h(r,0)}{\partial \varepsilon^j} \tag{29a}$$

$$y_j(r,0,0) \;=\; \frac{1}{j!}\frac{\partial^j g(r,0)}{\partial \varepsilon^j} \tag{29b}$$

boundary condition :

$$x_j(0,t,\tau) \;=\; x_j(1,t,\tau) \;=\; y_j(0,t,\tau) \;=\; y_j(1,t,\tau) \;=\; 0 \tag{29c}$$

Also the expansion for the bifurcation parameter Da_1, assuming it to be analytic in ε neighborhood of Da_{1c} can be written as,

$$Da_1(\varepsilon) \;=\; Da_{1c} + Da_1'(0)\varepsilon + \frac{1}{2}Da_1''(0)\varepsilon^2 + O(\varepsilon^3) \tag{30}$$

In terms of these expansions the linear and nonlinear operators become,

$$L(\gamma) = \begin{pmatrix} \eta D\Delta-(1+Da_1e^{\alpha\theta}) & -\alpha x_s Da_1 e^{\alpha\theta} \\ Da_1e^{\alpha\theta} & D\Delta+\alpha x_s Da_1 e^{\alpha\theta}-Da_2-1 \end{pmatrix}$$

$$+ \ \varepsilon \begin{pmatrix} -Da_1'(0)e^{\alpha\theta} & -\alpha x_s Da_1'(0)e^{\alpha\theta} \\ Da_1'(0)e^{\alpha\theta} & \alpha x_s Da_1'(0)e^{\alpha\theta} \end{pmatrix}$$

$$+ \ \frac{1}{2}\varepsilon^2 \begin{pmatrix} -Da_1''(0)e^{\alpha\theta} & -\alpha x_s Da_1''(0)e^{\alpha\theta} \\ Da_1''(0)e^{\alpha\theta} & \alpha x_s Da_1''(0)e^{\alpha\theta} \end{pmatrix} \tag{31}$$

and,

$$N(Da_1,u) = \varepsilon^2 \begin{pmatrix} -\alpha e^{\alpha\theta} Da_{1c}x_1y_1 \\ \alpha e^{\alpha\theta} Da_{1c}x_1y_1 \end{pmatrix}$$

$$+ \ \varepsilon^3 \begin{pmatrix} -\alpha e^{\alpha\theta}[Da_{1c}(x_1y_2+x_2y_1)+Da_1'(0)x_1y_1] \\ \alpha e^{\alpha\theta}[Da_{1c}(x_1y_2+x_2y_1)+Da_1'(0)x_1y_1] \end{pmatrix} \tag{32}$$

and the derivative term becomes,

$$\frac{\partial}{\partial t} = \frac{\partial}{\partial f}+\left[Da_1'(0)\varepsilon+\frac{1}{2}Da_1''(0)\varepsilon^2+O(\varepsilon^3)\right]\frac{\partial}{\partial\tau} \tag{33}$$

Here onwards, the tilde ~ on t will be dropped.

From Eqs. (12) and (31), collecting terms of equal powers of ε we obtain following linear equations,

$$L\begin{pmatrix} x_1 \\ y_1 \end{pmatrix} = \begin{pmatrix} \frac{\partial}{\partial t}-[\eta D\Delta-(1+Da_{1c}e^{\alpha\theta})] & \alpha x_s Da_{1c}e^{\alpha\theta} \\ -Da_{1c}e^{\alpha\theta} & \frac{\partial}{\partial t}-[D\Delta+\alpha x_s Da_{1c}e^{\alpha\theta}-(1+Da_2)] \end{pmatrix}\begin{pmatrix} x_1 \\ y_1 \end{pmatrix} \tag{34}$$

$$L\begin{pmatrix} x_2 \\ y_2 \end{pmatrix} = \begin{pmatrix} -Da_1'(0)\frac{\partial x_1}{\partial\tau}+x_1(-Da_1'(0)e^{\alpha\theta})+y_1(-\alpha x_s Da_1'(0)e^{\alpha\theta})-x_1y_1\alpha e^{\alpha\theta}Da_{1c} \\ -Da_1'(0)\frac{\partial y_1}{\partial\tau}+x_1(Da_1'(0)e^{\alpha\theta})+y_1(\alpha x_s Da_1'(0)e^{\alpha\theta})+x_1y_1\alpha e^{\alpha\theta}Da_{1c} \end{pmatrix}\begin{pmatrix} x_2 \\ y_2 \end{pmatrix} \tag{35}$$

$$L\begin{pmatrix} x_3 \\ y_3 \end{pmatrix} = \begin{pmatrix} -Da_1'(0)\dfrac{\partial x_2}{\partial \tau} - \dfrac{1}{2}Da_1''(0)\dfrac{\partial x_1}{\partial \tau} + x_2(-Da_1'(0)e^{\alpha\theta}) + y_2(-\alpha x_s Da_1'(0)e^{\alpha\theta}) \\ + \dfrac{1}{2}x_1(-Da_1''(0)e^{\alpha\theta}) + \dfrac{1}{2}y_1(-\alpha x_s Da_1''(0)e^{\alpha\theta}) \\ -\alpha e^{\alpha\theta}[Da_{1c}(x_1y_2 + x_2y_1) + Da_1'(0)x_1y_1] \\ \\ -Da_1'(0)\dfrac{\partial y_2}{\partial \tau} - \dfrac{1}{2}Da_1''(0)\dfrac{\partial y_1}{\partial \tau} + x_2(Da_1'(0)e^{\alpha\theta}) + y_2(\alpha x_s Da_1'(0)e^{\alpha\theta}) \\ + \dfrac{1}{2}x_1(Da_1''(0)e^{\alpha\theta}) + \dfrac{1}{2}y_1(\alpha x_s Da_1''(0)e^{\alpha\theta}) \\ + \alpha e^{\alpha\theta}[Da_{1c}(x_1y_2 + x_2y_1) + Da_1'(0)x_1y_1] \end{pmatrix}$$

.........(36)

The solution of Eq. (34) is,

$$\begin{pmatrix} x_1(r,t,\tau) \\ y_1(r,t,\tau) \end{pmatrix} = \mathrm{Re}\sum_{n=1}^{\infty}\left\{c_n^+(\tau)e^{\lambda_n^+ t}\Xi_n^+(r) + c_n^-(\tau)e^{\lambda_n^- t}\Xi_n^-(r)\right\} \tag{37}$$

Here the dominant eigenvalue is $\lambda_{n_c}^+ = 0$, while all other decay exponentially with t. Eq. (37) therefore reduces to,

$$\begin{pmatrix} x_1(r,t,\tau) \\ y_1(r,t,\tau) \end{pmatrix} = c_{n_c}^+(\tau)\Xi_{n_c}^+(r) + (\text{e.d.t}) \tag{38}$$

where (e.d.t.) denotes exponentially decaying terms.

The coefficients $c_{n_c}^+(0)$ can be obtained using Eqs. (27), (28) and (A7) as,

$$c_n^{\pm}(0) = \frac{<\hat{\Xi}_n^{\pm} | \begin{pmatrix} h_\varepsilon(r,0) \\ g_\varepsilon(r,0) \end{pmatrix}>}{<\hat{\Xi}_n^{\pm} | \Xi_n^{\pm}>}$$

$$= 2\int_0^1 \{\sin n\pi r(h_\varepsilon(r,0) - \alpha x_s M n^{\pm} g_\varepsilon(r,0))\, dr\} \tag{39}$$

Thus, constants $c_n^{\pm}$ are directly expressed in terms of the initial condition (27). Using the definition of Fredholm alternative the coefficient $c_{n_c}^{\pm}(\tau)$ can be obtained from the ε^2 equation in the set of Eqs. (34-36). It is convenient to introduce the following average which is useful when we take the limit $t \to \infty$.

$$<<\hat{\Xi}_{n_c}^{+} | f>> = \lim_{t \to \infty} \frac{1}{T} \int_0^T <\hat{\Xi}_{n_c}^{+} | f> dt \tag{40}$$

where f is some arbitrary function in this equation. All products of $\hat{\Xi}_{n_c}^{+}$ with e.d.t. then vanish according to this definition.

From Eqs. (35), (40) and (A9) we obtain,

$$\frac{1}{2} Da_1'(0) \frac{dc_{n_c}^{+}(\tau)}{d\tau}(1-\eta) = \frac{Da_1'(0)}{4} e^{\alpha\theta} c_{n_c}^{+}(\tau)$$

$$\times \left\{ \frac{2[\eta(\alpha x_s Da_1 e^{\alpha\theta} - (1+Da_2)) + (1+Da_1 e^{\alpha\theta})] - 2Da_1 e^{\alpha\theta}(1+\alpha x_s \eta)}{Da_1 e^{\alpha\theta}} \right\}$$

$$+ \; c_{n_c}^{+2} <\hat{\Xi}_{n_c}^{+} | \left[\frac{1}{2} \frac{\partial^2}{\partial c^2} N(\gamma, u) \right]_{\varepsilon=0} > \tag{41}$$

where,

$$< \hat{\Xi}^{+}_{n_c} \mid \left[\frac{1}{2} \frac{\partial^2}{\partial c^2} N(\gamma, u) \right]_{\varepsilon=0} > \;=\; \left\{ \frac{\alpha e^{\alpha\theta} Da_{1c}[\eta(\alpha x_s Da_1 e^{\alpha\theta} - (1+Da_2)) + (1+Da_1 e^{\alpha\theta}) - 2\alpha x_s \eta Da_1 e^{\alpha\theta}]}{2\alpha x_s Da_1 e^{\alpha\theta} \frac{3}{4} n_c \pi} \right\}$$

when n_c is odd

$$= \; 0$$

when n_c is even (42)

When n_c is odd and $< \hat{\Xi}^{+}_{n_c} \mid \left[\frac{1}{2} \frac{\partial^2}{\partial c^2} N(\gamma, u) \right]_{\varepsilon=0} > \neq 0$, then we have,

$$\frac{dc^{+}_{n_c}(\tau)}{d\tau} \;=\; \nu \left[1 - \frac{c^{+}_{n_c}(\tau)}{c^{+}_{n_c}(\infty)} \right] c^{+}_{n_c}(\tau) \qquad (43a)$$

where,

$$\nu \;=\; \frac{1 - \eta(1+Da_2)}{Da_1(1-\eta)} \qquad (43b)$$

$$c^{+}_{n_c}(\infty) \;=\; -\frac{3 n_c \pi Da_1'(0) x_s}{4} \;\; \mathbf{x} \;\; \frac{1 - \eta(1+Da_2)}{Da_{1c}[1 + Da_1 e^{\alpha\theta}(1 - \alpha x_s \eta) - \eta(1+Da_2)]} \qquad (44)$$

Integrating Eq. (43a) we obtain,

$$c^{+}_{n_c}(\tau) \;=\; \frac{c^{+}_{n_c}(0)\, c^{+}_{n_c}(\infty) e^{\nu\tau}}{c^{+}_{n_c}(\infty) - c^{+}_{n_c}(0)\,(1 - e^{\nu\tau})} \qquad (45)$$

From Eqs. (37) and (45) and after substituting for, $Mn^{+}_{n_c}$ from Eq. (A8), we obtain to first order in ε.

$$\varepsilon\begin{pmatrix} x \\ y \end{pmatrix} \cong \varepsilon c_{n_c}^{+}(\infty)c_{n_c}^{+}(0)\exp\left[\frac{-xy(Da_{1c}-Da_1)t}{c_{n_c}^{+}(\infty)-c_{n_c}^{+}(0)\left[1-\exp[-\nu(Da_{1c}-Da_1)t]\begin{pmatrix} 1 \\ M_{n_c}^{+} \end{pmatrix}\sin n_c\pi r\right]}\right]$$

$$+\varepsilon c_{n_c}^{-}(0)e^{\lambda_{n_c}^{-}t}\begin{pmatrix} 1 \\ M_{n_c}^{-} \end{pmatrix}\sin n_c\pi r + \varepsilon \operatorname{Re}\sum_{n\neq n_c}^{\infty} c_n^{\pm}(0)e^{\lambda_n^{\pm}t}\begin{pmatrix} 1 \\ M_n^{\pm} \end{pmatrix}\sin n\pi r + O(\varepsilon^2) \qquad (46)$$

if the trivial solution is to be asymptotically stable for $Da_l > Da_{lc}$. To have such a case $c_{n_c}^{+}(\tau)=0$ for $t\to\infty$. This is obtained by imposing a condition,

$$\nu\tau = \nu(Da_1 - Da_{1c})t < 0 \quad \text{at} \quad t\to\infty. \qquad (47)$$

It follows from above that,

$$\nu = \frac{1-\eta(1+Da_2)}{Da_1(1-\eta)} < 0 \qquad (48)$$

Since $\eta > 1$, we have, $\eta(1+Da_2) < 1$.

Eq. (48) can also be stated as follows :

$$\frac{\partial L(\gamma_c)}{\partial\varepsilon} = \begin{pmatrix} -Da_1'(0)e^{\alpha\theta} & -\alpha x_s Da_1'(0)e^{\alpha\theta} \\ Da_1'(0)e^{\alpha\theta} & \alpha x_s Da_1'(0)e^{\alpha\theta} \end{pmatrix} \qquad (49a)$$

Then, using Eq. (31), it can be shown that,

$$<\hat{\Xi}_{n_c}^{+} \mid \left[\frac{\partial L(\gamma_c)}{\partial\varepsilon}\right]_{\varepsilon=0} \Xi_{n_c}^{+}> = \frac{(1-\eta)\nu}{2} \qquad (49b)$$

Hence, equivalently Eq. (48) can be stated as,

$$<\hat{\Xi}_{n_c}^{+} \mid \left[\frac{\partial L(\gamma_c)}{\partial\varepsilon}\right]_{\varepsilon=0} \Xi_{n_c}^{+}> < 0. \qquad (50)$$

For the sake of simplicity, we choose $Da_1'(0)=1$ in Eq. (30). This gives,

$$Da_1 - Da_{1c} = \varepsilon + O(\varepsilon^2) \qquad (51a)$$

To first order in ε, we then have the solutions x and y as,

$$x \cong c^+_{n_c}(\tau)\,(Da_1 - Da_{1c}) \sin n_c \pi r$$

$$\text{and } y \cong c^+_{n_c}(\tau) M^+_{n_c} (Da_1 - Da_{1c}) \sin n_c \pi r \qquad (51b)$$

If $c^+_{n_c}(0)$ and $c^+_{n_c}(\infty)$ have the same sign, with $Da_1 < Da_{1c}$, then as $t \to \infty$, the following asymptotic state will be reached.

$$\begin{pmatrix} x(r) \\ y(r) \end{pmatrix} \sim \begin{pmatrix} x_s \\ \theta \end{pmatrix} + c^+_{n_c}(\infty) \begin{pmatrix} 1 \\ M^+_{n_c} \end{pmatrix} (Da_{1c} - Da_1) \sin n_c \pi r + O[(Da_{1c} - Da_1)^2] \qquad (52)$$

In more explicit terms, this becomes,

$$\begin{pmatrix} x(r) \\ y(r) \end{pmatrix} \sim \begin{pmatrix} x_s \\ \theta \end{pmatrix} + \left\{ \frac{3 n_c \pi Da_1'(0) x_s}{4} \times \frac{1 - \eta(1 + Da_2)}{Da_1[1 + Da_1 e^{\alpha\theta}(1 - \alpha x_s \eta) - \eta(1 + Da_2)]} \right\} \times \begin{pmatrix} 1 \\ M^+_{n_c} \end{pmatrix} (Da_{1c} - Da_1) \sin n_c \pi r + O[(Da_{1c} - Da_1)^2] \qquad (53)$$

The derivation assumes that the signs of $c^\pm_n(0)$ and $c^\pm_n(\infty)$ are similar. In the instance the signs of these differ, the denominator in Eq. (45) vanishes for a time interval of the order of $[\nu(Da_{1c} - Da_1)]^{-1}$. The solution after this time goes out of the ε region. Also, when Da_1 is slightly larger than Da_{1c} we would obtain the same equation for x and y; however, the solution is now unstable and the neighboring concentration profiles diverge with time. The initial perturbation for this case with the signs of $c^\pm_{n_c}(0)$ and $c^\pm_{n_c}(\infty)$ different, will decay and the solution will culminate into the trivial asymptotically stable point.

The calculation of $c_n^{\pm}(\tau)$ for the case when n_c is even requires us to consider the next higher order Eq. (36). After some algebraic manipulations we then have,

$$\left[\frac{\partial}{\partial t} - L(\gamma_c)\right]\begin{pmatrix} x_2 \\ y_2 \end{pmatrix} = \begin{pmatrix} -\alpha e^{\alpha\theta} Da_{1c} M_{n_c}^{+} \\ \alpha e^{\alpha\theta} Da_{1c} M_{n_c}^{+} \end{pmatrix} c_{n_c}^{+2} \sin^2 n_c \pi r + (e.d.t.) \tag{54}$$

The particular solution to Eq. (54) is written as,

$$u_2^{\mathrm{ps}} = \sum_{n \neq n_c} \beta_n^{\pm}(\tau) \Xi_n^{\pm}(r) \tag{55}$$

Knowing that,

$$L(\gamma_c)\Xi_n^{\pm}(r) = \lambda_n^{\pm}(r) \tag{56}$$

the Eqs. (54) and (56) give,

$$\sum_{n \neq n_c} \beta_n^{\pm}(\tau) \lambda_n^{\pm} \Xi_n^{\pm}(r) = \begin{pmatrix} 1 \\ -1 \end{pmatrix} M_{n_c}^{+} \alpha e^{\alpha\theta} Da_{1c} c_{n_c}^{+2} \sin^2 n_c \pi r + (e.d.t.) \tag{57}$$

Using Eq. (A7), we get the result,

$$\beta_n^{\pm}(\tau) = \begin{Bmatrix} \rho_n^{\pm} c_{n_c}^{+2}(\tau) & \text{for odd n} \\ 0 & \text{for even n} \end{Bmatrix} \tag{58}$$

where,

$$\rho_n^{\pm} = \frac{8n_c^2}{n(n^2 - 4n_c^2)\pi\delta_n^{\pm}} \frac{Da_{1c}(1 + \alpha x_s M_n^{\pm})\{\eta[\alpha x_s Da_1 e^{\alpha\theta} - (1 + Da_2)] + (1 + Da_1 e^{\alpha\theta})\}}{2x_s Da_1 (1 - \alpha x_s M_n^{\pm 2}} \tag{59}$$

The general solution of Eq. (54) then reduces to,

$$u_2 = b_{n_c}^{+}(\tau)\Xi_{n_c}^{+}(r) + c_{n_c}^{+2}(\tau)\Omega(r) + (e.d.t.) \tag{60}$$

where,

$$\Omega(r) = \begin{pmatrix} \omega(r) \\ \xi(r) \end{pmatrix} = \sum_{\substack{n \neq n_c \\ \text{n is odd}}} \rho^{\pm} \Xi_n^{\pm}(r) \tag{61}$$

Substituting Eqs. (60) and (61) into Eq. (36) we obtain,

$$\left[\frac{\partial}{\partial t} - L(\gamma_c)\right] u_3 = -\frac{1}{2} Da_1''(0) \frac{\partial u_1}{\partial \tau} + L_{\text{II}}(\gamma_c) u_1 + N_{\text{III}}(\gamma_c, u_1, u_2) \tag{62}$$

where,

$$L_{\text{II}} = \left[\frac{1}{2}\frac{\partial^2 L(\gamma_c)}{\partial \varepsilon^2}\right]_{\varepsilon=0} = \begin{pmatrix} -1 & -\alpha x_s \\ 1 & \alpha x_s \end{pmatrix} \frac{Da_1''(0)}{2} e^{\alpha\theta} \tag{63a}$$

and

$$N_{\text{III}}(\gamma_c, u_1, u_2) = \begin{pmatrix} -1 \\ 1 \end{pmatrix} \alpha e^{\alpha\theta} Da_{1c}(x_1 y_2 + x_2 y_1) \tag{63b}$$

Multiplying Eq. (62) with $\hat{\Xi}_{n_c}^{+}(r)$ and applying Fredholm alternative with Eq. (40), the result is,

$$\frac{Da_1''(0)}{2} \frac{dc_{n_c}^{+}}{d\tau} = \frac{Da_1''(0)}{2} \nu c_{n_c}^{+} - \beta \nu c_{n_c}^{+3} \tag{64}$$

where,

$$\nu = \frac{1 - \eta(1 + Da_2)}{Da_1(1 - \eta)} \tag{65}$$

and,

$$\beta \;=\; \frac{-Da_{1c}\{\alpha x_s \xi(r)\,[Da_1 e^{\alpha\theta}(\alpha x_s \eta - 1) - \eta(1+Da_2)+1]\}}{2\,(1-\eta(1+Da_2))}$$

$$+\frac{-Da_{1c}\{\omega(r)\,[1+Da_1 e^{\alpha\theta} - \eta[(1+Da_2)+\alpha x_s Da_1 e^{\alpha\theta}]]\}}{2\,(1-\eta(1+Da_2))} \qquad (66)$$

In the limit $\tau \to \infty$ one notices that,

$$c^{+}_{n_c}(\infty) \;=\; \pm\,[Da_1''(0)/2\beta]^{1/2} \qquad (67)$$

Therefore Eq. (64) using Eq. (67) becomes,

$$\frac{dc^{+}_{n_c}}{d\tau} \;=\; \nu c^{+}_{n_c}\left[1-\frac{c^{+2}_{n_c}(\tau)}{c^{+2}_{n_c}(\infty)}\right] \qquad (68)$$

Integrating Eq. (68) we obtain,

$$c^{+}_{n_c}(\tau) \;=\; |\,c^{+}_{n_c}(\infty)\,|\,c^{+}_{n_c}(0)\,e^{\nu\tau}\left[c^{+2}_{n_c}(0)\,(e^{2\nu\tau}-1)+c^{+2}_{n_c}(\infty)\right]^{1/2} \qquad (69)$$

It is interesting to note that depending on the positive or negative sign of $c^{+}_{n}(0)$, the solution $c^{+}_{n}(\tau)$ goes to $|\,c^{+}_{n}(\infty)\,|$ or $-c^{+}_{n}(\infty)$. The dissipative structure at $t \to \infty$ therefore depends only on the sign of the initial conditions. The asymptotic expansion of the solution in this case gives,

$$\begin{pmatrix} x(r,t,\varepsilon) \\ y(r,t,\varepsilon) \end{pmatrix} \;=\; \begin{pmatrix} x_s \\ \theta \end{pmatrix} + \varepsilon \begin{pmatrix} 1 \\ M^{+}_{n_c} \end{pmatrix} c^{+}_{n_c}(\tau)\sin n_c \pi r$$

$$+\varepsilon c^{-}_{n_c}(0)\begin{pmatrix} 1 \\ M^{+}_{n_c} \end{pmatrix} e^{\lambda^{\pm}_{n} t}\sin n_c \pi r + \varepsilon \sum_{n \neq n_c}^{\infty} c^{\pm}_{n} e^{\lambda^{\pm}_{n} t}\begin{pmatrix} 1 \\ M^{\pm}_{n} \end{pmatrix}\sin n\pi r \qquad (70)$$

As $t \to \infty$,

$$\begin{pmatrix} x(r) \\ y(r) \end{pmatrix} \;\cong\; \begin{pmatrix} x_s \\ \theta \end{pmatrix} \pm \left(\frac{Da_1 - Da_{1c}}{\beta}\right) \mathrm{x} \begin{pmatrix} 1 \\ Mn^{+}_{n_c} \end{pmatrix} \sin n_c \pi r + O(|\,Da_1 - Da_{1c}\,|) \qquad (71)$$

Conclusively, we can say in the end that, when $Da_l > Da_{lc}$, then the trivial solution is asymptotically stable, and vice-versa in the case of odd n_c.

8.3 Stability analysis of Limit Cycle

We shall begin with the neutral stability curve given by Eq. (22),

$$Da_1 e^{\alpha\theta}(\alpha x_s - 1) - (Da_2 + 2) \quad = \quad \pi^2 D(1+\eta) \tag{72}$$

and note that the critical eigenvalue from Eq. (20) is,

$$\lambda_1^{\pm} \quad = \quad \pm i \left\{ (Da_1 e^{\alpha\theta})^2 \alpha x_s - (\pi^2 D \eta + 1)^2 \right\}^{1/2} \tag{73}$$

From Eq. (21), we have,

$$M_1^{+} \quad = \quad \frac{-[\pm i\omega + (1 + Da_1 e^{\alpha\theta}) + \pi^2 D\eta]}{\alpha x_s Da_1 e^{\alpha\theta}} \tag{74}$$

We assume the solution to Eq. (34) with $n_c = 1$, as,

$$u_1(r,t,\tau) \quad = \quad \mathrm{Re}\{c_1^{+}(\tau) e^{i\omega t} \Xi_1^{+}(r) + c_1^{-}(\tau) e^{-i\omega t} \Xi_1^{-}(r)\} + (e.d.t) \tag{75}$$

The above equation contains two coefficients, which are unknown. It would be appropriate to define a new coefficient as follows,

$$c_1(\tau) \quad \equiv \quad \frac{1}{2}[c_1^{+}(\tau) + c_1^{-*}(\tau)] \tag{76}$$

In addition, we have, $M_1^{-} = M_1^{+*}$ and $e^{-i\omega t}\Xi_1^{-}(r) = [e^{i\omega t}\Xi_1^{+}(r)]^{*}$ we can then write,

$$u_1(r,t,\tau) \quad = \quad c_1(\tau) e^{i\omega t} \Xi_1^{+}(r) + c.c. + (e.d.t.) \tag{77}$$

where $c.c.$ stands for complex conjugate

The initial condition for $c_1(\tau)$ is given by,

$$c_1(0) \quad = \quad \frac{2\int_0^1 \{h_\varepsilon(r,0) - \alpha x_s M_1^+ g_\varepsilon(r,0)\} \sin \pi r\, dr}{(1 - \alpha x_s M_1^{+2})} \tag{78}$$

Substitution of Eq. (75) into Eq. (35) gives,

$$\left[\frac{\partial}{\partial t} + (1 + Da_1 e^{\alpha\theta}) - \eta D\Delta\right] x_2 - \alpha x_s Da_{1c} e^{\alpha\theta} y_2$$
$$= \{-Da_1'(0)\sin \pi r(c_1' e^{i\omega t} + c.c.) + (c_1 e^{i\omega t} + c.c.)\sin \pi r[-Da_1'(0)e^{\alpha\theta}]$$
$$+ (c_1 e^{i\omega t} M_1^+ + c.c.)\sin \pi r(-\alpha x_s Da_1'(0)e^{\alpha\theta}) + \sin^2 \pi r[(M_1^+ + M_1^{+*}) \mid c_1 \mid^2$$
$$+ c_1^2 e^{2i\omega t} M_1^+ + c.c.]\,(-\alpha e^{\alpha\theta} Da_{1c})\} + (e.d.t) \tag{79}$$

and,

$$\left[\frac{\partial}{\partial t} - [\alpha x_s Da_{1c]} e^{\alpha\theta} - (1 + Da_2)] - D\Delta\right] y_2 + Da_{1c} e^{\alpha\theta} x_2 \quad =$$
$$\{-Da_1'(0)\sin \pi r(c_1' M_1^+ e^{i\omega t} + c.c.) + (c_1 e^{i\omega t} + c.c.)\sin \pi r(Da_1'(0)e^{\alpha\theta})$$
$$(c_1 e^{i\omega t} M_1^+ + c.c.)\sin \pi r(\alpha x_s Da_1'(0)e^{\alpha\theta})$$
$$+ \sin^2 \pi r[(M_1^+ + M_1^{+*}) \mid c_1 \mid^2 + c_1^2 e^{2i\omega t} M_1^+ + c.c.]\,(\alpha e^{\alpha\theta} Da_{1c})\} + (e.d.t.) \tag{80}$$

Now, defining an average,

$$\ll [\hat{\Xi}_1^+] \mid f \gg \quad = \quad \lim_{T \to \infty} \frac{1}{T} \int_0^T < \hat{\Xi}_1^+ \mid f > e^{i\omega t} dt \tag{81}$$

and using Fredholm's alternative one sees that $Da_1'(0) = 0$, if c_l is nonvanishing. Now, for the eigenvalue problem for the operator $L(u_2)$ we have,

$$\sum_{n \neq n_c} \beta_n^{\pm}(\tau)\lambda_n^{\pm}\Xi_n^{\pm}(r)$$

$$= \begin{pmatrix} \alpha e^{\alpha\theta} Da_{1c}[(M_1^+ + M_1^{+*}) \mid c_1 \mid^2 + c_1^2 e^{2i\omega t} M_1^+ + c.c.] \\ -\alpha e^{\alpha\theta} Da_{1c}[(M_1^+ + M_1^{+*}) \mid c_1 \mid^2 + c_1^2 e^{2i\omega t} M_1^+ + c.c.] \end{pmatrix} \sin^2 \pi r + (e.d.t.) \tag{82}$$

Appiying Eq. (A7) we obtain,

$$\beta_n^{\pm} = \frac{< \hat{\Xi}_n^{\pm} \mid f(r) >}{< \hat{\Xi}_n^{\pm} \mid \Xi_n^{\pm} >}$$

$$= \frac{2 < \begin{pmatrix} \sin \pi r \\ -\alpha x_s M_n^{\pm *} \sin n\pi r \end{pmatrix} \Bigg| \begin{pmatrix} \alpha e^{\alpha\theta} Da_{1c}[(M_1^+ + M_1^{+*}) \mid c_1 \mid^2 + c_1^2 e^{2i\omega t} M_1^+ + c.c.] \\ -\alpha e^{\alpha\theta} Da_{1c}[(M_1^+ + M_1^{+*}) \mid c_1 \mid^2 + c_1^2 e^{2i\omega t} M_1^+ + c.c.] \end{pmatrix} \sin^2 \pi r >}{(1 - \alpha x_s M_n^{\pm 2})} \tag{83}$$

Integration of the system in Eq. (79) and (80) yields,

$$u_2(r,t,\tau) = b_1(\tau) e^{i\omega t} \Xi_1^+(r) + c.c. + c_1^2(\tau) e^{2i\omega t} \Omega(r) + c.c.$$
$$+ \mid c_1(\tau) \mid^2 [\Omega(r) + c.c.]_{\omega = 0} + (e.d.t.) \tag{84}$$

where,

$$\Omega(r) = \begin{pmatrix} \omega(r) \\ \xi(r) \end{pmatrix} = \sum_{\substack{n=3 \\ n \text{ is odd}}}^{\infty} \frac{\rho_n^{\pm}}{2i\omega - \lambda_n^{\pm}} \times \{M_1^+(1 + \alpha x_s M_n^{\pm})\} \, \Xi_n^{\pm}(r) \tag{85}$$

and,

$$\rho_n^{\pm} = \frac{-8}{n(n^2 - 4)} [1 - \alpha x_s M_n^{\pm 2}] \,, \tag{86}$$

$$[\Omega(r)]_{\omega = 0} = \sum_{\substack{n=3 \\ n \text{ is odd}}}^{\infty} -\frac{\rho_n^{\pm}}{\lambda_n^{\pm}} \{M_1^+(1 + \alpha x_s M_n^{\pm})\} \, \Xi_n^{\pm}(r) \tag{87}$$

To obtain $c_1(\tau)$, we substitute for u_1 and u_2 from Eq. (77) and (84) respectively into Eq. (36), with $Da_1'(0) = 0$. Multiplication of the result with $\hat{\Xi}_1^+(r)$ and using the identity in Eq. (81) as before, yields following differential equation,

$$\frac{Da_1''(0)}{2}\frac{\partial c_1^*}{\partial \tau} = \frac{Da_1''(0)}{2}\nu c_1^* + |c_1|^2 c_1^* \kappa \tag{88}$$

where,

$$\nu = \frac{-e^{\alpha\theta}(1+\alpha x_s M_1^{+*})^2}{(1-\alpha x_s M_1^{+*2})} \tag{89}$$

and,

$$\kappa =$$

$$\frac{-2\int_0^1 \sin^2 \pi r\, dr\, \alpha e^{\alpha\theta} Da_{1c}[\xi^*(r) + [\xi(r)+c.c.]_{\omega=0} + M_1^+\omega^*(r) + M_1^{+*}[\omega(r)+c.c.]_{\omega=0}] \times \{1+\alpha x_s M_1^{+*}\}}{(1-\alpha x_s M_1^{+*2})}$$

.....(90)

Writing, $c_1(\tau) = c(\tau)e^{-i\beta(\tau)}$ where $c(\tau)$ and $\beta(\tau)$ are yet to be specified, and then separating the real and imaginary parts in Eq. (88) gives us,

$$\frac{Da_1''(0)}{2}\frac{dc}{d\tau} = \frac{Da_1''}{2} c\,\mathrm{Re}\,\nu + c^3\,\mathrm{Re}\,\kappa \tag{91a}$$

$$\frac{Da_1''(0)}{2}\frac{d\beta}{d\tau} = \frac{Da_1''(0)}{2}\mathrm{Im}\,\nu + c^2\,\mathrm{Im}\,\kappa \tag{91b}$$

From Eq. (91a), as $\tau \to \infty$ we can write,

$$c(\infty) = \left[-\frac{Da_1''(0)}{2}\frac{\mathrm{Re}\,\nu}{\mathrm{Re}\,\kappa}\right]^{1/2} \tag{92}$$

Using Eq. (92), Eq. (91b) can be rewritten as,

$$\frac{dc}{d\tau} \;=\; \mathrm{Re}\,\nu\left[1-\frac{c^2}{c(\infty)^2}\right]c \tag{93}$$

The solution to this equation is,

$$c(\tau) \;=\; \frac{c(0)c(\infty)\,e^{\mathrm{Re}\,\nu\tau}}{\{c(\infty)^2+c(0)^2[e^{2\mathrm{Re}\,\nu\tau}-1]\}^{1/2}} \tag{94}$$

The solution to unknown phase can be written using Eqs. (91b) and (94),

$$\beta(\tau) \;=\; \beta(0)+\tau\,\mathrm{Im}\,\nu+\frac{2\,\mathrm{Im}\,\kappa}{Da_1''(0)}\int_0^{\tau} c^2(s)\,ds \tag{95}$$

which for large values of time becomes,

$$\beta(\tau) \;\cong\; \tau\left\{\mathrm{Im}\,\nu-\frac{\mathrm{Im}\,\kappa\,\mathrm{Re}\,\nu}{\mathrm{Re}\,\kappa}\right\} \tag{96}$$

Finally, to first order in ε, the following result is obtained

$$\begin{aligned} u(r,t,\varepsilon) \;\cong\;& \varepsilon\frac{2c(0)c(\infty)\exp[-(Da_{1c}-Da_1)\,\mathrm{Re}\,\nu t]}{\{c(\infty)^2+c(0)^2\{\exp[-2(Da_{1c}-Da_1)\,\mathrm{Re}\,\nu t]-1\}\}^{1/2}} \\ &\times\begin{pmatrix} 1 \\ -\dfrac{2[1+Da_1e^{\alpha\theta}+\pi^2D\eta]}{\alpha x_s Da_1e^{\alpha\theta}}\end{pmatrix}\times\cos[\omega t-\beta(Da_1-Da_{1c})t] \\ &+\varepsilon\,\mathrm{Re}\sum_{n=2}^{\infty}c_n^{\pm}(0)\times e^{\lambda_n^{\pm}t}\,\Xi_n^{\pm}(r)+O(\varepsilon^2) \end{aligned} \tag{97}$$

Eq. (97) reduces to following form as $t\rightarrow\infty$,

$$\begin{pmatrix} x(r,t) \\ y(r,t) \end{pmatrix} \cong \begin{pmatrix} x_s \\ \theta \end{pmatrix} + 2\left[\frac{\mathrm{Re}\,\nu}{\mathrm{Re}\,\kappa}(Da_{1c}-Da_1)\right]^{1/2} \begin{pmatrix} 1 \\ -\dfrac{2[1+Da_1 e^{\alpha\theta}+\pi^2 D\eta]}{\alpha x_s Da_1 e^{\alpha\theta}} \end{pmatrix} \times \sin \pi r$$

$$\times \quad \cos\left[\omega + (Da_{1c}-Da_1)\left(\mathrm{Im}\,\nu - \frac{\mathrm{Im}\,\kappa\,\mathrm{Re}\,\nu}{\mathrm{Re}\,\kappa}\right)\right] t + O(|\,Da_1 - Da_{1c}\,|) \qquad (98)$$

8.4 Conclusions

The chapter employs the two-time scale method to obtain the limit cycle and global non-uniform solutions for an exponentially autocatalyzed reaction-diffusion system. Sufficient condition for the steady uniform distribution of reactants in the presence of diffusion is established and stability of such states are examined. Global nonuniform solutions depending on whether n_c, the critical wave number, is even or odd, are then constructed and given respectively by Eqs. (46) and (70). Conditions under which the dissipative structures are asymptotically stable or when the inhomogeneous steady state solutions lose their stability are also identified. In a similar fashion Eq. (97) describe the limit cycle solution, the stability of which depends on whether Da_l exceeds Da_{lc} or not. In addition, we observe that, for sufficiently large values of diffusion parameters the limit cycle may not exist.

The important feature of the method of multiple time scales is that in addition to allowing us to construct the nonuniform and limit cycle solutions, it affords information on their stability. The detailed account of the evolution of initial disturbances upon the trivial steady state of the system is thus possible.

APPENDIX I

8.5 Linear operator properties

In this section, we will describe some of the important properties of the linear operator $L(\gamma)$ defined in Eq. (9), which are relevant to the analysis presented in this paper [6,7].

(1) If the eigenvalues $\lambda_n^{\pm}$ are complex, then the eigenvector $M_n^{+} = M_n^{+*}$, where * denotes complex conjugation.

(2) Let F be the space of analytic functions $(u(r), v(r))$ such that

$$u(0) = u(1) = v(0) = v(1) = 0,$$

then, the inner product is defined as,

$$<u\,|\,\overline{u}> = \int_0^1 \{x^*(r)\overline{x}(r) + y^*(r)\overline{y}(r)\}\,dr \tag{A1}$$

(3) From the definition of the eigenfunctions, we can write that,

$$M_n^{+} M_n^{-} = \frac{1}{\alpha x_s} \tag{A2}$$

(4) Let $\hat{L}(\gamma)$ be the adjoint operator of $L(\gamma)$ and

$$\hat{\Xi}_n^{\pm}(r) = \begin{pmatrix} \sin n\pi r \\ N_n^{\pm}\sin n\pi r \end{pmatrix},$$

the eigenfunctions of the adjoint operator with same b.c. Then, we have a relation,

$$N_n^{\pm} = -\alpha x_s M_n^{\pm *} \tag{A3}$$

(5) Also, we have following inner products,

$$<\hat{\Xi}_m^{\pm}\,|\,\Xi_n^{\pm}> = \frac{1}{2}(1 - \alpha x_s M_m^{\pm} M_n^{\pm})\,\delta_{n,m} \tag{A4}$$

and,

$$<\hat{\Xi}_n^{\pm}\,|\,\Xi_n^{\pm}> = 0 \tag{A5}$$

Thus, the orthogonal set of $\Xi_n^{\pm}(r)$ in F is defined, and for any arbitrary function $f(r)$ belonging to F we have an expansion,

$$f(r) \quad = \quad \sum_{n=1}^{\infty} (\beta_n^{+}\Xi_n^{+}(r) + \beta_n^{-}\Xi_n^{-}(r)) \tag{A6}$$

where,

$$\beta_n^{\pm} \quad = \quad \frac{2 < \hat{\Xi}_n^{\pm} \mid f >}{(1 - \alpha x_s M_n^{\pm 2})} \tag{A7}$$

(6) At the critical point, $Da_1 = Da_{1c}$ if the eigenvalue with vanishing real part is real (i.e. simple zero eigenvalue), then,

$$M_{n_c}^{+} \quad = \quad -\frac{1}{2\alpha x_s Da_1 e^{\alpha\theta}} \{\eta[\alpha x_s Da_1 e^{\alpha\theta} - (1 + Da_2)] + (1 + Da_1 e^{\alpha\theta})\} \tag{A8}$$

(7) Using Eqs. (23) and (A8), we obtain,

$$\eta \quad = \quad \alpha x_s M_{n_c}^{+*} \tag{A9}$$

8.6 Notation

c_n	constants in Eq. (15)
D_1, D_2	diffusivities of the two species
Da_1, Da_2	Damkohler numbers for the two species
Da_{1c}	critical value of Da_1
h, g	functions in perturbation expansions in Eq. (27)
$L(\gamma)$	linear differential operator
M_n	eigenvector in Eq. (16)
n	wave number

$N(\gamma, u)$	nonlinear operator
n_c	critical wave number
r	dimensionless space variable
t	dimensionless time
t	fast time scale
T	time period of oscillation
u	deviation vector
x, y	deviations from steady state for X and Y
X, Y	dimensionless concentrations of species
$X_{in}(r)$, $Y_{in}(r)$	inlet boundary condition
x_o, y_o	dimensionless initial concentrations
x_s	steady state value of X

Greek Letters

α	exponential autocatalytic parameter
γ	bifurcation control parameter of the system
Δ	operator in space dimension
ε	smallness parameter in perturbation expansion
τ	slow time scale
λ	eigenvalue
η	ratio of diffusivities ($= D_1/D_2$)
θ	steady state value of Y

Ξ	eigenvector
$\zeta(r)$, $\kappa(r)$	components of eigenvector

8.7 References

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CHAPTER IX

SUMMARY AND CONCLUSIONS

9.1 Conclusions

The present thesis chooses exponential autocatalysis as a model reacting system and extensively uses the armour of applied mathematical techniques, essentially expounding the importance of perturbation theories, for obtaining analytical results under variations in parameter values. The model reaction system has been choosen primarily because its relevance in several biochemical systems as also in explaining varied features in combustion type of reactions. The physical form of the model was suggested primarily to reflect the strong nonlinearity, resemblance to Semenov type of law and generality to behavior depicted by rate constant upon variations of temperature.

The present work begins with identifying the bounds on the steady state solutions of the system of nonlinear equations. The transcendental nature of the functions presents considerable difficulties in this analysis and recourse to linearization becomes necessary. This, however, restricts the scope of the analysis to significantly smaller values of parameter α and in the subsequent work more rigorous bounds on the steady state solutions are derived. The stability of the steady state solutions has also been determined using the linear stability theory. The baic framework also gives rise to methodologies by which the nonhomogeneous and nonnegative steady states appearing as dissipative structures can be constructed. These nonhomogeneous solutions are constructed using Sattinger's theory and an estimate of its size is provided.

The analysis of reaction-diffusion system then moves on to study the system behavior near the Hopf bifurcation point. The reductive perturbation theory is employed here to reduce the set of equations to a universal form decsribed as Ginzburg-Landau equation. The reduction of the system to this form has several advantages and behavior of reacting system can now be quantified in terms of the constants tht appear in this equation. The criteria for existence of rotating and spiral waves, chemical turbulence etc. can now be identified in terms of these parameters and would help in fixing the behavior of the system *a priori*. The formulation of reaction-diffusion equations in the form of Ginzburg-Landau equation requires special techniques which while have been practised in the general area of applied mathematics, have been employed in the analysis of reaction engineering systems for the first time. The singular perturbation theory has also been applied to this reaction-diffusion system with a view to construct nonuniform solutions arising due to the effects of the diffusion. Additionally, limit cycles have also been analyzed within the framework. The stability of the steady state solutions are also examined.

The present work puts heavy emphasis on deriving analytical results for a model system which exhibits a variety of interesting features ranging from stable state solutions, periodic, nearly periodic behavior, multipeak periodic and chaotic behavior. The general emphasis in the literature has been on deriving the various criteria using numerical techniques. The present work makes an attempt to arrive at these results using analytical techniques.

LIST OF PUBLICATIONS

1.	S.R. Inamdar, V. Ravi Kumar and B.D. Kulkarni	Dynamics of reacting systems in presence of time delay	Chem. Engg. Sci. (*Accepted*).
2.	S.S. Tambe, S.R. Inamdar, J.K. Bandopadhyay and B.D. Kulkarni	Parametric Sensitivity of Complex Reaction Systems	Chem. Engg. J, (*In Press*)
3.	S.S. Tambe, S.R. Inamdar and B.D. Kulkarni	Sensitivity Coefficients of Oscillatory Reaction Systems	Chem. Engg. J., (*In Press*).
4.	S.R. Inamdar and B.D. Kulkarni	Bounds on steady states for nonsystemically autocatalysed reaction-diffusion system	J. Phys. A : Math. & Gen., 23, L461, (1990).
5.	S.R. Inamdar, P. Rajani and B.D. Kulkarni	Reduction of reaction-diffusion system to Schrodinger-like equation	Chem. Engg. J., (*Communicated*)
6.	S. R. Inamdar and B.D. Kulkarni	Homoclinic orbits in exponential autocatalysis	I & EC., (*Communicated*)
7.	S.R. Inamdar, P. Rajani and B.D. Kulkarni	Chemical Instabilities and Bifurcations in Encillator	J. Phys. Chem., (*Communicated*)
8.	S. R. Inamdar, P. Rajani and B.D. Kulkarni	Diffusive Instability Near Hopf Bifurcation for Exponentially Autocatalyzed Reaction-Diffusion System	J. Phys. A : Math. & Gen., (*Accepted*)

9.	S.R. Inamdar, P. Rajani and B.D. Kulkarni	Multi-time scale approach to analysis of exponential autocatalysis : Limit cycle and Global non-uniform steady patterns	(*Under preparation*)
10.	S.R. Inamdar and B.D. Kulkarni	Bifurcation analysis of exponentially autocatalized reaction-diffusion equations - I : Linear stability analysis of steady state solutions.	Chem. Engg. J., (*Communicated*)
11.	S.R. Inamdar and B.D. Kulkarni	Bifurcation analysis of exponentially autocatalized reaction-diffusion equations - II : Dissipative structure and its properties.	Chem. Engg. J., (*Communicated*)